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PREFACE

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A Brief Review on Failure of Turbine Blades

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ABSTRACT

A common failure mode for turbine machine is high cycle of fatigue of compressor and turbine blades due to high dynamic stress caused by blade vibration and resonance within the operating range of machinery. Studies and investigations on failure of turbine blades are continuing since last five decades. Some review papers were also published during this period. The basic aim of this paper is to present a brief review on recent studies and investigations done on failures of turbine blades. It is not the intention of the authors to provide all the detailed literature related with the turbine blades. However, the main emphasize is to provide all the methodologies of failures adopted by various researches to investigate turbine blade. The paper incorporates a candid commentary on various factors of failure. The paper further deals with the detailed survey on these factors.

Keywords: *Corrosion failure, Corrosion fatigue, failure, fretting fatigue failure, turbine blade.*

NOMENCLATURE

Put nomenclature here.

1. INTRODUCTION

With increase in generating capacity and pressure of individual utility units in the 1960s and 70s, the importance of studying large steam turbine reliability and its efficiency is greatly increased. With increase in turbine size and changes in design (i.e., larger rotors, discs and longer blades) resulted in increased stresses and vibration problems and enforce the designers to use of higher strength materials. Turbine blades are subjected to very strenuous environments inside a gas/steam turbine. They face high temperatures, high stresses, and a potentially high vibration environment. All three of these factors can lead to blade failures, which can destroy the engine. That is why turbine blades are carefully designed to resist those conditions. The components most commonly rejected are the blades, from both the compressor and the turbine, and the turbine vanes. Generally, there are various factors causing failures of turbine blade. However, the factors which significantly influence the blade life time are as follows

- Corrosion failure
- Fretting fatigue failure
- Fatigue-creep failures

The present paper incorporates a candid commentary on the various factors of failures. The next section will present the various factors of turbine failures.

2. Various Factors of Turbine Failures Applied To Investigate Turbine Blades

This section presents the various factors, which are mainly responsible of turbine failure. Various studies of turbine blade have been contributed by many researchers which are included in this survey.

2.1 Corrosion Failure

A corrosion failure occurs when the metal wears away or dissolves or is oxidized due to chemical reactions, mainly oxidation. It occurs whenever a gas or liquid chemically attacks an exposed surface, often a metal. Corrosion is accelerated by warm temperatures and by acids and salts. Unacceptable failure rates of mostly blades and discs resulted in initiation of numerous projects to investigate the root causes of the problems [1].

Low-pressure blades of a steam turbine are generally found to be more susceptible to failure than IP (Intermediate pressure)

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and HP (High pressure) blades [2] as shown in figure 1. The most common failure mechanisms which occur within low-pressure blade are Corrosion fatigue (CF), Stress corrosion cracking (SCC), Pitting and Erosion-Corrosion in steam turbines [3]. Hata et al [4] concluded that corrosion fatigue is the leading mechanism of damage in low-pressure steam turbine and all fatigue cracking should be considered corrosion fatigue. It is considered that the corrosive chemical enrichment in the wet/dry transient zone and the corrosive environment have a strong relationship with blade corrosion fatigue damage [5]. From fractography result analysis many researchers have confirmed that corrosion fatigue cracks often originate from pits by intergranular cracking and then proceeding as a flat fatigue fracture with beach marks and striations [6].

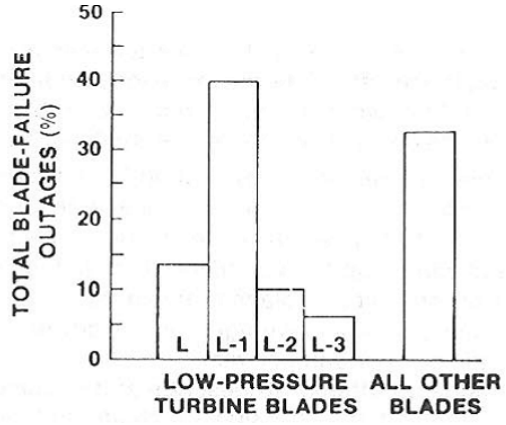

Figure1: Distribution of blade failure in US fossil turbines [7]

An analysis of the cause of fracture in a steam turbine of low pressure stage blade root was investigated by Kubiak et al [8]. The metallurgical investigation revealed that the crack was propagated by a combined process corrosion-fatigue. The analysis concludes that the metallurgical mode of the blade root failure was the corrosion-fatigue at the zone of the highest stress concentration caused by mismatch and errors in the installation between the blade root platform and the rotor fastening tree. Also, the crack was propagated by the vibrations around of the first mode of vibration. The failure analysis of 12% chromium martensitic stainless steel blades of the medium-pressure stage of a thermoelectric centre turbo-blower was presented by Tschiptschin [2]. The results indicated that at least one of the blades of the medium pressure stage failed by a corrosion-fatigue mechanism, whose nucleation was associated with the presence of corrosion pits on its suction side. The high-pressure blades presented hardness bellow the specification and presence of corrosion pits and cracks.

Das et al. [9] identified the root cause of failure of a LP (low pressure) turbine blade i.e., whether it was due to material related problem or due to change in operational parameter arising from grid frequency, boiler water chemistry etc.. Several pits/grooves were found on the edges of the blades and chloride was detected in these pits. These were responsible for the crevice type corrosion. The probable carriers of Cl were Ca and K, which were found on the blade. The failure mode was intergranular type and failure was due to corrosion-fatigue. The cause and process of the crack of the fourth stage rotor blade in the low-pressure turbine of a 500 MW steam turbine was investigated by Kim [10]. The microstructural investigation of the blade revealed the presence of corrosion pits at the leading edge of the blade and EDS analysis detected oxide-scale as corrosion media inside the corrosion pits. Thus the crack was propagated by a combined process corrosion-fatigue. Corrosion can affect blade structural reliability since fatigue cracks can nucleate from the corrosion pits and grow accelerated rate [11].

The failure of a second stage blade in a gas turbine was investigated that serious pitting was occurred at the leading and trailing edges on the blade surfaces and there were evidences of fatigue marks in the fracture surface. It was found that the crack initiated by the hot corrosion from the leading edge and propagated by fatigue. The ANSYS code was applied for generating and simulating a FE model of fractured blade [12].

The desire to achieve increased output with increase efficiency has paved way for the development of advanced alloys and surface coatings for turbine blades. Turbine blades are normally protected with sophisticated coatings, usually based on chromium and aluminium, but often containing exotic elements such as yttrium and platinum group metals to provide resistance to corrosion and oxidation in service [14]. Several surface treatment methods corresponding to operation environment have been applied for prevention of erosion damage by solid particles and water droplets, fouling on the flow path and corrosion fatigue [15]. Recently developed and improved methods are boronizing, ion plating, plasma transfer arc welding and radical notarizations plus nickel phosphate multilayer hybrid coating [4]. Hata et al [16] investigated corrosion fatigue phenomenon and studied various surface treatment methods applied to actual blades to improve anti-corrosion and anti fouling. They have developed preventive coating and blade design method against fouling and corrosive environments. Steam turbine efficiency deterioration prevented by PTFE Ni-P hybrid coating, online wash and wide pitch nozzles. Also RT22 nickel-aluminide coating has superior rupture properties of Ni-base superalloy blade material in saline atmosphere [17].

Jonas and Machemer [18] discussed the basics of corrosion, steam and deposit chemistry, and steam turbine corrosion and deposition problems, their root causes and solutions. The most deleterious impurities, which reduce fatigue strength of turbine blades, are NaCl and NaOH. The important role of corrosion pit and intergranular fracture were stressed in corrosion fatigue failure for steam turbine blade [19]. Published literature of EPRI [5] shows that corrosion fatigue resistance of shot peened 12% Cr steel does improve in 22% Nacl solution. Prabhugaunkar et al. [20] studied and investigated the role of shot peening on surface residual stresses and its effect on SCC and corrosion fatigue has been investigated in 3.5% NaCl solution. They concluded that higher peening depth is beneficial for improving corrosion resistance. Other surface treatments for protection against corrosion, such as coatings and electroplating, have been evaluated [21].

2.2 Fretting Fatigue Failure

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One common area for fretting failures to occur is blade/disk attachment at the fir tree joint as shown in figure 2, in gas turbine engines is one of critical components which can fail due to fretting fatigue [22]. Although this joint is nominally fixed, micro-scale relative movement at the interface occurs between contacting bodies experience both centrifugal and oscillatory tangential movement vibrations [23] resulting in damage and causes a significant reduction in fatigue life [24]. This phenomenon is known as fretting fatigue and often occurs in the blade and disk attachment region of gas turbines and jet engines [25].

Figure 2: The remaining fir tree root region of the fractured blade [27]

The fretting cracks are initially quite small, but may eventually lead to severe component damage. Eliminating or reducing slip at the interface is the only method for preventing fretting fatigue, and it must be accomplished during the design process [26]. Fretting fatigue leading to crack nucleation, growth, and eventually failure faster than that under the conventional fatigue condition without fretting (plain fatigue) [27]. A complex interaction between high cycle and low-cycle fatigue leads to fretting-fatigue induced failure in turbine disks [28].

Based on fractographic observations many researchers find three distinct regions of fracture surface a fretting fatigue zone created by crack propagation [29], a crack growth zone and a tensile region which gives rise to fracture of specimen when it is sufficiently weakened by the crack zone development were identified on the failure surface of the fractured blade which had failed at the top firtree root in the blade/disc joint as shown in figure 3 and transition from stable cyclic crack growth to unstable fast fracture was accompanied by a change from transdendritic to interdendiritic fracture mode.

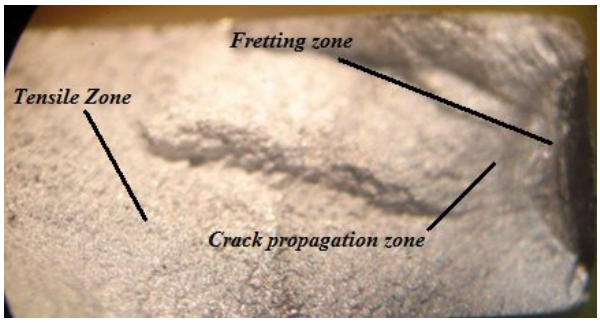

Figure 3: Fracture surface of a specimen after failure by fretting fatigue [29]

The formation of typical striation markings characteristic of progressive crack growth under high cycle fatigue conditions [30]. Therefore, a complex interaction between high cycle and low-cycle fatigue leads to fretting-fatigue induced failure in turbine disks [28].

Barella et al. [26] studied the fracture on the 3rd stage turbine blade of 150 MW unit of a thermal power plant located at the top fir tree root. They identified that fracture mechanism was high cycle fatigue originated by fretting on the fir tree lateral surface (i.e. fretting fatigue) and concluded that the absence of shot peening at the time of refurbishment is a relevant cause of failure. Tang et al. [31] investigated the cause of failure of low pressure aero turbine (LPT) blade. Borescope inspection reported intermediate pressure turbine (IPT) and LPT airfoil damage. The fracture mechanism of first stage LPT (LPT1) blade which caused the in-flight shutdown was fretting fatigue. Farhangi and Fouladi Moghadam [27] investigated the fracture of second stage Udimet 500 superalloy turbine blades in a 32 MW unit in a thermal power plant. Detailed examinations of the blades indicated that the primary failure event was related to the fracture of a turbine blade at the top fir tree root.

Hojjati Talemi et al. [32] investigated the effect of elevated temperature on fretting fatigue life of Al7075-T6 and further the effect of temperature is studied using numerical codes such as ABAQUS and FRANC2D/L. They validate the numerical results by fretting fatigue tests. Also Mutoh and Satoh and Jina et al have been examined Fretting fatigue life of materials. The Palmgren–Miner linear damage hypothesis is very widely used for the prediction of life under conditions of varying or changing stress amplitudes. Namjoshi and Mall [28] Investigated the fretting-fatigue behavior of titanium alloy Ti-6Al-4V, which is typically used for blades and disks in turbine engines, under a variable-amplitude (V-A) fatigue loading and compares linear cumulative damage rule with non-linear method of damage accumulation, the Marco–Starkey cumulative damage theory, to predict the fretting fatigue life of Ti-6Al-4V alloy during V-A loading. Namjoshi and Mall concluded that a non-linear method of damage accumulation is more appropriate than a linear method for estimating the fretting-fatigue life under the variable amplitude loading.

Traditionally there have been two predominant methods for preventing fretting failures in dovetail joints.

1. Coatings are commonly used because they would rub away preventing cracks from initiating and parts from coming out of tolerance.
2. Shot peening is used to induce compressive residual stresses in the body and roughen the surface. Compressive residual stresses increase fatigue life while roughening the surface reduces adhesion.

Cu-Ni-In is commonly used coating for resistance to fretting fatigue in compressor blade root dovetail joint. Selivanov and Smyslov [33] examined Titanium alloy BT6 specimen for various surface treatment methods from surface defects development at fretting corrosion and concluded that that nitrogen ionic implantation with subsequent vacuum plasma coating deposition of titanium nitride (Ar + i.i. + Ti) was the most perspective method to increase fretting resistance of titanium alloys. Shepard et al [34] demonstrated the

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feasibility of using advanced CNC controlled low plasticity burnishing (LPB) process for improve fretting fatigue performance, the performance of LPB treated Ti-6Al-4V specimens was superior in terms of enhanced surface finish and the deeper, more thermally stable compressive residual stresses.

Shot peening and ultrasonic impact treatment (UIT) method used for treating fretting fatigue, thereby inducing compressive stresses under the surface to increase the fatigue strength [26]. UIT removed tensile stresses to a greater depth. More recently it has been demonstrated that other surface treatment approaches, such as laser shock processing (LSP) can have a beneficial effect on fretting fatigue performance.

2.3 Fatigue Failure

Steam/Gas turbine blades are subjected to very high levels of stress and temperature during each engine operating cycle and due to vibrations produced in the turbine during transient loads the predominant blade failures are due to fatigue. A study conducted by Dewey and Rieger [35] reveals that high cycle fatigue alone is responsible for at least 40% failures in high pressure stages of steam turbine. In the year 1992 another study was also conducted by the Scientific Advisory Board of the US Air Force and concluded that high-cycle fatigue (HCF) is the single biggest cause of turbine engine failures in military aircraft [36]. The blades in a turbo-machine experience resonance in transient conditions, when the rotor accelerates or decelerates during start-up or shut-down operations and the instantaneous nozzle passing frequency or its harmonics coincide with any of the natural frequencies of the blade [14]. Mazur et al. [37] studied the effect of the pressure fluctuation, flow recirculation and counter flows, in conjunction with the negative incidence angle flow striking on the blades, can develop excessive vibratory stresses causing fatigue fracture. It is important to limit the dynamic stresses under such conditions of operation to avoid fatigue failure and increase the life of the turbine [38]. Most of the researchers concluded that for fatigue failure, when a cracked blade was investigated under fractography using SEM, the crack observed is usually of transgranular type at low temperature [37; 42; 53] and beach marks found on the fracture surface [39].

The distinction between high-cycle fatigue and low-cycle fatigue is made by determining whether the dominant component of the strain imposed during cyclic loading is elastic (high cycle) or plastic (low cycle), which in turn depends on the properties of the material and on the magnitude of the stress. Blade airfoil fatigue fracture was probably originated during transient events (low load and low vacuum) and not during continuous (stable) operation under vibratory stresses.

Mazur et al. [37] investigated the failure of last stage turbine blades. On the basis of metallographic examination, unit operational parameters, blade/rotor natural frequencies, blade stresses and fracture mechanics. Mazur et al concluded that the L-0 blades failure initiation and propagation was driven by a high cycle fatigue mechanism. This conclusion also indicates that fatigue failure of the blades was not originated during continuous operation under vibration stresses, but during transition events. Mazur et al. [40] also investigated last stage (L-0) turbine blades failure at a 28 MW geothermal unit. Blades had cracks in their airfoils initiating at the trailing edge, near the blade platform. Based on the analysis of results from the last stage blade metallographic examination, unit operational parameters, blade natural frequencies and blade stresses, they concluded that the blade high cycle fatigue failure initiation and propagation by erosion/corrosion processes.

Romeyn [41] in his study of aero engine fatigue failure observed that alternating stresses may be created in turbine blades through the excitation of a resonant state through variations in gas impulse loads and these variations were due to the creation of a non-uniform temperature and pressure distribution across the face of the turbine through abnormalities in the combustion process, and the creation of gas velocity differences through abnormalities in the shape of individual turbine nozzles. Author concluded that the turbine blade failure is primarily due to High cycle fatigue cracking developed at the location of the flexural node and recommended that by maintenance directed at maintaining uniformity of the combustion process and uniformity of the shape of turbine blade the HCF failure can be prevented.

Kim et al. [42] performed low cycle fatigue tests on GTD-111 superalloy in order to predict the low cycle fatigue life at different temperatures. The fatigue lives that were predicted by Coffin-Manson method and strain energy methods were compared with the measured fatigue lives at different temperatures. Authors concluded that the stress range decreases and plastic deformation area increases with increasing of temperature and presents cyclic hardening behavior. Kim [43] studied the fracture on the blade in an aircraft gas turbine to see the cause of crack initiation. The turbine blades of Ni-base superalloy were fabricated by directional solidification (DS) investment casting. The crack initiated at the trailing edge of the blade and propagated by the fatigue under the cyclic loading experienced by the blade during service. Kubiak et al. [44] investigated the catastrophic failure of 150MW gas turbine which experienced a forced break down because of extremely high vibrations. Before the break down, the turbine was operated by approximately 1800 hours in intermittent mode, with a record of 65 start-ups in total. They were found that the blades mainly destroyed were from the first row of the moving blades, with four missing blades. The results of further investigation lead to establish that the former cause of the blade failure was low cycle fatigue that originated a crack in the securing pin hole (stress raiser) located at the root of the blade and propagated.

Resonance of second type axial vibratory mode with nozzle passing frequency was the source of high cycle fatigue load [41; 45; 46]. Zi-Li Xu [45] investigated the Cracking of blade fingers occurred in a few numbers of low pressure 1st stage steam turbine blades. The cracking of the blade finger has been caused by the high cycle fatigue, and surface defect coming from rough machining induces the initiation of crack. Based on the investigation done on the fractured blade by Zi-Li Xu revealed that resonance of second group axial modes with nozzle passing frequency was dangerous for blade groups, and by changing the number of blades in the blade group is an effective way to adjust the natural frequency to avoid axial mode resonance.

Park et al. [47] investigated the fracture of a turbojet engine turbine blade and observed that the turbine blade had

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initially cracked by a fatigue mechanism over a period of time and then failed by overload at the last moment. The cracked turbine blade was severely damaged by hot gas flow and discolored. This heat damage made the gamma prime phase in the matrix (Ni-base super alloy) coarsens and lowered the fatigue strength of the base material assisting to the premature fatigue fracture. The decrease of the strength of the material due to degradation of gamma prime phase was verified by hardness measurements. The possible relevance of other parts attached to the engine shaft to the fracture was also reviewed.

Hou et al. [46] employed a non-linear FEM to determine the steady-state stresses and dynamic characteristics of the turbine blade. The steady-state stresses and dynamic characteristics of the blade were evaluated and synthesized in order to identify the cause of blade failures and a pre-stressed modal analysis was performed to examine the dynamic behaviour of the blade and disc assembly under service conditions. From the analysis Hou et al concluded that the first bending vibration mode was not a significant contributor to failure. The second vibration mode is a possible cause of fatigue because the maximum stress corresponding to this mode is coincident with the point of crack initiation. Wang et al. [39] constructed fault tree to analyze the possible causes for final stage blade cracking of the low pressure blades of steam turbine. It was found that the failure mechanism of blades is the environment assisted fatigue fracture. In order to decrease the blade cracking susceptibility author recommended that the suction side of low pressure blade was heat treated through high-frequency quenching method, corresponding temper and shape-righting followed.

Bhaumik et al. [48] analyzed the failure of a blisk that took place during the development runs of an aircraft engine for a specific application. Cracks were observed at the trailing edge of the blades of a turbine rotor blisk of a gas turbine engine during inspection. The factors responsible for such cracking were the unfavorable columnar grain orientation in the airfoil and high operating temperature. Once the initial crack is formed due to stress rupture, it is natural that the crack will propagate under the cyclic loading experienced by the blade during service. The presence of beach marks and striations confirmed the second stage growth of the crack by a fatigue mechanism. Author recommended that coarse columnar grains with high aspect ratio in the airfoil section will improve the elevated temperature strength and stress rupture property. Jayakumar et al [13] investigated and concluded that the most of the failures in the aero-engine turbine blades are due to microstructural changes at elevated temperatures, hot corrosion and degradation of mechanical properties leading to creep and creep fatigue failure.

Singh et al. [49] presented a case study for failure of steam turbine blade caused by natural frequency shift due to solid buildup. In their study the damage was believed to have been caused by a solid build up at the blade root that shifted a natural frequency into an interference region, and changed the response characteristic of the bladed disk assembly.

A major technical challenge of the US Air Force is to reduce turbine engine blade high cycle fatigue failures. To prevent HCF failures, design methodologies are required that identify the critical levels of precursory microstructural damage which can lead to such failure [36]. With probabilistic method approach turbine blade designers can design blades to avoid high cycle fatigue failure. The use of probabilistic methods give engineers a more thorough understanding of how the parameter variations affect the distribution in response. These failures are driven by variations from nominal design geometry that causes variation in the blade natural frequency and modal stress. Improved reliability will be achieved by more accurately accounting for variation in response with probabilistic methods. Brown [50] presented a probabilistic methodology that uses MSC.Nastran to predict the probability distributions of blade frequency and modal stress. Brown used Monte Carlo sampling method. Each Monte Carlo iteration obtained random blade geometry, modifies a MSC.Nastran data file, runs the solution, and stores the new frequency and modal stress values. The distribution of response gives the engineer a broader understanding what input variations are influential on response variation and the margin their systems have.

The coating crack initiation was probably due to a thermal fatigue mechanism, as a result of high thermal transient loads (i.e., trips, start-ups, and slow-downs) and crack grain boundary initiation and propagation in the substrate by a creep mechanism (high steady state loads) [51]. The substrate intergranular crack initiation and propagation were due to a creep mechanism [52]. The nickel-base superalloy alloy commonly used for gas turbine blades is strengthened by precipitation of γ' phase [47]. The microstructural changes due to blade operation at high temperature include irregular growing of γ' particles (rafting) and formation of carbides in grain boundaries and matrix. The γ' elongation in nickel-base alloys is related to gradual decrease of the total blade life and leads to alloy creep properties reduction [51].

Mazur et al. [51] carried out the failure analysis of the 70 MW gas turbine first stage blades made of nickel-base alloy Inconel 738LC. The blades experience internal cooling hole cracks in different airfoil sections assisted by a coating and base alloy degradation due to operation at high temperature. A detailed analysis of all elements which had an influence on the failure initiation was carried out. It was found that the coating/substrate crack initiation and propagation was driven by a mixed fatigue/creep mechanism. Naeem et al. [52] investigated the failure analysis of a gas turbine with first and second stage blades made of nickel-based alloy. Micro-cavities were found on fracture surfaces that served as an origin of a creeping failure mechanism, decreasing of alloy ductility and toughness due to carbides precipitation in grain boundaries, and degradation of the alloy γ' phase (irregular growing of γ' particles). Finally, it was concluded that the cause of the rotor blade failure may be increased in blade length and contact between blade tip and casing as a consequence of creep after an extended period in service.

Aside from alloy improvements, a major breakthrough was the development of directional solidification (DS) and single crystal (SC) production methods. These methods help greatly increase strength against fatigue and creep by aligning grain boundaries in one direction (DS) or by eliminating grain boundaries all together (SC) [53]. Another major improvement to turbine blade material technology was the development of thermal barrier coatings (TBC). Where DS and SC

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developments improved creep and fatigue resistance, TBCs improved corrosion and oxidation resistance, both of which become greater concerns as temperatures increased [54]. Further from the various surface enhancement processes the laser peening process have greater advantage to increase the resistance of aircraft gas turbine engine compressor blades to foreign object damage (FOD) and improve high cycle fatigue (HCF) life. [55] The process creates residual compressive stresses deep into part surfaces – typically five to ten times deeper than conventional metal shot peening. Laser peening may also be referred to as laser shock processing (LSP).

Conclusions

Based on literature and studies reported above, following conclusions can be drawn.

1. Low pressure turbine blades are the critical component in any steam/gas turbines and corrosion fatigue has caused most of the damage in that part of the turbine due to wet/dry transient zone. Further, presence of corrosion pits and intergranular cracks initiates the corrosion fatigue cracks which results in failure of low pressure (LP) turbine blades. However, the efficiency of LP turbine blades can be enhanced by taking proper protective measures against corrosion such as surface treatment techniques, improve blade design and online washing.
2. Fretting fatigue is the cause of failure that generally occurs at the top of the blade root. To avoid this, fretting fatigue resistance can be increased by advance coating techniques, laser shock processing treatment, low plasticity burnishing process, shot peening and ultrasonic impact treatment.
3. High thermal transient events/loads are the main cause to produce high cycle fatigue failures in high pressure (HP) steam/gas turbine blades. To avoid this type of failure designers generally used probabilistic method approach for design of blades.
4. By the use of directional solidification (DS) and single crystal (SC) production methods of turbine blades, strength against fatigue and creep failure can be increased. Further for the high temperature operated gas turbine blades the thermal barrier coating (TBC) have been suggested to increase the resistance against hot corrosion and oxidation.

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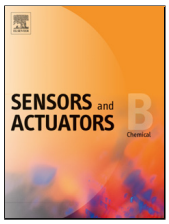

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A Micro Interdigitated Thin film Metal Oxide Capacitive Sensor for Measuring Moisture in the range of 175-625 ppm

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Abstract

In this paper we present the development of a nano-structured hyper thin film sensor for the measurement of humidity in ppm level using the micro sized interdigitated electrode capacitive structure. The sensor electrode has been fabricated using the optical lithography technique on the oxide sensing film deposited on the quartz substrate. The nanoporous metal oxide thin film of γ-Al_2O_3 has been fabricated by simple sol-gel drop coating method. The electrical characteristics of the sensor have been determined in the moisture range from 175 to 625 ppm by Agilent 4294A impedance analyzer at 1 kHz, 50 kHz and100 kHz respectively. The sensor has excellent yield ratio because of complete avoidance of shorting problem of the electrode. The response time is very fast (T_r = 12s) in comparison to the conventional commercial parallel plate gold electrode capacitive thin film aluminium oxide sensor. The proposed sensor can be useful for

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measuring moisture dispersion inside electronic gadgets and packages where the performance of the devices is deteriorated due to moisture entrapment.

Keywords: Interdigitated electrode, sol-gel thin film, capacitive moisture sensor, electrical characteristics

1. Introduction

Moisture measurement in ppm level below 1000 ppm is still a notorious challenging issue [1]. There are numerous applications where moisture measurement in ppm or ppb level is required [2]. Most of the sensors found application in RH range [4, 5]. Large numbers of research articles on humidity sensors are published in various journals but the literature of moisture measurement in ppm level is [3, 6]. The moisture sensors for industrial applications must have good sensitivity, low response time, good reproducibility, small hysteresis, long lifespan, resistance against contaminants, negligible temperature dependence and low cost [7]. The sensitivity, resolution and stability are very important characteristics for humidity sensors used in certain special gases applications [2, 4]. Yield ratio, which represents the success of the sensor fabrication, and is another important parameter which can significantly affect the overall cost of the sensor is rarely mentioned in the literature. The alumina thin film sensor is used as an absolute sensor and it is suitable for large dynamic range moisture measurement [7]. Among different technologies employed for moisture measurement in trace level [8, 9], the parallel plate capacitive alumina sensor offers low cost solution, but the cost of such sensor is still high in ppm range. A single sensor costs around 1000-1200 US dollar for ppm range measurement whereas a RH sensor is available for only 20-30 US dollar or even less [3].

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Table I COMPARISON OF PPM LEVEL MOISTURE SENSORS IN THE LITERATURE

Prior Art	**Response time (s)**	**Recovery time (s)**	**Sensitivity**	**Hysteresis**	**Operating range (ppm)**	**Technologies**
Faramarz Hossein-Babaei [10]	~ 120	~ 600	2Ω/ppm	Not study	1 – 5000	Resistive humidity sensor
Xentaur Corporation (LPDT, USA) [11]	180	NM	0.5pF/ppm	Not available	NM	Al_2O_3 Capacitive Sensor
Shaw [12]	20	< 120	1.05pF/ppm	1%	0 – 1000 ppm	Capacitive Sensor
GE [13]	5	10	-	2%	-80 to 20^{0}C	Planar gold/aluminum oxide capacitance
K-Sen Gupta[14, 15]	67	121	4.2pF/ppm	Not available	1-10%RH	Al_2O_3 Capacitive Sensor
	30	40	1.5pF/ppm	Not available	4-18ppm	Al_2O_3 Capacitive Sensor
T. Islam [16, 17]	47	118	2.24pF/ppm	0.33%	2.5-25ppm	Al_2O_3 Capacitive Sensor
	158	216	0.13pF/ppm	Not available	3.5-800	Al_2O_3 Capacitive Sensor
Xiaolei Shi [18]	≥ 120	160	15nm/100ppm	Not available	10-200ppm	Al_2O_3 coated microcantilevers (MCLs)
Zhi Chen [1]	5	5	NM	0.043 pF/ppm	0-23000ppm	Capacitive anodic spark Al_2O_3

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Because of the disadvantages of all practical moisture measurement systems, there is an urgent need to design and fabricate a sensor which can work in corrosive and contaminating gaseous environment is sensitive and fast enough to sudden and drastic changes of moisture, requires minimum maintenance and is available at low cost with relatively long calibration period. To obtain a low cost sensor for trace level moisture measurement, several works utilizing sol-gel aluminium oxide thin film have been recently reported in literature [15-19]. The salient response characteristics of the aluminium oxide sensors available in commercial dew point meters and in literature are given in Table 1. Most of the sensors employ parallel plate capacitive structure with costly gold electrode. From the table we observed that most of the parallel plate capacitive sensors have high response and recovery time [10 -12, 15- 18], high hysteresis [12, 13] and there is no data for yield ratio. A very fast and long term stable alumina moisture sensor has been reported in [2] but the device has very small sensitivity from 0-1000 ppm moisture and there is no data about the yield ratio. Also in [2, 12-13] response time is determined over a wide humidity range. Even if the nanostructure sensing layer of high surface area in thin film form may offer high sensitivity, resolution, fast response and recovery, high reproducibility, low hysteresis [16-17], the small thickness of the film in case of parallel plate capacitor sometimes shorts the electrodes which ultimately affects the yield ratio of the sensor. The failure of the device fabrication will cause the wastage of costly gold electrode and hence will affect the overall cost of the sensor. The preparation of thin film metal oxide includes sputtering, chemical vapor deposition, pulsed laser deposition, electrochemical anodization and recently sol–gel process [2, 14-17]. Of these processes sol–gel deposition has attracted recently significant interest due to the excellent compositional control and homogeneity of the film at lower crystallization temperature, combined with deposition of thin film of few hundreds of nanometer

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thickness [20, 22]. The interdigitated electrode is most often used in RH level humidity sensor [2]. The interdigitated electrode eliminates the electrode shorting problem even though the sensing film is of few hundreds of nanometer thickness. There is no work reported so far as our knowledge is concerned to sense moisture below1000 ppm using interdigitated capacitive hyper thin film of Al_2O_3.

In the present work we have investigated the fabrication of interdigitated micro electrode capacitive aluminium oxide hyper thin film of nearly 10-20 nm thickness for ppm level moisture detection. The nanostructure of high specific surface area γ-Al_2O_3 has been obtained by sol-gel method [23]. Thin film of Al_2O_3 was prepared by drop coating technique on quartz substrate. The effective sensing area is varied by varying the dimension of the microelectrode deposited on the quartz substrate using the optical photolithography technique. The device offers fast response and recovery time, negligible hysteresis and excellent yield ratio, whereas the fabrication completely eliminates the shorting of electrode.

2. Working of the microsize interdigitated capacitive sensor

It has been investigated that keeping pore morphology of nanostructred thin film identical, the sensitivity can be increased by simply optimizing the configurations of both bulk parallel plate or membrane type interdigitated capacitors [18, 24]. However, if the electrode area increases, the size of the device will increase and it will create problems when packaging the sensor in the small sample chamber. But if we make several identical parallel plate capacitors (interdigitated) on the quartz substrate and connect them in parallel, we can significantly increase the sensitivity without increasing the device size. Also, if the gap between the fingers is reduced to very a small

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value (few μm), the sensitivity of an interdigitated capacitor (which is normally used in RH range) can be improved to a great extent for ppm level as well. Hence it may be possible to measure the humidity in ppm level below 1000 ppm by utilizing the micro size interdigitated electrode deposited on thin film of highly hygroscopic metal oxide film. In our earlier work (or in other publications), the capacitive humidity sensor was fabricated on one side of alumina substrate by depositing the sensing film in-between the gold plates using the sol-gel dip coating method. It has the disadvantage that identical thin sensing film deposited on the opposite side of alumina substrate remains unused [11, 14-17]. In addition, due to small thickness of the sensing film, sometimes electrodes get shorted causing device failure. The thickness of the film plays an important role in improving the sensitivity and it is also an important feature of the sensor. For the parallel plate capacitive structure generally employed in commercial aluminium oxide based dew point meter, the thickness of the aluminium oxide film cannot be reduced in nm [11-12]. This is because such small thickness will short the parallel plate electrodes causing failure of the sensor which finally affects the yield ratio of the device. This shorting problem can be totally avoided in interdigitated capacitive humidity sensor although the thickness of the sensing film is very small. The schematic of the structure proposed is shown in Fig. 1. The total capacitance C_{IDT} of the micro IDT can be determined from the following equation given in [25].

$$C_{IDT} = C_{UC}(N-1)L \tag{1}$$

where C_{IDT} is the capacitance of the micro IDT, C_{UC} is the capacitance of unit cell in the structure, N is the number of fingers and L is the length of each finger. C_{UC} can be further written or the IDT structure

$$C_{UC} = C_1 + C_2 + C_3 \tag{2}$$

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The capacitance C_1 and C_2 are calculated by conformal mapping K[x] of the two semi-planes with dielectric constants ε_1 and ε_2 into two parallel-plate capacitors [25].

$$C_1 + C_2 = \varepsilon_0 \frac{\varepsilon_1 + \varepsilon_2}{2} \frac{K\left[\left(1 - \left(\frac{a}{b}\right)^2\right)^{1/2}\right]}{K\left[\frac{a}{b}\right]} \quad (3)$$

where a is the gap between the two fingers, b is the distance between the adjacent fingers, ε_0 is the dielectric constant in the free space, ε_0= 8.8542 $\times 10^{-12}$ F/m and ε_1 and ε_2 are the dielectric constants of the substrate and the sensing film in presence of moisture. The capacitance C_3 is given by

$$C_3 = \varepsilon_0 \varepsilon_2 \frac{h}{a} \quad (4)$$

where, h is the thickness of the finger. As the gap (a) between the fingers is inversely related with C_3, decreasing the gap between the electrodes or increasing the number of fingers (actual sensing area) may increase sensitivity towards lower humidity range.

3. Experimental

3.1. Preparation of nanostructure thin film of aluminium oxide and morphology studies

The nanostructure of alumina film having high effective surface area has been fabricated using the sol-gel solution method. The sol solution is prepared by hydrolyzing the metal alkoxide such

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as aluminium sec. butoxide ($C_{12}H_{27}AlO_3$) precursor in excess water [23, 26-28]. The steps followed for the preparation of alumina sol of Al_2O_3 are

(i) Hydrolysis of alumina precursor in excess amount of DI water (1:100)

(ii) The peptization of the sol solution by adding a fixed amount of HCl acid (0.07 mol/mol)

(iii) Refluxing of sol solution to remove organic impurities

(iv) Addition of the binder namely polyvinyl alcohol (PVA) of molecular weight 125,000.

The solid thin film of nanometer thickness has been formed on the polished side of ST-X quartz substrate. Thin film was deposited on the substrate by a drop coating method using Nordson drop coating system (model no 741MD-SS MicroDot). The film was initially dried at around 100°C for few minutes and then sintered at nearly 400°C for 1 hr. The film is properly laminated on the substrate.

The γ-Al_2O_3 nanostructure film was assessed by X-ray diffraction (XRD) using a Philips X'pertpro advance diffractometer with Cu K –α, X-rays of wavelength = 1.541874 Å in the 2θ range of 10–90°, with a scanning rate of 0.05°/s. Experimental results of XRD are shown in Fig 2. The peak intensity indicates the presence of gamma phase of the alumina. By sintering the film at different temperatures, other phases of the alumina can be obtained but the gamma phase gives maximum micro pore volumes and suitable morphology of the porous structure [26]. The pore morphology of the porous alumina has also been characterized by field emission scanning electron microscope (FESEM) using the Carl Zeiss model no SUPRA55 (USA). The resolution

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of the FESEM instrument is 1.5 nm. Fig. 3 shows the FESEM image of the porous structure of the γ-Al_2O_3 at very low magnification of 100 nm. From the FESEM image we see that the pores are almost spherical in shape with smooth surface. The film is highly porous having microspores in the range of 4.9–13.3 nm. The average pore size is around 8.7 nm. The roughness of the surface is studied by the atomic force microscopy (AFM) by using the model no 5600LS of Agilent Technology (USA). Fig. 4 shows the AFM image of the film. The root mean square value of the roughness of the porous surface is 4.6 nm, which is quite significant.

3.3 Fabrication of the micro size interdigitated electrode capacitive sensor

The performance of the micro size interdigitated electrode based capacitive humidity sensor depends on the (i) structure and size of the interdigitated electrode (ii) surface area of the sensing film (iii) pore morphology (iv) thickness of the film and (iv) uniformity of the film. For low level humidity detection, the micro size interdigitated electrode is fabricated on nanostructure thin film of γ-Al_2O_3 of nanometer thickness (10-15 nm). Effort has been made to optimize the dimension of the micro size of interdigitated electrode (IDT) and morphology of the film.

3.4 Fabrication of the micro size interdigitated electrode for humidity sensors:

The micro size interdigitated electrodes are fabricated using the optical photolithography process on quartz substrate having zero temperature coefficient of delay. After proper cleaning of the substrate aluminium (99.999% pure) metallization has been done using the thermal evaporation technique [29]. Using the wet etching process, the aluminium interdigitated electrode has been fabricated on the substrate. The gap between two fingers of the interdigitated electrode (IDT) is only 13.1μm and the device chip size is 30 mm×10mm. To deposit thin layer of sensing film, the IDT of the device was initially cleaned in the oxygen plasma for 60 s at 100cc/min flow and

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100W power. The oxygen plasma removes the undesirable impurities from the IDT of the substrate. The Al_2O_3 film was then deposited on the electrode by dropping the sol- gel solution on the IDT using drop coating system. The sensitive film formed on the electrode was dried in oven at 400 ^{0}C for 1 hr [16, 27]. Thickness of the film has been optimized to increase sensitivity. The Al_2O_3 film thickness has been measured using the SOPRA optical ellipsometry (Sopra Inc., Palo Alto, CA, USA) system. The film thickness of the sensor is in the range of 10-15 nm only. Fig. 5 shows the actual optical photograph of the parallel micro sized electrodes based capacitive impedance sensor device and Fig. 6 shows the sensor cell which has been designed for packaging the fabricated device.

4. Electrical characteristics of the sensor

Electrical characteristics of the sensors were investigated by passing moist N_2 gas to the sensor. The moisture concentration of the moist N_2 gas was monitored by commercial dew point meter. The reference dew point meter employs hyper thin film metal oxide parallel plate capacitive sensor (model no SADPTR-R, SHAW UK) [12]. The measurement range of the dew point meter is 0-1000 ppm with accuracy ± 1 ppm. Both the dew point meter and the sensor were refreshed to the minimum moisture concentration of around 175 ppm with dry N_2 gas at the flow rate of 6 l/m. The concentration of the moisture in the N_2 gas was varied by adding dry N_2 gas and precisely controlled using precision needle valve. Experiments were carried out at room temperature of 25°C. The initial moisture content of N_2 gas cylinder used for creating moist gas with fixed concentration was 3-5 ppm. The concentration level of moist gas for sensors testing was varied from 175 ppm to 625 ppm. The terminals of the sensor were connected to the test fixture of the Impedance Analyzer (Model 4294A, Agilent, USA) with short length shielded

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cable. Care was taken to ensure a minimum capacitance effect of the cable length used for connecting the sensor to the impedance analyzer. The impedance analyzer was interfaced with a PC through a IEEE 488 bus. The sensor was excited with an input ac voltage of 500 mV (rms) and frequencies of 1 kHz, 50 kHz and 100 kHz respectively. The observations recorded in Cp-D mode of the impedance analyzer with moisture variation from 175 to 625 ppm at different excitation frequencies are shown in Fig. 7. It is observed that as moisture level increases, the capacitance value increases. It shows that the sensor has significant change in capacitance above 175 ppm. Up to 350 ppm the capacitance increases almost linearly but above 400 ppm it increases more rapidly. We have noticed in the graph that the slope of capacitance change is much smaller at lower ppm than at higher ppm. The cause of such behavior is different sensing mechanisms at different moisture concentration. Studies have explained that the sensing of water molecules in porous alumina film is governed by (i) chemisorption and physisorption of water vapor, (ii) pore morphology and (iii) the geometries of the electrodes of the sensor [35-36]. The chemisorption of water molecules takes place at lower ppm and physisorption takes at higher ppm [34]. Due to lower concentration of water vapor, high surface area porous film is partially filled causing less change in effective dielectric constant. Thus the little change occurs in capacitance value below 350 ppm. However, when concentration increases, more and more water molecules will be physisorbed on chemisorbed layer and subsequently multilayer physisorbed water molecules will be formed. The physisorbed water molecules will condense in the nano order pores of the film with radius less than the Kelvin radius [30] causing large change in effective dielectric constant of the sensor. The large change in dielectric constant leads to abrupt increase in capacitance value. The sensor has the ability to give response above 625 ppm. To ascertain the saturation level of the sensor further experiments have been carried out that

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confirmed the sensor saturates around 7000 ppm. However, only results up to 625 ppm have been included in the current study, since our aim is to detect the moisture in lower ppm range. The high capacitance change indicates significant variation in effective dielectric constant of the film even though the moisture concentration is in ppm level. For determining the other important parameters such as response (T_r) and recovery time (T_c), the transient response curve of the sensor for step change in moisture concentration from 175 to 625 ppm is shown in Fig. 8. The response of the sensor is very fast. It takes very little time (T_s ~12 s) to raise the output for the step change of moisture. The recovery time of the sensor is also ~12 s which is very small compared to other capacitive humidity sensors reported earlier [12, 14-17]. It is observed that the output of the sensor is stable and recovered fully when the sensor is refreshed by dry N_2 gas. The repeatability of the sensor output for the same humidity change for several cycles is shown in Fig 9, which shows that sensor output is highly reliable and does not deviate for identical repeatable exposure to the moisture. The stability of the sensor output over long periods of time is another important parameter of the sensor. If the output is not stable, it cannot be used for real time applications. The drift of the sensor is determined after 120 days with the same moisture range (175 to 625 ppm) at different excitation frequencies. It has been found that the sensor output stays the same which proves that there is no drift. The results of aging effect of the sensor at 1 kHz excitation frequency are shown in Fig. 10.

5. Results and discussion

Humidity sensitivity is defined as the ratio of change in capacitance (ΔC) to the change in humidity (Δppm)

$$S\ (\%) = \frac{\Delta C}{\Delta ppm} \times 100 \qquad (5)$$

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The basic aim of determining the sensitivity of the sensor is to investigate its utility for sensing moisture in dry gas above 100 ppm level. However, the results show that the sensor is responsive above 175 ppm. The sensitivity of the sensor is determined using the Eq. (5) and it is found to be 14.25 pF/100 ppm which is very good and can be easily measured by the interface electronics circuit [17]. When the sensor is exposed to a certain concentration of humidity thermodynamic phenomena of adsorption and desorption take place. The equilibrium between these two decides the quantity being adsorbed on the film. Vapor molecules initially condense on the porous surface and then condense in the pores through capillary condensation causing change in the effective dielectric constant of the sensor. The response behavior is also governed by other factors namely (1) the pore morphology of the hygroscopic film which includes surface to volume ratio, the average dimension of the pores, the distribution of the pores, thickness of the porous layer, (2) the configuration of the electrode in both size and the gap between the fingers [30]. Capillary condensation of water in the porous matrix depends on the mean free path and size of incident moisture cluster which varies with the change in moisture concentration in the gas. An optimum pore size comparable to the mean free path governed by the Kelvin radius (R_k), given below, is desirable for humidity sensing [21].

$$R_K = \frac{2\gamma M_w \cos\theta}{\rho_w RT \ln(P_w/P_s)} \quad (6)$$

where γ is the surface tension, θ is the contact angle of vapor molecule, ρ_w is the density of water molecules, M_w is the molecular mass, P_w is the water actual vapor pressure, P_s is the saturation vapor pressure at a specified temperature, R is the universal constant and T is the temperature. Thus the size R_K will vary according to the concentration of water the sensor is exposed to. Since R_k varies with different moisture, the distribution of nano order pores is also important. To obtain desired sensitivity for measuring humidity in trace level, the optimum pore size should be in the nano meter range [30]. The morphology of the nanostructure, electrode geometry and the dielectric constant of vapor molecules have a significant role in improving the characteristics of the sensor [31-33]. It has been noticed that as the sensing area of the sensor increases the sensitivity increases. It is obvious that as the area will increases more water molecules would be adsorbed in the nanostructured porous film resulting in an increase in change of the effective dielectric constant and in more capacitance change with moisture. The actual sensing area of the

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interdigitated electrode for the same device size is much smaller than the area of the parallel plate capacitive structure. Since the concentration of moisture below 175 ppm is not sufficient to cause the measurable change in effective dielectric constant, the sensitivity is insignificant.

The response and recovery times of the sensor are very fast (T_r = 12s) because, the sensor takes very little time to reach 90% of its maximum value and takes very little time to desorb during degassing to the initial value (due to the very thin sensing layer).

Hysteresis error, which is the percentage deviation of capacitance value at the same moisture level measured for both increase and decrease in moisture is found to be ~0.24%. As shown in Fig.11 the sensor shows negligible hysteresis when it was exposed to humid gas in reverse order. This happens because the sensor is coated with a thin sensing layer of Al_2O_3 where the moisture desorbs quickly [34]. Generally speaking the hysteresis is normally observed for any humidity sensor which is having a porous film and works on adsorption and desorption phenomenon. Due to incomplete adsorption and desorption of water molecules hysteresis error arises and for a good sensor it should be as small as possible. The hysteresis error also depends on the pore morphology and the sensing layer thickness [19]. Furthermore, it can be ascertained that the capacitance change from 175 ppm to 350 ppm is almost linear but for the full range (175ppm to 625 ppm) the response is nonlinear, as shown in Fig 12. This nonlinear curve can be linearized by dividing the response in two linear segments, one for 175 to 350 ppm and other for 350 ppm to 625 ppm, as shown in Fig. 13 (a) and Fig 13 (b) respectively. The output of the sensor is free from drift due to aging, as observed in Fig. 10. The impedance change from 175 to 625 ppm is almost linear and quite significant, as shown in Fig. 14. Because of very small film thickness (10-15 nm), and very small gap between the electrodes (13.1 μm), improved electrical characteristics of the sensor are observed. Table II summarises the important specifications determined from experimental results for measuring humidity in ppm.

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Table II PARAMETERS OF THE SENSOR

Operating moisture range	175-625 ppm
Nominal capacitance	100 ± 1 pF
Sensitivity	14.25 pF/100ppm
Response time(t_{90})	12s (175-625 ppm)
Recovery time (t_{90})	12s (175-625 ppm)
Nonlinearity	1.05% (max [(C/Cmax) × 100])
Hysteresis	0.24% (at 175ppm)
Drift due to aging	Negligible
Operating frequency range	1 kHz ,50 kHz and 100 kHz

7. Conclusions

The present work proposes a micro size interdigitated electrode thin film moisture sensor with large sensing area fabricated by modern optical lithography technique. The characteristics of the moisture sensor were examined for 175 to 625 ppm moisture content in controlled moisture level gas, for 14.25pF/100ppm sensitivity. We have found that the sensor shows improved response characteristics in comparison to the sensors reported in the literature. For trace level humidity, pore morphology, thickness of the film and sensing area play an important role for a sensitive detection of humidity. It is known that thin film porous alumina based parallel plate sensor fabricated on alumina using gold electrode is used for trace moisture detection but they suffer

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from very poor yield ratio. Therefore the proposed micro size interdigitated electrode thin film sensor fabricated using optical lithography has excellent yield and can be used to detect trace moisture. However further improvement is necessary to sense the moisture below 175 ppm.

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Fig. 1 Schematic structure of interdigitated electrode.

Fig. 2 XRD results of γ-Al_2O_3 film deposited on quartz substrate.

Fig. 3 Field emission scanning electron micrograph (FESEM) of the nanoporous structure of γ-Al_2O_3 film deposited on quartz substrate.

Fig. 4 Atomic force micrograph of the nanoporous structure of γ-Al_2O_3 film deposited on quartz substrate.

Fig. 5 Microscopic image of the interdigitated electrode structure of the sensor.

Fig. 6 Photograph of the package with fabricated humidity sensor.

Fig. 7 Capacitance change of the thin film sensor with variation of humidity in the range of 175-625 ppm at different excitation frequencies.

Fig. 8 Transient response of the sensor for step change in humidity from 175 to 625 ppm.

Fig. 10 Aging effect of the thin film sensor for the 175-625 ppm humidity.

Fig. 11 Hysteresis effect of the sensor output for both increase and decrease in humidity from 175 to 625 ppm.

Fig. 12. Third order polynomial fitting of the capacitance change of the sensor with variation of humidity in the range of 175-625 ppm

Fig. 13. Approximate linear capacitance change of the sensor with variation of humidity (a) 175-350 ppm (b) 350-625 ppm.

Fig. 14. Impedance response (Z) of the sensor for increase in humidity from175-625 ppm.

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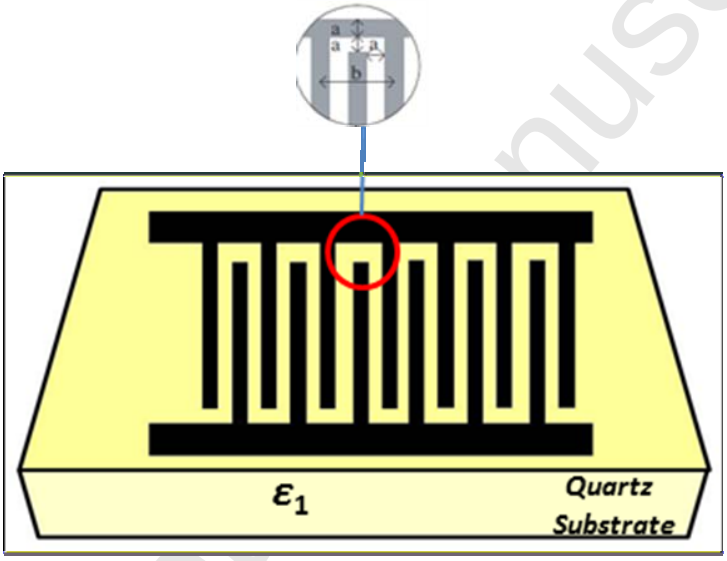

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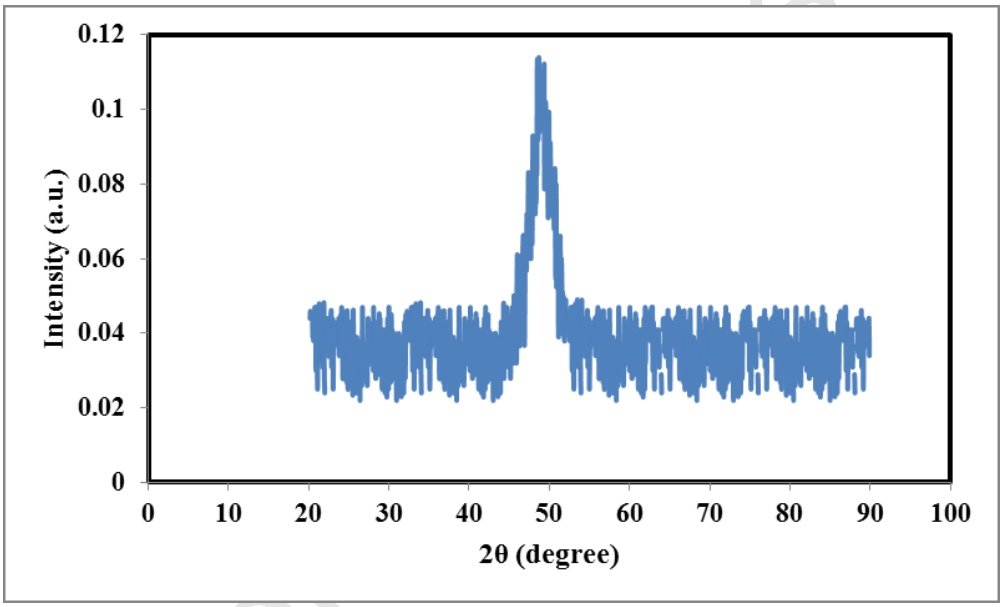

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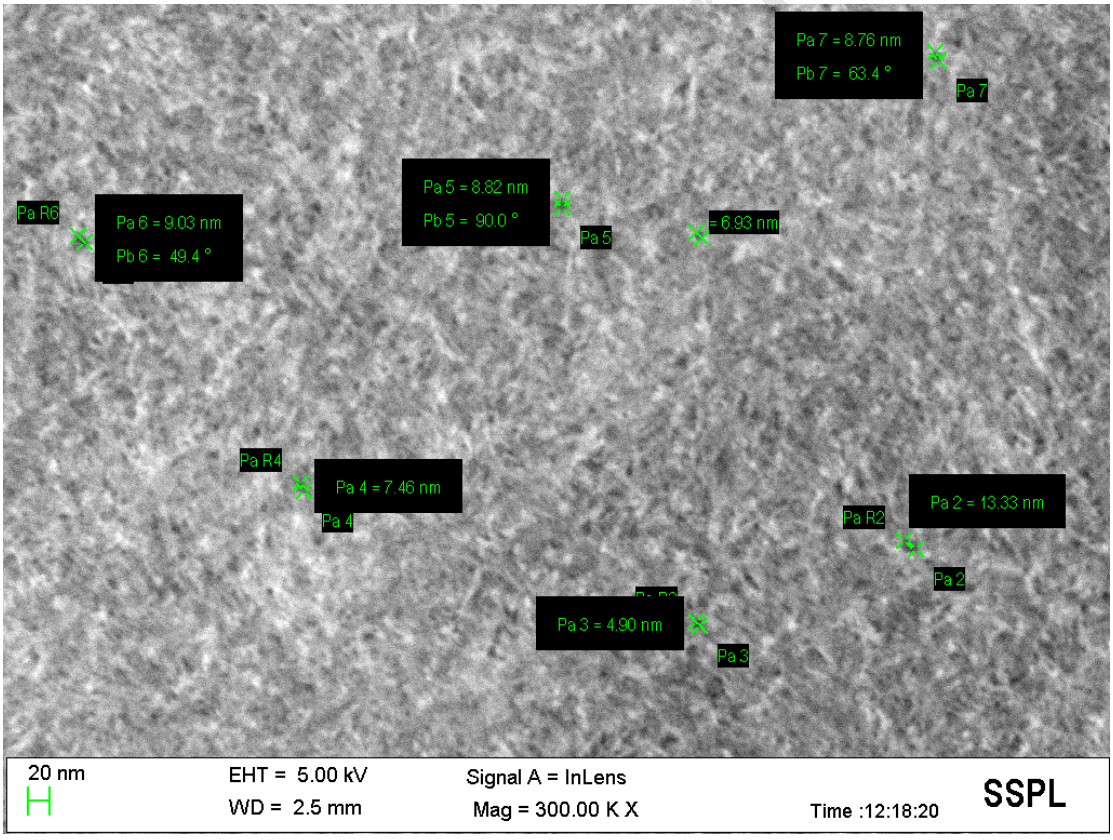

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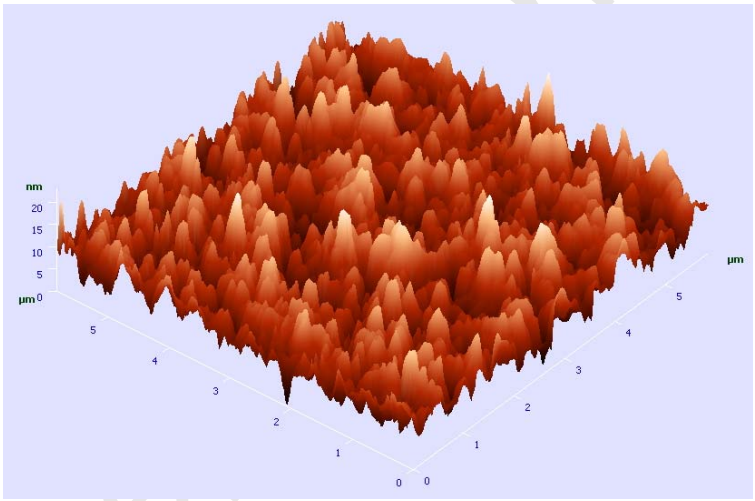

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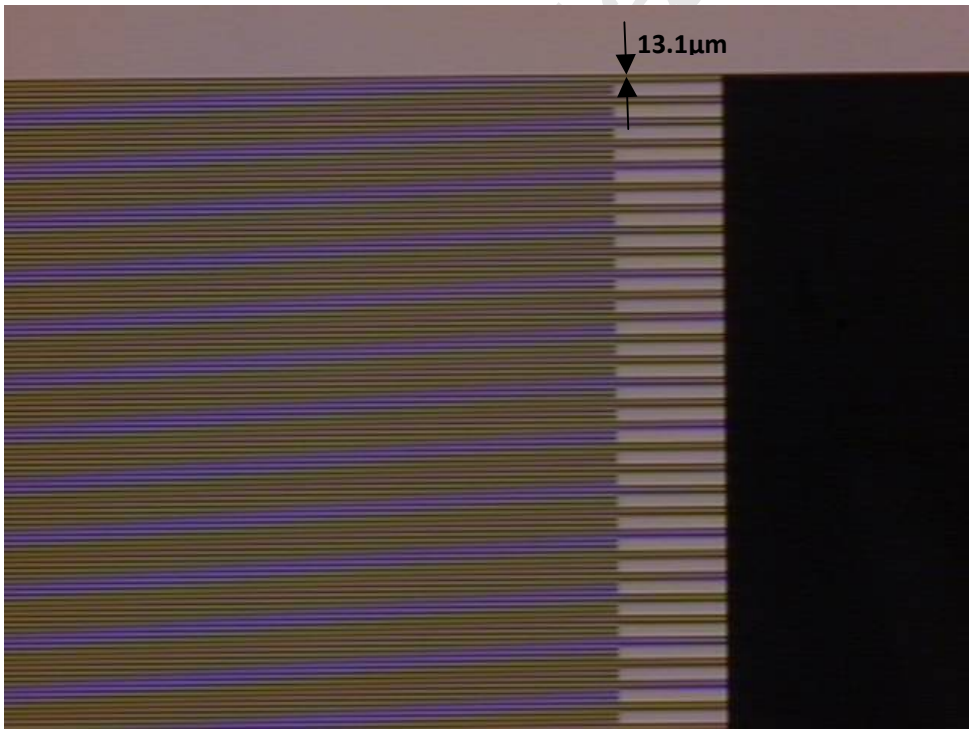

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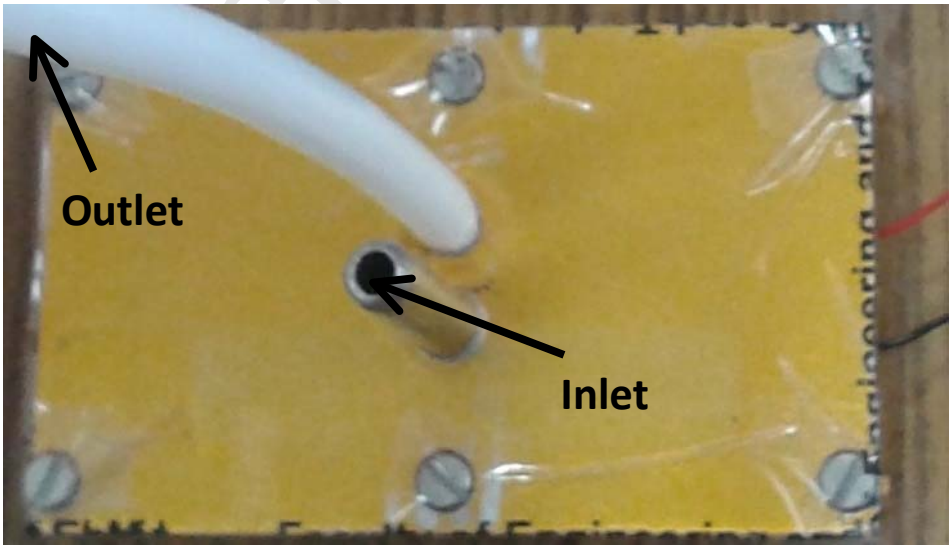

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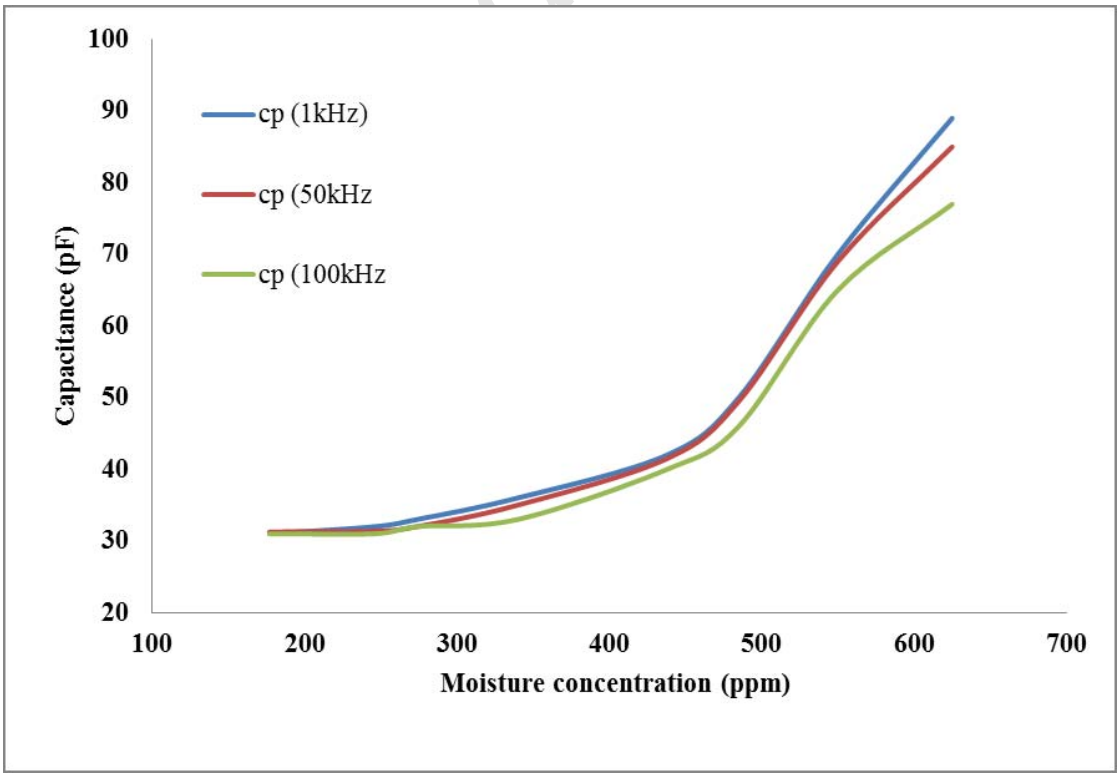

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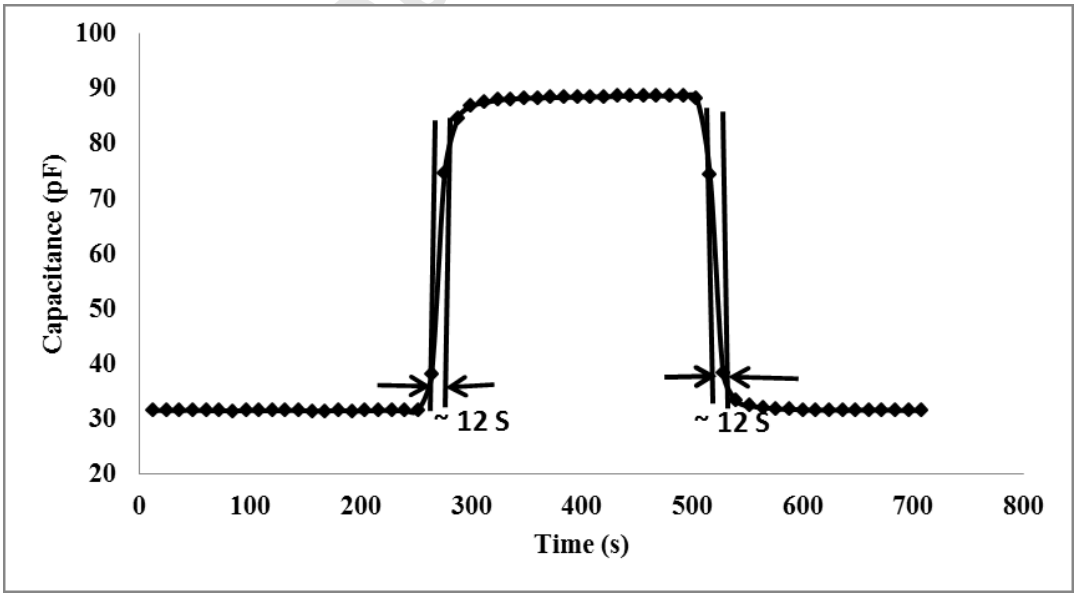

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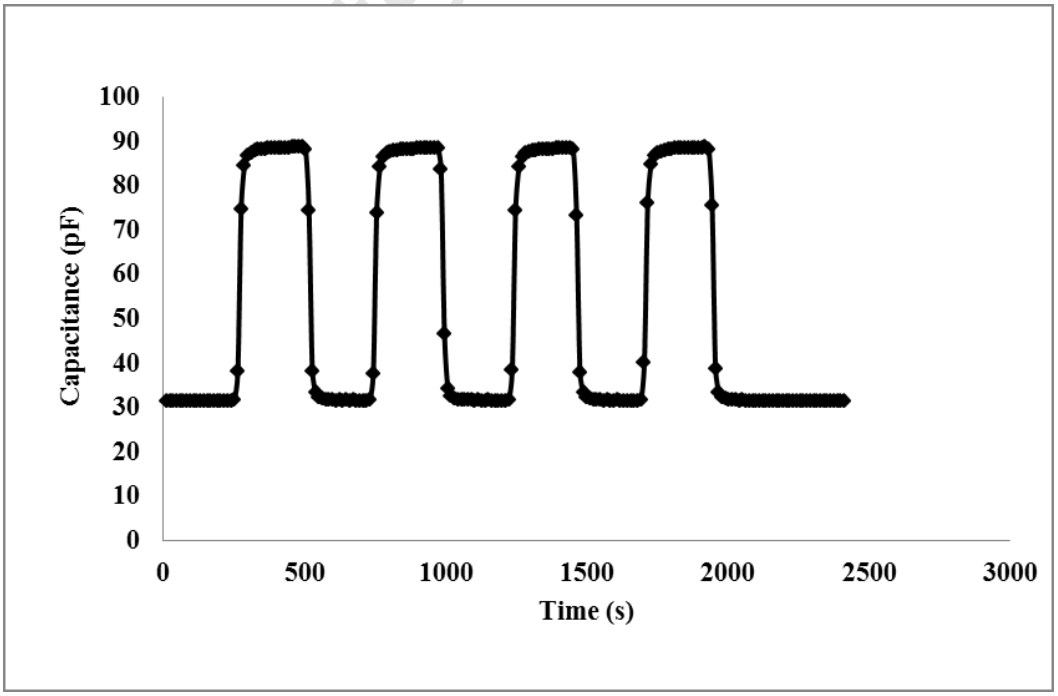

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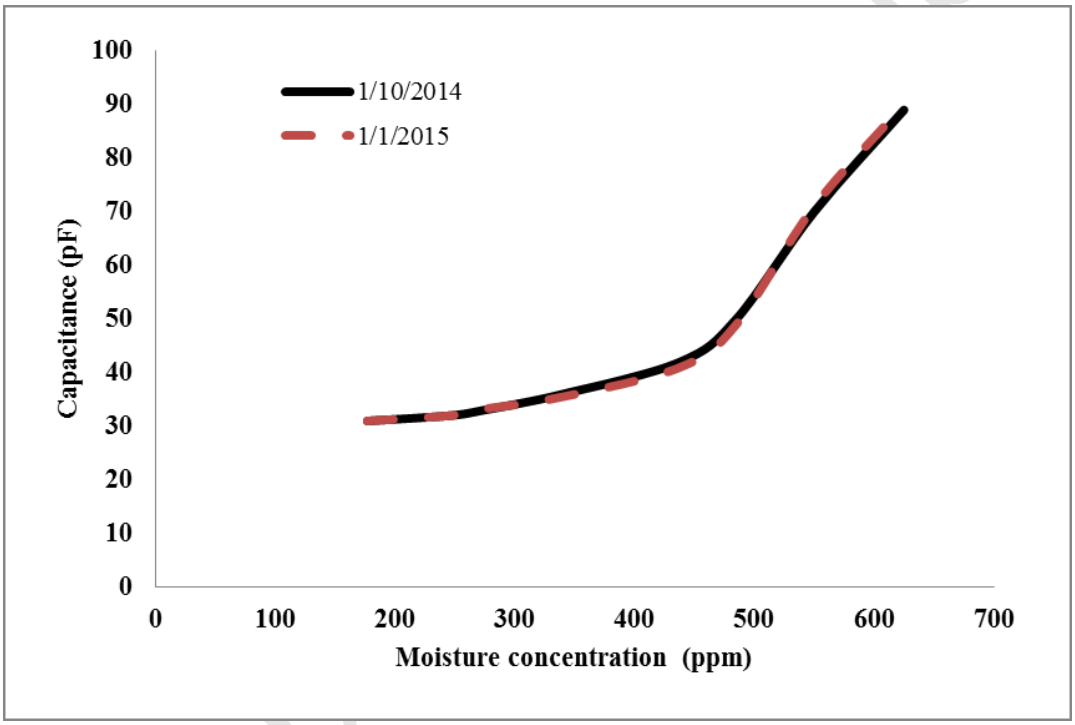

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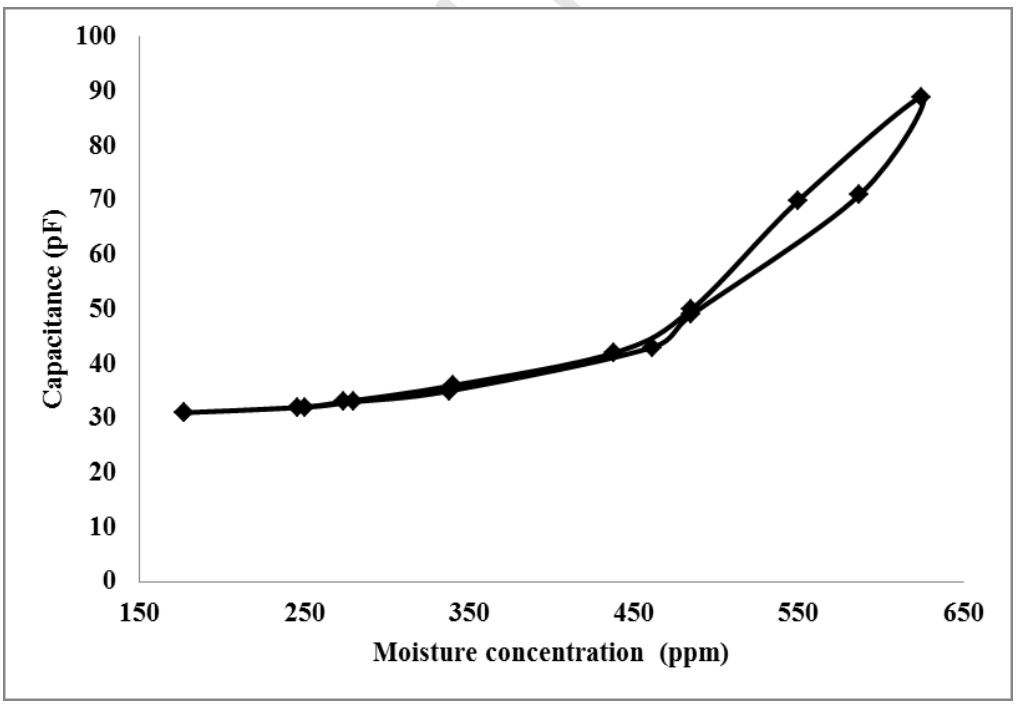

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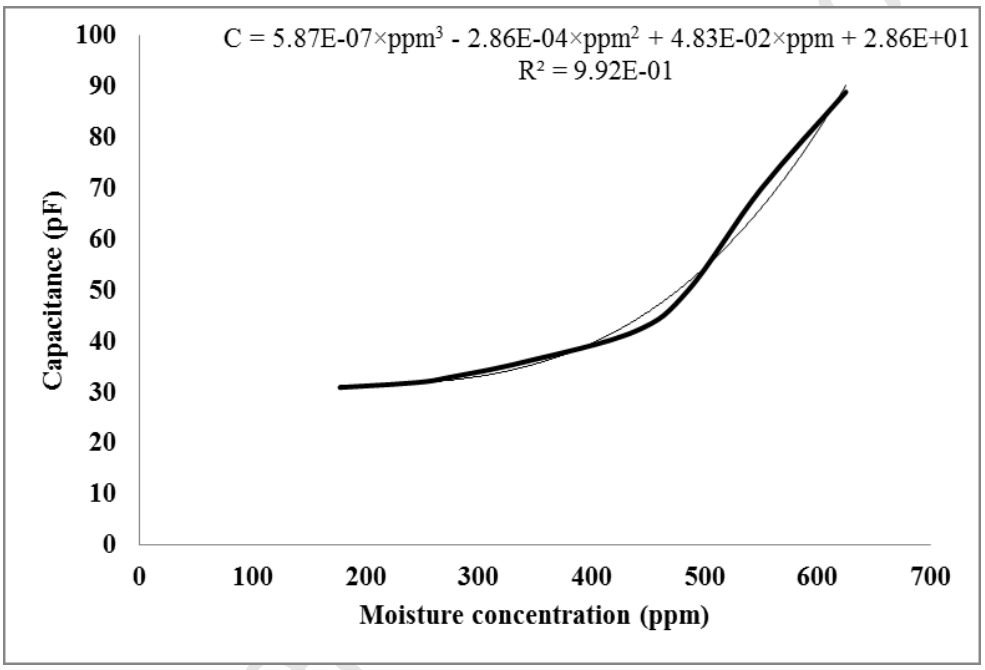

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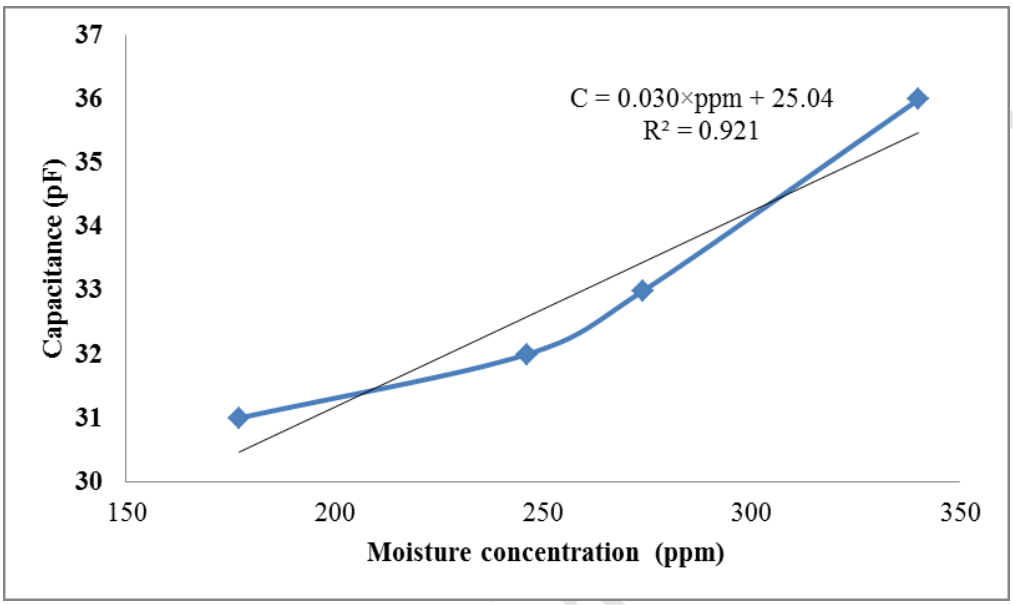

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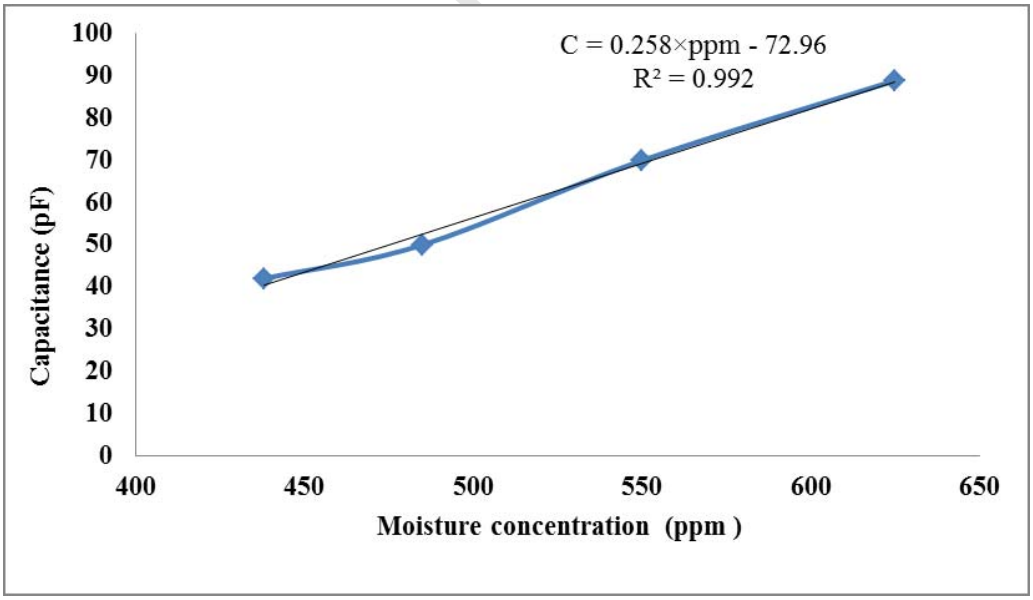

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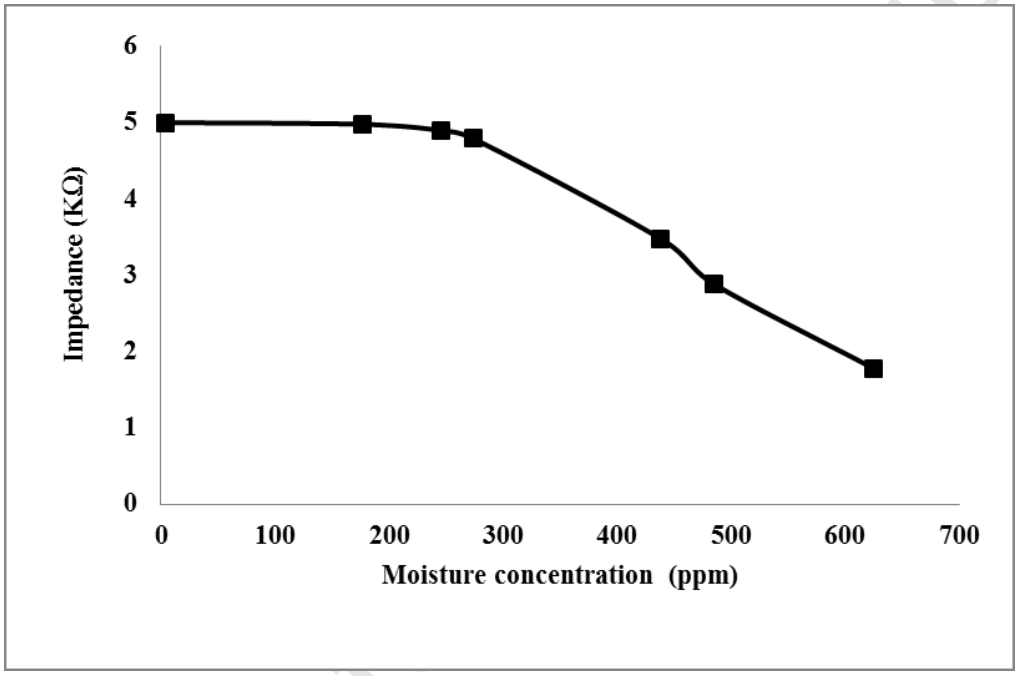

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A proficient process for Dynamic Location Management in Wireless Communication Networks

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Abstract - ***Every aspect of our lives have been touched by recent advances in cellular mobile. Mobile terminals (MTs) move randomly from one place to another inside a distinct environmental region. To provide appropriate services to mobile users, a demanding task is to track the location of the mobile successfully, so that the connection establishment delay is low. Typically, the network uses paging to decide the precise location of the mobile and this takes somewhere between 500ms to several seconds. The time factors for LU and paging are often reciprocally contradictory.***

In this paper, we productively set up a new analytical representation available for the analysis of the significant dynamic movement-based location management method for wireless networks with HLR/VLR architectures with intelligent paging scheme , to determine the total cost, comprise of paging cost and LU cost. Analytical results show that projected integrated new scheme, it reduces the total cost for location management compared to the preceding scheme, and obtain the improved performance, , thus reducing the call setup time. .

Key Words: *HLR, VLR, LA, LU, MSC, BS, CMR*

1. INTRODUCTION

Service area in wireless cellular networks is partitioned into location areas, and each location area contains a number of cells, as illustrated in Fig. 1 [5]. An mobile terminal is able to travel liberally within the location areas devoid of updating its location information and would just need to perform an location updates when it enters a new location areas. When an incoming call arrives, the network locates the mobile terminal by paging all cells within the location areas. A cell, usually represented with a hexagon, is served by a base station that transmits paging messages to all mobile terminals within the cell over a common broadcast channel. All BSs of the location areas are openly connected to the mobile switching centre (MSC) via the backbone network. MSCs are telephone exchanges which act as boundary between the mobile terminal and the PSTN/Internet. The LM system resides in the MSCs. While the MT-BS links are wireless, BS-MSC links are usually fixed and wired.

1.1 Location update schemes

There are two essential operations in location management: location update and paging. Location update is the procedure through which system tracks the location of mobile terminals that are not in conversations. The mobile terminal reports its current location information dynamically. A paging area (PA) may include one or more cells. When the incoming call arrives, the system searches for the mobile terminal by sending polling signals to cells in the Paging area. This searching process is referred to as paging. Performing location update or paging will acquire a major amount of cost (e.g., wireless bandwidth and processing power at the mobile terminals, the base stations, and databases), which must be minimized in the systems.

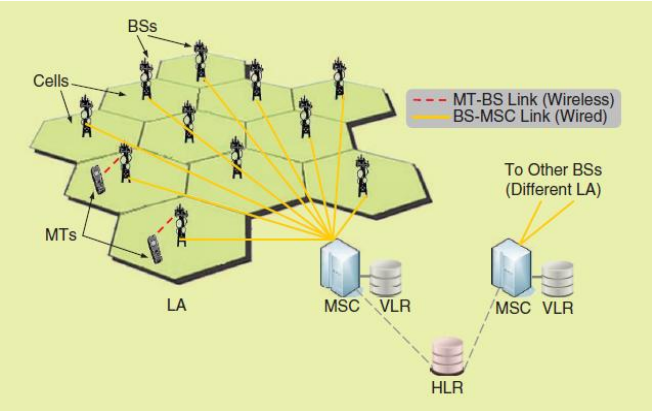

Fig 1: The LM architecture of existing 2G cellular mobile networks. [5]

LU are generally are of two types i.e. static LU and Dynamic LU. In dynamic schemes, the size of a LA is determined energetically according to the changes of mobility and calling pattern of mobile terminals. Three kinds of dynamic location management schemes have

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been planned [4], namely, distance based, movement based, and time based.

To implement the dynamic location update scheme in a actual PCS network, we have to consider the real network architectures with HLR-VLR databases. The location management have a bold task to design a high-quality strategy that can decrease the cost of the location update and paging at the identical time. In this paper, we test the obstacle of the performance assessment of the dynamic movement-based location management process for wireless networks with the HLR- VLR architectures all along with intelligent paging scheme.

1.2 Paging

Paging is performed at the onset of an incoming call and involves transfer a query message over the downlink signaling channel to every cell in the LA. All MTs keep an eye on the common control channel regularly to check whether it has been paged or not. When an MT finds a paging signal for itself, it thus responds by sending an acknowledgement note over the uplink signaling channel. The entire area to be paged (i.e., the PA), in its basic form, equals the LA and depends on the exactness and frequency of LU. A straightforward trade-off exists here - the enhanced the location prediction through LU, the smaller is the size of PA. A smaller PA results in a compact paging cost as the paging cost is comparative to the number of paged cells. To decrease the paging cost additional, as an alternative of paging all the cells within the LA at one go, the LA can be partitioned into several PAs that will be polled in succession.

Intelligent paging: The design of selective paging can be carried forward with more intelligent paging strategy. By intelligent paging, we refer to a group of schemes where the sequential paging scheme is further customized by computing the paging order of the different PAs based on pre-established probability metrics. The key goal is to poll the correct PA in the first pass with a high degree of success. As expected, intelligent strategies require even more computational overhead.

1.3 CMR

An added significant characteristic in the current topic is the call to mobility ratio (CMR). CMR is computed by dividing the average number of incoming calls by the average number of cell crossings the user makes in a given period of time. Users with lesser CMR values have need of more frequent location updates than users having higher CMRs.

The novel scheme could decrease the total LU cost drastically for high CMR, and thereby reduce the total cost. The rest of this paper is structured as follows. In section II, we present the related work. In section III, we discuss location update and paging strategy. Performance comparison is addressed in section IV. Finally, we present the conclusion in section V.

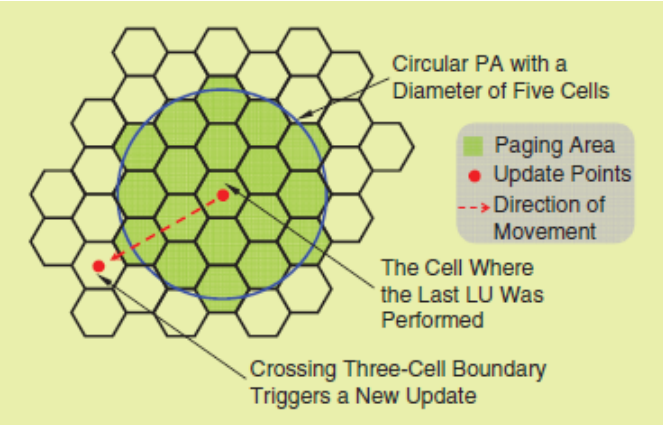

Fig 2 : The PA for movement-based LU with d =3 [5]

2. Related work

The wireless networks coverage area is separated into LAs, each one of which consists of tens or hundreds of cells and is serviced by a VLR. A mobile terminal resides in a cell it visits for a random time interval and moves on to the next cell.

In the movement-based location update scheme, the mobile terminal registers at a new VLR and its new location is reported to HLR when it moves across cells since the last location update, where 'd' is a threshold value. For ease, a location data update in HLR is referred to as a HLR location update and a set of registration and deregistration operations in VLRs is referred to as a VLR location update.

We define the center cell to be the cell where the last VLR location registration took place, for the movement-based location update method. The network initiates the terminal paging process to locate the called mobile terminal, as soon as a call for a mobile terminal arrives. The PA is the covering area within a distance from the centre cell. The PA is the same as an LA, for the system with the static location update scheme. [3]

In the dynamic movement-based location management with HLR/VLR architecture, there are costs for location update and paging. Furthermore, in the HLR/VLR network architectures, there are two kinds of location updates: HLR location updates that update the location data in HLRs and VLR location updates that update the location data in VLRs.

Denote the expected costs per call arrival of HLR location updates, VLR location updates, and the paging by Chlr, Cvlr and Cp respectively. The total costs of location update and paging per call arrival is the sum of HLR and VLR location updates and the cost of paging.

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TCmb = Chlr + Cvlr + Cp (1)

The costs function of location update in database HLR [3]:

Chlr = δhlr . (λm / λc) (2)

The expected cost function of location updates in VLRs per call arrival is obtained as follows [3]:

$$C_{\text{Vlr}} = \delta_{\text{Vlr}} \left(\frac{\rho_{sm}^{d}}{1-\rho_{sm}^{d}} \frac{\rho_{mc}}{1-\rho_{mc}} + \frac{\rho_{sc}^{d}}{1-\rho_{sc}^{d}} \right). \quad (3)$$

Here,

d = cell boundaries (d=1 to d=15)
δhlr = HLR update cost
δvlr = VLR update cost

In the analysis, it is supposed that the residence time of a mobile terminal in an LA is an exponentially scattered random variable with rate λm and the call arrival to each mobile terminal is a Poisson process with rate λc

Further, we have

ρmc = (λm)/(λm+ λc)
ρsc = (λs)/(λs+ λc)
ρsm = (λs)/(λs+ λm)

where,

λm = 1/ Tm
λs = 1/ Ts
λc = 1/ Tc

Tm is mean LA residence time, Ts is mean cell residence time and Tc is mean time between consecutive phone calls to mobile handset. For brevity, we skip the part of derivation.

When there is a call to arrive the mobile terminal, the network will hunt all the range in the LA to found the mobile terminal [7]. In the RBPS strategy, the paging strategies can be either sequential paging or blanket paging. Both strategies have benefit and drawback. In the sequential paging [8] Search speed is sluggish but the paging load is very little. Blanket paging [8]: Search speed is quick but the paging load is very vast. Apart from these two, intelligent paging method has rapid search speed as blanket paging and the paging load is little just like the sequential paging.

The cost of the selective paging is as follows [2] :

$$\sum_{x=\max(i-j+1,1)}^{\min(i+j-1,d)} \rho_{i,x,j} \cdot nc_PA_{x,j} \cdot \lambda_c \quad (4)$$

where ,

ρi,x,j = probability for an MT to move from ith PA to xth PA.

nc_PAx = Number of cells in the xth PA

λc = inverse of the mean time between two consecutive phone calls to MT

3. PROPOSED METHOD

In the previous strategy, the location update is done when the mobile terminal move across periphery of cell threshold d. If the quantity of crossing the boundary surpasses the earlier defined threshold value, the mobile terminal would carry out a LU.

In this section, we set collectively the dynamic movement-based location management with HLR/VLR architecture with the selective paging approach together. Under the joint scheme, the total cost could be represented as:

$$TC = \{ \delta_{hlr} . (\lambda_m / \lambda_c) \} + \left\{ \delta_{\text{Vlr}} \left(\frac{\rho_{sm}^{d}}{1-\rho_{sm}^{d}} \frac{\rho_{mc}}{1-\rho_{mc}} + \frac{\rho_{sc}^{d}}{1-\rho_{sc}^{d}} \right) \right\} + \left\{ \sum_{x=\max(i-j+1,1)}^{\min(i+j-1,d)} \rho_{i,x,j} \cdot nc_PA_{x,j} \cdot \lambda_c \right\} \quad (5)$$

In this paper, the size and shape of a cell are in some way reflecting by the cell residence time value. In the small cell size, the mean residence time will be relatively small and vice versa. In the live cellular phone systems, all cells in the Paging area or the location area are paged every time when an incoming call arrives, but the intelligent paging scheme are being used here.

The different parameters are used to analyze the materialization of the new scheme and evaluated the results with the previous scheme, and the total cost obtained from the new proposal and the previous method is compared. The wireless network with widespread hexagonal cell configurations shown in Fig. 3. For the hexagonal cell formation, cells are hexagonal shaped and each cell has six neighbors. There are many rings of cells in the hexagonal cell formation. The innermost ring (i.e., ring "0") consists of only the center cell in the movement-based location update scheme. Ring "1" surrounds ring "0", which in turn is surrounded and so on.

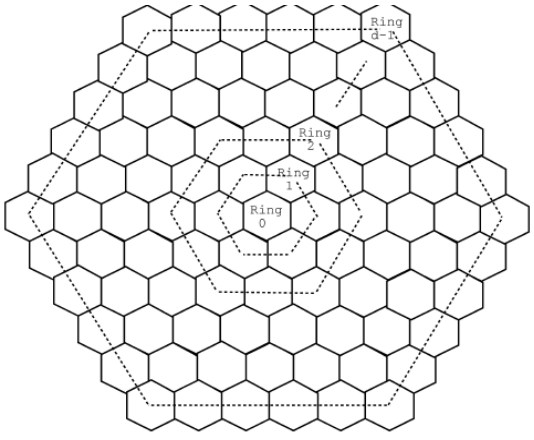

Fig 3 : The hexagonal configuration [3]

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4. PERFORMANCE COMPARISION

In the proposed scheme, the dynamic movement-based location management cost with HLR/VLR architecture is added with the scheme of selective paging together. Thus, under the combined scheme, the total cost is represented as in (5)

The total cost obtained from the new scheme and the previous schemes are compared here. The costs of various boundary crossing threshold d are evaluated when λc=0.1 & 1 i.e. Tc (time elapsed between termination of a call & arrival of the next call to mobile handset) is 10 and 1 respectively.

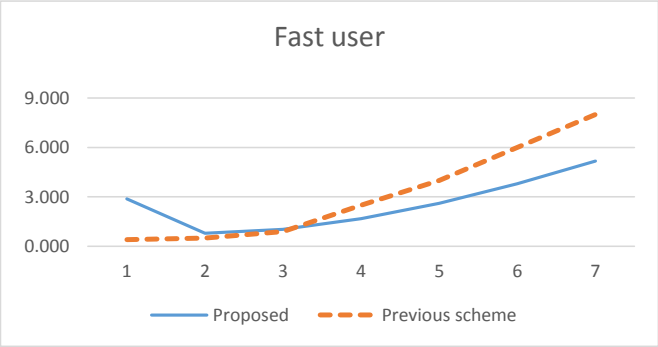

Fig 4: Cost at various boundaries when λc=0.1

Figure 4 shows that when the value of d is 1 i.e. the location update count, the high location update cost is high. When d ranges from 2 to 7, there is decrease in the number of location updates. With the increase in the d value, there is reduction in the number of location update and there is drop in the location update cost step by step. However, increase in the value of d would cause the paging area to increase also, and thus increase the paging cost. The proposed scheme still has good performance in d = 2 to 7. Moreover, the numerical results show that the proposed scheme outperforms the previous scheme. But when the threshold d ranges from 2 to 7, it is obvious that the paging cost of new strategy is lower than the previous scheme.

From Fig.5, we could see that the proposed strategy has better performance than the previous scheme when d ranges from 2 to 7.

It is evident from the graph that there is decrease in the performance improvement when Tc increases (i.e λc decreases). It is usual because with the lower mobility (i.e., the larger value of Tc), it is better to not perform the registration operation frequently and vice versa. From the graphs it is evident that as the cost decreases, the value of d also decreases. It is expected because an increase in the movement threshold results in an increase of the PA of the mobile terminal and, thus, decreases the HLR and VLR update costs.

The numerical experiments with different system parameters are broadly conducted. Due to the limitation of space, we provide the typical results here.

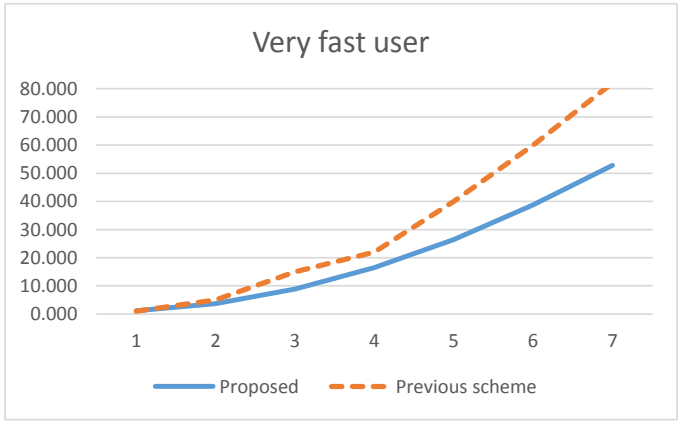

Fig 5: Cost at various boundaries when λc=1

5. CONCLUSION

In this paper, an analytical model to study the dynamic movement-based location management for wireless networks with HLR/VLR architectures is developed. The paging scheme with movement based location update scheme is combined, where different movement threshold value d was selected.

The acquired methodical formulations are simple and uncomplicated to be used. By using the analytical model, performance evaluation is demonstrated and the result compares with the previous strategy to prove that the new strategy can obtain better performance under the same environment. Location update cost is successfully reduced using the new scheme under various parameters of mobility and calling patterns. Finally, the total location management cost is reduced and do better than the previous scheme. The analyzed results in Figure 6-7 proves that the new scheme is effectual in dropping the total network cost consisted of location update cost and the terminal paging cost.

This model can provide good analysis for the system design and implementation of the dynamic location management for cellular networks. The precision of the analytic model may be verified by the computer imitation or actual measurements. Ideally, the results obtained by the computer simulation should be the same as that obtained by the analytic method with the same stochastic model and assumptions. Computer simulation may also incorporate more details in studying the performance of cellular networks

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BIOGRAPHIES

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A Survey of Black Hole Detection Techniques in WSNs

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Abstract: Wireless Sensor Networks (WSN) is a trending technology now-a-days and has a wide range of applications such as battlefield surveillance, traffic surveillance, forest fire detection, flood detection etc. But wireless sensor networks are susceptible to a variety of potential attacks which obstructs the normal operation of the network. Black hole attack is one of severe security threat that affects the network from its normal functioning by maliciously advertising itself having shortest route to the destination and then drops all receiving packets. There are lots of mechanisms have been proposed to defend network from black hole attack, but none of the solution looks most promising to defend against black hole attack. So in this paper, we have surveyed and compared the existing solutions to black hole attacks on AODV protocol. Tabular representation of comparison depicts clear picture of these solutions.

Keywords: AODV, Black hole attack, IDS, Routing

I. INTRODUCTION

A Wireless Sensor Network (WSN) consists of large number of sensor nodes working in cooperation manner to gather the information from the monitoring region. Generally WSN have little or no infrastructure. There are two types of WSNs: structured and unstructured [1]. In unstructured WSN there are huge numbers of nodes deployed randomly to monitor the region. Due to unavailability of physical presence on the region, network maintenance activities are difficult. In a structured WSN, all the nodes are deployed in fixed and planned manner. Positive point of a structured network is that fewer nodes can be deployed and requires fewer maintenance and management cost. In a WSN the object performing task of sensing is called a sensor. Sensor nodes are low power devices equipped with one or more sensors, processor, memory, power supply, a radio, and an actuator [2]. A variety of mechanical power, thermal sensor, biological, chemical,optical sensor, and magnetic sensors can be attached to enhance the power of sensor nodes [1]. Since the sensor nodes
have limited memory and are deployed in harsh environment and in difficult locations, radio transmitter is implemented to transfer the collected data to base station. WSNs have many applications such as military target tracking and surveillance, disaster relief, health monitoring, environment exploration seismic sensing to measure the environment.

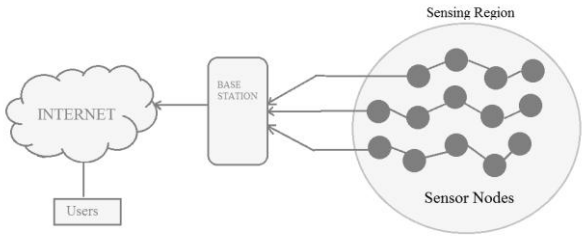

Figure 1.1 WSN model

The remainder of the paper is structured as follows. In next section we discuss about some constraints of WSN and fundamentals of security that are essential to be considered as key concepts before implementing any protocol. In Section 2, we discuss some of the possible attacks in WSN. Section 3 describes the Black hole attack in both reactive and proactive routing protocols. A review of existing techniques to handle black hole attack is presented in section 4. In section 5, Comparison of discussed techniques is performed. Finally, section 6 concludes the paper and points out future research directions.

II. CONSTRAINTS FOR WSNS

In the wireless sensor network, sensors are organized into the specific configuration to satisfy the requirements of ad-hoc applications. Unfortunately, the connectivity cannot remain unchanging at any working time. The sensor network is a broadcast network in which any signal can be captured by adversaries at any time. These features make wireless ad-hoc sensor networks more vulnerable than wired networks [2].
Resource Constraints:

Energy Constraints: Energy is one of the important constraints for WSNs. In sensor nodes energy consumption can be categorized in three parts: Sensor transducer, Communication among sensor nodes, microprocessor computation.

Memory Limitation: A sensor is a tiny device with a small amount of memory and storage space. Sensor nodes memory is usually includes flash memory and RAM (used for storing application programs, sensor info & intermediate results of computations). Usually, there is not sufficient space to run complicated programs or codes after loading the OS and application code.

Lack of Central Control: Because of resource constraints and network dynamics it is not feasible to have a central

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point of control in sensor networks. Therefore security solutions must be decentralized and nodes must be able to achieve security [5].

Remote Locations: As sensor nodes are deployed in hard-to-reach locations so it will be infeasible to continuously monitor and protect the nodes from attacks. That why it will be difficult maintain a secure network.

Error-prone Communication: Unreliable communication is a dangerous threat to sensor security. Packets in WSNs may be lost due to collision, channel errors or routing failures. This may interfere with security mechanisms.

III. FUNDAMENTALS OF NETWORK SECURITY

Computer and network security is the collection of all policies, mechanisms, and services that protect a computer system or network from unauthorized access or unintended use. So, to ensure Network as secure some security mechanisms are applied that are Non-repudiation, Integrity, Availability, Privacy, Confidentiality, Authorization, Authentication, Freshness[3].

IV. ATTACKS IN WSN

There are different kinds of attacks possible by malicious nodes to harm the network and make the network unreliable for communication and proper functioning. Some of such kinds of attacks are:

a) *Jamming*: Jamming attack is related with disrupting or interfering the radio frequencies used by sensor nodes. Attacker may get physical access to some nodes and creates jam in the network to disrupt the network. Jamming attack come under physical layer attack.

b) *Tampering:* Refers to gaining physical access to a set of sensors by tampering with their hardware configuration and making nodes to act as adversary node. Tampering is possible at physical layer.

c) *Sybil Attack:* Sybil attack is defined as a malicious device illegitimately taking on multiple identities. In Sybil attack an adversary can appear to be in multiple places at the same time. A single node presents multiple identities to other nodes in the sensor network either by fabricating or stealing the identities of authenticated nodes. It is a Network layer attack.

d) *Wormhole attack:* Wormhole attack is a critical attack in which the attacker records the packets (or bits) at one location in the network and tunnels those to another location. This generates a false scenario that the original sender is in the neighbourhood of the remote location. The tunnelling procedure forms wormholes in a sensor network. The tunneling or retransmitting of bits could be done selectively.

e) *Hello Flood Attack:* Hello flood attack uses HELLO packets as a weapon to convince the sensors in WSN. In this type of attack an attacker with a high radio transmission range (termed as a laptop-class attacker) and processing power sends HELLO packets to a number of sensor nodes which are dispersed in a large area within a WSN.

f) *Black hole:* In Black hole attacks, a malicious node acts as a black hole to attract all the traffic in the sensor network through a compromised node or malicious node. A compromised node is placed at the center or any respective position, which looks attractive to neighboring nodes and attracts nearly all the traffic of surrounding nodes that was destined for a base station.

Black hole attack:

V. BLACK HOLE ATTACK

In this attack, a malicious node falsely advertises optimal paths (e.g. the shortest path or the most stable path) to the destination node during the path-finding process (in reactive routing protocols), or in the route updates messages (in proactive routing protocols). The intention of the malicious node could be to hinder the path-finding process or to intercept all data packets being sent to the destination node. A more delicate form of this attack is known as the grayhole attack, where the malicious node intermittently drops the data packets thereby making its detection even more difficult [4].

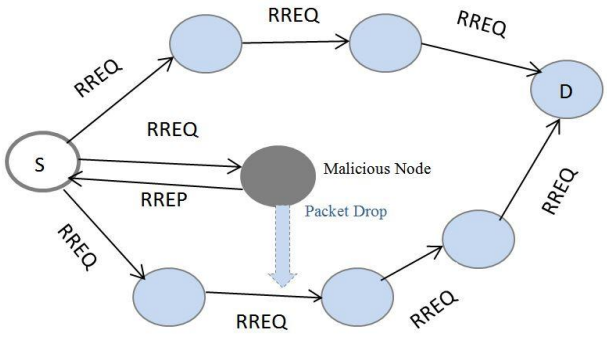

Figure 2. Black Hole Attack

Black hole attacks are classified into two categories:

- *Single Black Hole Attack*: In single black hole attack only one node act as malicious or compromised node which misbehaves within the network. It is also known as black hole attack with single malicious node.
- *Collaborative Black Hole Attack:* In collaborative black hole attack multiple nodes behaves as malicious node in the network and work in co-operative manner. It is also known as the black hole attack with multiple malicious nodes.

VI. SURVEY OF BLACK HOLE DETECTION TECHNIQUES

S. A. Arunmozhi et.al. [4] Discussed a defence scheme for detecting black hole node. The detection is based on the timing information and destination sequence numbers that is maintained in the Neighbourhood Route Monitoring Table. The table manages the record of time of Reply. A black hole node will send a route reply message without checking the routing table as the legitimate node normally does. This reduced reply time is used to detect the black hole node. To improve the security further, the destination sequence number is checked with the threshold value, which is dynamically updated. This protocol not only detects black hole attack but also improves the overall performance. Limitation is that it cannot prevent the

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network from co-operative black hole attack because of assumption that black hole node cannot work in group.

SwarnaliHazra et.al. [5] proposed a trusted on-demand routing approach to prevent black hole attack depending on their trust model with different levels of trust computations. In this approach, black hole attackers are identified and isolated on context of data forwarding.

Fei Shi et.al [6] provides a cluster-based scheme form preventing black hole attacks in MANETs. It first employee's a powerful analytic hierarchy process (AHP) methodology to elect cluster heads (CHs). Then CHs are required to implement the black hole attack prevention scheme to not only detect the existence of black hole attacks but also identify the black hole nodes. Positive point with this scheme is that it is feasible and efficient in preventing black hole attacks.

R. TANUJA et al. [7] this article propose technique to eliminate Black Hole and False Data Injection attacks initiated by the compromised inside nodes and outside malicious nodes respectively using a new acknowledge scheme with low overhead. Advantage with this scheme is that it can successfully identify and eliminate 100 % black hole nodes and ensures more than 99 % packet delivery with increased network traffic.

Harsh Pratap Singh and Rashmi Singh [8] has proposed broadcast synchronization (BS) and relative distance (RD) method of clock synchronization which is used to prevent the black hole nodes. BS (Broadcast Synchronization) is very famous technique for clock synchronization process in Mobile-ad hoc Network. This paper has BS technique for removal of cooperative black hole attack. Sometimes the detection process for worms is failed in the clock synchronization. In this case this paper imposed another method for black hole detection using Relative Velocity distance.

Ming-Yang Su[9] in this several IDS (intrusion detection system) nodes are deployed in MANETs in order to detect and prevent selective black hole attacks. The IDS nodes must be set in sniff mode in order to perform the so-called ABM (Anti-Black hole Mechanism) function, which is mainly used to estimate a suspicious value of a node according to the abnormal difference between the routing messages transmitted from the node. When a suspicious value exceeds a threshold, an IDS nearby will broadcast a block message, informing all nodes on the network, asking them to cooperatively isolate the malicious node. This study employs ns2 to validate the effect of the proposed IDS deployment, as IDS nodes can rapidly block a malicious node, without false positives, if a proper threshold is set. Advantage with this is that it is multipath passed protocol and packet loss rate can be decreased to 11.28% and 14.76%. Drawbacks: Failed at co-operative black hole attack detection.

Muhammad Raza et.al [10] They have proposed a novel architecture of FRIMM (A Forced Routing Information Modification Model) prevents black hole attacks in wireless Ad Hoc network by introducing automatic error correction in routing information that leads the node to select correct path thus secure transmission will take place between source and destination.

*NeelamKhemariya et.al [11]*have proposed an algorithm and it is implemented on AODV (Ad hoc on demand Distance Vector) Routing protocol. The algorithm can detects both the single Black hole attack and the Cooperative Black hole attack. These algorithms first identify black hole nodes from the network and then remove their entries from the routing table. The advantage of the algorithm is that it not only detects the black hole nodes in case when the node is not idle but it can also detect the Black hole nodes in case when a node is idle as well.

SubhashisBanerjee,MousumiSardar et.al[12] have proposed trust based mechanism for detection and mitigation of black hole nodes from the network. They have introduced mechanism which detects malicious nodes from the network without introducing additional control packets and without modifying routing table. Detection is originator initiated hence there is no need to rely on intermediate nodes. Trust mechanism

KashifSaghar et.al[13] have proposed RAEED (Robust formally Analyzed protocol for wireless sensor networks Deployment), which is able to address the problem of black hole attacks using formal modeling and proves that RAEED avoids such kind of attacks.

SatyajayantMisra et.al[14] have propose an efficient technique that uses multiple base stations deployed in the network to counter the impact of black holes on data transmission their work is based on how to deploy the base stations for collecting the information gathered by nodes deployed in hostile environment. Simulation shows packet delivery ratio was 99% and detection rate was 100% but no. of base stations was not optimal.

Sonika Malik et.al [15] Have proposed the solution to black hole attack by using data routing table that stores routing information of neighbor nodes. This analyze the data routing table of nodes and send check packet to the neighbor nodes to get the information about nodes and from this information they finds the trust worthy and reliable nodes and eliminate the malicious black hole nodes by rising global alarm to warn the network about malicious nodes.

Anurag Gupta et.al[16] Have proposed the solution to avoid denial of service and black hole attack in mobile adhoc network. In this the solution to detect the malicious node has been presented, for that all nodes in the network are listed together and counter clock is applied to every node and any misbehavior is detected by using RREQ time, Current time, Expire time Source sequence number and Destination Sequence number. Malicious nodes are added to malicious list and when session expires malicious nodes are removed from malicious list because they assume that after some time malicious node stops doing malicious activity.

Anishi Gupta [17] Proposed a new method MEAODV(Modified Enhanced AODV), based on EAODV(Enhanced AODV).The MEAODV is based on route discovery process for mitigating black hole effect. It does not have any overhead to the network. The similar logic is used as in EAODV but has few different condition parameters for checking the RREP message for better

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route discovery mechanism. Performance is compared with EAODV and performance delivery ratio is slightly higher. But negative point is that it does not consider co-operative Black hole attack.

H.Shafieiet.al[18] proposed two techniques to detect sinkholes in the network. In the first approach, base station samples the residual energy of sensing nodes deployment region using a geostatistical method and estimates a parameter called statistical estimator. Base station utilizes this parameter to estimate the presence of energy holes in deployment region using geostatistical frailty survival model. Energy holes around the base station are neglected whereas presence of energy holes in rest of the network ensures occurrence (presence/ existence) of sinkholes in network. Base station then instructs all of network nodes to avoid the suspicious region in their routing to mitigate the attack or ignore it. Second approach is Distributed monitoring method comprising two phases: Distributed residual energy query phase and Distributed estimation and detection phase. Distributed monitoring method detects region with lower average residual energy level and applies a mitigation method to eliminate sinkholes.

S. S. Bajwa and M. K. Khan [19] proposed Grouped Black Hole Attack Security Model (GBHASM) to prevent grouped black hole attacks in Ad hoc On-demand Distance vector (AODV) protocol in wireless ad hoc networks. This model is based on two modules. First module describes how a new node becomes member of network. After having joined the network, this node is assigned node code (NC) pkk1 and pkk2. When node requests for shortest path to destination with a packet having pkk2, then each node matches Node Code pkk1 with pkk2. If they match within Time to Live (TTL), routing information is shared with intermediate node otherwise packet is forwarded to next node. This model has low delay and high performance.

Varshney et al., [20] proposed a monitoring method called Watchdog AODV mechanism to form detect black hole nodes in mobile adhocnetworks.In this method nodes act as watchdogs monitor their neighbors locally using control messages by listening to all nodes within transmission range to detect misbehaving as well as black hole node. Black hole node once detected, is excluded from the path of transmitting messages. Limitation of Watchdog AODV is that it is vulnerable to attack of two consecutive nodes. It can monitor only first node while the consecutive node performs attack. Watchdog AODV has higher packet delivery ratio and lower overhead than AODV.

M. Mohanpriya, I. Krishanamurthi [21] presented Modified Dynamic Source Routing protocol (MDSR) to detect and prevent selective black hole attack by analyzing forwarding behavior of nodes. This approach detects the presence of gray hole attackers in source route based on difference between number of packets source node sends and number of packets that are actually received by destination. IDS nodes deployed in network broadcast the block message to all nodes and then suspected malicious nodes are isolated from the routing path as well as network. Advantages of MDSR are that it reduces packet drop ratio by 64 % but increased overhead ratio by 8 %.MDSR has less end to end delay as compared to DSR protocol.

S. Vidhyaand T. Sasilatha [23] proposed a black hole detection scheme in wireless sensor network by adding energy to sensor nodes externally through batteries that increases network lifetime. The author provided a solution to black hole attack by a public key encryption through Message Digest MD5 cryptographic function with 128 bithash value. While relaying messages from source to destination, confidentiality, authenticity and integrity of data packets is to be kept in mind. Nodes are in network in such a way that a node acting as a mobile agent monitors the activities of neighboring nodes and informs trust manager about any changes in status of nodes. Trust manager verifies identity of each node in the network and intimates to neighbors about the malicious behavior of a node if it finds any to keep the network safe. MD5 marks a node malicious if it uses another node's signature and packets are forwarded to neighbors through alternate route. Providing energy externally increases network lifetime, packet delivery ratio, as well as throughput.

N. Chaudhary and L. Tharani [24] proposed a Timer based detection mechanism to detect and eliminate black hole nodes launched over AODV in mobile adhoc networks. This scheme utilizes a trust value defined by every node on its neighbors. Initially all neighbors are assigned max_trust value and a timer is set with each data packet. A node does not communicate with its neighbor if neighbor's trust value is less than min trust. The node checks by listening to wireless transmission whether have been received by next hop before timer expires. If node could not hear wireless transmission of next hop, it reduces trust value of next hop and broadcasts this information to all nodes in network so that they can update their routing tables. If node's next hop continues to drop packets, its trust value goes on decreasing and becomes less than min_trust. All nodes in network put such a node in their blacklist table. In this way, all blackhole nodes get eliminated from the network. Packet delivery ratio gets improved as black hole nodes are detected and removed from the network.

Siddiqua et al., [25] proposed a secure knowledge algorithm to detect and mitigate black hole attack on AODV by taking packet drop reasons into consideration before declaring a trusted node as black hole node. Each node monitors the behavior of its neighbor by listening to packet transmission wirelessly. Every node compares the neighbor information with its knowledge table information. The nodes monitor the control packets as well as data packets to prevent selective dropping. When packet dropping reaches to a threshold then before declaring a node to be malicious the algorithm first checks whether suspected node is destination or not. It also checks packet drop reasons such as Time to live (TTL) and residual energy. If suspected node is detected to be a black hole, its id is broadcasted to all other nodes in network so that malicious node can be avoided in routing process. Secure AODV shows better performance in terms of throughput and delay as compared to existing AODV.

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VII. COMPARISON

Various techniques are discussed based on various criteria, which are base routing protocol used, Modifies routing table or not, new control packets introduced or not, type of black hole detected and simulation tool used.

Sr No.	Technique	Routing Protocol Used	Modifies Routing Table (YES/NO)	New Control Packets (YES/NO)	Simulation TOOL	Performance Matrices	Results	Year
1.	NRMT[4]	AODV	YES	YES	NS2	Routing overhead, PDR, CPU usage, Memory usage, Delay	Network Performance Improved	2012
2.	CST-AODV[5]	AODV	YES	YES	-	Packet loss Rate	Packet Loss Rate are negligible	2014
3.	Cluster Based [6]	AODV	YES	NO	NS2	PDR w/s traffic load	Improved Packet delivery ratio under black hole attack.	2013
4.	BHnFDIA [7]	MAC	NO	YES	MATLAB	PDR w/s compromised nodes	Gives 100% packet filtering efficiency and 99% packet delivery ratio	2013
5.	Secure Path Based[8]	OLSR	YES	YES	NS2	Throughput end to end delay, PDR, Jitter	Effective performance in terms of PDR, Throughput, end to end delay	2014
6.	IDS Based[9]	AODV	YES	YES	NS2	Total packet loss rate	Packet loss reduced to 10.05% and detection rate 100%	2011
7.	FRIMM[10]	AODV	YES	NO	-	-	-	2011
8.	Neelam et.al [11]	AODV	NO	YES	NS2	Throughput, PDR, end to end delay	Improve network performance	2013
9.	Trust Based[12]	AODV	NO	NO	-	-	-	2013
10.	RAEED [13]	INSENS	YES	NO	TOSSIM	% of nodes blocked	Robust and lower overhead	2014
11.	BAMBi[14]	-	NO	NO	Realistic simulation	Packet delivery success, packet delivery failure	Packet delivery ratio is 99% Detection ratio is 100%	2011
12.	Alarm Based[15]	AODV	YES	YES	NS2	-	-	
13.	DSN Based[16]	AODV	YES	YES	NS2	Throughput, end to end delay	Better throughput and end to end delay	2015
14.	MEAODV[17]	AODV	YES	YES	NS2	PDR, end to end delay, no. of malicious nodes.	Better PDR as compared to EAODV	2013
15.	Geostatistical based[18]	AODV	NO	NO	OMNET++	False positive false negative	Adopted 95% confidence level	2014
16.	GBHASM[19]	AODV	YES	YES	NS2	No. of RREQ and RREP	High performance less delay	2010
17.	Watchdog AODV[20]	AODV	YES	YES	NS2	PDR, MAC load, end to end delay	Improved PDR and end to end delay	2014
18.	MDSR[21]	DSR	YES	YES	GLOMOSIM	Packet drop ratio, end to end delay, PDR, overhead	Percentage of Packet loss rate is better	2013
19.	ACK based[22]	AODV	NO	YES	OPNET			2014
20.	MD5 based[23]	AODV	NO	NO	NS2	PDR, Throughput, end to end delay	Improved overall network performance	2014
21.	Timer based[24]	AODV	YES	YES	EXata-cyber	PDR w/s no. of attacker	Improved PDR	2015
22.	Knowledge based[25]	AODV	YES	YES	NS2	PDR w/s no. of malicious nodes	Effective PDR	2015

VIII. CONCLUSION

Wireless Sensor Networks are vulnerable to many types of attacks due to deployment of sensor nodes in an unattended environment. These types of networks are suffered from the black hole attack as there is no centralized security management. This paper provided a survey on various countermeasures for black hole attack. In this survey, firstly we have given the security goals of a network. Next, we have presented some of the possible network layer attacks in WSNs. This survey also gives the tabular analysis of various security mechanisms to prevent network from black hole attack. It is to be believed that this survey will help future researches in developing a good knowledge about the attacks and their countermeasures.

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A Voltage mode biquad with lowpass, bandpass and notch outputs using Voltage Differencing Current Conveyor

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Abstract: The present work deals with voltage differencing current conveyor and its application in analog circuit design. There have been several major developments in the area of analog circuits which have taken place during the past four decades. There is a bulk of material available about the various active blocks developed past Current Conveyors.Among various modern active building blocks, Voltage Differencing Current Conveyor(VDCC), is emerging as quite flexible and versatile building block for analog circuitdesign. In this paper an attempt has been made to highlight the realization of the VDCC active block using MOSFETs and a VDCC based biquad filterusing three active blocks has also been realized. This VDCC based voltage mode biquad filter gives low-pass, band-pass and notch outputs. The workability of the circuit is supported by PSPICE simulations using TSMC 0.18µm parameters.

Keywords: voltage differencing current conveyor, biquad filter, low-pass, band-pass, notch

I. INTRODUCTION

In the past many circuits for the simulation of voltage mode biquadsusing different active building blocks such as operational amplifiers, current conveyors, current feedback amplifiers, current differencing buffered amplifiers, current differencing transconductance amplifiers, operational transconductance amplifiers, operationalmirrored amplifiers, voltage differencing differentialinput buffered amplifiers, and voltage differencingtransconductance amplifier have been reportedin the literature.

In recent times, many active building blocks have been presented, and VDCC is one of them [5]. The usefulness of recently introduced active building block "VDCC" is well-defined in [1]. In [1], the authors proposed a MOSFET model for realization of VDCC active block and then realized grounded inductance simulator circuits using single VDCC and two passive components.

The objective of this paper is to propose a multifunction filter based on two integrator loop topology first proposed by Kerwin Heulsman and Newcomb (KHN) which is realized using VDCC as the active analog block. First of all the VDCC block was realized using MOSFETs[1] and then using three VDCC blocks and some passive elements the biquad filter was realized.

II. VOLTAGE DIFFERENCING CURRENT CONVEYOR

The circuit symbol of the recently proposed active element,VDCC, is shown in Fig. 1, where p and n are input terminals andz, x, $W_p$and $W_n$are output terminals.

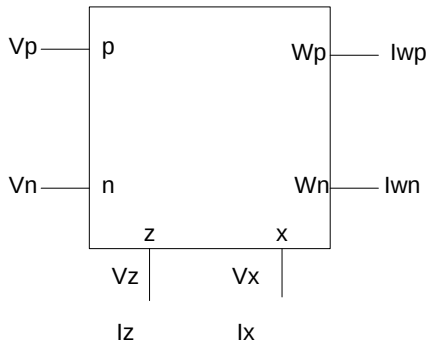

Fig.1: Symbol of VDCC

All of the terminals exhibithigh impedance, except the x terminal.Using standard notation, the port relations of an ideal VDCCshown in Fig. 1, can be characterized by[2]

$$\begin{bmatrix} I_n \\ I_p \\ I_z \\ V_x \\ I_{Wp} \\ I_{Wn} \end{bmatrix} = \begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ g_m & -g_m & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & -1 \end{bmatrix} \begin{bmatrix} V_p \\ V_n \\ V_z \\ I_x \end{bmatrix}$$

According to the above matrix equation, the first stage can be realized by a balanced transconductance amplifier to convert thedifference of the input voltages ($V_p - V_n$) into the output current (I_z)with transconductance gain of $g_m$and the second stage is a currentconveyor used for transferring x-terminal current to $W_p$and W_n terminals. For a balanced CMOS transconductance amplifier,the parameter $g_m$can be given as

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$$g_m = \sqrt{I_{B1}\mu_n C_{ox}\left(\frac{W}{L}\right)_1}$$

where $\mu_n$is the mobility of the carrier for NMOS transistors, C_{ox}isthe gate-oxide capacitance per unit area, W is the effective channelwidth, L is the effective channel length and $I_{B1}$is bias current.

III. THE PROPOSED VDCC BASED MULTIFUNCTION BIQUAD FILTER

The block diagram of the proposed voltage mode multifunction biquad filter is shown in fig. 2 which contains two lossless integrators, one summer and proportional gain blocks. It is similar in configuration to the filter based on CCII proposed in [3]. In this, most important thing is that all the passive elements are used as grounded elements [4]. So, it is easy to fabricate in the form of IC.

By analysis of the circuit shown in fig.2, the transfer function expressions are given as

$$\frac{V_{out\,1}}{V_{in}} = \frac{\frac{G_1 G^2}{C_1 C_2 (G_1+G-G_2)}}{D(s)} \quad (1)$$

$$\frac{V_{out\,2}}{V_{in}} = \frac{\frac{-sG_1 G}{C_2 (G_1+G-G_2)}}{D(s)} \quad (2)$$

$$\frac{V_{out\,3}}{V_{in}} = \frac{\frac{s^2}{(G_1+G-G_2)} + \frac{G_1 G^2}{C_1 C_2 (G_1+G-G_2)}}{D(s)} \quad (3)$$

$$D(s) = s^2 + \frac{G^2}{C_1(G_1+G-G_2)}s + \frac{G^2}{C_1 C_2} \quad (4)$$

From equations (1)-(4) it can be seen that a lowpass response is obtained from $V_{out\,1}$, a bandpass response is obtained from $V_{out\,2}$and a notch response is obtained from$V_{out\,3}$.

The proposed circuit uses three VDCCs, two grounded capacitors and eight resistors.

The design methodology of using only grounded capacitors is attractive, because grounded capacitor can be implemented on a smaller area than the floating counterpart and it can absorb equivalent shunt capacitive parasitics [6-8].

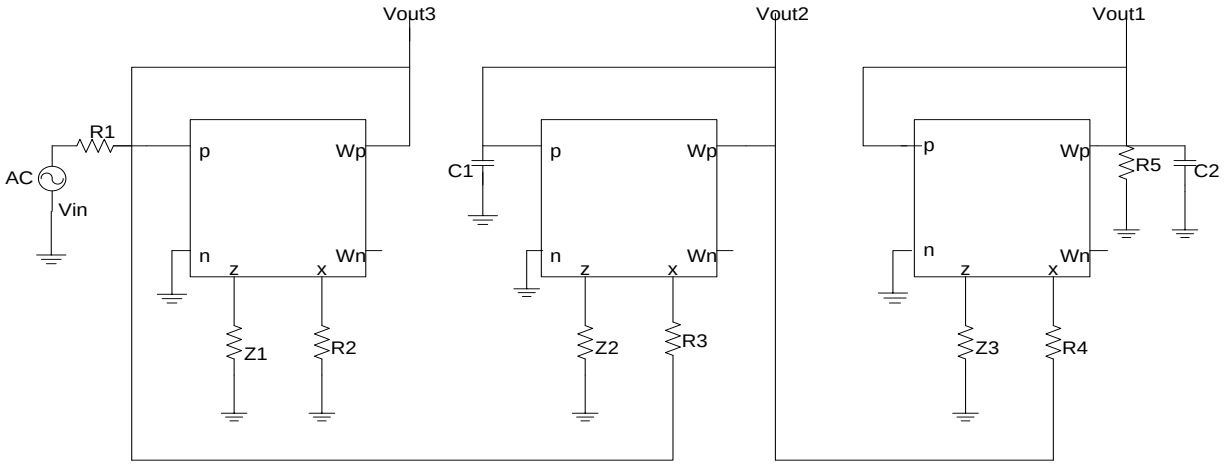

Fig: 2: Block Diagram of Proposed Biquad Filter

In all cases, the resonance angular frequency *ωo* and the quality factor *Q* are given by

$$w_0 = G\sqrt{\frac{1}{C_1 C_2}} \quad (5)$$

$$Q = \frac{(G_1+G-G_2)}{G}\sqrt{\frac{C_1}{C_2}} \quad (6)$$

The resonance angular frequency can be controlled by *G*. The quality factor can be orthogonally controlled by *G*1 or *G*2.

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IV. SENSITIVITY ANALYSIS

The sensitivities of the proposed circuit are given as:

$$S_G^{w_0} = 1\ ;\ S_{C_1}^{w_0} = S_{C_2}^{w_0} = -\frac{1}{2}$$

$$S_{G_1}^{Q} = \frac{G_1}{G + G_1 - G_2}\ ;\ S_{G_2}^{Q} = \frac{G_1}{G + G_1 - G_2}$$

$$S_G^{Q} = \frac{-G_1 + G_2}{G + G_1 - G_2}$$

$$S_{C_1}^{Q} = -S_{C_2}^{Q} = \frac{1}{2}$$

V. SIMULATIONS

The proposed circuit was simulated using PSPICE. The VDCC was implemented using the MOSFET model proposed in [1] using TSMC 0.18µm parameters. Thesupply voltages are chosen as ± 0.9 V. The following setting was selected to obtain the lowpass, bandpass andnotch filters: $R1 = R2 = R3 = R4 = R5 = 1k\Omega$, $C1 = C2 = 1nF$with $Q = 1$ and f_o= 159.15 KHz. Figs. 3 and 4represent the simulated frequency responses for thelowpass (*Vout*1), bandpass (*Vout*2) and notch (*Vout*3) filtersoffig.2, respectively. While fig. 3 shows the low-pass, band-pass and notch responses, fig.4 shows the phase response for the three outputs. The simulation results are coherentwith the theoretical analyse

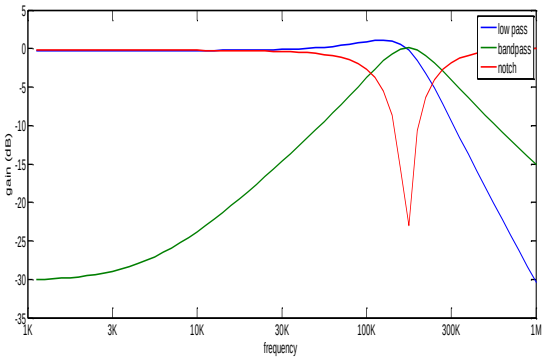

Fig.3 Magnitude response of the proposed biquad filter showing low-pass, band-pass and notch outputs

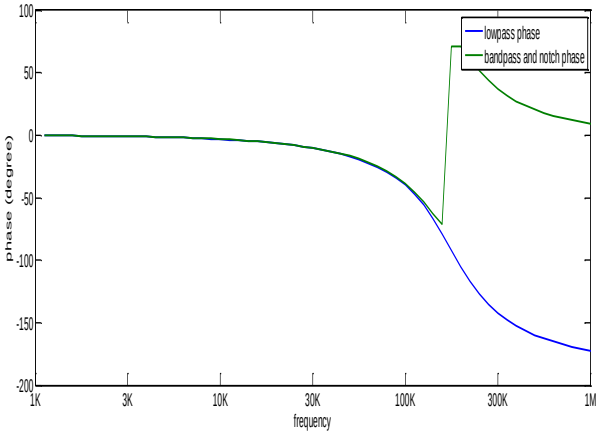

Fig.4 Phase response of the proposed biquad filter

VI. CONCLUSIONS

In this paper, a new single input and three outputs voltage-mode biquadratic filter is presented. The proposed circuit uses three VDCCs, two grounded capacitors and eight resistors. The new circuit offers several advantages, such as the realization of lowpass, bandpass, and notch filter functions, simultaneously, in the same circuit configuration; the use of only three VDCCs; orthogonally controllable resonance angular frequency and quality factor and the use of only grounded capacitors.

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An Empirical Study of Face-to-Face and Distance Learning Sections of a Core Telecommunication course

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Abstract

We present an empirical study that compared the student learning outcomes of face-to-face and distance learning sections of a Telecommunications course. Student performance was assessed based on the course grade, which included the final exam, quizzes, assignments, and midterm exam scores. Both classes were taught by the same instructor, and had similar content and assessment measures. The study factored in the students' demographics such as gender, work and residency status to assess their impact on student learning. In addition, data stored in the learning management system (LMS), BlackBoard ™, were collected and used to understand student activities within the system, and determine their relation with student performance. The number of times the material was accessed and the time duration spent on assessments are some of the examples of the data that were included in the study. The results show that there is a correlation between students' use of Blackboard and student performance. We found a significant statistical difference between course grades of the face-to-face and distance learning sections. We did not find any evidence for significant difference across a range of demographic factors.

1. Introduction

Over the years, as the available technologies and student demographics [6] have changed, higher education institutions have begun offering more and more distance education (DE) classes to their students. According to [2], the number of students taking at least one online class was about 6.7 million in 2012, which is more than 30% of total enrollment. Although research on distance learning (DL) has been conducted since its early adoption, there are few comparative studies between distance and face-to-face (F2F) classes. As institutions increase their offerings of online courses they often face the challenging task of finding the right balance between face-to-face and online offerings and therefore it is important to understand the issues across a range of courses and contexts.

In this study we compare two sections of the same course offered in the same semester. Both two classes used a learning management system (LMS) called Blackboard™ (BB) to facilitate content delivery, store assignments, send announcements, create discussion forums, and manage grades. BB is the official LMS of the institution and is used by instructors to upload the course materials (e.g. lecture slides, lecture and lab videos for the distance learner, syllabus, etc.), conduct quizzes, and communicate with the students. Students used it to download and submit their assignments, complete the quizzes, access course materials, and see their grades.

In this paper, section 2 is a literature review of online and face-to-face class comparisons. We describe our study in section 3 where we elaborate on the data and methods used. Section 4 analyzes the data and reports the results of data

analytics. Section 5 is on conclusion and future directions that concludes our findings, and recommends changes and modifications in subsequent studies for future research.

2. Literature review

For more than two decades, online and F2F education has been of rising interest among researchers, including in engineering [1], because of the significant progress distance education has made in the practical arena. Many of the studies done so far have focused on academic performance measurement to gauge the differences between online and F2F learning, and to assess student satisfaction with the course [11].

An extensive review [8] summarizes the efficacy of the outcomes of online and F2F education. The review involved 355 comparative studies and raised what's known as "No Significant Difference" phenomena. Russell concluded there is no significant difference between online and traditional classroom education outcome. However, his results were criticized for several reasons [3]. The review included some studies of low quality, without qualification. In addition, it accepted the null hypothesis, which does not deny the existence of the difference, where the sample does not include studies with significant difference.

Another meta-analysis [5] reviewed 73 studies that compared online and traditional education during 1992-2002. This meta-analysis shows half of the studies found no significant difference between online and F2F learning outcomes. Interestingly, most of the remaining studies show distance learning students outperform their counterparts of F2F learning environment. It also reports more than half of the studies, which compared student satisfaction with the course, found F2F students are more satisfied with the course in comparison with the online students. In summary, distance learning is as effective as face-to-face learning considering student performance with exams. Another meta-analysis for the period (1996- July 2008) also confirmed that on average students in online settings do better than students in F2F class [7]. However, more recent study [12] indicates that there is a significant difference in overall student performance between F2F and distance education sections. Students taking the course in F2F section have a better performance, but the study does not specify the course being taught.

Bernard et al. [3] conducted a meta-analysis comparing F2F and DL courses, but in their study the DL courses were split into synchronous and asynchronous classes. Synchronous classes require students to be available at specific times to watch streamed lecture videos and participate in live discussions. Asynchronous classes allow students to access the class materials at their convenience. The analysis reported that students in F2F classes outperform the synchronous DL students. However, asynchronous online classes outperform F2F classes.

In a recent study, academic leaders were asked to rate the online learning outcomes. The survey reported 77% of academic leaders believe distance education

outperform face-to-face education. This is a major shift from the survey done on 2003 where only 57.2% of academic leaders perceived the same [2].

Many studies have compared the effectiveness of DL and traditional F2F classes [3, 5, 9, 12]. But, most encountered methodological weaknesses such as small nonrandom samples, lack of factoring demographic variables, and substantial differences in course materials and assessments [4, 12]. To address these shortcomings, the objective of our study was to compare student outcomes of a F2F web-facilitated class and an asynchronous DL class of a core Modern Telecommunication undergraduate course. We factored in demographics data using identical materials and assessments of both sections.

3. Research Study

This empirical study involved two classes. The first class was a web-facilitated F2F course where students met in a classroom during the scheduled class time. It used BB LMS to accommodate a segment of online learning that facilitated course material access, and communication with the instructor and classmates. The second class was an online course. Here most the activities like accessing the materials, watching the lectures, completing the assessments, etc. was done online. The class did require the students to meet face-to-face in a classroom on campus two times a semester to take the midterm and the final exams. Both sections were taught by the same instructor and used the same type of assessments. Both sections had similar enrollment of 34 students each, but their demographics were different. Table 1 summarizes the demographic data of each section.

We defined the type of classes in the study based on the definitions stated in the BSRG report. There are four different types of courses categorized based on the proportion of content delivered online: 1. Traditional course, where there is no technology involved in the content delivery; 2. Web-facilitated course, where technology is used 1%-29% of the course to facilitate content delivery with the use of some type of learning management system. However, most of the course is conducted face-to-face; 3. Hybrid course that entails 30%-79% of the course delivery to be online. Typically, hybrid courses offer blended F2F and DL classes; 4. Online course offers more than 80% of the content via online delivery [2].

Table 1: Demographics distribution of DL and F2F sections

	Gender		Work		Age		Commuting distance		Related work	
	M	F	Full-time	Part-time	<30	>=30	<10	>=10	Yes	No
F2F section	30	4	12	22	26	8	3	31	7	27
Distance learning section	26	8	17	17	25	9	9	25	10	24

A questionnaire was developed to collect students' demographic information. The data includes gender, working status, age, commute distance to campus, and whether their work is related to the course. The data were mapped to the students as part of the analysis.

In both sections, assignments and other course materials were delivered to students using BB. Quizzes were also conducted via BB in both sections. F2F and DL classes had similar assessment evaluation mechanisms. Students in both sections were given identical questions and same amount of time to complete their assessments, and were evaluated by the same instructor using the same grading rubric.

Although there is a huge amount of data available in BB, we were selective in choosing the variables that would possibly have impact on student performance. The variables selected are: time spent completing the assessment, number of times the materials had been accessed, and the time when the students started their assessments.

The course grade was used as an indicator of students' academic performance in the course. It is commonly used as a reliable indicator of how well students meet the course objectives [4, 10]. The course grade composed of four different components: home assignments, midterm exams, quizzes, and final exam. During the semester, there were 6 home assignments that totaled 30% of the course grade, two midterm exams, two quizzes which were mix of multiple choice, short answer, and essay questions (30% weight for two midterms, and 20% for both quizzes), and the final exam (20% of course grade), which was also a mixture of questions similar to the midterm exams.

Research questions:

A. Is there a correlation between the students' demographics and their performance?

B. How did the students perform in distance learning and F2F sections? Is there a significant difference in the outcome (course grade)?

4. Analysis and Results

A. Demographics correlation with course grade

The data used to determine whether there is a correlation between demographics and performance were accumulated from both sections. The majority of students fell in the following categories: male, living off campus (commute distance more than 15 minutes), less than 30 years old, and has no related work experience with the course. The data was not equally distributed among the demographic variables. To resolve the discrepancy of data distribution, it was normalized and expressed as percentage. Figure 1 shows the different demographic variables and the course grade distribution of each variable.

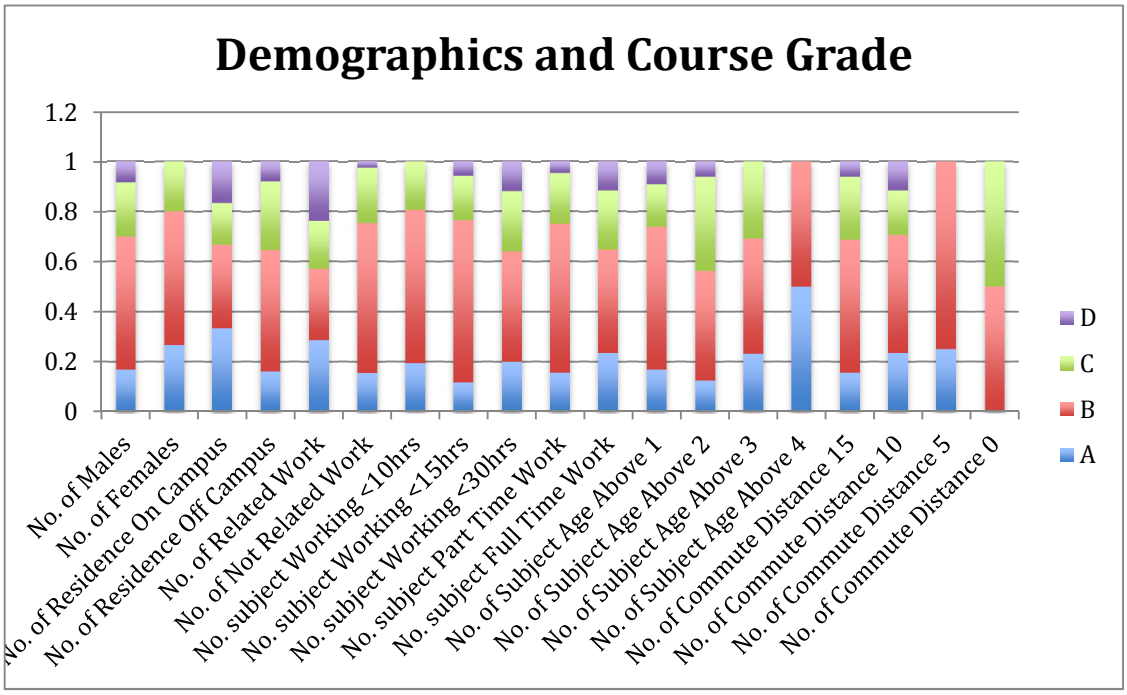


Figure 1: Demographics represented in percentage. The graph shows the percentage of students who earned a course grade of A, B, C, or D of each demographic variable.

The Fisher's exact statistical test was used to analyze the data and find out whether there is a significant relationship between demographic variables and the distribution of course grade. This test was chosen because of the small sample size and the categorical nature of data. In this test, the exact deviation from the null hypothesis is calculated (p-value) rather than relying on approximation.

Table 2 shows the p-value calculation for each demographic variable in its distribution across the course grades (A, B, C, and D). The null hypothesis for each variable: there is no significant relationship between the demographic variable "x" and the course grade. In other words, the number of subjects for each variable, for example, gender (female, and male), is distributed in the course grade represented by (A, B, C or D). These numbers represent the data to be used in the calculation. The test shows that all demographic variables do not have significant difference between the two groups in their category in terms of their course grade distribution, except related work variable (Table 2). The p-value for "related-work" is 0.00027, which means there is a significant difference between the students who have related work experience and those who does not. From the data we discovered on average students with related work experience to the course earned a lower course grade. This finding could be due to external factors; future investigation may reveal clearer insights.

Table 2: Fisher's exact test and p-value of each demographic variable

Demographic Variable x	P-value	Result
Gender (Male, Female)	0.71	No significant difference
Related work (Yes, No)	0.00027	Significantly different
Working hours (<30, >=30) hrs	0.15	No significant difference
Age (<30, >=30) yrs old	0.42	No significant difference
Commuting distance (<10, >=10) miles	0.71	No significant difference

The data collected from Blackboard were based on students' behavior of: the time they started their homework; the time they spent doing it; and the number of times the resource had been visited. Figure 2 shows the correlation between these variables and the course grade. The x-axis represents the course grade, and the y-axis represents the time or number after amplification to show the correlation. The study reveals students who received an A grade tend to do the assignment earlier than others. This is inferred from the average time students begin to do the assignment for each group. Moreover, it reveals that there is a correlation between the number of times students access the resource and the course grade. From the graph, we can see the average number of times students access the resource decreases as the student grade deteriorates. Finally, the average time spent on doing the assignment has no correlation with the grade. Majority of the students have the same average time spent on doing the assignment, except for those who do not pass the course.

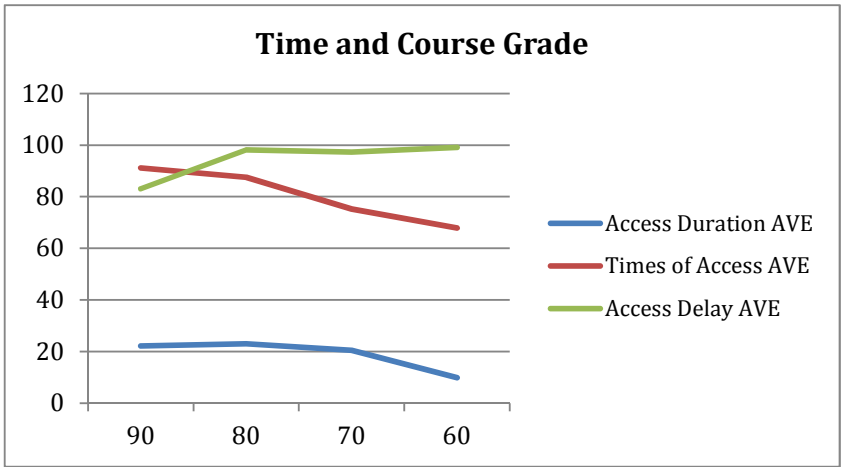


Figure 2: Correlation between the students' behavior in Blackboard and their performance

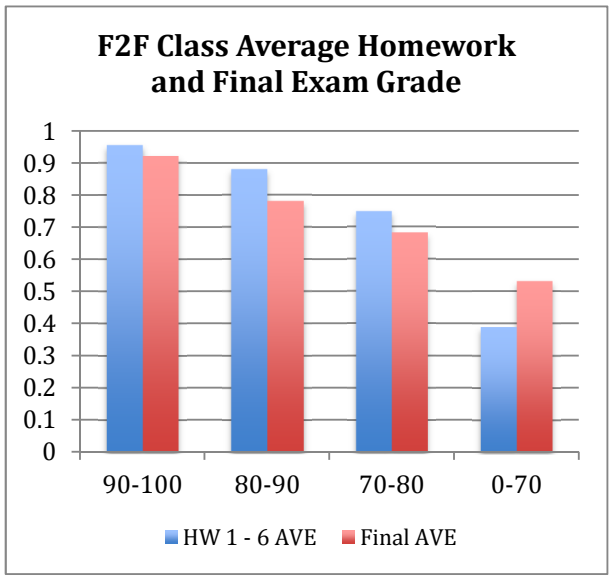
To get statistical inferences from the graph, the correlation coefficient was used to determine the relationship between two variables. The correlation coefficient between the grade and the average "# of times resource accessed" is 0.98, which means there is a strong relationship between the two variable. The student who frequently accessed the resource tends to do a good job in completing the assignment and earn a better grade. The average time spent doing the assignment and the delay time in starting the assignment both show a correlation of 0.83, and 0.80 respectively.

We also performed a simple linear regression to determine if there was a statistically significant relationship between the three variables and the course grade. Using a significant level $\alpha=0.05$, the p-value for the access duration time, access delay time and number of times a resource was accessed were as the following 0.16, 0.20, and 0.02. Thus, we do not reject the null hypothesis for the first two variables and concluded that there were no significant relationships between the access duration time, or the access delay time and the course grade. However, the test (ρ-value=0.02<α) showed that there was a significant relationship between the numbers of times a resource accessed and the course grade.

B. Distance Learning and F2F:

Due to the small size of data, this section will provide a descriptive observation of the data collected. First, the number of female students in a distance learning class is double the size of females in the F2F class, and there is less number of students who commute more than 10 miles (Table1). Second, there are more students who scored 70 or less (4 students) in the distance learning section as opposed to the F2F section (1 student).

On the performance side, F2F students perform better in the final exam, quizzes and midterm exams in comparison with their counterparts in the distance learning class. On the same token, DL students did better in their average homework, particularly the students with 80 or below course grade. Figure 3 and Table 3 reveals this information.



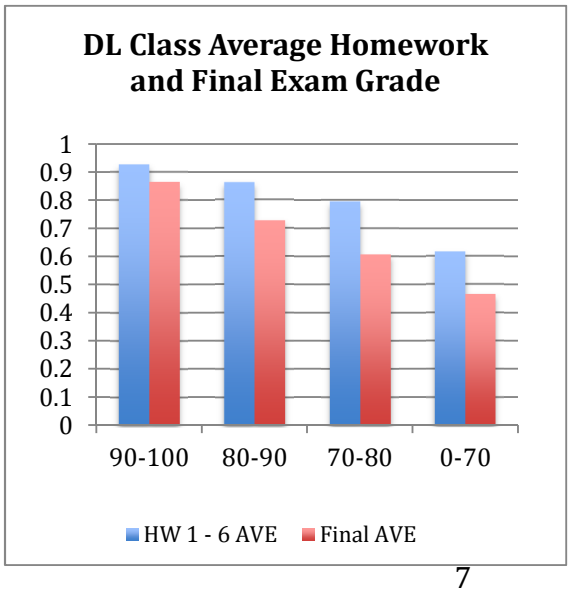


Figure 3: Comparison of Average Homework and Final Exam grades in both sections

Another observation of both classes: students who are 30 years or older have similar performance with quizzes and final exam. In both sections, we observed students who are 30 year old (the common variable) doing poorly with their quizzes but earning better grades in their final exam. This is contradictory because students in general, perform the best in assignment, then quizzes and least in the final exam.

Table 3 shows the two classes are significantly different with course grade, but not the final exam, assignments, quizzes, or midterms grades (A, B, C and D). In other words, the distribution of students who earned A, B, C or D is significantly different with the overall course grade (4-A, 15-B, 14-C, and 1-D) in F2F while in distance learning class the distribution of students is (8-A, 17-B, 4-C, 5-D). Although the number of students in the distance learning section who received A grade is higher, it is also true that the number of them earning D grades is higher.

Table 3: Fisher's exact test results for the assessment variable and their relationship with the distribution of the students in terms of their overall course grade

Assessment x	P-value	Result
Course grade	0.0188	Significantly different
Final exam	0.3268	No significant difference
Average Homework	0.521	No significant difference
Average quizzes	0.267	No significant difference
Midterm1	0.475	No significant difference
Midterm2	0.999	No significant difference

When comparing the two classes, the mean and standard deviation (SD) were used to perform the t-test. Table 4 shows the mean and SD for each assessments used in the class. The result shows the difference between the two classes. DL class outperform F2F class in terms of its average homework scores, however, F2F class outperform DL with the remaining assessments.

Table 4: The mean and standard deviation of each assessment in both sections

F2F Class					
	AVG HW Grade	AVG Quiz Grade	AVG Midterm Grade	Final Exam Grade	Course Grade
Mean	81.73	81.19	76.80	75.24	82.71
SD	0.13	0.16	0.10	0.11	0.07
DL Class					
Mean	83.96	80.05	76.24	69.44	81.81
SD	0.11	0.15	0.15	0.21	0.12

5. Conclusion and Limitations

The study shows the following: there is no evidence found for student demographics independently having a relationship with the student's performance (course grade), except the students who have related work experience; their performance was worse when compared to those who do not have related work experience (based on their overall course grade average). Blackboard data also shows the correlation between student's behaviors in LMS and their grade. The time spent doing an assessment, the time when students start their assessment, and the number of times students access the resource all have a strong correlation with the student grade. Finally, F2F students statistically, significantly outperform distance learning students with their overall course grade. However, both classes in this study obtain similar grades in all the assessments.

Limitations

Our sample is too small to consider all the demographic variables along with the performance to derive at more accurate inference. The combination of more than 6 variables may result in a large number of groups. If we assumed 6 variables and each variable had 2 options (values), then we may end up with 64 different combinations of groups. This is why 100 or 200 subjects are considered quite small to make solid conclusive inferences. If the same course were taught multiple times using the same settings, it would be easier to generalize the findings.

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SHORT COMMUNICATION

Analysis of the Effect of Microphone Parameters in Reciprocity Calibrations Using Taguchi Method

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Abstract: The paper presents parametric study investigating the relative influence of the various microphone parameters affecting the closed coupler reciprocity measurements while computing the sensitivity of reference standard microphones using the well known *MP.EXE* program used by National Metrology Institutes of various countries. A design of experiments perspective using L_9 (3^4) orthogonal array and analysis of variance (*ANOVA*) method is presented for LS1P and LS2P microphones. The relative importance of microphone parameters on its sensitivity is evaluated in terms of percentage contribution using *ANOVA* methodology.

Keywords: *ANOVA* analysis; L_9 (3^4) orthogonal array; Reciprocity method; *MP.EXE* program

1. Introduction

The primary standard for sound pressure in air, with lowest levels of uncertainty of measurement is realized and maintained through the calibration of laboratory standard microphones (LS1P and LS2P) in a closed coupler cavity by reciprocity technique in the frequency range of 31.5 Hz to 25 kHz with an expanded uncertainty of 0.05–0.17 dB ($k = 2$ and 95 % confidence level) [1]. The reciprocity calibration apparatus of the National Physical Laboratory, India (NPLI) is Brüel & Kjær (B&K) type 9699 system [1, 2]. A recent investigation on measurement of microphone parameters has led to reaffirmation of measurement uncertainties ($k = 2$ and 95 % confidence level) in range 0.04–0.15 dB [3, 4]. The designation LS1P refers to a laboratory standard microphone of mechanical configuration 1 having nearly constant pressure sensitivity as a function of frequency [5, 6]. The pressure sensitivity measurement of microphones is influenced by various factors affecting the electrical- and acoustic transfer impedances contributing to the expanded measurement uncertainty. Precise measurement of the volume of the cavity including the equivalent volume of the microphone is pivotal factor in reciprocity method. NPLI had been using the nominal values of microphone parameters specified by B&K for the past few years for the sensitivity fitting exercise for two standard plane wave couplers in *MP.EXE* software until the convergent results are obtained. The experience gained in the recent key comparison exercises viz., bilateral comparison of NPLI with the DPLA, APMP.AUV.A-K1 and APMP.AUV.A-K3 comparison have not only inculcated a confidence in the system procedure and methodology realized, but also provided a scope for further improvement for achieving the highest levels of accuracy and precision on par with other NMIs [7–10]. Thus, it is imperative to continuously upgrade the primary standard for achieving highest levels of accuracy and precision and establish a strong traceability chain throughout the country. The present work focuses on ascertaining the significance of the microphone parameters used in the sensitivity fitting exercise in *MP.EXE* program used by many NMIs of world. This study uses the well known technique of Taguchi method utilizing the L_9 (3^4) standard orthogonal array (*OA*) and analysis of variance (*ANOVA*) analysis to investigate the significance of microphone parameters for both LS1P and LS2P microphones in measurement frequency range of 31.5 Hz to 25 kHz. The relative importance of microphone parameters on its sensitivity is evaluated in terms of percentage contribution using

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ANOVA. Such a design of experiment perspective in context with the reciprocity calibration of microphones had been rarely reported except a recent study reported by Tan [11] wherein 2^6 factorial design is considered to analyze the significance of six microphone back plate parameters on sensitivity, bandwidth and mechanical–thermal noise.

2. Factors Affecting the Reciprocity Calibrations

The sensitivity of one of the three microphones calculated as per reciprocity method is calculated as [12]:

$$M_{\mathrm{p},1}^2 = \frac{R_{12}R_{13}}{R_{23}}\frac{V_{\mathrm{o},12}V_{\mathrm{o},13}}{V_{\mathrm{o},23}}\frac{P_{\mathrm{s},23}}{P_{\mathrm{s},12}P_{\mathrm{s},13}}\frac{\kappa_{23}}{\kappa_{12}\kappa_{13}} \times \frac{\mathrm{Cor}_{\mathrm{HW},12}\mathrm{Cor}_{\mathrm{HW},13}}{\mathrm{Cor}_{\mathrm{HW},23}}C^{-1}, \quad (1)$$

where R_{12}, R_{13} and R_{23} are voltage ratios for the three pairs of microphones, $V_{\mathrm{o},12}$ is cavity volume plus low frequency equivalent diaphragm volume of microphones 1 and 2, $P_{\mathrm{s},12}$ is the static pressure during measurement with microphones 1 and 2, κ_{12} is the ratio of specific heat capacities of cavity gas with microphones 1 and 2, $\mathrm{Cor}_{\mathrm{HW},12}$ is correction factor for heat conduction and wave motion of coupler with microphones 1 and 2 and C is capacitance of series capacitor. B&K type 9699 system is inhouse traceable to the respective standards of voltage, capacitance, dimensional, temperature, pressure and relative humidity realized at NPLI. The variations in environmental conditions from reference value (23 °C, 101.325 kPa, 50 % RH) have a major influence on the sensitivity of microphone determined by reciprocity method. For static pressure changes, only the radiation mass is affected, resulting in a slightly lower resonance frequency. However, changes in temperature not only affect the radiation impedance but also the diffraction around the microphone due to corresponding change in speed of sound [13]. The maximum variation in sensitivity due to variation in pressure by 5 kPa is 0.23 dB at 25 kHz, while that for 2 °C change in temperature is 0.03 dB at 16 kHz. Humidity has least effect as a variation of 20 % shall inculcate a change in sensitivity level by 0.02 dB. The two major corrections considered in the reciprocity measurements, i.e., the wave motion correction is dependent on length of cavity and speed of sound in cavity, while the heat conduction correction is function of cavity length–diameter ratio, volume–surface area ratio, and also depends upon thermal diffusivity and ratio of specific heats of air [12]. Figure 1 shows the cause-and-effect analysis diagram showing the various factors affecting the microphone sensitivity measured using reciprocity set up.

In a pressure reciprocity calibration of microphones using closed couplers, the resulting uncertainties can be divided in three major groups referring to: the measurement of the electrical transfer impedance, i.e., the uncertainties and errors related to the measurement technique and instrumentation used for the calibration; the determination of the acoustical transfer impedance, i.e., the uncertainties and errors related to the calculation procedure and the software used and determination of the acoustical impedances and microphone parameters [14]. The greatest contribution to the standard uncertainty at low frequencies is uncertainty of equivalent volume of diaphragm when determining the acoustic impedance of the microphone. This contribution reduces as frequency increases [15]. The variation of 0.1 mm in cavity depth induces a maximum deviation of 0.02 dB at 16 kHz, 0.03 dB at 20 kHz and 0.07 dB at 25 kHz for a LS2P microphone. Thus, it is imperative to ascertain the significance of deviations in the microphone parameters on sensitivity determination in measurement frequency range for achieving lowest levels of uncertainty of measurement especially when an uncertainty of 0.03 dB is stated by some National Metrology Institutes. Table 1 compares the nominal values of microphone parameters stated by manufacturer and the NPLI reported values in key comparison exercises.

Figure 2 shows the percentage difference of NPLI values in comparison with pilot laboratories for each microphone parameters. The maximum deviation in sensitivity for LS1P microphone w.r.t. pilot laboratory observed in range 200 Hz to 2 kHz is within ±0.02 dB, while highest deviations of 0.06 dB is observed at higher frequencies. In case of LS2P microphone, the maximum deviation in sensitivity determination w.r.t. pilot laboratory observed in range 200 Hz to 2 kHz is within ±0.03 dB, while highest deviation of 0.11 dB is observed at 25 kHz. A maximum difference of 6.36 % in front cavity volume, 12.84 % in equivalent volume, 8.32 % in cavity depth measurement, 4.54 % in loss factor and 13.76 % in resonance frequency determination has been observed in the key comparison exercise for B&K 4180 microphones in comparison with pilot laboratory.

3. Measurement Methodology and Instrumentation

The sensitivities of both LS1P and LS2P microphones were determined by means of reciprocity method wherein the microphone under test is acoustically coupled in pairs with two microphones in a closed coupler. The sensitivity of the microphone was obtained from measurements of the electrical transfer impedance between the pair of microphones and acoustical transfer impedance between the microphones in compliance with IEC 61094-1992. The electrical transfer impedance was measured using the main unit of B&K reciprocity set up 5998, Sine generator, type B&K 1051, a band pass filter, type B&K 1617 and a digital

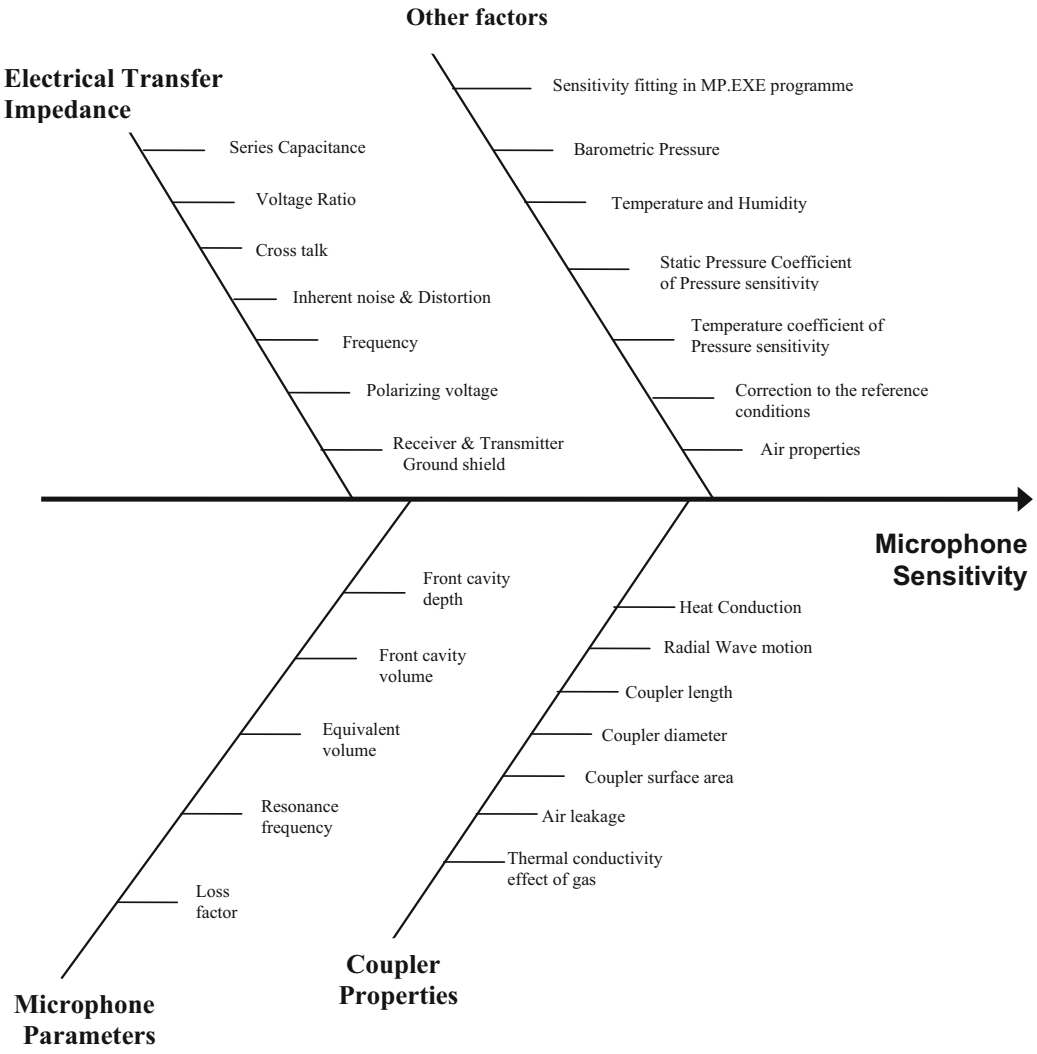

Fig. 1 Cause-and-effect analysis diagram for factors affecting the microphone sensitivity (in dB re 1 V/Pa) measured using the reciprocity set up

Table 1 Comparison of nominal values of microphone parameters stated by manufacturer and the NPL, India reported values in key comparison exercises [7–9]

Nominal values			Measured values in key comparison exercises					
Microphone parameters	LS1P (B&K 4160)	LS2P (B&K 4180)	B&K 4160 in APMP.AUV.A-K1		B&K 4180 in APMP.AUV.A-K3		B&K 4180 in DPLA-DFM and NPL, India	
			S. No. 2142622	S. No. 2302533	S. No. 1763688	S. No. 2341431	S. No. 1124046	S. No. 1395455
Front cavity volume (mm^3)	535	34	535	535	34	32.8	34.2	35.1
Cavity depth (mm)	1.95	0.50	1.95	1.95	0.463	0.504	0.50	0.51
Equivalent volume (mm^3)	136	9.2	139.6	137.6	7.56	9.64	9.24	9.14
Resonance frequency (kHz)	8.2	22.0	8.4	8.4	22.4	22.4	24.8	24.8
Damping factor	1.05	1.05	1.05	1.05	1.05	1.07	1.05	1.05

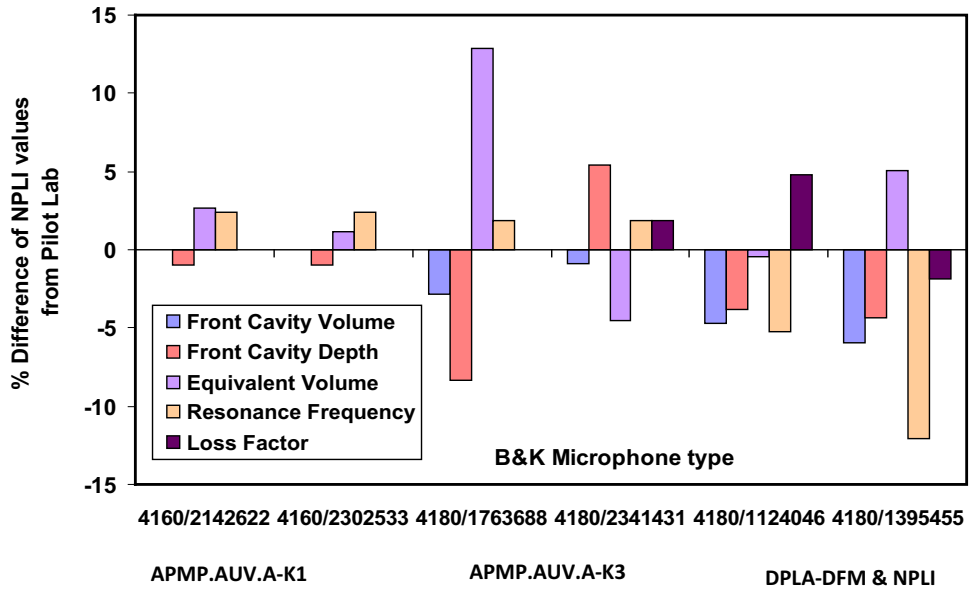

Fig. 2 Percentage difference of NPLI values in comparison with pilot laboratories for each microphone parameters

voltmeter, Datron 1281. The polarising voltage applied to the microphones was 200 ± 0.01 V. All measurements were conducted in a temperature controlled laboratory at (23 ± 2) °C and relative humidity within the range 40–60 % RH. While conducting the reciprocity measurements, it was ensured that standard deviation of measurements STDEV <400 ppm and *S*/*N* ratio is greater than 46 dB [12]. Each single calibration run comprehended three cycles of measurements for three microphones pairs for a single coupler. Two plane wave couplers were used in each measurement for LS1P and LS2P microphones. The long coupler and short coupler used in case of LS1P microphones were of 18.6 mm diameter and nominal length 7.5 and 15 mm, while that in case of LS2P microphones had nominal length 4.7 and 9.4 mm and each had diameter of 9.3 mm. It may be noted that short coupler measurements cater to frequency range 31.5 Hz to 25 kHz, while that in case of long coupler, the measurement range extends from 31.5 Hz to 2 kHz. The measurement data was analysed using computer software *MP.EXE* developed by B&K. The temperature and pressure correction coefficients used to adjust the sensitivity to standard conditions were −0.002 dB/K and −0.016 dB/kPa in case of LS1P microphone. The temperature and pressure correction coefficients used to adjust the sensitivity to standard conditions were −0.0012 dB/K and −0.0055 dB/kPa in case of LS2P microphone.

It may be noted here that these measurements enable only the electrical transfer impedance to be determined, but this is not at all influenced by the choice of microphone parameters. However, the acoustic transfer impedance of the coupler including the thermal conductivity effect of fluid must be modelled precisely to obtain the accurate sensitivity of microphones from the electrical transfer impedance [16]. The microphone parameters influence the acoustic transfer impedance which is derived from analytical calculations [12]. The uncertainty of measurement of microphone sensitivity determined by reciprocity method for LS1P and LS2P microphones is discussed in details in [2, 3], respectively.

4. Taguchi Method and Its Application

The Taguchi method developed by Genuchi Taguchi is a statistical method used to improve the product quality and is commonly used in improving the product quality [17]. Taguchi designs experiments using specially constructed tables known as "orthogonal array" (*OA*). The method based on *OAs* is widely used in industrial and research applications as in this approach fewer number of experiments are required to obtain optimum level of process parameters. An *OA* is a fractional factorial design used to ascertain the effects of multiple process variables on the performance characteristic while minimizing the number of test runs. The use of these tables makes the design of experiments very easy and consistent [18] and it requires relatively lesser number of experimental trials to study the entire parameter space. As a result, considerable savings in time, cost, and labour is achieved using this innovative technique. The Taguchi technique includes the following steps summarized as:

- selection of the control factors affecting the output and their respective levels,

- selection of an appropriate *OA* as recommended in Taguchi method,
- conducting the experiments as enunciated by the *OA*,
- analysis of the data using *ANOVA* and determine the optimal levels of control factors,
- investigate the relative influence of all these parameters,
- performing the confirmation experiments and obtaining the confidence interval,
- improving the quality characteristics through optimization.

A statistical *ANOVA* is performed to investigate which process parameters are statistically significant. The analysis of sensitive factors can be accomplished using main effects plot whereby the average value of the output parameter at each level of control factors considered is plotted. The present work is only restricted to the investigation of the relative influence of microphone parameters as the confirmation run is not required.

Table 2 Selected microphone parameters (LS1P and LS2P) at different levels

Microphone parameters	Level 1		Level 2		Level 3	
	LS1P	LS2P	LS1P	LS2P	LS1P	LS2P
A						
Front cavity volume, FCV (mm^3)	540	36	535	34	530	32
B						
Equivalent volume, EQV (mm^3)	135	7.5	140	8.0	145	8.5
C						
Damping factor, DF	1.06	1.06	1.05	1.05	1.04	1.04
D						
Resonance frequency, R_f (kHz)	8.0	20	8.5	22	9.0	24

4.1. Selection of Orthogonal Array (*OA*)

The parametric investigations were conducted to analyze the significance of microphone parameters using the Taguchi method. The selection of control factors, i.e., microphone parameters and their levels were made on the basis of experience gained in periodic calibration exercise conducted at Acoustics and Vibration Standard, CSIR-NPLI. Thus, considering the variation of these microphone parameters as revealed in recent key comparisons participated as shown in Fig. 2, four parameters: front cavity volume, equivalent volume, damping factor and resonance frequency were selected for investigations. The sensitivity of microphone under test (in V/Pa) was the output parameter to be analyzed. The front cavity depth, which is another vital parameter especially for high frequency sensitivity measurements, has not been considered as a separate parameter here as it is already used in calculation of the front cavity volume. It may be noted here that other factors influencing the Eq. (1) in conjunction with static temperature and pressure coefficients used for calculation of microphone sensitivity were kept constant here in order to analyze the significance of microphone parameters exclusively. Each of the four factors were considered at three levels as shown in Table 2. The choice of three levels has been made such that the effect of these factors on the performance characteristics may vary nonlinearly.

An L_9 (3^4) standard *OA* [18] as shown in Table 3 was used in present work. An *OA* is fractional factorial design that facilitates the minimum number of test runs required to reach a conclusion with a particular level of confidence whereby the effect of multiple process variables on performance characteristic can be estimated simultaneously. The array is most suitable to provide the minimum degrees of freedom as 9 [$= 1 + 4 \times (3 - 1)$] required for an experimental investigation. The selection of an appropriate *OA* requires prior estimation of degrees of freedom.

Table 3 L_9 (3^4) standard orthogonal array

Experiment Nos.	Front cavity volume, FCV, (mm^3) *A*	Equivalent volume, EQV (mm^3) *B*	Damping factor, DF *C*	Resonance frequency, R_f (kHz) *D*
1	36	7.5	1.06	20
2	36	8.0	1.05	22
3	36	8.5	1.04	24
4	34	7.5	1.05	24
5	34	8.0	1.04	20
6	34	8.5	1.06	22
7	32	7.5	1.04	22
8	32	8.0	1.06	24
9	32	8.5	1.05	20

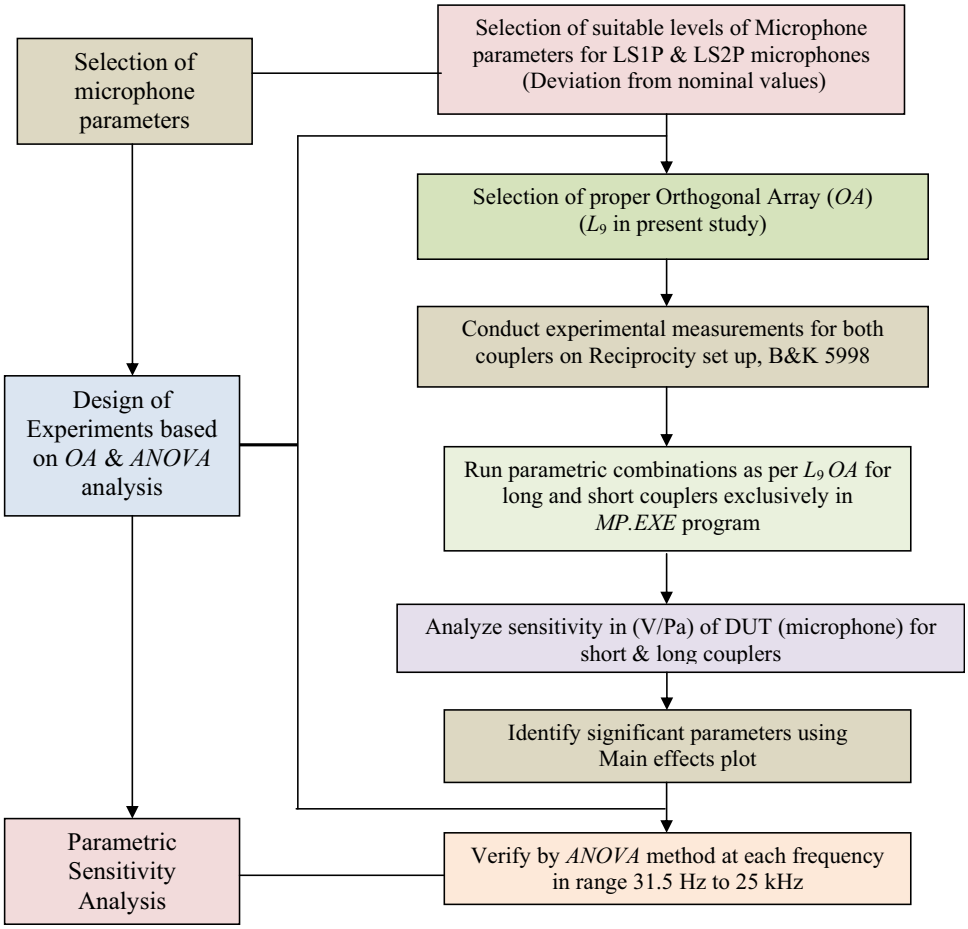

Fig. 3 Methodology adopted for ascertaining the significant microphone parameters in reciprocity calibrations

Basically the degree of freedom for an *OA* should be greater than or at least equal to those for the process parameters influencing the output [19].

Four control factors each identified at three levels viz., A_1 (540 mm^3), A_2 (535 mm^3), A_3 (530 mm^3), etc., can be investigated using an L_9 *OA*, while the intersections or correlations were considered to be negligible. The array has nine rows and four columns and each row represent an experimental run, while each column accommodates a specific process parameter. The factors investigated were identified as *A*, *B*, *C* and *D* and while conducting the experiment, all intersections amongst parameters *A*, *B*, *C* and *D* were ignored. The methodology adopted for ascertaining the significant microphone parameters is shown in Fig. 3. The three levels of microphone parameters were selected such that it corresponds to deviation from the nominal values (Level 2) as reported in key comparisons. The experimental measurements were conducted for the two couplers on reciprocity set up B&K 5998 as discussed in Sect. 3. All parametric combinations as desired by L_9 *OA* for long and short couplers were run exclusively for microphone under test in *MP.EXE* program. As reciprocity measurements require three microphones for measuring the sensitivities, the parameters viz., front cavity volume, equivalent volume, resonance frequency, damping factor, static pressure and temperature coefficients were kept constant for the other two microphones used along with the microphone under test. The sensitivity of device under test in V/Pa (V/Pa $= 10^{M_p/20}$, M_p in dB re 1 V/Pa) for long and short couplers was analyzed exclusively and significant parameters using main effects plot were investigated. It may be noted here that the present investigations don't have objective of either maximizing or minimizing the sensitivity, thus an average sensitivity for three levels is analyzed instead of ascertaining the *S/N* ratio for larger-the-better or smaller-the-better is followed in routine application of Taguchi method [19]. The main effects plot shows the average sensitivity value in dB re 1 V/Pa for each value of the control factor considered at three levels as listed in Table 3. For instance, for the front cavity volume parameter, the average sensitivity value in dB re 1 V/Pa for a LS2P microphone for three experimental runs (1–3, 4–6, 7–9 as listed in Table 3) determined at three respective levels considered, e.g., 36, 34 and 32 mm^3 is

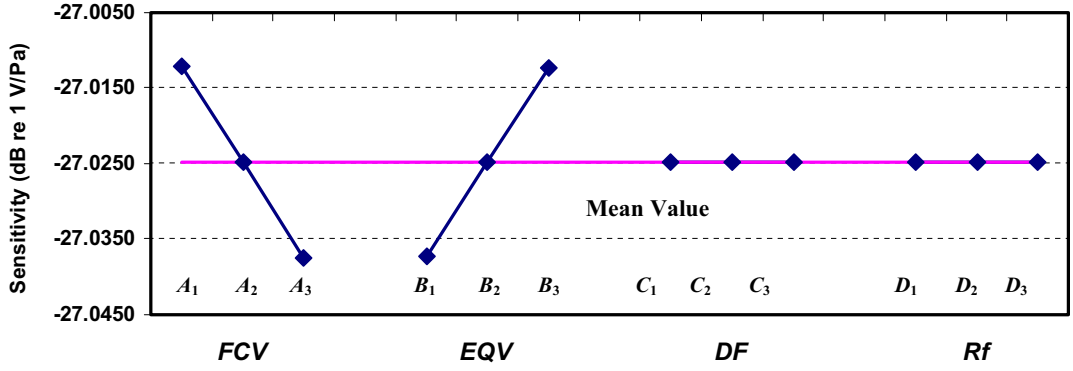

Fig. 4 Main effects plot for average sensitivity (in dB re 1 V/Pa) at three levels of a LS1P (B&K 4160) microphone at 250 Hz

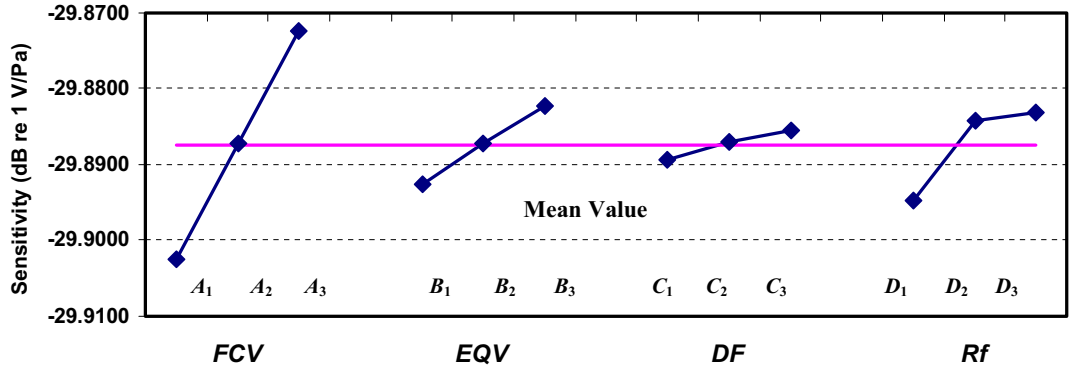

Fig. 5 Main effects plot for average sensitivity (in dB re 1 V/Pa) at three levels of a LS1P (B&K 4160) microphone at 10 kHz

plotted in main effects plot. The parameters having a larger variation at three levels considered indirectly indicates their higher sensitivity to the output value. Also, the present investigations were exclusively undertaken for three microphones to ascertain the repeatability of the results of *ANOVA* methodology. With all these parametric combinations as desired by L_9 *OA*, the heat conduction and wave motion correction may have altered resulting in the change in the output value (sensitivity).

Figures 4 and 5 show the main effects plot for average sensitivity (dB re 1 V/Pa) at three levels (shown in Table 3) of a B&K 4160 microphone at 250 Hz and 10 kHz. At 250 Hz, the front cavity volume and equivalent volume plays a significant role, while at 10 kHz, the front cavity volume is the most significant parameter. At 10 kHz, the resonance frequency also plays a prominent role. These investigations revealed following conclusions when analyzed for B&K 4160 microphones for the complete frequency range from 31.5 Hz to 10 kHz as:

- Front cavity volume plays a significant role in the entire measurement frequency range,
- Equivalent volume is significant up to 5 kHz after which its significance diminishes,
- Resonance frequency plays a dominant role after 5 kHz,
- Damping factor has no statistical significance,
- *ANOVA* analysis for both the long and short couplers reveals the same results.

Figures 6 and 7 show the main effects plot for average sensitivity (dB re 1 V/Pa) at three levels of a B&K 4180 microphone at 250 Hz and 25 kHz. It can be observed that at 250 Hz, front cavity volume is most prominent parameter, while equivalent volume has little significance. At 25 kHz, front cavity volume is the most significant parameter as compared to other parameters. These investigations revealed following conclusions when analyzed for B&K 4180 microphones for the complete frequency range from 31.5 Hz to 25 kHz as:

- Front cavity volume plays a significant influence in the entire frequency range,
- Equivalent volume hasn't major influence in measuring the final sensitivity derived using the *MP.EXE* program,
- Resonance frequency plays a dominant influence above 4 kHz,
- Damping factor has no statistical significance,
- *ANOVA* analysis for both the long and short couplers reveals the same results.

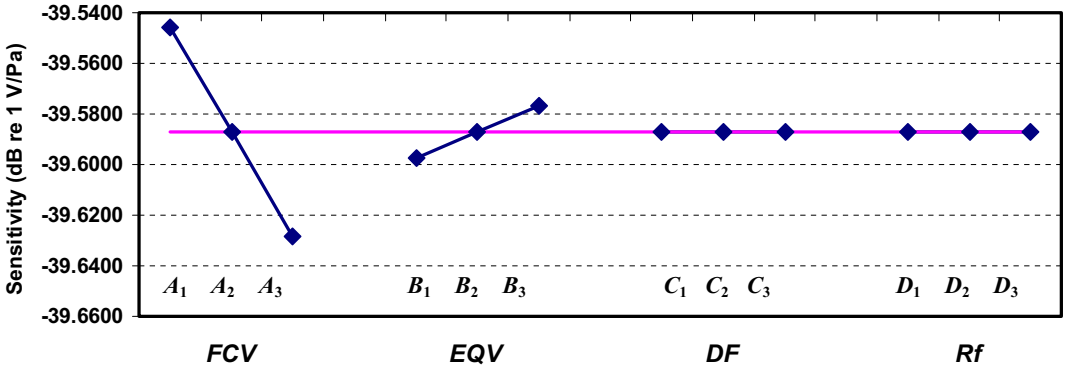

Fig. 6 Main effects plot for average sensitivity (in dB re 1 V/Pa) at three levels of a LS2P (B&K 4180) microphone at 250 Hz

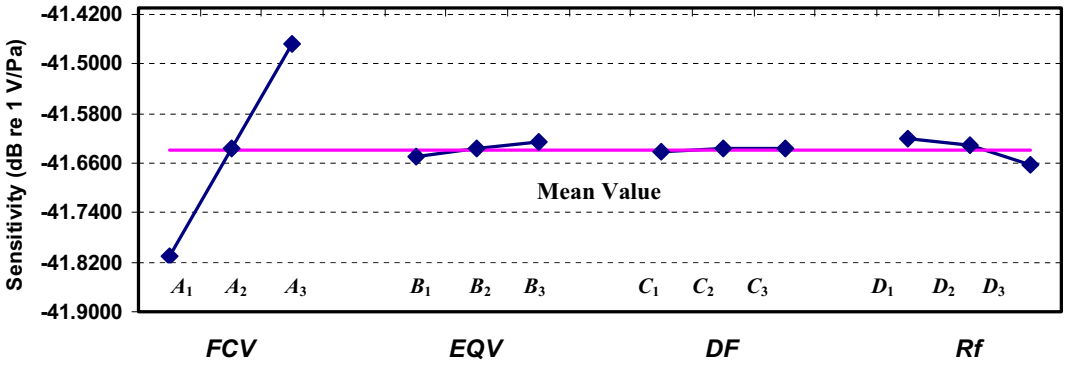

Fig. 7 Main effects plot for average sensitivity (in dB re 1 V/Pa) at three levels of a LS2P (B&K 4180) microphone at 25 kHz

4.2. *ANOVA* Analysis

The *ANOVA* is performed to investigate the relative influence of significant parameter. *ANOVA* was used to investigate the significance of design parameters significantly affecting the quality characteristic. The total sum of squared deviations from means (SS_T) can be calculated as [19, 20]:

$$SS_T = \sum_{i=1}^{n} y_i^2 - \frac{1}{n}\left[\sum_{i=1}^{n} y_i\right]^2, \tag{2}$$

where n is number of experiments in the *OA* (e.g., 9 in L_9 *OA*) and y_i is resultant output (sensitivity in V/Pa) for ith experiment. The total sum of squared deviations is decomposed into two sources: the sum of squared deviations due to each design parameter and the sum of squared error. The sum of squared deviations due to each process parameter (SS_p) is calculated as:

$$SS_p = \sum_{j=1}^{t} \frac{(\bar{y})^2}{t} - \frac{1}{n}\left[\sum_{i=1}^{n} y_i^2\right]^2, \tag{3}$$

where p represents one of the experimental parameters, j is the level number of this parameter p, t is the repetition of each level of parameter, $\bar{y}_i$ is sum of output involving this parameter p and level j. The sum of squares for each error parameter (SS_e) in L_9 *OA* considering four parameters at three levels is then calculated as:

$$SS_e = SS_T - \sum_{i=1}^{4} SS_i, \tag{4}$$

where SS_i is sum of squared for each of the four microphone parameters viz., A, B, C and D calculated using Eq. (3). The percentage contribution by each of the design parameters is a ratio of the sum of squared deviations due to each design parameter to the total sum of squared deviations [19, 20]. The mean of squares deviation is calculated as ratio of sum of squared deviations due to each parameter to degree of freedom, wherein degree of freedom of each parameter is $(t - 1)$. F-ratio for each design parameter is the ratio of the mean of squared deviation to the mean of squared error and is used to statistically ascertain the significance of design variable. Table 4 shows the computed results for *ANOVA* analysis with 95 % confidence level. The F-ratio of the microphone parameters for LS1P microphones at 250 Hz and 10 kHz are quantified in Tables 4 and 5 at 95 % confidence level.

Table 4 Results of analysis of variance (*ANOVA*) for an LS1P (B&K 4160) microphone at 250 Hz

Parameters	Degree of freedom (DOF)	Sum of squares (*S*)	Mean square	*F*-ratio	Percentage contribution
A					
Front cavity volume	2	0.02518	0.01259	2E06[a]	50.8
B					
Equivalent volume	2	0.02439	0.012195	2E06[a]	49.2
Pooled error	4	5.72E−08	2.86E−08		
(Damping factor and resonance frequency)					
Total	8	0.04957			100.0

From *F*-Table, $F_{0.05;1,2} = 18.5$

[a] Factors are significant at 95 % confidence level

Table 5 Results of analysis of variance (*ANOVA*) for an LS1P (B&K 4160) microphone at 10 kHz

Parameters	DOF	Sum of squares (*S*)	Mean square	*F*-ratio	Percentage contribution
A					
Front cavity volume	2	0.01836	0.00918	59.6[a]	74.5
B					
Equivalent volume	2	0.00212	0.00106	6.9[b]	7.5
D					
Resonance frequency	2	0.00344	0.00172	11.2[a]	13.0
Pooled error		0.00030			5.1
(Damping factor)					
Total	8	0.02423			100.0

From *F*-Table, $F_{0.05;1,2} = 18.5$, $F_{0.1;1,2} = 8.53$

[a] Factors are significant at 95 % confidence level

[b] Factor is insignificant at 90 % confidence level

The analysis shows that at 250 Hz the front cavity volume and equivalent volume plays a pivotal role in affecting the microphone sensitivity. The measure of relative significance is ascertained by *F*-ratio, whereby the factors having high probability typically higher than 95 % are confirmed as significant factors. Larger the *F*-ratio, the greater is the effect on the performance characteristic due to change of the process parameter.

The inactive and smaller effects were added together to obtain a non-zero estimate of the error variance called 'pooling up' which can be used to combine factors or interaction effects with low magnitude of sum of squares [18–21]. Table 5 shows the *ANOVA* analysis of B&K 4160 microphone at 10 kHz, wherein it can be observed that front cavity volume and resonance frequency plays a pivotal role with 95 % confidence level. The equivalent volume is insignificant at 90 % confidence level and thus constitutes the pooled error along with damping factor at 10 kHz. These investigations when extended in the entire frequency range also reveal an interesting fact that the percentage contribution of equivalent volume and front cavity volume on final sensitivity is relatively constant within the frequency range 200 Hz to 2.5 kHz for LS1P microphones. In case of LS2P microphones at low frequency, the front cavity volume is the most significant parameter as shown in Table 6. The damping factor and resonance frequency constitutes the pooled error at 250 Hz. At 25 kHz, the front cavity volume has even more relative significance as compared to 250 Hz. The resonance frequency and equivalent volume have little influence although these parameters are significant at 95 % confidence level as shown in Table 7. These investigations when extended in the entire frequency range revealed the fact that the percentage contribution of equivalent volume and front cavity volume on final sensitivity is relatively constant with the frequency range 200 Hz to 4 kHz in case of LS2P microphones. The significance of equivalent volume diminishes after 16 kHz and thus the front cavity volume plays a prominent role in determination of the final sensitivity at higher frequencies. Thus, it is imperative to

Table 6 Results of analysis of variance (*ANOVA*) for an LS2P (B&K 4180) microphone at 250 Hz

Parameters	Degree of freedom (DOF)	Sum of squares (*S*)	Mean square	*F*-ratio	Percentage contribution
A					
Front cavity volume	2	0.01510	0.00755	9E7[a]	94.2
B					
Equivalent volume	2	0.00094	0.00047	5E7[a]	5.8
Pooled error	4	8.11E−10	4.05E−10		
(Damping factor and resonance frequency)					
Total	8	0.01604			100.0

From *F*-Table, $F_{0.05;1,2} = 18.5$

[a] Factors are significant at 95 % confidence level

Table 7 Results of analysis of variance (*ANOVA*) for an LS2P (B&K 4180) microphone at 25 kHz

Parameters	Degree of freedom (DOF)	Sum of squares (*S*)	Mean square	*F*-ratio	Percentage contribution
A					
Front cavity volume	2	0.15942	0.07971	3673.2[a]	97.9
B					
Equivalent volume	2	0.00082	0.00041	18.9[a]	0.5
D					
Resonance frequency	2	0.00250	0.00125	57.5[a]	1.5
Pooled error	2	0.00004	2.2E−05		0.1
(Damping factor)					
Total	8	0.16278			100.0

From *F*-Table, $F_{0.05;1,2} = 18.5$

[a] Factors are significant at 95 % confidence level

have the highest levels of accuracy and precision associated with the measurement of front cavity volume for determination of the sensitivity with a definite uncertainty.

The present investigations also recommends the range of 200 Hz to 2 kHz in case of LS1P microphone and range of 200 Hz to 4 kHz in case of LS2P microphones as a good match of the sensitivities for long and short couplers while doing the sensitivity fitting exercise. Apart in this range, the relative heat conduction and wave motion corrections are small. This fact is consistent with the previous investigations reported by Wagner et al. [22] and B&K user manual [12].

5. Discussion and Conclusions

The paper presents a design of experiment perspective by utilizing the *OA* approach and *ANOVA* methodology of well known Taguchi method for ascertaining the significance of the microphone parameters viz., front cavity volume, equivalent volume and resonance frequency used in determination of the sensitivity (in dB re 1 V/Pa or V/Pa) while conducting the sensitivity fitting exercise with *MP.EXE* program. An L_9 standard *OA* was used to accommodate four control factors each at three levels for adjudging their parametric sensitivity. The sensitivity results were obtained on *MP.EXE* program for nine parametric combinations as shown in Table 3 for both the LS1P and LS2P microphones. The conclusions drawn from the present work were as follows:

- Front cavity volume is the most significant parameter in the entire measurement frequency range for both LS1P and LS2P microphones. Thus, it is imperative to measure this value with a definite uncertainty for achieving the highest levels of accuracy and precision in reciprocity calibrations, which also implies a higher accuracy and precision associated with measurement of front cavity depth.
- Equivalent volume is significant up to 5 kHz in case of LS1P microphones after which its significance

diminishes. In case of LS2P microphone calibrations, equivalent volume hasn't any major role on the final sensitivity derived using the *MP.EXE* program computations.

- As obvious, resonance frequency plays a vital role at higher frequencies. In case of LS1P microphones, it plays a significant role after 5 kHz, while in case of LS2P microphones, it plays a significant role after 4 kHz. This can be interpreted as the frequency variation in sensitivity for LS1P microphones depends strongly on wave motion in cavity behind the back plate for frequencies higher than 0.5 f_0.
- The percentage contribution of equivalent volume and front cavity volume on the final sensitivity of microphone under test is relatively constant within the frequency range 200 Hz to 2.5 kHz for LS1P microphones. In case of LS2P microphones, the percentage contribution of equivalent volume and front cavity volume on final sensitivity is relatively constant with the frequency range 200 Hz to 4 kHz. The corrections for heat conduction and wave motion are also small in this frequency range and thus this range may be considered as good match of the sensitivities for long and short couplers while doing the sensitivity fitting exercise. The above mentioned frequency range is optimum for sensitivity fitting as at low frequencies, it is difficult to separate the influence of equivalent volume and the front cavity volume and accordingly the total volume is to be adjusted for best match between different couplers at low frequencies.
- Damping factor has no statistical significance as revealed from the *ANOVA* analysis.
- *ANOVA* analysis performed for the short coupler in frequency range 31.5 Hz to 2 kHz revealed identical results as that for the long coupler for both the LS1P and LS2P microphones. Also, the sensitivities of the other two microphones was unaffected by changing the microphone parameters while performing the sensitivity fitting exercise in *MP.EXE* program for the device (microphone) under test as is confirmed by the observed maximum standard deviation to be 0.001 dB for LS1P microphone at 10 kHz and 0.0039 dB for LS2P microphone at 25 kHz for the nine experimental runs shown in Table 2.

Interestingly, the sensitivity computation for nine parametric combinations as decided by L_9 standard *OA* for LS1P microphone had shown that standard deviation was less than 0.02 dB in measurement frequency range of 31.5 Hz to 10 kHz, while that for LS2P microphone, the standard deviation of nine set of measurements was observed to be less than 0.04 dB in frequency range 31.5 Hz to 20 kHz. At 25 kHz, the standard deviation had been observed to be 0.15 dB. It may be noted that the statistical insignificance of damping factor and equivalent volume at higher frequency in case of LS1P microphone shouldn't be misinterpreted as the irrelevance of lowest uncertainty of measurement associated with the measurement of these parameters especially when an uncertainty levels of 0.03 dB are reported by some National Metrology Institutes. Future work in this regard focussed on the intersections of parameters for ascertaining the correlations amongst the microphone parameters especially at lower frequencies using suitable *OA* shall be indispensable in analyzing the significance and correlations of microphone parameters and their influence on the acoustic transfer impedance of the cavity. It is imperative to focus on these studies for realizing the primary standards with lowest levels of uncertainty of measurement for strengthening the measurement traceability chain throughout the country [23–26].

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Application of Membrane Bioreactor Technology for Waste Water Treatment and Reuse: Case Study of MBR Plant in Luxury Hotel in Delhi

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Abstract

The availability of potable water has become severely limited in the past decade and the quality of current water supplies is deteriorating rapidly . Water contamination by disposal of untreated sewage into water bodies ,water scarcity ,salinity intrusion are common problems faced by many cities in India. Recycling and reuse of wastewater by commercial complexes,residential colonies,industries is the need of the hour.It would eliminate the need for large centralised treatment plants, reduce demand on local supplies and pollution of water bodies.Membrane bioreactors is an ideal solution for the water problems in urban areas. MBR processes produce effluent of high quality enough to be discharged to coastal, surface waterbodies used for irrigation,flushing and other purposes depending upon the quality of treatment . Membrane bioreactors combine conventional biological treatment processes with membrane filteration to provide an advanced level of organic and suspended solids removal. Membrane bioreactor technology has been gaining popularity over past few years all over the world.. Many countries like Singapore are using membrane treatment successfully for supplementing water supplies. MBR technology is yet to gain popularity in India as preferred treatment method over conventional treatment methods for industrial and domestic wastewater treatment. This paper focuses on performance of membrane bioreactors in wastewater treatment in a MBR plant in a hotel in Delhi and the suitability of treated water for reuse and recycling..Samples of raw sewage water and treated water were taken from the plant and tested in laboratory to analyse the efficiency of wastewater treatment by MBR technology. Composite samples were taken for 5 days in the month of October. The changes in wastewater composition were evaluated by measuring changes the total amount of organic matter in terms of BOD, COD, suspended solids (SS,phosphates,nitrogen content of raw water and treated water samples.

Keywords: membrane bioreactor, activated sludge, water quality, waste water treatment, recycle and reuse

I. INTRODUCTION

Wastewater management in urban India is based on centralised systems of sewerage networks for treatment and disposal. The centralised conventional technologies of sewage collection and treatment are capital intensive and not effective in urban areas were the population density is high . Nearly 50-80 perecent of domestic wastewater mostly untreated are disposed off in the water bodies. The increasing population and sewage generation has resulted in pollution of water bodies and drinking water supplies have been affected . There is a need for developing decentralised sewage treatment plants at community level with good,effective treatment methods which enables wastewater reuse . This will considerably reduce the load on municipal treatment plants and reduce pollution of water bodies.

Membrane Bioreactor technology can be effectively used for wastewater treatment in residential,commercial complexes,hotels,industries to achieve enhanced nutrient and organic matter removal .The treated water can be effectively utilised for various purposes like horticultiure ,flushing etc. This results in reduced net daily water requirements from Tube wells/Municipal sources for landscape/ horticulture and lesser withdrawal from underground aquifer water sources.It also reduces dependence on the public utilities for water supply and sewerage systems.Sludge generated from the Sewage Treatment Plant is rich in organic materials and is excellent manure for horticulture purpose.

This paper aims to analyse the performance and efficiency of waste water treatment process by MBR technology in a luxury hotel in Delhi . This paper gives the results and discussion of the test analysis done on the the treated water from the plant and its suitability for reuse and recycling for various purposes within the hotel.

II. MEMBRANE BIOREACTOR TECHNOLOGY CHARACTERISTICS AND COMPARISON WITH CONVENTIONAL METHODS

Membrane processes are classified based on membrane pore size,mechanisim,membrane material and configuration. The commercially successfully membrane seperation process are Ultrafilteration (UF) and Micro filteration (MF) and Nanofilteration (NF). The typical pore size are as follows :MF 0.1 -0.2 µm, UF 0.002- 0.1 µm and for NF 0.0001- 0.001 µm .

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All the three processes rely on hydrostatic pressure differences for filteration. Microfilteration and Ultrafilteration is most commonly used membrane sizes used for municipal and commercial wastewater treatment .(Stacy Scott).

A. Membrane Configuration

The MBR systems are of two types submerged configuration (membranes are placed inside the bioreactor tank) and external configurations (placed outside the tank). In a submerged configuration ,the membrane module is submerged in aeration basin and and the filteration is done by suction removal of effluent by pumps . The external configuration is pressure driven filteration and is more prone to membrane fouling than submerged MBR due to high permeate flux . The transmembrane pressure (TMP) varies from 1-4 bar and permeate flux varies from 50 – 120 $L.h^{-1}.m^{-2}$ in external configuration while in submerged configuration TMP is around 0.5 bar and permeate flux varies from 15-50 $L.h^{-1}.m^{-2}$ (B.Marrot,2004) .Submerged configuration is usually preferred for domestic waste water treatment as it relies on coarse bubble aeration for mixing which maintains solids in suspension and leads to better biodegradability.Submerged systems are more economical than external systems as the energy consumption is significantly lower as it does not require pumps for recycling Submerged configurations operate at lower flux with good removal efficiency.

B. Membrane Materials

Membranes are usually made from ceramic and organic polymer materials but metallic membranes also exist. The most widely used commercially successful membranes are made from cellusloses,polyamides,polysulphone and polymeric substances such as polyvinylidene difluoride(PVDF) polyacrylonitrile (PAN), polyethylsulphone (PES), polyethylene (PE), and polypropylene (PP). These polymeric membranes have good chemical and physical resistance.

C. Biological Performance

1) Bod And Cod Removal

In conventional waste water treatment processes like activated sludge process removal of COD and BOD5 varies from 80-95 % while in MBR process can reach upto 96-99 % depending upon the quality and pore size of membranes. The pollutant uptake rate of MBR is higher than conventional processes due to high number of micro organisims in the reactor tanks .This leads to better degradation of organic matter in a given time span and smaller requirement of reactor volumes than the conventional methods.

Cic¸ek et al. conducted a study in 1999 to compare the ASP and MBR process for treatment of waste water , where a synthetic effluent similar to domestic effluent was used. The operating conditions of both systems were similar except for the sludge retention time (SRT) which was 30 days for the membrane bioreactor system and 20 days for activated sludge system . This study stated that removal of COD and dissolved organic matter in MBR was found to be higher at 99 % and 94.5 % respectively than the conventional ASP where removal of COD was 96.6 % and dissolved organic matter was 92.7 % .

2) Nutrient Removal

In urban areas nutrient removal from domestic sewage is primary concern especially in areas prone to eutrophication. In conventional ASP nitrification and denitrification technologies are applied besides phosphorous removal by enhanced biological phosphorous method (EBPR). MBR technology is an attractive alternative for nitogen and phosphorous technologies applied in conventional ASP method to achieve low nutrient effluent.

3) Sludge Yield

The membrane bioreactor is characterized by a complete retention of the biomass inside the bioreactor because of the use of membrane separation unlike the conventional activated sludge system. This increases the sludge retention time (SRT) high SRTs increases the sludge concentration and the applied organic load, thereby increases the pollutant degradation.(Marrot et al , 2004)

III. STUDY AREA

The study area is a MBR plant with a design capacity of 500 KLD located in a luxury hotel in Delhi .Samples of raw sewage and treated water from the MBR plant were taken and analysed in labroratory to evaluate the performance of MBR plant. The membrane used in the bioreactor are made of PVDF material and of 0.2 microns poresize.The membranes were stacked in form of cassettes. The filterate from the MBR is removed by means of MBR filterate pumps. Return activated sludge pumps are provide in the MBR chamber to maintain the continuous circulation of the mixed liquor between the aeration tank and MBR chamber.The filterate from the MBR is collected in treated water tank.

IV. METHODOLOGY

A. Sampling Period

Samples were taken for 5 days in the month of October 2014 from the inlet and outlet of the MBR facility.

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B. Sampling Materials and Methods

The experimental method consisted of collection of composite samples of raw sewage and treated water from the inlet and outlet of MBR plant in a one litre bottle.Sampling was conducted from 9 am to 2 pm which has peak sewage flow for 5 days .

The efficiency of MBR treatment was examined by conducting tests in laboratory on samples and measuring changes in concentration of the total amount of organic matter in terms of BOD, COD, suspended solids (SS),Ammonia, nitrate,Phosphate of raw sewage and treated water. The samples of raw sewage and treated water collected from the outlet is shown in figure below

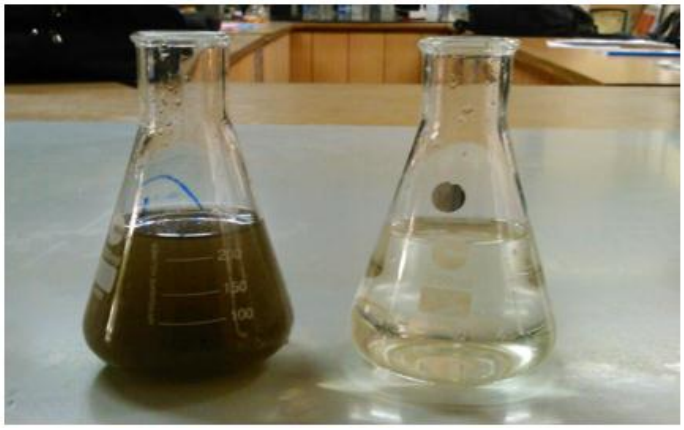

Fig. 2 : Sample collected from inlet and outlet of MBR plant

C. Laboratory Analysis

All measurements were conducted in research laboratory of Environmental Engineering Department of Delhi Technological University . Laboratory analysis conducted is given in Table 1.

Table – 1
Laboratoty Analysis Methods

PARAMETER	*METHOD*
pH	*pH meter*
COD	*Open reflux*
BOD	*Winkler method*
TSS	*Gravimetric Method*
TDS	*Gravimetric Method*
NITRATE	*Brucin -Spectrofotometric Method*
TKN	*Kjeldahl Method*
TOTAL PHOSPHATE	*Stannuous Chloride –spectrofotometric Method*
HARDNESS	*EDTA method*
SODIUM ,POTTASIUM	*Flame photometer*

V. RESULTS AND DISCUSSION

Raw Sewage and Treated water characteristics Based on the laboratory analysis conducted on the inlet and outlet samples for different primary parameters following results were drawn from the study .

A. Characteristics Of Inlet And Outlet Wastewater.

The pH of the inlet and outlet varied from 7.38 to 8.45 which was measured using a pH meter . The ratio of $BOD_{5/}$ COD indicates the biodegradability of wastewater and the higher the ratio higher the biodegradability of the wastewater The ratio of BOD to COD indicates the extent to which the organic matter in wastewater is degradable by aerobic microorganism and if biological processes is suitable for treatment of the particular type of wastewater. The BOD5/COD ratio varied from 0.54 -0.61 at inlet indicating suitability for biological treatment by Membrane Bioreactor Process

B. BOD Removal Efficiency

BOD is described as the dissolved oxygen used by aerobic microorganism in biochemical oxidation of organic matter (Davis and Cornwell, 1991).

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The BOD 5 of the raw sewage from the hotel at inlet varied from 280- 400 mg/L over the five day sampling period. The BOD5 of outlet treated water varied from 20-28 mg/L which is within the permissible limits as given by DPCC. BOD removal is indicative of the efficiency of biological treatment processes .The efficiency of removal of BOD 5 varied from 91-93 % with an overall average removal efficiency around 92.9 %

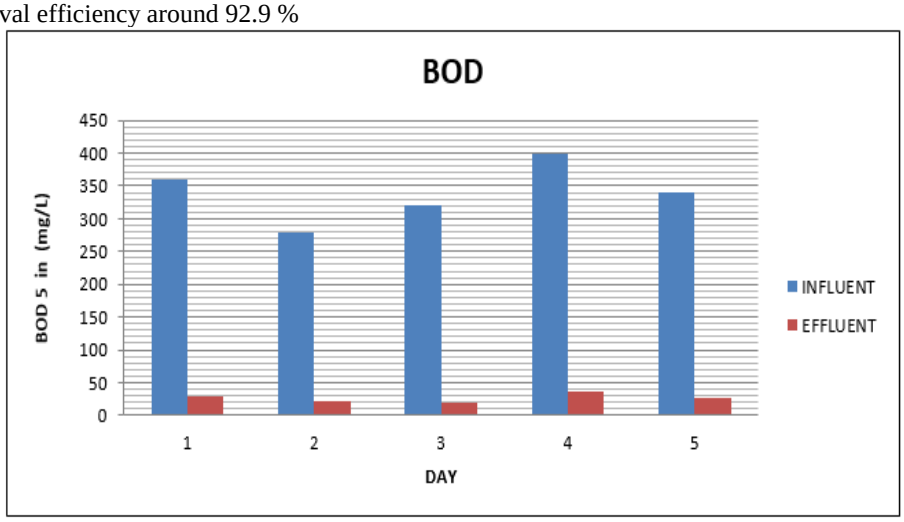

Fig. 2: BOD in inlet and outlet samples

C. COD removal efficiency

Chemical oxygen demand of the inlet varied from 420- 580 mg/L while at outlet varied from 28- 46 mg /L . The COD value determines the efficiency of biological process of treatment plant . The removal efficiencies varied from 89 -91 % overall average of removal being 90.9 % for 5 day sampling period.

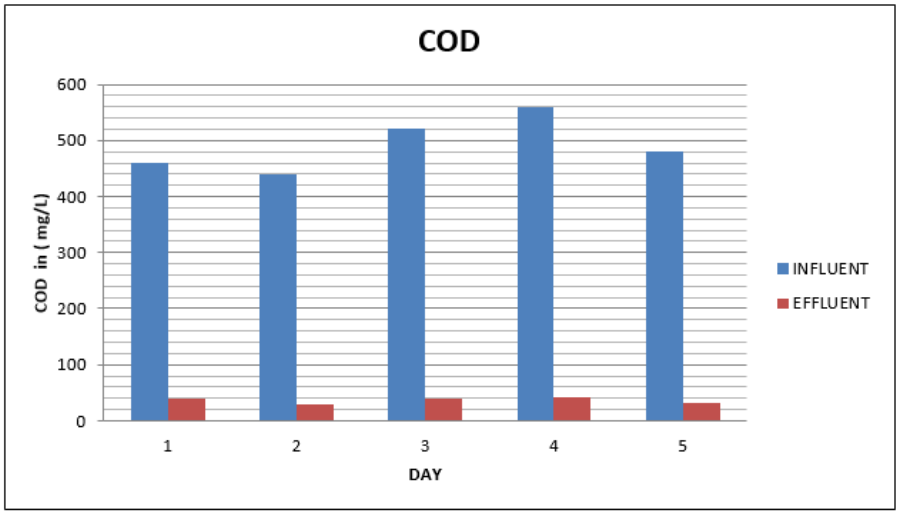

Fig. 3: COD in inlet and outlet samples

D. Phosphate removal efficiency

The available phosphate concentration in treated water varied from 7.32- 9.2 ppm with average removal efficiency around 61 %. The total phosphate in outlet varied from 8.44 -11.365 ppm with removal efficiency around 68 %.

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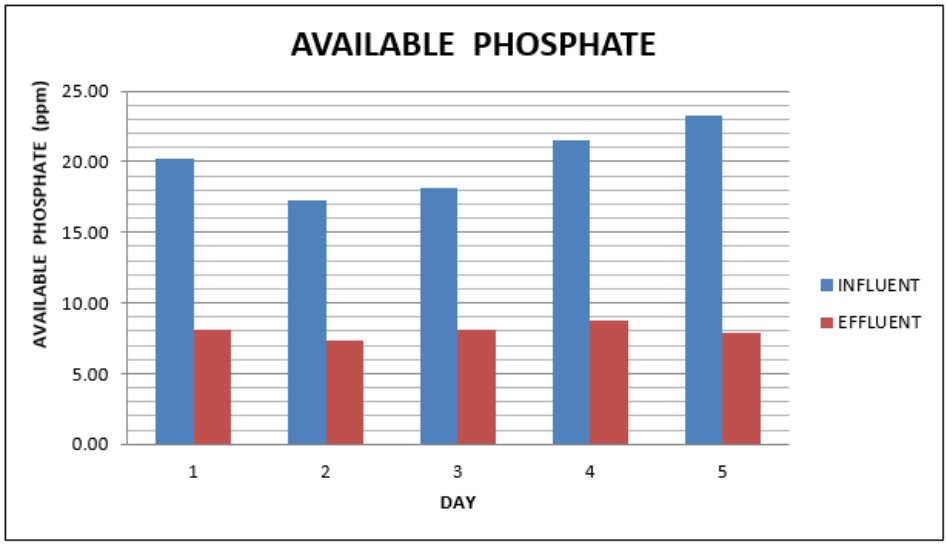

Fig. 4: Available phosphate in inlet and outlet samples

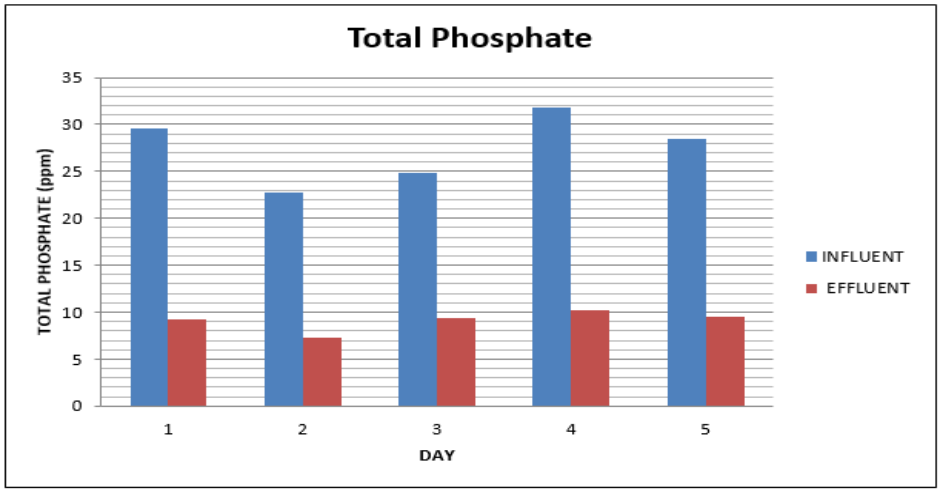

Fig. 5: Total phosphate in inlet and outlet samples

E. Ammonia and Nitrate removal efficiency

The Total Kjeldahl Nitrogen concentration varied from 18.20 -25.80 ppm in samples collected from outlet with average removal efficiciency of 61 % . The nitrate concentration in treated water samples varied from 7.54 -9.10 ppm with removal efficiency of around 65 % .

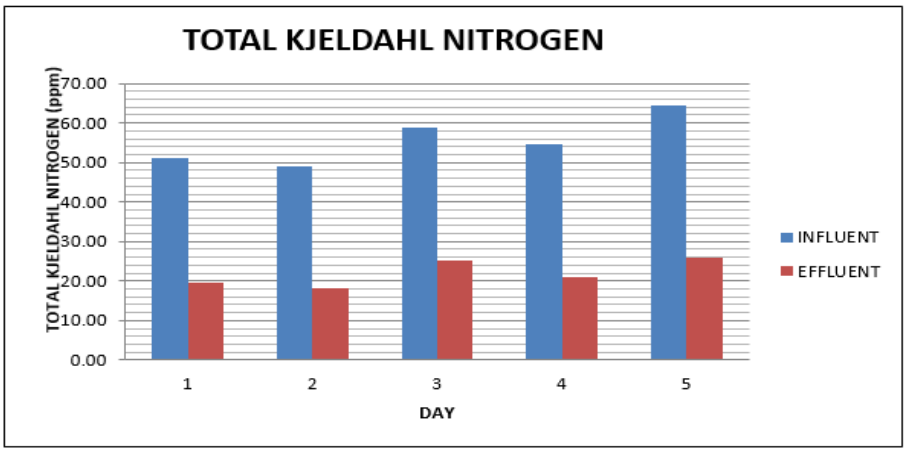

Fig. 6: Total Kjeldahl Nitrogen in inlet and outlet samples

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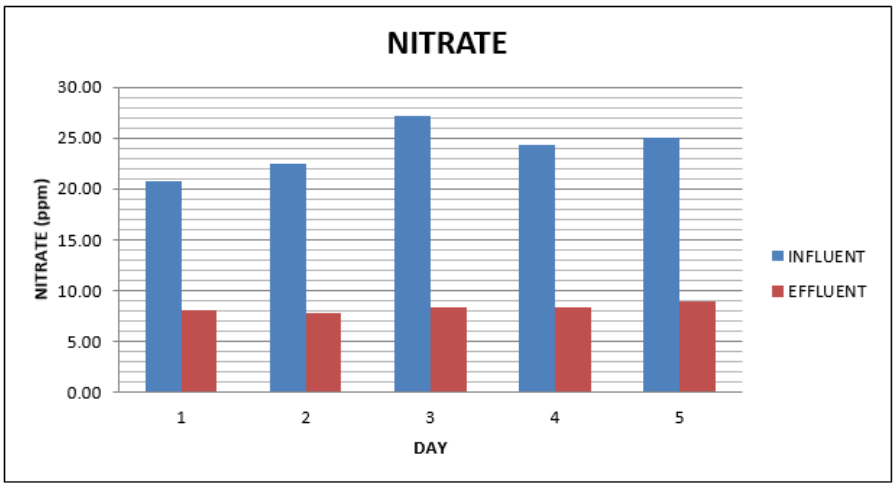

Fig. 7: Nitrate in inlet and outlet samples

F. TSS and TDS removal efficiency

MBR technology has very high TSS removal efficiency rate than normal treatment methods . The TSS and TDS values of inlet varied from 318-458 mg/L and 2231-3892 mg/L measured using gravimetric method . The TSS at outlet varied from 22-35mg/L with an average removal efficiency of around 93 % .

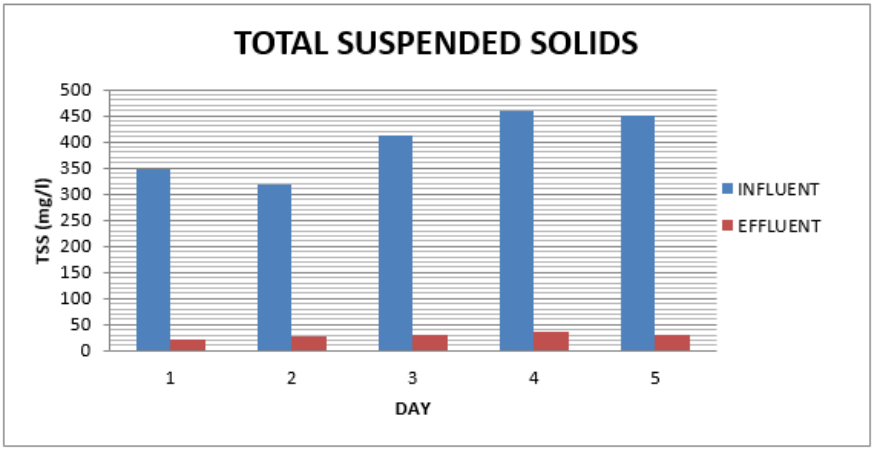

Fig. 8: TSS in inlet and outlet samples

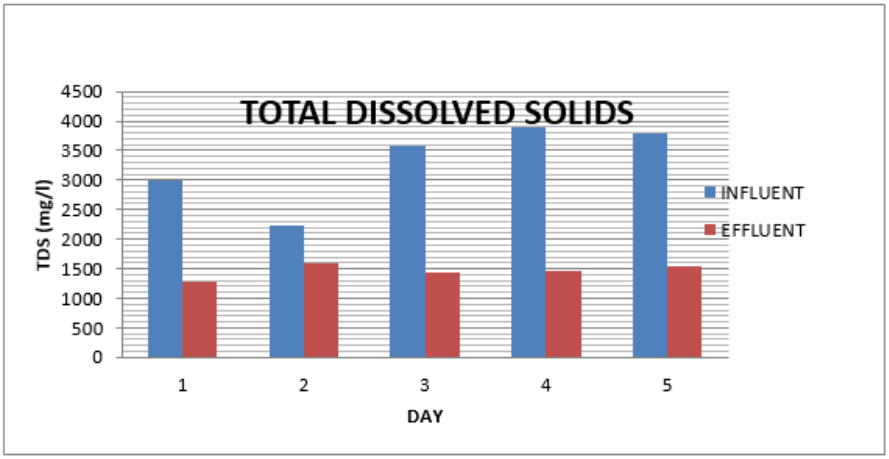

Fig. 9: TDS in inlet and outlet samples

The average removal efficiency of BOD 5 and COD was around 90-92% which is very high as compared to conventional treatment methods.. The phosphate and nitrogen removal was found to be around 65-70 % and not so effective as predicted by the manufacturer. The TSS removal by MBR was found to be really effective with removal efficiency varying from 93- 94 %.

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The treated water was very clear . The low efficiency of removal of phosphate and nitrogen can be due to low MLSS in the bioreactor tank. The MLSS content needs to be regulated and monitored periodically for effective removal at all times. Addition of cow dung in the recirculation tank can prove effective for removal of nitrogen and phosphate content in wastewater . The treated water from MBR has better removal efficiency as compared to conventional methods of treatment but has lower efficiency from the MBR prototypes. The comparison of the removal efficiencies is given in table below.

Table – 2
Comparison of removal efficiencies of phsio-chemical parameters

PARAMETERS	*CONVENTIONAL M ETHODS*	*THEORETICAL MBR EFFICIENCY*	*REMOVAL EFFICIENCY AT PLANT*
COD	*80-85*	*99*	*90.9*
BOD	*85-95*	*98-99*	*92.9*
TSS	*60*	*99*	*93.25*
NITROGEN	*95*	*97-99*	*61.61*
PHOSPHOROUS	*88*	*96-99*	*68.28*

The results of the testing and analysis were compared with the DPCC guidelines for disposal of effluents from commercial complexes and except for the phosphate the treated water met with the effluent standards of DPCC.

Table – 3
Comparison of treated water with effluent standards by DPCC GUIDELINES

PARAMETERS	*EFFLUENT STANDARDS*	*TREATED WATER*	*REMARKS*
pH	*5.5-9*	*7.4*	*WITHIN LIMIT*
COD	*-*	*52mg/L*	*-*
BOD	*30 mg/L*	*29.5*	*WITHIN LIMIT*
TSS	*50 mg/L*	*26.75 mg/L*	*WITHIN LIMIT*
OIL AND GREASE	*10*	*NOT DETECTABLE*	*WITHIN LIMIT*
PHOSPHATE	*1*	*5.73*	*EXCEEDING LIMIT*

G. Suitability for Irrigation

Treated water can be used for horticulture if conforms with the standards for water used for irrigation. The standards for irrigation water in India are given in *Guidelines* for Quality of Irrigation Water, *Is 11624 -1986.*

Table - 4
Guidelines for water used for irrigation

WATER CLASS	*SODIUM %* *(Na)*	*ELECTRICAL CONDUCTIVITY µmhos/c.m at 25 C*	*SAR*
Excellent	*<20*	*<250*	*<10*
Good	*20-40*	*250-750*	*10-18*
Medium	*40-60*	*750-2250*	*18-26*
Bad	*60-80*	*2250-4000*	*>26*
Very Bad	*>80*	*>4000*	*>26*

The treated water was tested for sodium,pottasium and Ca,Mg content. The SAR ,sodium absorption ratio and electrical conductivity was measured and calculated to evaluate its suitability for irrigation and horticulture .The results are given below.

Table – 5
Suitability of treated water for irrigation and horticulture

PARAMETERS	*DAY 1*	*DAY 2*	*DAY 3*	*DAY 4*	*DAY 5*
Na+	*356.3*	*394.2*	*348.4*	*364.1*	*358.2*
Ca+	*482*	*534*	*468*	*448*	*320*
Mg+	*430*	*398*	*450*	*389*	*625*
K+	*32.6*	*38.5*	*36.4*	*33.2*	*32.9*
TDS	*1281*	*1582*	*1433*	*1450*	*1530*

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ELECTRICALCONDUCTIVITY (mS/c.m)	*3.16*	*3.13*	*3.12*	*3.18*	*3.15*
SAR	*16.66*	*18.59*	*16.26*	*17.79*	*16.47*
Na%	*27.38*	*28.85*	*26.74*	*29.49*	*26.8*

The electrical conductivity in treated water varies from 3.12- 3.18 mS/c.m for the 5 day samples. The SAR ratio varies from 16-18 which is good quality water for horticulture. The sodium % varies from 25-28 which is also of good suitability for horticulture.

VI. CONCLUSIONS

MBR technology is being used for decentralised wastewater treatment plants for the past few years .The efficiency of MBR prototypes, pilot studies show very high efficiency of removal of organic matter and impurities but in actual treatment plants the efficiency of removal may vary.

The BOD,COD removal efficiency for this study was 92.9 and 90.5 % respectively which is higher than the conventional processes which have removal efficiency range from 80 -85 %. The TSS removal rate is 93.9 % which is higher than the conventional processes too. The nitrogen and phosphate removal efficiency is not so high in the particular plant. This is due to variation and low concentration of MLSS and improper sludge recirculation. The efficiency of treatment can be increased in MBR plants with proper monitoring of MLSS concentration in reactor tanks and proper sludge recirculation ..

Though the overall efficiency and effluent quality from MBR plant is not as high as reported for membrane bioreactors ,it is higher than that by conventional processes. The treated water from the MBR plant of study area is successfully being used in flushing and HVAC purpose in the hotel . MBR technology can be effectively used for waste water treatment in decentralised wastewater treatment and disposal of treated water onto water bodies with lesser pollutant load. The characteristics of the MBR process makes it ideal for small communities, commercial complexes to meet the discharge limits prescribed by authorities . MBR systems have minimal operator interface and smaller carbon footprints than conventional waste water treatment plants .MBR systems are ideal for residential colonies ,offices, commercial complexes looking to minimise the impact of WWTP , reuse and recycle the waste water thereby reducing water demand and waste water discharge . There is a need for monitoring the MLSS concentration and sludge recirculation to improve the working efficiency of treatment of Membrane Bioreactor Plants and to optimize the cost of MBR treatment for popularising this technology.

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REPORT

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BARAPULLA ELEVATED ROAD PROJECT: PAST, PRESENT AND FUTURE

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Summary

Express corridors have been planned by Govt. of Delhi to reduce the travelling time between distinct far ends. Elevated Road Project over Barapulla Nallah is one such corridor connecting East and South Delhi. The Project has been conceived in three phases with nodal locations as Mayur Vihar in East Delhi and Aurobindo Marg in South Delhi with intermediate locations as Sarai Kale Khan and Jawahar Lal Nehru Stadium. An Elevated road, 4 Kms long connecting Sarai Kale Khan and Jawahar Lal Nehru Stadium has been completed in recent past as 1st Phase. Work from Nehru Stadium to Aurobindo Marg is presently in progress in 2nd Phase, while the 3rd Phase for future, in planning stage will serve as the last link between Sarai Kale Khan and Mayur Vihar to complete the South-East link. Since the alignment of the corridor was over a drain (Nallah), and other Engineering measures for environmental related issues like use of fly ash, high strength concrete for reducing carbon footprints etc., the project is graded as an environmentally sustainable Project.

Keywords: Elevated Road, Precast segmental, post tensioning, pre-tensioned I girders, Deck to deck continuity, pre-stressing couplers, pre-stressed voided slab

1. Introduction

The Proposed Barapulla Nallah Corridor has been conceived as East-south corridor as an alternative route to congested section of Ring Road between Sarai Kale Khan and AIIMS that facilitates the immediate need of Commonwealth Games and in long run for the movement of freight, goods, people, and utilities. The alignment which is along Barapulla Nallah (drain) collects the discharges of other internal, peripheral and trunk drains to further discharge its contents-1,25,000 Kld of domestic sewage into the Yamuna. Barapulla Nallah in its east west orientation starts from Ring Road to INA, crosses major screen line i.e. Mathura railway track, several Arterial Roads namely Nizamuddin Railway Station Road, Mathura Road near Jangpura, Lala Lajpat Rai near CGO Complex, Bhishm Pitamaha Marg near Sewa Nagar Flyover, and meeting Aurobindo Marg before being covered under Dilli Haat. The Nallah with a width of 70 m. on an average covers an area of 9.60 Ha. The areas

along the Barapulla Nallah include INA, Sewa Nagar, JLN Stadium, CGO complex, Jangpura, Nizammuddin, Siddhartha Extension and Sarai Kale Khan Village.

2. Execution of Project in Phases : Past, Present and Future

As defined in the Summary itself, the Project has been conceived and its execution planned in 3 phases.

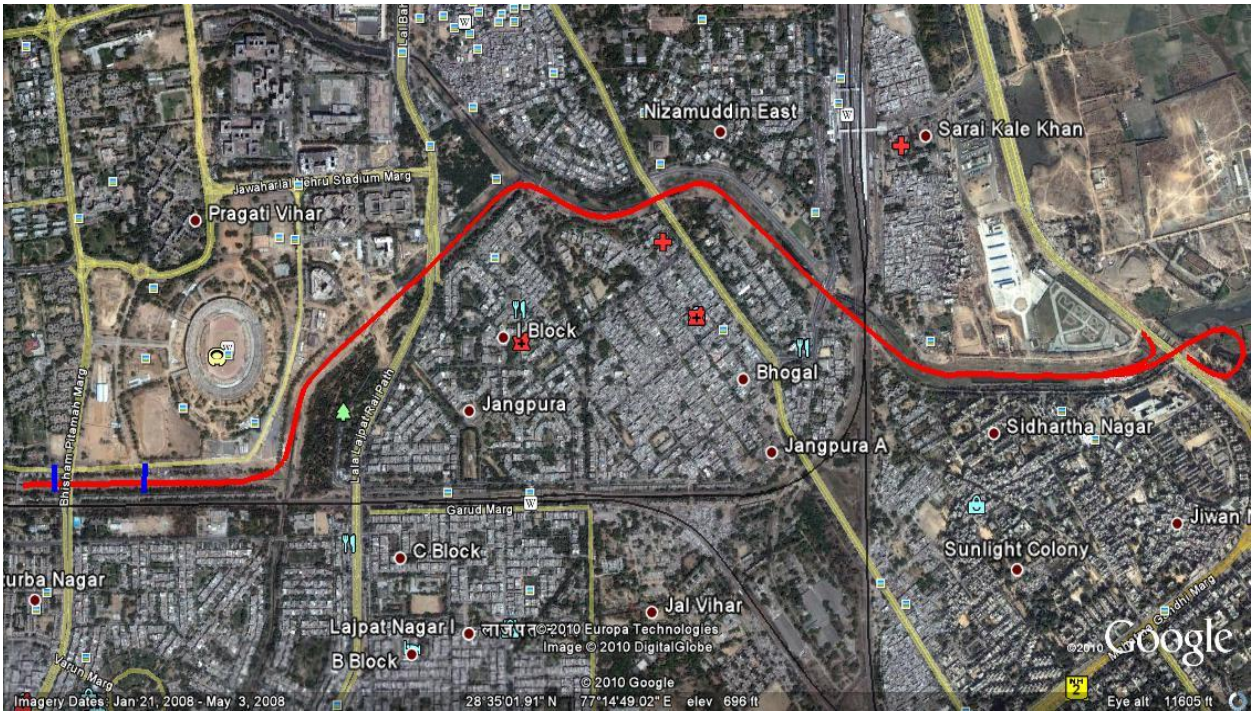

Fig. 1 : Phase I of Barapulla Corridor on google Map

Phase 1 (Past) : In phase 1, an Elevated road, 4 Kms long connecting Sarai Kale Khan and Jawahar Lal Nehru Stadium has been completed in recent past in 2010 to facilitate the movement of sports persons and sports lovers to reach Jawahar Lal Nehru Stadium and enjoy the Common Wealth Games 2010 without facing the traffic hassles of Delhi.

Phase 2 (Present) : In Phase 2, at present, the construction of connectivity from Jawahar Lal Nehru Stadium to INA is in progress. In addition to this connectivity, there are certain intermediate loops connecting the elevated road constructed in Phase 1 with the major arterial roads crossing on the way. Also the missing facilities for ascending and descending to the elevated corridor at Sarai Kale Khan are being added in 2nd phase. The works in Phase 2 are expected to be completed and operational in 2015.

Phase 3 (Future) : In phase 3, the major link to connect the elevated corridor with East Delhi at Mayur Vihar after crossing Yamuna will be provided. The major planning of the Project is completed with all mandatory clearances from Local Bodies and Project has been planned to start in the current Financial Year so that the complete corridor is operational by 2017.

3. Phase 1 from Sarai Kale Khan to Jawahar Lal Nehru (JLN) Stadium

Phase 1 of the Project completed and made operational in 2010 for the commonwealth Games, was constructed as Precast Segmental Construction, to complete the construction in lmited time frame and without causing much disturbance to the flowing traffic in Delhi.

For spans other than at major crossing, this technique of construction was successfully employed. Here, a span is constructed by joining together several precast units of length ~ 3.0 m & pre-stressing them. For facilitating standardisation of segments, the cables were so profiled that they draped down/up only in the segments near end but followed horizontal

profile in the middle segments. By taking out some of segments from central zone, various span lengths were possible. This offered flexibility in planning of substructure location depending on site conditions. The construction was span-by-span sequentially starting at one end of continuous stretch and finishing at other end. It was possible to erect a typical 34 m span within 2.5 days.

Fig. 2 : Main Flyover (Phase 1) in operation

To minimize the expansion joints to offer pleasant riding, it was decided to provide deck continuity. Expansion joints were provided after every three spans.

At major crossings, three/ five span continuous units have been provided. The central piers were made integral to superstructure. To offset the effect of temperature change, creep and shrinkage due to integral structure, twin leaf slender piers were provided in place of one thick pier which could absorb much of the deformation without development of excessive moments. These obligatory crossings are in precast segmental construction. As the depth for these girders varies from 2.450m to 4.584 m with additional requirement for crash barrier dowels, transportation of segments from casting yard to site was carefully planned. Special low bedded trailers were employed for transportation of these segments.

Fig. 3 Structure at Sarai Kale Khan

Fig. 4 Loop at Sarai Kale Khan

Fig. 5 Pre-cast segmental construction

Fig. 6 Precast Segmental Technique: Overhead Launching Truss

Special lifters were procured from NRS for lifting the segments, aligning them and keeping them in position till these were glued to already cast structure through temporary/ permanent pre-stressing. Segment on leading side was lifted, aligned, epoxy glue applied on the surface and locked to structure through temporary pre-stressing. After this the balancing segment on other side was lifted, aligned, epoxy glue applied on surface and temporary pre-stressing applied. After this, the permanent cantilevering cables were threaded and stressed to complete the erection of one pair of cantilevering segment. Five nos. of lifters were employed for the project. Each lifter weighed round 90 t. The lifter had capability of lifting from ground, rotating, aligning and transporting the segments over the already cast structure.

Fig. 7 View of Special Crossing at Sarai Kale Khan

At obligatory location, it was not possible to lift the segments from directly below the bridge. At such location, the segments were lifted from the other (lateral span) side and transported over the already cast structure. At certain locations, it was impossible to lift segments directly under the bridge from any of the sides. At such locations, segments were lifted using cranes. The end portion of end spans was erected using ground supported trestles. Precast segments were placed on the trestles with PTFE sliding plates at the soffit location for effecting pre-stressing. Central stitch was made cast-in-situ.

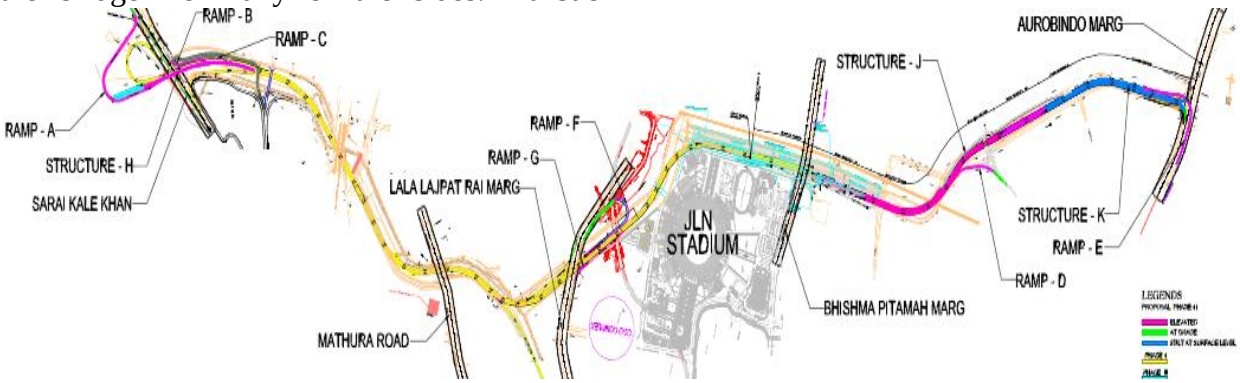

Fig. 8 Combined Layout Plan of Phase I and II

4. Phase 2 from JLN Stadium to INA

Phase 2 of the Project is under construction since 2013 and expected to be operational by 2015. In this Phase the Corridor dropped at Nehru Stadium in the previous phase is being taken ahead to INA to touch the Aurobindo Marg. In addition to this there were certain loops not taken up in Phase 1 due to paucity of time are being added to make the corridor better functional and useful to more number of citizens.

In Phase 1 there was limited facility of ascending and descending in this corridor at Sarai Kale Khan i.e. only ascending for the traffic coming from ITO side and descending to ITO side was permitted. Now with the addition of two more loops at this location, Traffic coming from Ashram side will be able to ascend to this corridor and traffic bound for Ashram will be able to descend from this corridor. Also the location where this corridor is crossing Lal Lajpat Rai Marg, two loops are being added to get down to this Marg from both the carriageways.

There are many more intricacies involved in Phase 2 due to which the distinct types of designing technologies have been adopted as detailed below.

4.1 Pre-cast segment for construction

Most of the spans have been designed with pre-cast segmental technique. But here the continuity in spans just not limited to the deck slab continuity, but total structure is made continuous by providing pre-stressing couplers between pre-stressing cables.

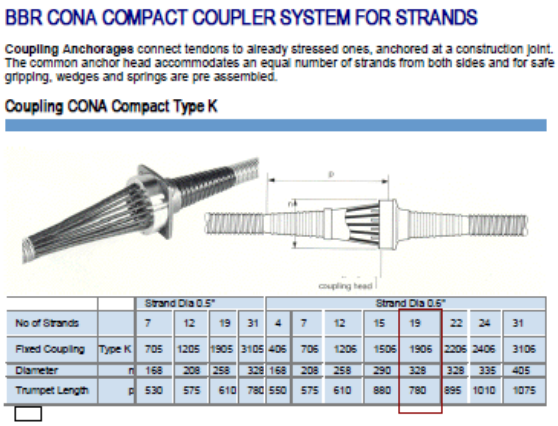

Fig. 9 BBR Cona Compact Coupler system

In the first stage of launching for three (or four) span continuous structure, 1¼ span is launched and pre-stressed in the usual manner. The pre-stressing cables can be taken further by joining next set of cables through the pre-stressing couplers and the launching of **2¼** (or **3¼)** span is completed and so on till last ¾ span is left over for final launching of a module and finally pre-stressed. This system proves to be economical in comparison to conventional system of providing Deck slab Continuity by about 10%. Moreover, the constructability is also simplified.

Fig. 10 : Phase II under construction to take off from the termination point of Phase I at Sarai Kale Khan

4.2 Cantilever Structure Technique

The corridor is required to cross the Ring road at one location at Sarai Kale Khan and railway tracks at Sewa Nagar (2 carriageways). Since the Railways are insisting to place the piers out of their land, the railway tracks are being negotiated in a 98 m curve with a radius of about 230 m and 49° Skew Angle. As per the design, the depth of the segment at the end span is about 5.5 m. In Phase-I also the corridor is crossing major roads of Delhi as well as railway tracks but the spans were in straight line and also about 85 m length which are possible with pre-cast segments as a depth of any segment was limited to 4 m. In the instant case, due to deeper segments, it will not be possible to transfer the segments through the heavy traffic and decision has been taken to

substitute from precast to in-situ balanced cantilever structure.

Fig. 11 Pile Cap(3 m deep) of CLC span under preparation at Sarai Kale Khan with sheet piling all around

Accordingly, all these 3 crossings (one at ring road 2 over Railway Tracks) will be constructed as in-situ Cantilever structure technique monolithic with the twin flexible piers.

4.3 Pre-cast I-Girders

There are locations were the radius of the curves is too less to cast the segment with sufficient accuracy and launch them at site. At such locations, the construction will be carried out with pre-cast pre-tensioned I Girders of approximately 20 m Length.

Fig. 12 Pre-cast Pre-tensioned beams stacked in casting Yard

In addition to above locations, the structure meeting Aurobindo Marg for a length of about 300 m will be just over the Nallah. In such a location, there is a limitation of the depth of the structure as deeper segments will cause obstruction to the free flow of Nallah. At such locations, the structure has been designed as pre-tensioned, pre-cast I-Girders with a pre cast and in-situ slab for the ease of constructability. .

4.4 Steel Arch Bridge

Interestingly, it was noticed that DMRC is also planning an underground tunnel which is crossing the Barapullah Corridor at grade.

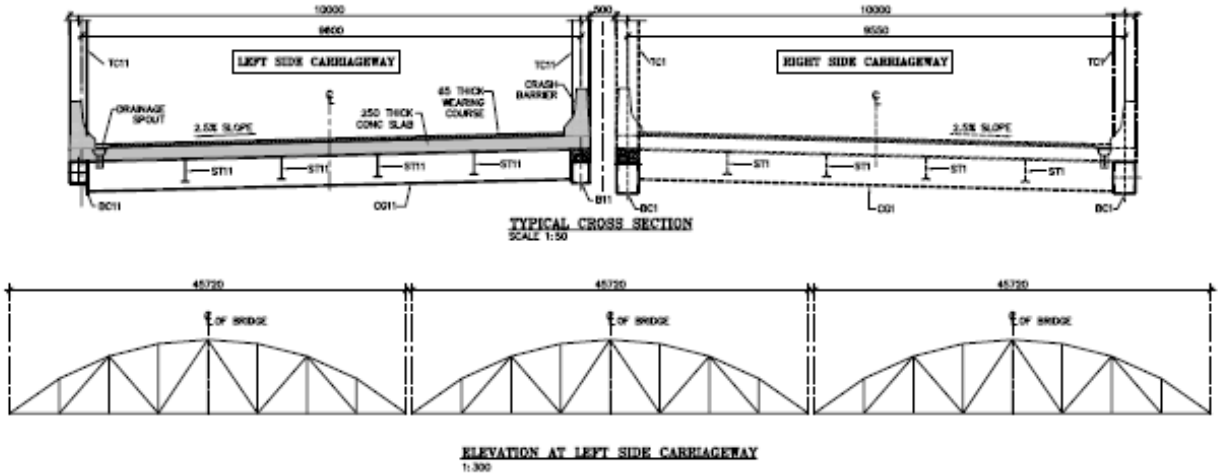

Fig. 13 Drawing of Steel Structure Arch Briadge over DMRC Tunnel area

The location of pile and piles caps were to be tailor made along the direction of the Tunnel so as to avoid any conflict between the two structures. Again there is a limitation of depth of the structure to be provided and span of the structure varying from 45-65 m in order to accommodate tunnels between the pile caps. Here a decision has been taken to provide steel arch truss.

On one carriageway, it is 3 spans of 45 m each, while on the other carriage way it is 2 span of 65 m each.

4.5 In Situ Solid/ voided Slab

There are certain locations like a structure passing through Silver Oak Park, the only solution was to negotiate the curve with in-situ solid slab monolithic with the piers due to non standard spans and also in Loop C, where there is possibility of Channel water rising up to the deck level.

Fig. 14 Preparation of solid slab monolithic over circular piers in progress

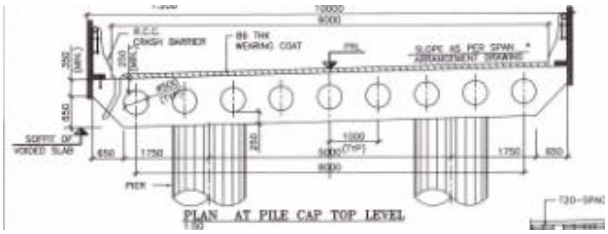

Fig. 15 A section through the voided slab showing voiders

The start point of Phase II beyond Nehru Stadium was found to be having underground cellular foundation structure provided for DTC bus depot constructed over the Nallah just abutting the Barapullah Corridor. Since the foundation structure was continuous, it was not advisable to puncture or dismantle the foundation for boring the piles and therefore, the alignment was to be shifted slightly by about 10 m. This shifting resulted into very limited areas for the placement of foundation and substructure. Accordingly decision was taken to provide structure over single pier for a length of about 200 m. For such a length of corridor, the structure is being provided as in Situ pre-stressed voided slab with shorter spans for making it lighter in weight and casting monolithically with single piers.

5. Phase III from Sarai Kale khan to Mayur Vihar

This is the 3rd phase of the project for which planning is in process and PWD has already been taken the approval from all the local bodies including Yamuna Standing Committee. After providing this connectivity, there will be a direct connection from Mayur Vihar in East Delhi to INA in South Delhi. Phase III will pass through Yamuna river and Yamuna Banks. "Yamuna Bachao Abhiyan" requested PWD to provide a design which total corridor over Yamuna and its Banks on stilts. Though it will increase the cost of structure, but considering the environmental up-gradation achieved, the increase in cost of structure is insignificant. The Preliminary cost of structure amounting to Rs. 1285 crores has already been submitted to Government of Delhi for necessary approval. Bids have been invited from consultants for providing a bridge with good aesthetics and unique design features. The structure will meet Mayur Vihar where already there is a unidirectional flyover on the Noida link road and now another flyover in other direction will be provided in Phase-III parallel to the existing flyover and the junction at Mayur Vihar will be converted to 4 arm junction with the creation of Barapulla Phase III. Additional Loops and. Clover leaves will be added to make the new 4 arm junction signal free for movement in all directions.

6. Sustainability Considerations and Achievements

(1) The feasibility study of alignment connecting Ring Road at Barapula Nala and INA near Dilli Haat demanded the most direct, economical, aesthetic, traffic worthy intersections and interchanges and its speedy constructability. The project has enhanced the visual quality of the urban space. Interventions adjacent to historic monuments are very sensitive.

(2) The work has been executed without disrupting the traffic by carefully planning

the sequence of operations so that the traffic moves unhindered at all times.

(3) The Barapulla Bridge of Mughal Era is aesthetically visible while driving from Sarai kale khan to INA on new Elevated Corridor.

(4) The alignment of the road with reference to Khan-e-Khana's Tomb has been kept more than 100 meters boundary away from the notified monuments designated as Prohibited Area within which no construction is permitted. Archeological Survey of India (ASI) suggested engaging a heritage consultant for Khan-e-Khana's Tomb and Barapulla Bridge. It was found that the earlier preferred alignment option is contrary to the stipulations of the Ancient Monuments and Archeological Sites and Remains Act 1958.

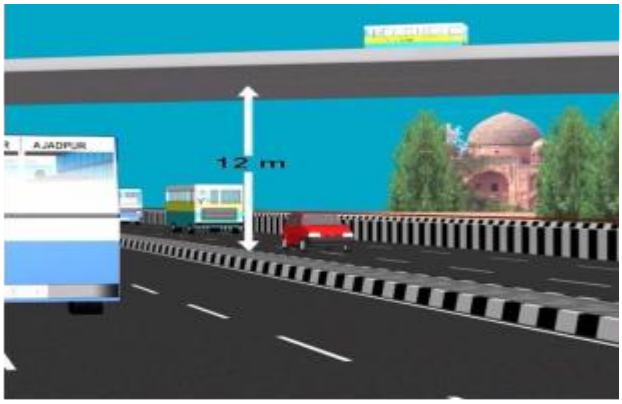

Fig. 16 Planning of Khan−e−Khana Tomb

Fig. 17 Khan−e−Khana Tomb in View

(5) Alignment was shifted towards east to provide 107 m distance between the Monument and structure soffit level was raised from 5.5 m to 12 m above Mathura Road Level. Elevated Road provides unhindered visibility to Khan-e-Khan tomb compiling to the ASI observations.

(6) In order to safeguard the disturbance to road and rail traffic, segmental construction was planned and the sequence of operation were such that the road as well as rail traffic moved uninterrupted at all times of construction.

Fig. 18 No Disturbance to Road Traffic during Precast Segmental Construction

Fig. 19 No Disturbance to Rail Traffic during Construction

(7) Turfing has been done on embankment Slopes as per the recommended practice for treatment of embankment for erosion control. Trees have been planted on both sides of the road and in the island formed near rotary.

(8) No disturbance has been caused to the existing drainage pattern. Side drains have been provided with its connectivity to main outfall drain. Sections of the corridor have been modified suitably along with the cross drainage structures.

(9) Safety of workers during construction was ensured by providing helmets, masks, safety goggles, etc. Adequate signage, barriers and persons with flags to control traffic had been provided during construction. Adequate drainage, sanitation, and waste disposal facilities were provided

at work places. Proper drainage was ensured around the sites to avoid water logging leading to any illness. At every workplace, potable and sufficient drinking and washing water supply is maintained to avoid water-related diseases and to secure the health of workers.

(10) All the construction and demolition waste is being taken to recycling plant, where it is getting converted into useful products like bricks, tiles, paver blocks etc,

(11) High grade concrete like M60 is being used to save overall cement and in turn reducing CO_2 emission to atmosphere.

(12) Maximum pre-casting is done to reduce pollution to city environment and also reducing the construction time period.

(13) A perfect coordination has been done with DMRC to allow the execution of both the projects simultaneously without any adverse impact on other project.

(14) The alignment wherever possible has been modified to save maximum number of trees. It may be appreciated that in complete project of Phase II, only 79 trees are to be removed and out of them about 20 trees are being transplanted.

Fig. 20 No Physical Disturbance to Heritage Structure

7. Discussions and Conclusions

1) It is true that civil constructions in urban areas are essential for overall development and benefits of the community, but same is successful only if equal importance is given to the environment and it is given due care for a sustainable development.

2) It is essential that every construction activity should be environment friendly as the Environment too has a right to remain protected. Engineering solutions to minimize the Environment impacts and for adopting the mitigation measures are available.

3) Many times it happens that planning a Project requires disturbance to heritage structures existing in the vicinity of the scheme. In such a situation, it requires the consultation with heritage experts. Solutions are available under such circumstances, but these may be more challenging for Engineers to plan and execution besides the cost factors. But importance of heritage structures, their restoration is essential and has to be given due importance.

4) Adoption of standard and safe construction practices is very much essential particularly in urban environment. It must be ensured at all times that workers adopt best safety protections in their own interest. Protection of Health, Safety and Environment should always be kept as the prime goal.

5) The right of respectful living of the residents around the construction sites should not be jeopardized. This should be given due regard without compromising on their comforts, safe movements and safe livelihood.

8. Acknowledgement

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Co-design Approach for Wide-Band Asymmetric Cross Shaped Slotted Patch Antenna with LNA

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Abstract The proposed work presents a co-design approach for a new asymmetric rectangular cross shaped slotted patch antenna with low noise amplifier that occupies 17.2–25.8 GHz wide-band for SDR applications. This co-design approach minimizes the chip area and noise and also improves integration system over the bandwidth of 8.6 GHz. Three different architectures have been designed in this work. Firstly, a two stage CMOS CG–CS LNA is designed using a technique of series–parallel resonant network as an input matching network and as inter-stage matching network between CG and CS LNA. In second architecture stage, a rectangular shaped microstrip antenna is designed and a slot of asymmetric cross shape is cut on the patch antenna. In third architecture the slotted antenna is integrated with low noise amplifier in order to form a co-design approach in which series–parallel resonant network is used as a band pass filter between slotted patch antenna and LNA. A two-stage CMOS LNA design is simulated and layout is made using foundry design kit for the TSMC 65 nm CMOS process in ADS.v.12. A simulation result of LNA achieves S_{11} of -21.4 dB with gain ranging from 7.4 to 21.3 dB over the wide-band of 19.1–28.8 GHz. The slotted antenna achieves S_{11} of -19 dB at 26 GHz and covers

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frequency range of 20.1–27.8 GHz with good radiation and receiving patterns. This co-design approach is analysed considering the 50 Ω impedance matching throughout the design and simulated on the platform of ADS.v.12. The best achievement of proposed co-design approach is reduced noise figure which is most suitable for SDR applications.

Keywords Software defined radio (SDR) · Low noise amplifier (LNA) · Complementary metal oxide semiconductor (CMOS) · Microstrip antenna

1 Introduction

In Last few years, a fastest growth for the wide range of wireless networks is continuously finding a new solution, which often comes either with new frequency bands or with new modulation schemes. Recently, the hardware and software system design have been done individually for every standard which overcomes the drawback of redesigning of hardware modules for every new standard. This suggests the integration of many communication devices into a single chip [1]. Moreover, there have been researchers for the already available spectrum for their efficient use e.g., cognitive radio. It is desirable to have a universal programmable hardware which gives the flexibility in designing the system by using software-defined radio (SDR) technique [2]. The first proposed idea of an SDR, developed by Mitola [3], is to perform all RF and baseband signal processing designs in both analog and digital domains. It brings the flexibility, cost efficiency and enhanced power in order to carry forward communication, resulting in benefits to the service providers [4]. The extensive progress of CMOS technology has enabled its application in SDR wireless networks. At present, the CMOS technology is one of the most attractive choices in implementing receiver due to its low cost and high level of integration [5]. In spite of having several advantages, the design of CMOS receiver in SDR applications exhibit various challenges and difficulties to which the designers should take care off. Although by using the integrated patch antenna with LNA, most of the performances parameters have been improved but SDR applications are not yet considered.

The most difficult task for the wide band co-design of low noise amplifier (LNA) with microstrip antenna are: (1) To take care of the performance parameters like impedance matching and noise over a wider range (2) To take care of size an effect of miniaturization and (3) Low power consumption for long lasting battery. Several authors have devoted their research about the many LNA's and different shaped slotted antennas which offered wider bandwidth [6, 7]. But the wide band co-design approach of slotted antenna with LNA concept is still needs exploration.

In [8], the return loss of filter degrades the noise figure (NF) when LC ladder filter has been placed at the input of a common source (CS) amplifier. Another inter-stage LC network is added to CG–CS stage that increase the power gain, but the NF is 6 dB at around 10 GHz [9]. In [10], coupled resonators have been used to design a wideband inter-stage matching network for a V-band cascaded CS amplifier. A wideband LNA operating in 23–32 GHz has been proposed in which coupled resonators are used as a load for the common-emitter stage [11]. In [12], design of wideband LNA's using parallel-series resonant matching network between CG and CS stages at 3–10 and 14–29 GHz achieved 9.6–12.7 and 8.25–1.65 dB gain but sacrificed NF. In [13], analysis of LNA-antenna co-

design for UWB system achieved 13 dB gains on the 3.25–5 GHz bandwidth but noise performances has not been discussed.

In this paper, a new approach of co-design of wide band asymmetric cross shaped microstrip antenna with LNA is proposed. Three architectures operating in the frequency ranges of 20.13–27.8, 19.1–28.8 and 17.2–25.8 GHz respectively are executed to verify this co-design approach. The designing of asymmetric cross shaped antenna is discussed in section II. Section III, presents the analysis of Wide band CMOS CG–CS topology using series–parallel resonant network. A co-design approach over wide band range is addressed in **Sect. 4. Finally, simulated results are discussed in Sect. 5 and are followed by conclusion in Sect. 6.

2 Design and Implementation of Asymmetric Cross Shaped Microstrip Antenna

The microstrip antenna is a small electrically thin patch having numerous advantages i.e. light weight, inexpensive, and easily integrable with active devices for improving system reliability. The schematic of the proposed antenna is shown in Fig. 1. The feedline of dimension $W_1 \times L_1$ is attached with a slot loaded rectangular patch of dimension $L \times W$ in the same plane. An asymmetric cross slot is cut in the rectangular patch. All the detailed dimensions are listed in Table 1. The proposed structure is designed on RT Duriod-5870 substrate. The height, dielectric constant and loss tangent of the substrate are 0.762 mm,

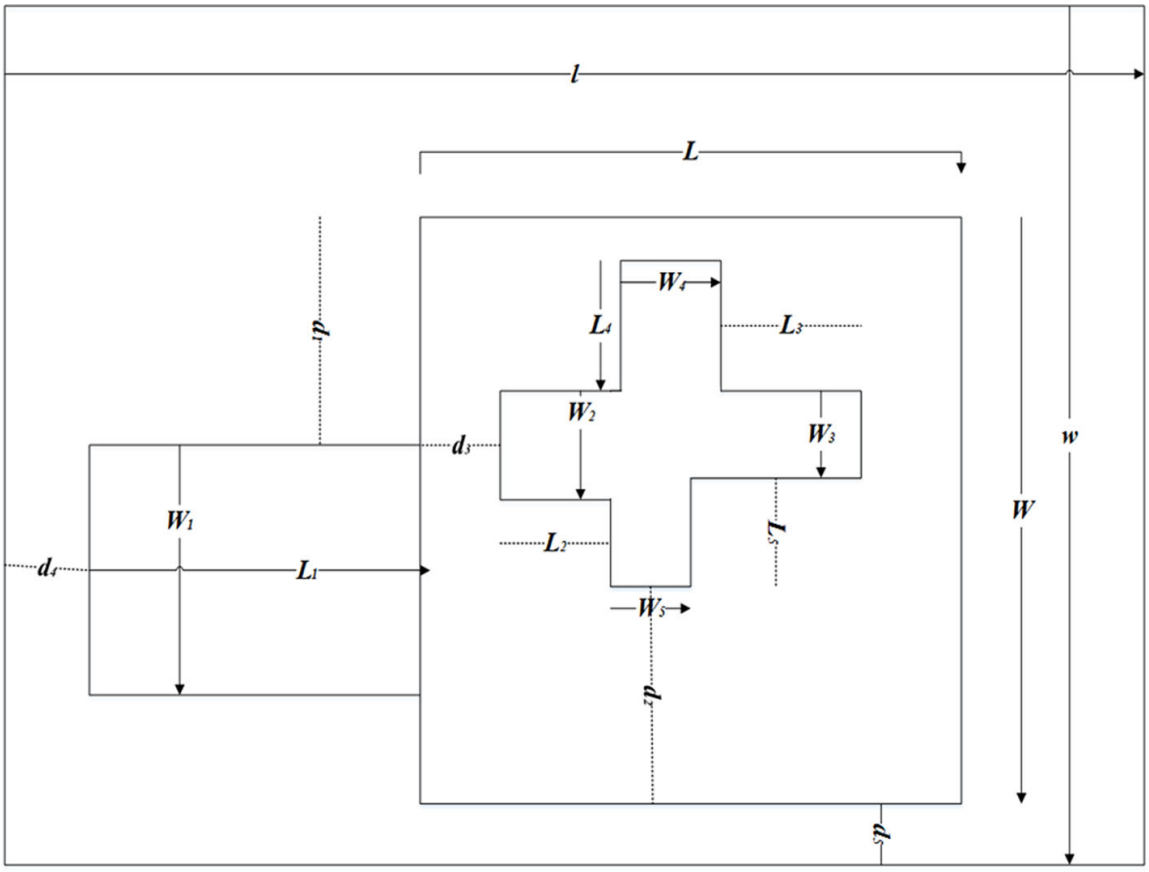

Fig. 1 Geometry of proposed antenna with asymmetric cross shaped slot

Table 1 Dimensions of patch antenna with cross shaped cut-slot

Dimensions	Values (mm)
w	9.2
W	4.6
W1	2.2
W2	0.9
W3	0.7
W4	0.7
W5	0.7
Ws	0.7
l	9.4
L	3.1
L1	1.6
L2	0.4
L3	1.2
L4	0.5
L5	1.1
Ls	1.1
d1	1.9
d2	1.9
d3	0.4
d4	2.2
d5	1.8

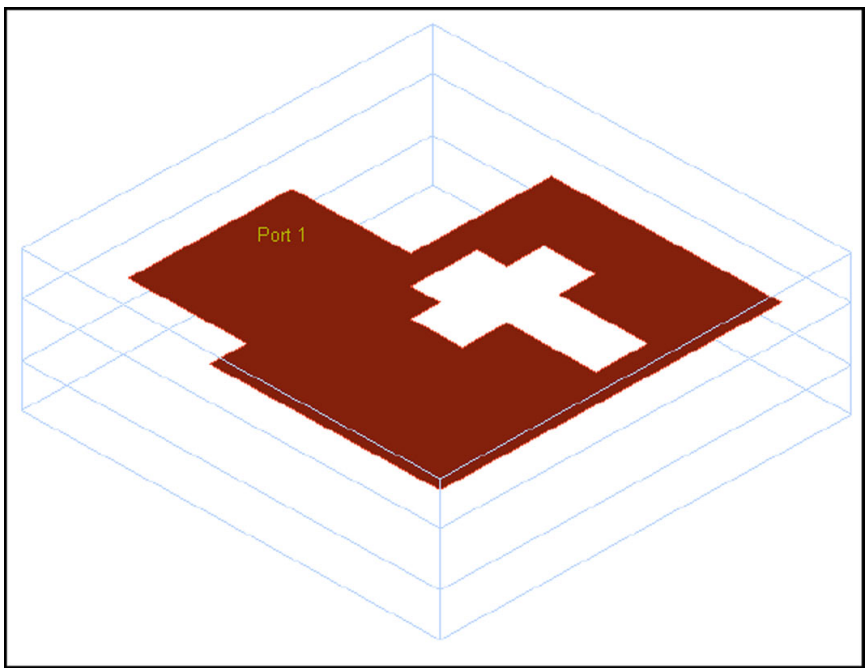

Fig. 2 3D view of asymmetric cross shaped slotted patch antenna

2.33, and 0.0012 respectively. The width of the smaller rectangular patch section (W_1) is adjusted to provide a 50 Ω microstrip line. By cutting a cross slot on the patch, additional resonances are created and much wider impedance bandwidth is produced. The 3D

isometric view of asymmetric shape slotted antenna is shown in Fig. 2. The simulated return loss and radiation at 26 GHz of the antenna is shown in Figs. 3 and 4 respectively. The return loss plot clearly shows two resonances eparated appropriately to create a wideband response. The bandwidth of the antenna ranges from 20.1 to 27.8 GHz providing a fractional bandwidth of 32.15 %. Figure 4 illustrates the simulated radiation pattern at resonant frequency of 26 GHz when phi rotates 90°. This plot shows electric field components of co and cross polarization.

3 Wide-Band CMOS LNA Analysis

In order to achieve the best impedance matching, gain and NF over a wide band range, many topologies are available [14]. Out of these topologies, CS and common gate (CG) are the most popular choices for LNA design. The CS with the source inductor degeneration technique achieves a good input impedance matching with ideal noiseless components providing a minimal NF and a higher gain whereas CG offers wideband operating performance with good linearity and input–output isolation property [15]. But at higher frequencies, cascaded CG–CS topology suffers with noise. Therefore, a series–parallel resonant network is used for CG–CS amplifier as an input and inter-stage matching network which improves the noise performance and other parameters. The details of the proposed structure of two stage CG–CS LNA using series to parallel resonant network are addressed below.

3.1 Series–Parallel Resonant Network

In [12], a parallel to series resonant network is used as a band pass filter is shown in Fig. 5. This resonant network achieved a band pass response and dual band response by selecting proper values of inductors and capacitors. For the parallel and series resonance networks, the impedances Z_p and Z_s are shown in Eq. (1) and (2) respectively [12].

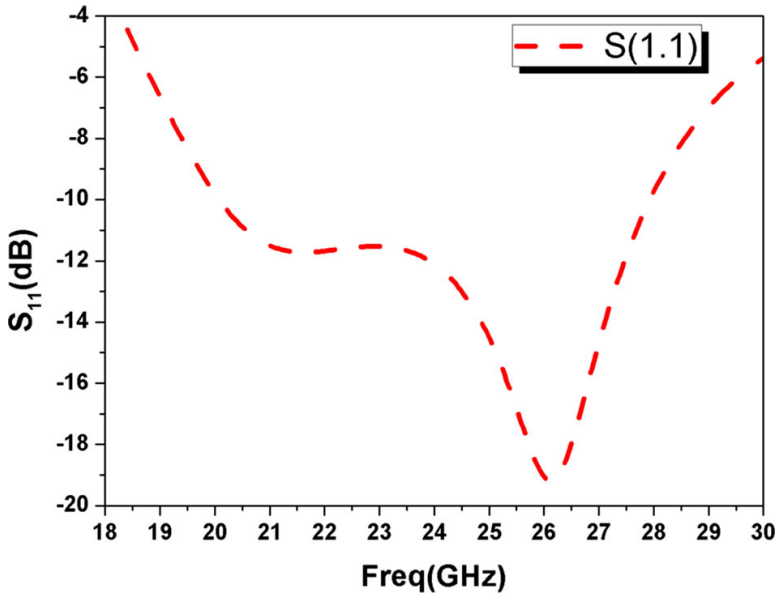

Fig. 3 Variation of return loss with operating frequency

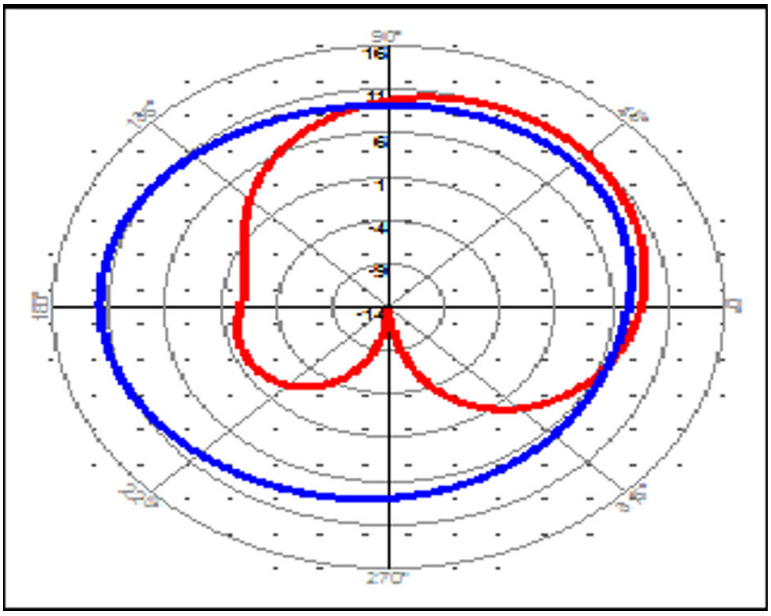

Fig. 4 Simulated radiation pattern of the proposed antenna at 26 GHz

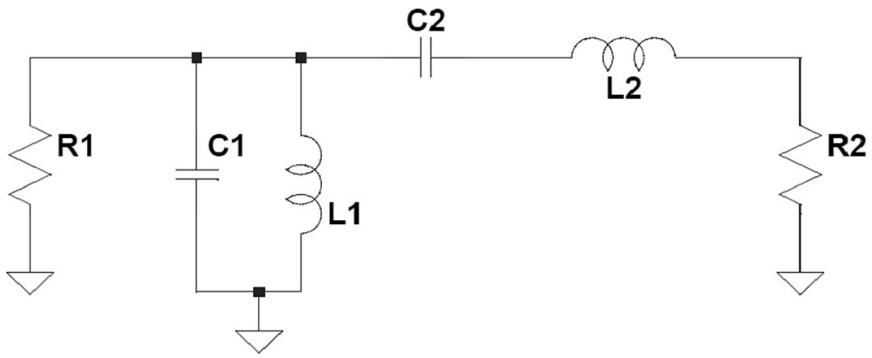

Fig. 5 Schematic of parallel-series resonant network

$$Z_p = \left(\frac{1}{R_1} + jwC_1 + \frac{1}{jwL_1}\right)^{-1} \tag{1}$$

$$Z_s = R_2 + jwL_2 - j\frac{1}{wC_2} \tag{2}$$

Here, the concept implies that different values of source and load impedances $R_1 = 250\ \Omega$ and $R_2 = 40\ \Omega$ in parallel to series resonant network offered dual band response with a dip in the middle. A wide band response is achieved when parallel-series network is used as inter-stage matching network between CG and CS LNA. The same concept is used in this work. However parallel-series resonant network is inverted as series–parallel resonance network which is used as matching network between CG and CS LNA for improving performance parameters like impedance matching, NF and gain over wider range of operating frequencies. A proposed two stage CMOS CG–CS LNA using inverted parallel-series resonant network is discussed in subsection *B*.

3.2 CG–CS LNA Using Series–Parallel Resonant Network

The proposed schematic of two stages CG–CS LNA using series–parallel resonant network is shown in Fig. 6. This is implemented using commercial TSMC design kit of 65 nm RF CMOS technology in Agilent Advanced Design System (ADS). The input matching and inter-stage matching networks of CG–CS LNA are composed of inductors and capacitors as L_1, L_2, L_3, L_4, C_1, C_2, C_4, C_5 having values of 0.48, 0.27, 0.83, 0.6 nH, 14.75, 30, 0.06 and 0.0835 pF respectively.

Selection of on-chip inductors is the key for the designing of a matching network, as it determines the performance quality of matching network. The input and inter-stage matching network is accomplished with the combination of a series–parallel LC impedance transformation network. In order to maintain the 50 Ω impedance matching, firstly a single stage of CG LNA using series to parallel resonant network as an input is designed that provides good reverse isolation parameter over a wide band range of operation. It is well known that the NF and high gain are the essential requirements of the LNA design. For improving these parameters further, the next stage i.e. CS with source degeneration via series–parallel resonant network is combined. For the two-stage of CG–CS LNA, the width of M_1 (WM_1) is calculated to be 492 μm using Eq. (3) as given in [14]. The second stage of CS device is designed to meet the desired performance criterion while width of M_2 (WM_2) is calculated as 532 μm using Eq. (4) as given in [14].

$$WM_1 = \frac{3}{2}\frac{c_{gs}}{L_{min}c_{ox}} \tag{3}$$

$$WM_2 = \frac{g_m^2 L_{min}}{2K_n I_D} \tag{4}$$

where, L is channel length, K_n is transconductance parameters, C_{ox} is gate oxide capacitance, I_D is the drain current, g_m is transconductance of device and C_{gs} is the gate to source capacitance. In this design, a more difficult task is to maintain an output impedance of

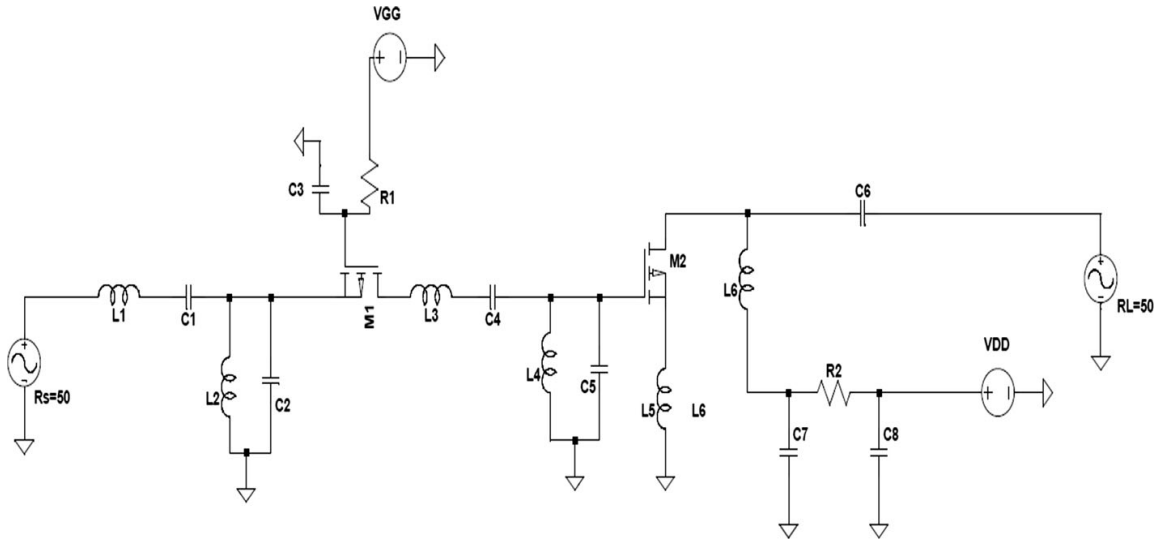

Fig. 6 Proposed schematic of CMOS CG–CS LNA using series to parallel network

250 Ω of CG stage and input impedance of 40 Ω of CS stage for obtaining wide band operation. The designed circuit of CG–CS LNA is simulated and reflection coefficient of −21.4 and −21 dB at operating frequency of 20.5 and 26.2 GHz is obtained respectively. This return loss shows a frequency band from 19.1 to 28.8 GHz with a fractional bandwidth of 40.5 % as shown in Fig. 7. It also shows transmission gain S_{21} of the circuit. The CMOS LNA provides a gain in the range of 7.4–21.3 dB for the entire band of operation with relatively constant NF of around 2.8 dB as shown in Figs. 7 and 8 respectively. The forward gain (S_{21}) shows a high gain over the bandwidth of 9.7 GHz ranging from 19.1 to 28.8 GHz as shown in Fig. 7. Using series–parallel networks a wideband impedance matching is obtained as shown in Fig. 9. It clearly indicates that the imaginary part of input impedance remains near zero value while real part is matched around 50 Ω within the band of operation. The total power consumption for two stage CG–CS LNA is 11.2 mW from 1.6-V power supply. Figure 10 shows layout of CG–CS LNA with final area of 0.74 mm^2. Table 2. Show the comparison of previous works with present one on various parameters.

4 Strategy of Combined Structure

In this section, the technique of proposed combined structure of slotted patch antenna with LNA is addressed. The schematic of this co-design is shown in Fig. 11. From the schematic, it can be observed that slotted patch antenna is integrated with the CMOS LNA which forms a co-design structure. In this structure, the input of CG–CS LNA i.e. series–parallel resonant network has been used as an inter-stage matching network between the asymmetric slotted patch antenna and the CG–CS LNA. As discussed above, the series–parallel resonant network which acts as a band pass filter is connected between slotted patch antenna and LNA to form a complete receiver system. The RF signal is applied to patch antenna with the help of two ports and the output from the antenna is connected to the microstrip line with help of another port while applying the approach of co-design, four major goals need to be fulfilled: (1) To sustain 50 Ω impedance matching throughout the design for achieving performance parameters (2) To achieve higher gain and lower NF that

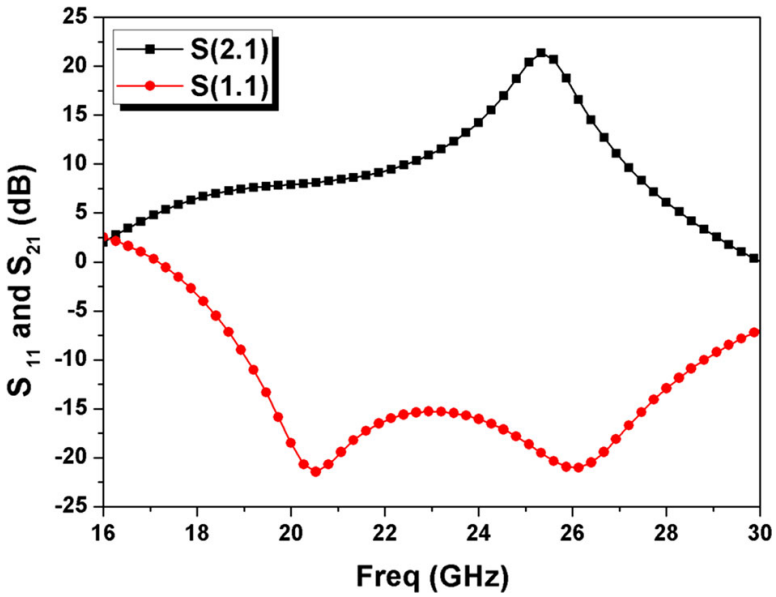

Fig. 7 Variation of return loss and forward gain of CG–CS LNA

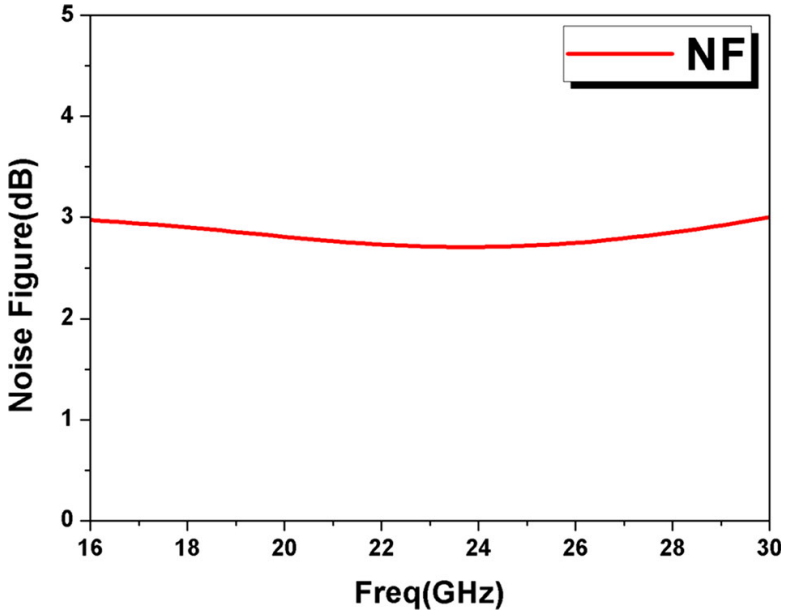

Fig. 8 Variation of NF with frequency

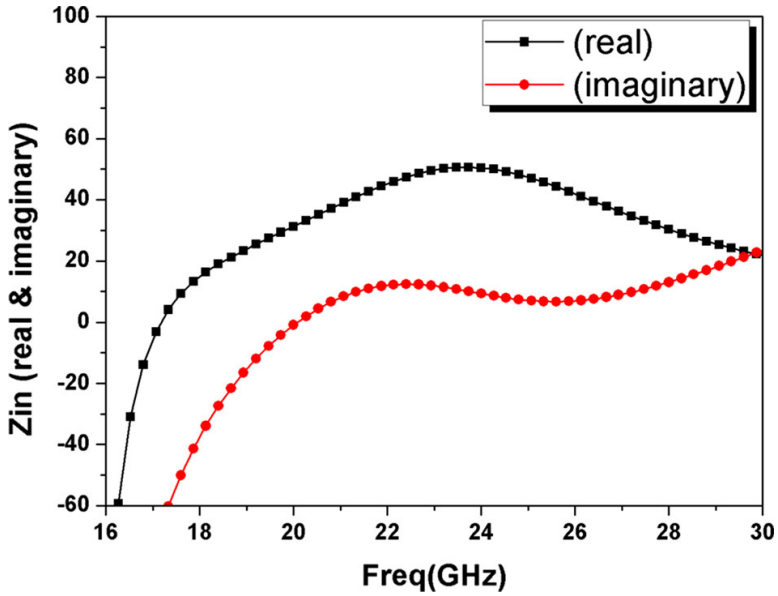

Fig. 9 Variation of Input impedance of CG–CS LNA with frequency

is essential for amplification (3) To minimize the chip area and (4) To achieve less power dissipation [16–18]. To predict the received signal, one port of RF signal with 50 Ω is attached on the slotted patch and the received signal is passed via series to parallel resonant network to the LNA for the amplification. Keeping above goals in mind, a strategy is adopted to combine the structure of slotted patch antenna and LNA that provides good results as per design specifications and that would be discussed in next section.

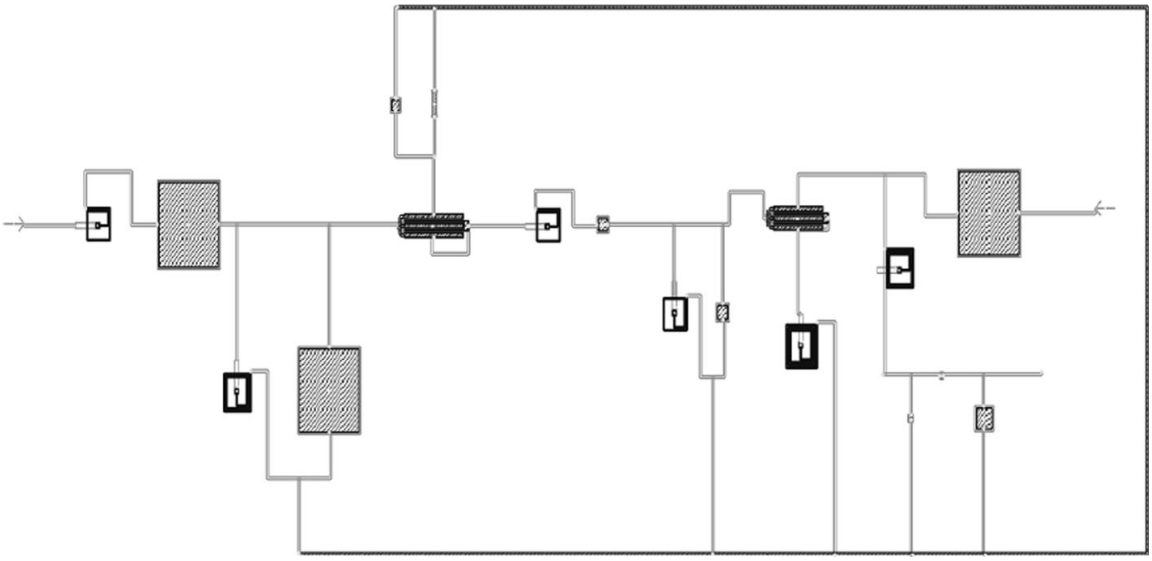

Fig. 10 Layout snapshot of CMOS CG–CS LNA

Table 2 Comparisons of LNA's with other reported papers

Design parameters	[19]	[20]	[12]	[12]	Present work
Technology	0.18 µm	0.18 µm	0.18 µm	0.18 µm	.065 µm
Peak Gain (dB)	12.4	12.9	12.7	8.95	21.3
NF (dB)	4.4–6.5	3.7–4.7	2.5–3.9	4.3–5.8	2.9–2.7
B.W (GHz)	0.4–10	1.5–11.7	3.1–10.3	14–29 GHz	19.2–28.8
Power (mW)	12	10.34	13.4	13.9	11.2
Area (mm^2)	0.42	0.536	0.68	0.54	0.74

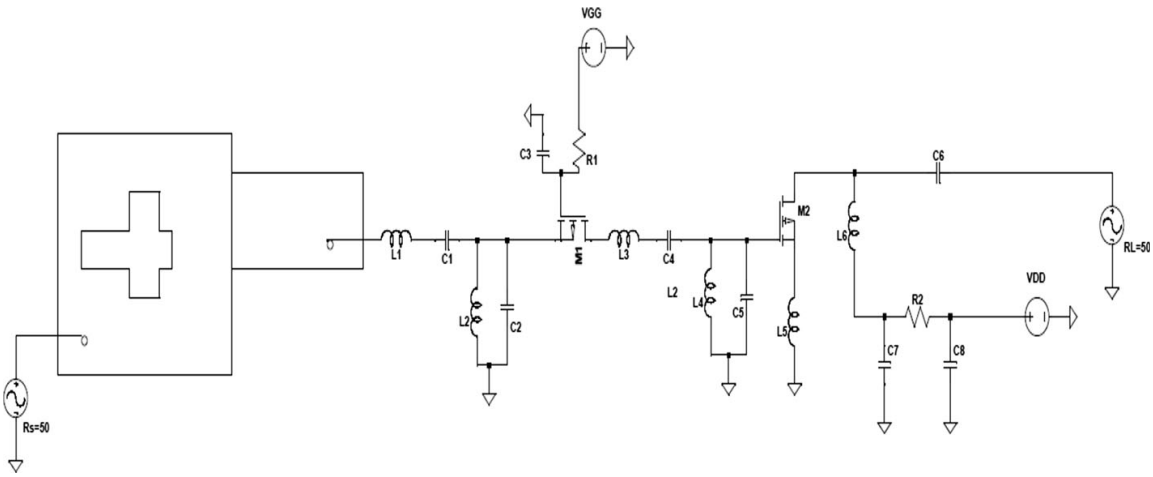

Fig. 11 Schematic of co-design of slotted patch antenna with LNA

5 Results Discussion of Co-design

From previously discussed results of slotted antenna and LNA in section II and III, it can be seen that the proposed asymmetric cross shaped antenna works on the wide band range of 20.1–27.8 GHz with fractional bandwidth of 32.15 % whereas LNA achieves a wide

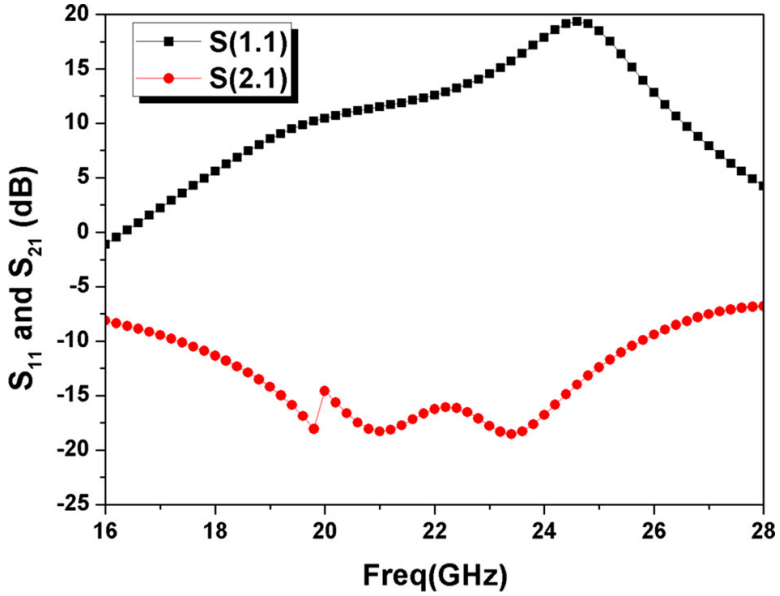

Fig. 12 Return loss and forward gain behavior for co-design strategy

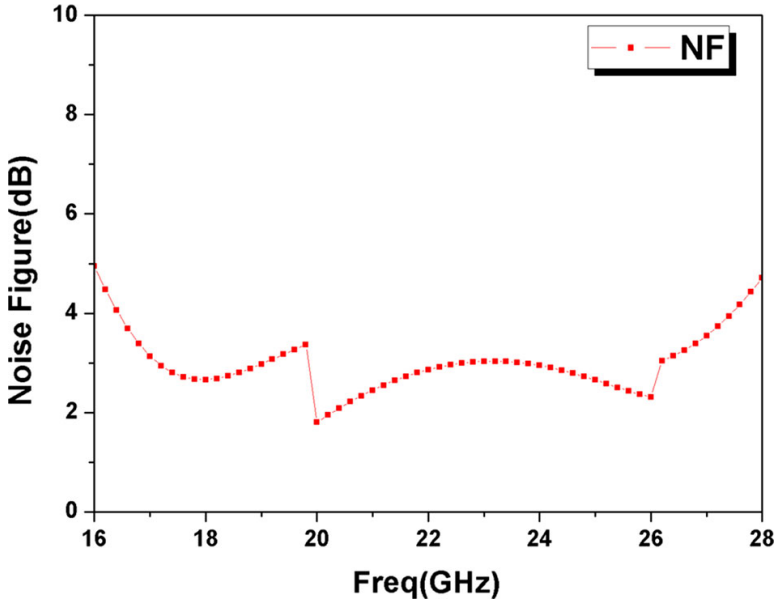

Fig. 13 NF variation with frequency for co-design system

range of 19.1–28.8 GHz with fractional bandwidth of 40.15 %. The obtained bandwidths of both the devices are approximately same and give the wide band when co-design approach is applied. Using above discussed strategy the two structures are combined, analyzed and simulated on ADS platform. The simulated result of co-design structure obtains the S_{11} of −18 dB at three different frequencies 19.8, 21 and 23.4 GHz with a wide band ranging from 17.2 to 25.8 GHz with fractional bandwidth of 40 % as shown in Fig. 12. The band of operation of the complete design shifts downward while the impedance matching of antenna and LNA remains within the acceptable limit. The best achievement of this co-design is to improve the performance parameters like gain and NF that is required for receiver system. The new band of operation is 17.2–25.8 GHz with gain ranging from 3.4–13 dB. The NF varies between 2.9–1.9 dB which is shown in Fig. 13.

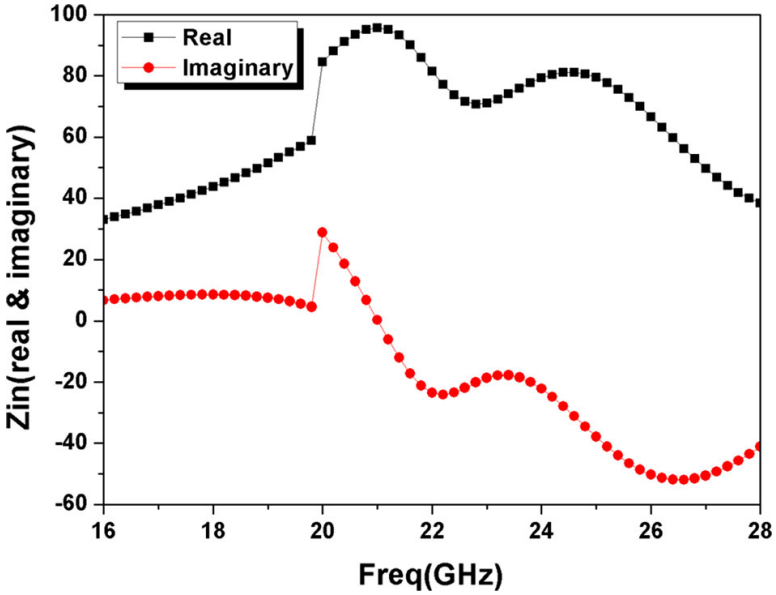

Fig. 14 Impedance variation with frequency for co-design system

Moreover, an impedance matching (real and imaginary) of co-design structure is also obtained and shown in Fig. 14. The calculated area of the slotted patch antenna is 9.2×9.4 mm^2 whereas the area of two stage CG–CS LNA is 0.92×0.81 mm^2. The total area of co-design layout is 9.2×10.2 mm^2.

6 Conclusions

The proposed method of co-design of asymmetric cross shaped patch antenna with LNA is discussed in the paper with achieving a wider bandwidth of 17.2–25.8 GHz. It is also found that the proposed antenna design exhibits an extremely wideband impedance by new type of slot cut in the cross shaped and also LNA design revealed an wideband by using series to parallel resonant network as a input and inter-stage matching network. The state of the art of this co-design work achieves S_{11} of -18 dB by proper impedance matching with wider gain variation from 3.1 to 13 dB and NF from 2.9 to 1.9 dB. Moreover, the proposed method of co-design system for SDR applications, increase the level of system integration, reducing chip area size thus, escalating the overall system performance.

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Regular paper

Comparative Analysis of PID, NARMA L-2 and PSO Tuned PID Controllers for Nonlinear Dynamical System

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Abstract- ***Practically almost all dynamical systems are complex and mathematically ill-defined due to the presence of model nonlinearities and uncertainties. The operation of dynamical systems with suitable adaptive controllers to maintain permissible performance levels under significant unanticipated model nonlinearities and uncertainties are necessary in high performance dynamical systems. In this paper the conventional Proportional Integral Derivative (PID), NARMA L-2, Particle Swarm Optimization tuned PID controllers are analyzed and their effects are compared through performance evaluation of a complex nonlinear dynamic system. The proposed controllers are able to drive uncertain complex dynamical systems with a greater degree of accuracy stably. The performance tests for these controllers were realized in the simulation environment on few selected type of nonlinear dynamical systems. The simulation results validate the superiority of the PSO tuned PID controller over conventional PID, NARMA L-2 controllers in terms of performance abilities and robustness.***

Keywords: Proportional-Integral-Derivative Controller, Nonlinear Autoregressive Moving Average, Particle Swarm Optimization, Nonlinear Dynamical System.

1. INTRODUCTION

Most of the physical systems are nonlinear and their analysis is usually complex when compared to the linear systems. Many significant attributes of system performance possibly ignored, if these nonlinear systems are analysed and designed by using linearization techniques. The nonlinear system behaviour is stable for one kind of input and may become unstable for another kind of input. There is no general solution method for nonlinear systems. However, a nonlinear dynamical system can be linearized to some degree, but discontinuity in nonlinear element characteristics such as coulomb friction, dead band, plant saturation, backlash, and hysteresis [1] restrict the linearization of these systems. Hence, development of nonlinear analysis techniques is important to predict the dynamical system performance. Several dynamical systems involve uncertainties in the model parameters due to sluggish or sudden change of plant dynamic parameters. A linear controller based on imprecise values of model parameters may exhibit significance performance degradation or even instability. In many systems, the nonlinearities are deliberately introduced to compensate the model uncertainties into the controller part of the dynamical systems. Moreover, certain other difficulties such as presence of unknown nonlinear function, uncertainty and computational complexity increase the design complexities of the dynamical system. Hence, the control systems are designed with intelligent controllers to deal with the above mentioned complexities and tackled by multi-disciplinary tools. Further

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the dynamics of the optimal system parameters are to be changed according to the operating point by the controller. When the time variable is discrete, the nonlinear dynamic system is modelled by difference equations otherwise it is modelled by ordinary differential equations and it is used to design adaptive controllers [2].The objective of this paper is to compare the performance of nonlinear dynamical system with conventional Proportional–Integral-Derivative (PID) controller to that of the Nonlinear Auto Regressive Moving Average Level-2 (NARMA L-2) and Particle Swarm Optimization (PSO) tuned PID.

For many control problems the conventional PID controllers are accepted by industries due to its simplicity, but still it has limitations like optimality and tuning rules [3-4]. In recent past NARMA L-2 controller were successfully presented to advance the performance of nonlinear dynamical systems, with no overshoot and excellent steady state performance over conventional PID controller [5]. J.Kennedy [6] et.al developed biologically inspired particle swarm optimization algorithm to solve unconstrained single objective function but later on it was modified to unconstrained, single or multi-objective problems. A. Oi [7] et.al suggested the PSO algorithm to search PID parameters for achieving the expected step response by PID tuning tool. P.L.Chen [8] et.al proposed online tuning of PID controller though the set point changes and load disturbance to obtain the good performance and stability. Nema.S and Padhy. P.K [9] presented a novel approach to design of PID controller for two input two output system using particle swarm optimization technique. W.Xin [10] et.al proposed PSO based self-tuning PID controller with variable parameters and reported that the controller is stable and reliable.

This paper is organized in four sections: Section 2 analyzes the modelling of nonlinear dynamical system. Section 3 discusses the three controllers followed by the case study in which each of the controller is applied to the test problem of nonlinear dynamical system. Section 4 simulation results and section 5 is conclusion.

2. MODEL OF NON LINEAR DYNAMICAL SYSTEM

The nonlinear dynamical system (NLDS) is represented using state equations, differential equations or difference equations. The nonlinear dynamical system considered in this paper is represented by the following equation [11], where y is output and u is input of the system:

$$\frac{d^2y}{dt^2} + 0.7\frac{dy}{dt} + 0.2y + 0.3\,y^3 = u \tag{1}$$

The state space representation of this system is described using two state variables x_1 and x_2 such that

$$x_1 = y \tag{2}$$

$$x_2 = \frac{dy}{dt} \tag{3}$$

Then,

$$\dot{x_1} = \frac{dy}{dt} = x_2 \tag{4}$$

$$\dot{x_2} = \frac{d^2y}{dt^2} = -0.7x_2 - 0.2x_1 - 0.3x_1^3 + u \tag{5}$$

The system can be compactly written as

$$\dot{x} = f(x) + g(x)u + d \tag{6}$$

Where,

$$f(x) = \begin{bmatrix} x_2 \\ -0.2x_1 - 0.3x_1^3 - 0.7x_2 \end{bmatrix}$$

$$g(x) = \begin{bmatrix} 0 \\ 1 \end{bmatrix}$$

$$d = 0$$

A Simulink model of the NLDS is shown in figure 1.

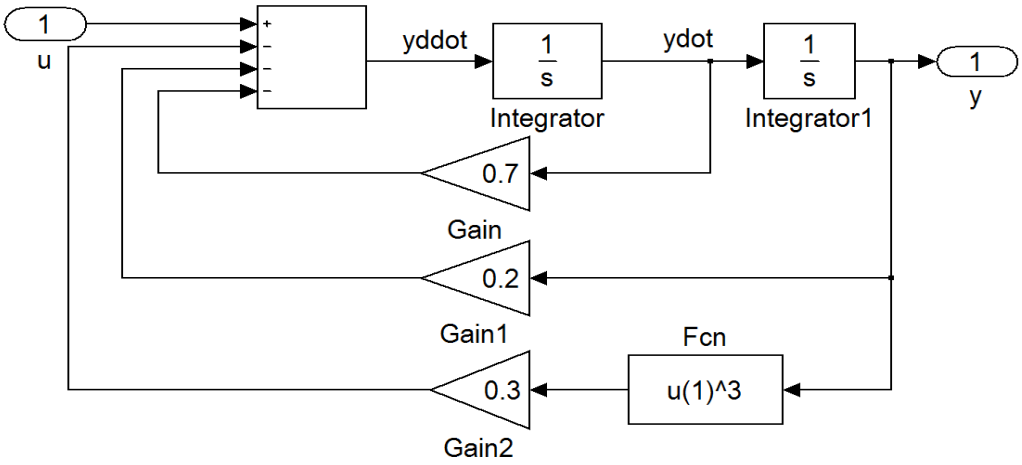

Figure 1.MATLAB Simulink model of the NLDS

The NLDS transient and steady state responses without any controller is shown in figure.2. The actual response is compared with a reference, [12] that represents the actual desired response of the controlled variable. This approach shows the tracking performance of underdamped system and also find the value of the adaptive parameters which are not exactly the same as that of the desired parameters, the tracking is achieved as time progressive tuning of controller.

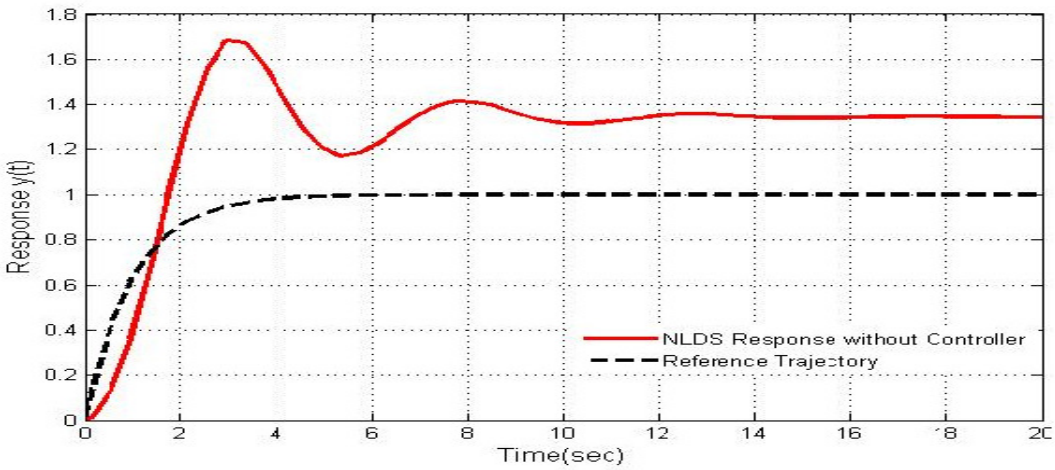

Figure 2. NLDS Responses without any controller

3. DESIGN OF CONTROLLERS FOR NONLINEAR DYNAMICAL SYSTEM

The controllers for dynamical systems are designed either by conventional or intelligent control techniques. The conventional PID controller is tuned by obeying the heuristic

Zeigler-Nichols rules [13] to attain stable control in the neighborhood of operating point. In conventional automatic control systems, the self-tuning controllers are not yet sufficiently advanced to cater to the effect of parametric changes in long term performance of dynamical systems. In these situations, an intelligent approach for development of dynamical models based on neural network controllers and bio-inspired search algorithms such as adaptive critic design, is currently attracting much renewed interest among the researchers.

3.1. PID Controllers

PID controllers have been used widely for the control of deterministic control systems for which the precise mathematical model can be formulated. The advantage of using a PID controller is that it has a very simple and easy to implement. It is robust and reliable. A conventional PID controller is shown in figure.3 and uses the reference signal to the NLDS, the error between the actual output and the reference signal along with a integral (K_i) and differential (K_d) coefficient, generate the control signal u [13] as given by equation (7)

$$u = K_p + K_i \int e dt + K_d \frac{de}{dt} \tag{7}$$

Where $e(t) = r(t) - y(t)$.

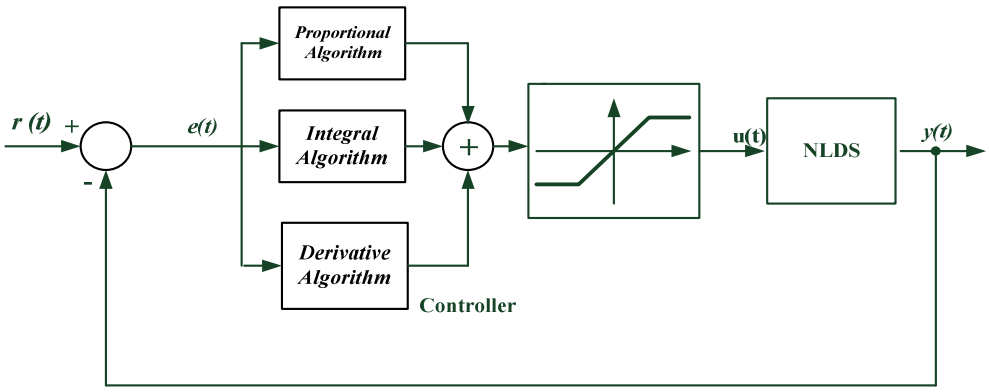

Figure 3. NLDS with PID Controller

The conventional PID control is based on linear control theory and hence is effective when used for simple practical linear processes. However when the system under consideration has nonlinearity or the system parameters vary under a wide range, the performance of conventional PID deteriorates considerably. This happens because the reference input given to the system are usually not continuous or smooth as they are subjected to the disturbance or noise signal, while the output of the system is required to be smooth and continuous. Since the smooth continuous output is taken as the direct objective of the output, the inertia influence of the system is neglected which causes unanticipated overshoot oscillations when used practically. In addition, the reference signals are usually un-differentiable signals which makes it problematic to achieve the differential signal of the error. The linear combination of conventional PID causes the conflict between the overshoot variable and the reference. Initially a high value of K_p would intensify the system response however as the error starts reducing, the K_p value must also change automatically so that there is no overshoot [14]. Also when the error is decreasing and the rate of change in error is increasing, the K_p must decrease gradually to reduce the overshoot and when the change of error is decreasing K_p must gradually decrease to avoid the overshoot. But due to the linear combination of the PID, this is not possible. Hence we need to find different nonlinear adaptive controllers to control such nonlinear dynamical system. The PID controller is auto tuned by heuristic Zeigler-Nichols rules for continuous time model. The simulation results for the control signal *u(t)* is shown in figure.4 and the response of NLDS with PID controller is shown in figure.5

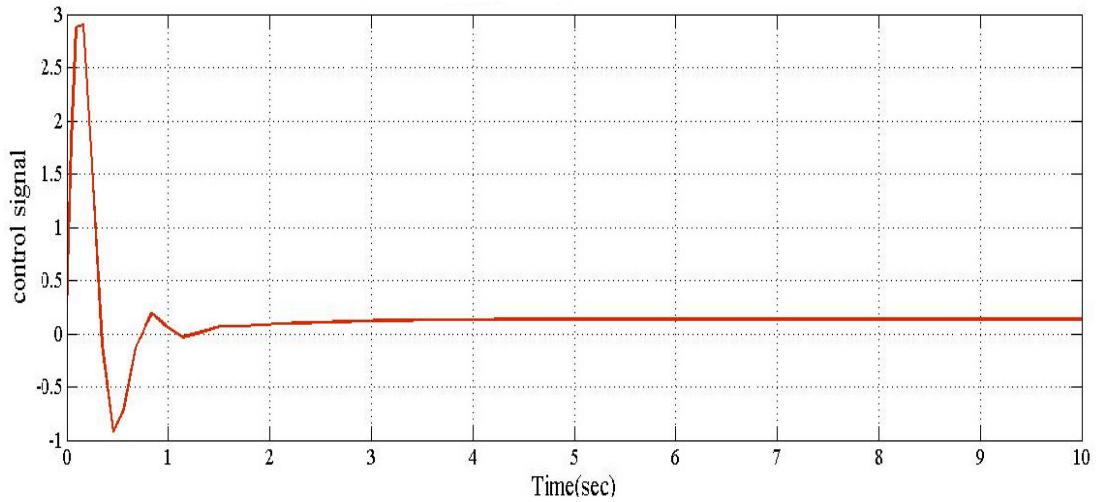

Figure 4 Control signal from PID Controller

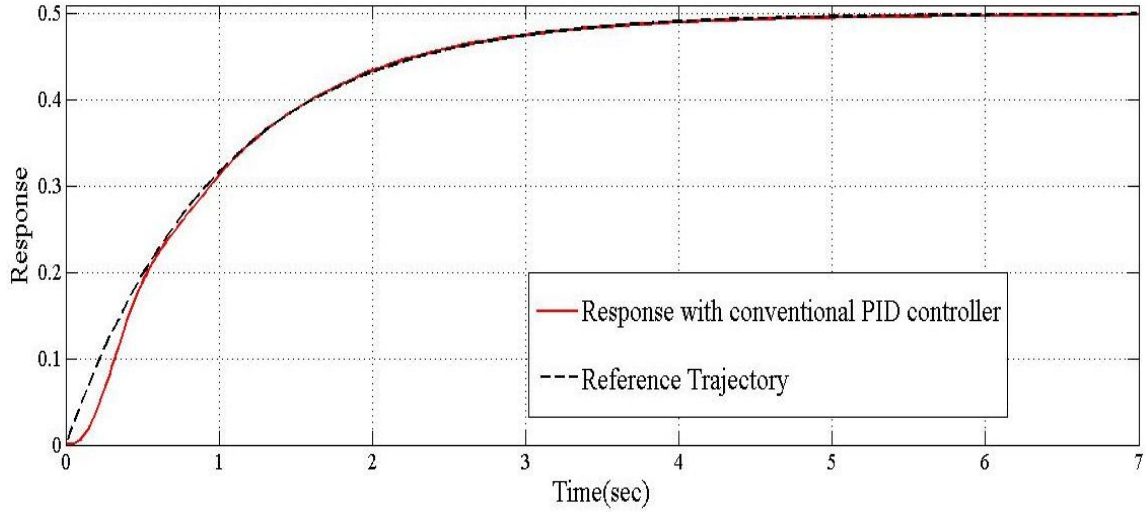

Figure 5 Response of NLDS with PID Controller

3.2.NARMA L-2 Controller

Neural networks (NN) have been extensively used in the identification and control of NLDS. Multilayer neural networks have the universal approximation capability which makes it a popular selection for modelling NLDS and for applying general purpose controller for NLDS. The two phases involved in neural network implementation are system identification and control design [15]. In the first phase, an identical NN model of the plant which is desired to be controlled has to be realized. Subsequently, the developed NN model is then used to train the controller. NARMA L-2 controller is simply a readjustment of the plant model that is trained off-line in batch process. It requires the least computation of most neural architectures as the only computation is forward pass through the neural network controller. The only drawback of this form of controller design is that the plant being controlled should be in companion form or must be capable of being approximated by a companion form model [16]. This type of control is also known as feedback linearization control. A standard model to denote general discrete-time nonlinear system is the nonlinear autoregressive-moving average (NARMA) model [16] expressed by equation (8).

$$y(k + d) = N[y(k), y(k -1),\ldots, y(k - n +1),u(k),u(k -1),\ldots, u(k - n +1)] \quad (8)$$

Where u (k), y (k) and'd' are the system input, system output and system delay respectively. For the identification phase, to train the NN, the nonlinear function 'N' is approximated. If the system output followed reference trajectory $y (k + d) = y_r (k + d)$, to develop a nonlinear controller [5] by using equation (9)

$$u(k) = G[y(k), y(k -1),\ldots, y(k - n +1), y_r (k + d),u(k -1),\ldots, u(k -m+1)] \quad (9)$$

Implementation of NARMA L-2 Controller is quite slow due to the dynamic back-propagation training and creation of a function 'G' to minimize the mean square error. The solution is to approximate the model by equation (10).

$$y (k+ d)= f [y (k), y(k-1)\ldots. y (k-n+1), u(k-1),\ldots., u(k- m+1)]+g [y(k),y(k-1)\ldots..,y(k-n+1),u(k-1),\ldots.,u(k-m+1).u(k) \quad (10)$$

This model is in companion form [16], where the next controller input u (k) is not confined inside the nonlinearity. The advantage of this form is that the control input that causes the

system output to follow the reference y (k + d) = y_r (k + d), can be determined. The consequential controller would take the form given in equation (11)

$$u(k) = \frac{y_r(k+d) - f[y, y(k-1), \ldots, y(k-n+1), u(k-1), \ldots, u(k-n+1)}{g[y(k), y(k-1), \ldots, y(k-n+1), u(k-1), \ldots, u(k-n+1)]} \quad (11)$$

Directly using the above equation the realization of problems [16] is achieved, as the control input u (k) has to be determined based on the output y (k), at the same time. Hence, instead of the previous model the revised model is used and given in equation (12).

$$y(k+d) = f[y(k), y(k-1), \ldots, y(k-n+1), u(k), u(k-1), \ldots, u(k-n+1)] + g[y(k), y(k-1), \ldots, y(k-n+1), u(k), \ldots, u(k-n+1)].u(k+1) \quad (12)$$

Where $d \geq 2$.The structure of a NN representation for NARMA L-2 controlled NLDS plant model is shown in the figure.6

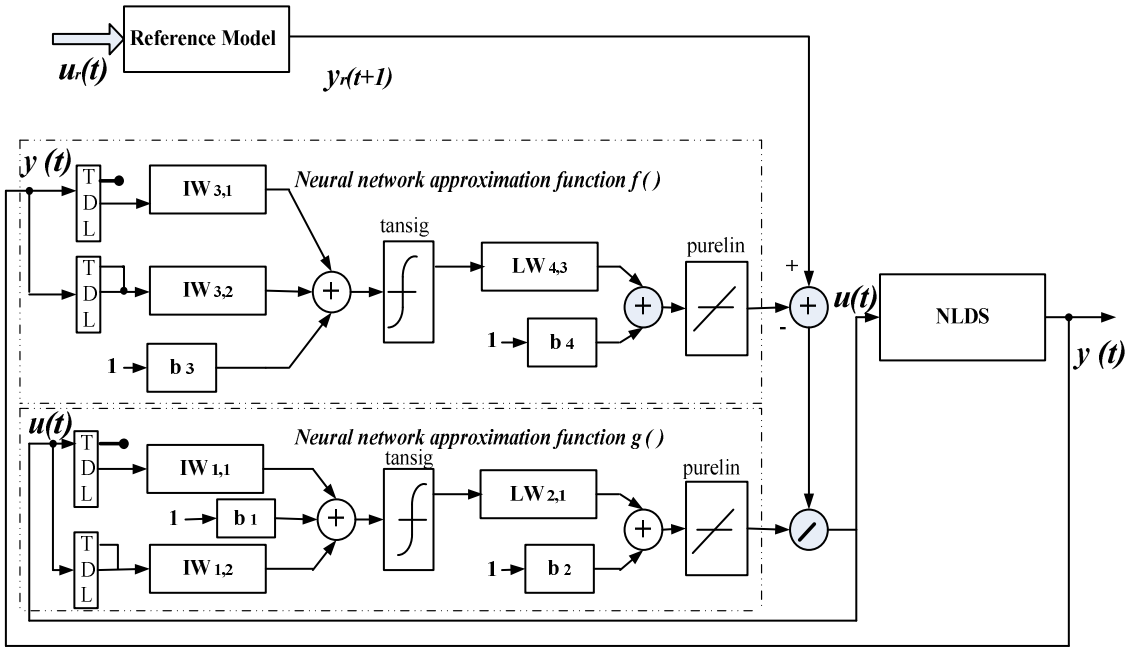

Figure 6. NARMA L-2 controlled NLDS Plant model

3.2.1. NARMA L-2 Controller Design

Neural networks are widely used now a days for identification of NLDS through NARMA L-2 controller by feedback linearization. Implementation of NARMA L-2 essentially consists of two steps. The first one is the identification of the plant shown in figure 7 which involves developing an approximate NN model of the NLDS.

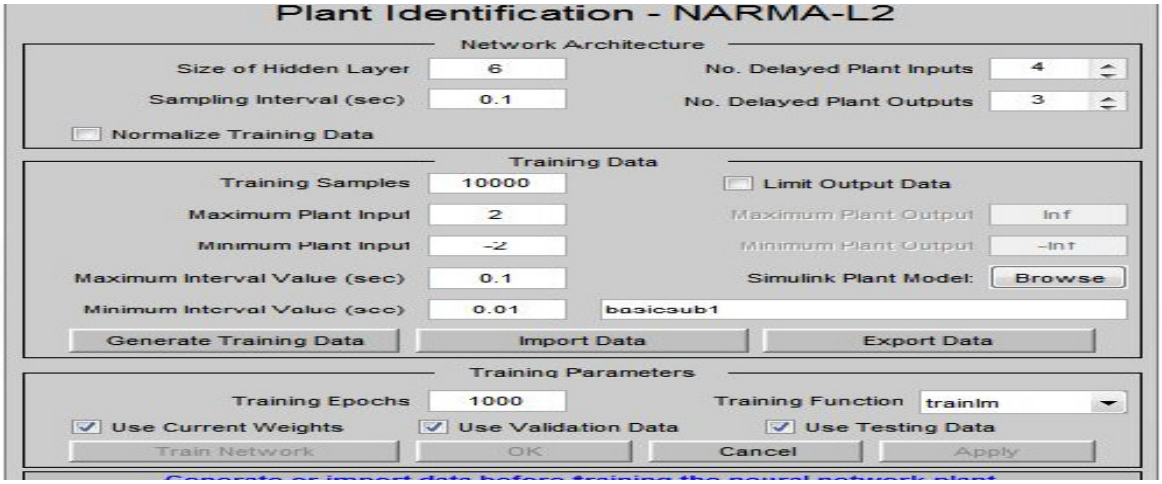

Figure 7 . NARMA L-2 Plant identification

The second stage is to obtain a NN model of the plant which is used to train the controller. The model of a NARMA L-2 controlled NLDS is shown in Figure.8 and the control signal from NARMA L-2 controller is also shown in figure.9

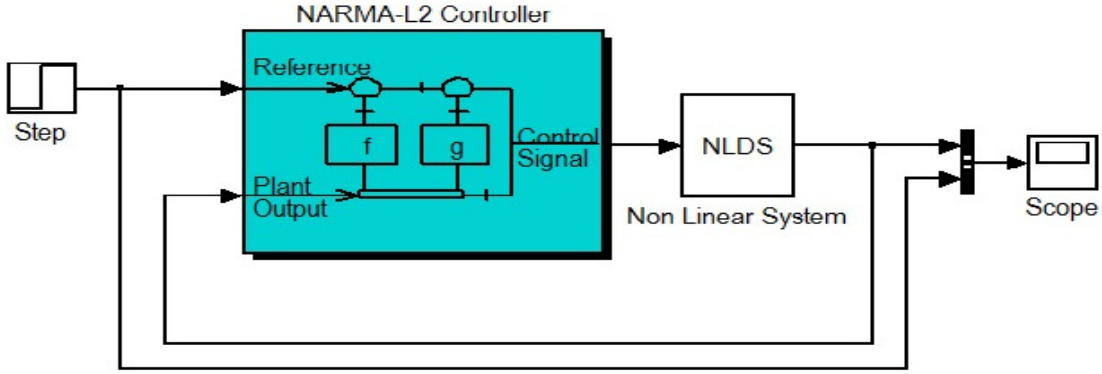

Figure 8. NARMA L-2 Controlled NLDS model

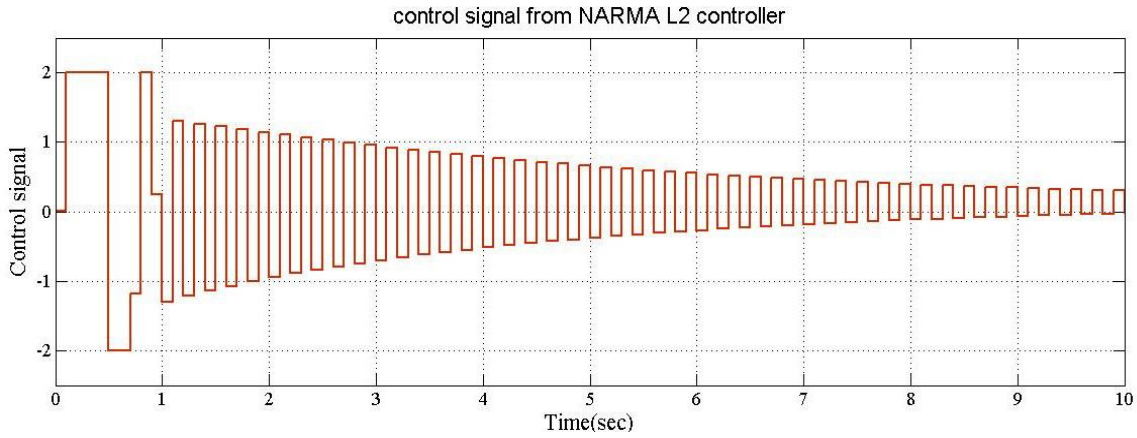

Figure 9.Control Signal of NARMA L-2 Controller

System identification mainly consists of gathering sufficient experimental data, estimating the best approximate model from the data and then validating the model with the data. For the plant identification, the controller bounds for the maximum and minimum inputs, outputs as well as the time interval for which the input to the system would remain constant [5,18]. Number of hidden layers required for the neural network is provided and the delays in the output and input of the system are also provided as 4 and 3 respectively. Since

information about the dynamic behaviour of the NLDS is used for system identification, a sufficient number of training samples (10000) were generated with the above specification. The number of epochs within which the mean squared error (MSE) will be minimized was set to 1000; the training algorithm used for the NLDS identification was Levenberg-Marquandt (trainlm) technique. The experimental data used for training the neural network is shown in figure 10. The testing and validation data sets for NARMA L-2 controller are shown in figure 11 and 12, respectively. After the validation of the training and testing data, the best validation performance is 3.0604 e^{-12} as shown in figure 13 and the response of the NARMA L-2 controlled NLDS is shown in figure.14. It is observed from the results that the NLDS system is stable.

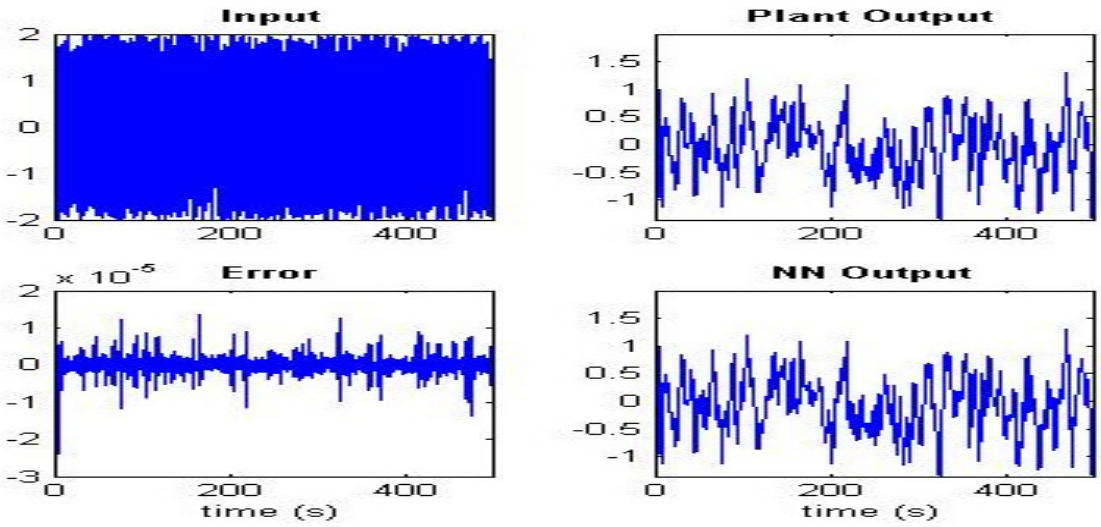

Figure 10. Training experimental data set for NARMA L-2 controlled NLDS

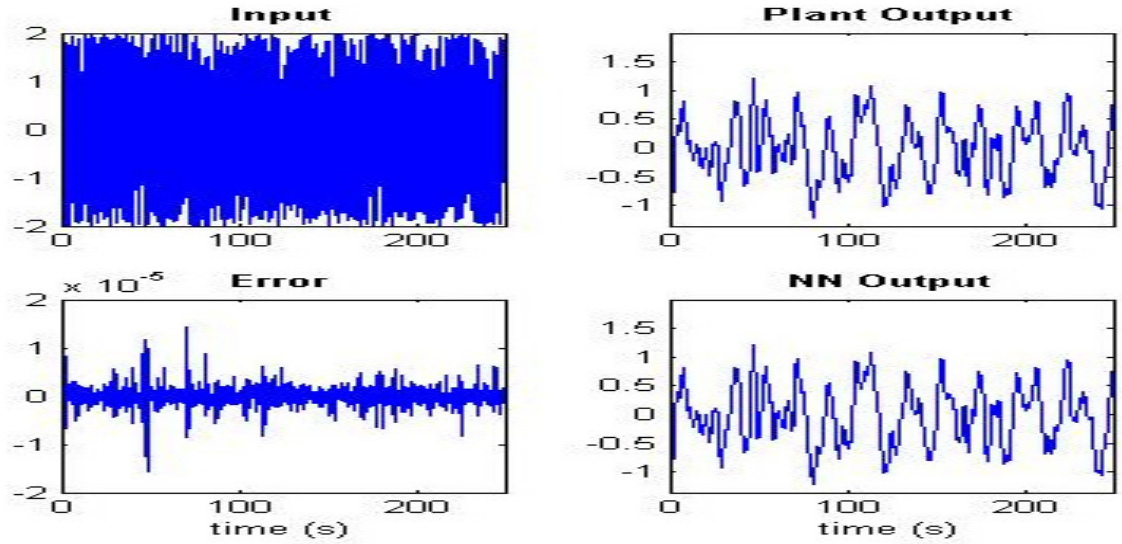

Figure 11. Testing data set for NARMA L-2 controlled NLDS

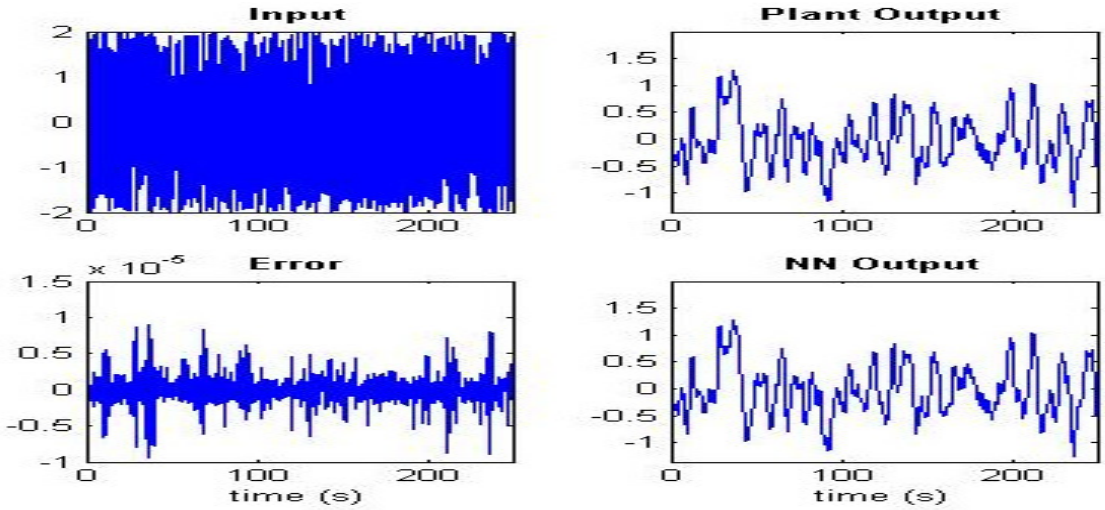

Figure 12. Validation data set for NARMA L-2 controlled NLDS

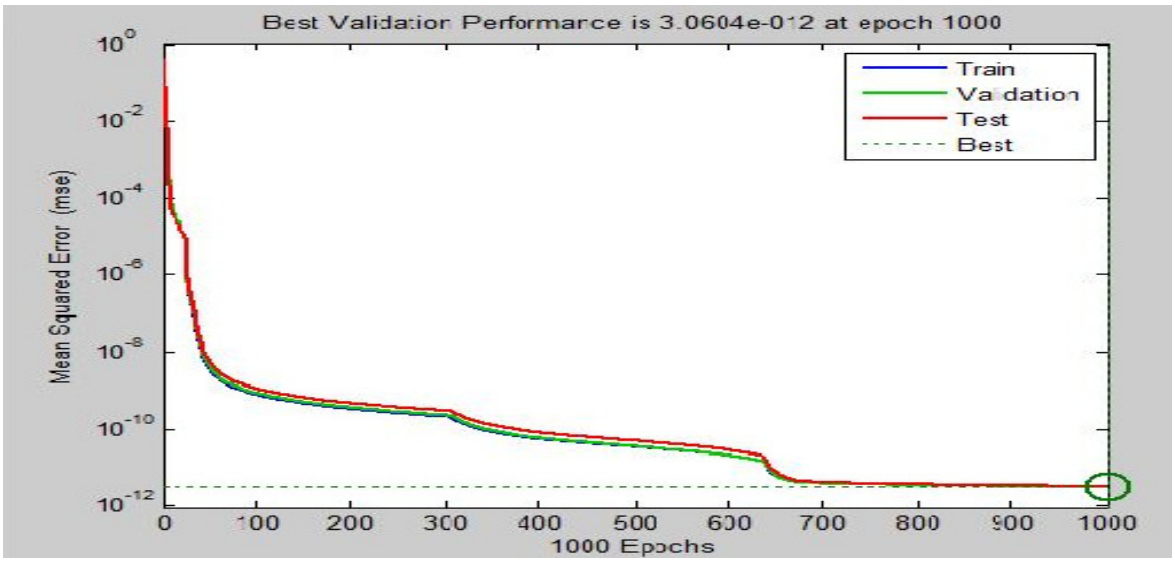

Figure 13. Best validation performance of NLDS

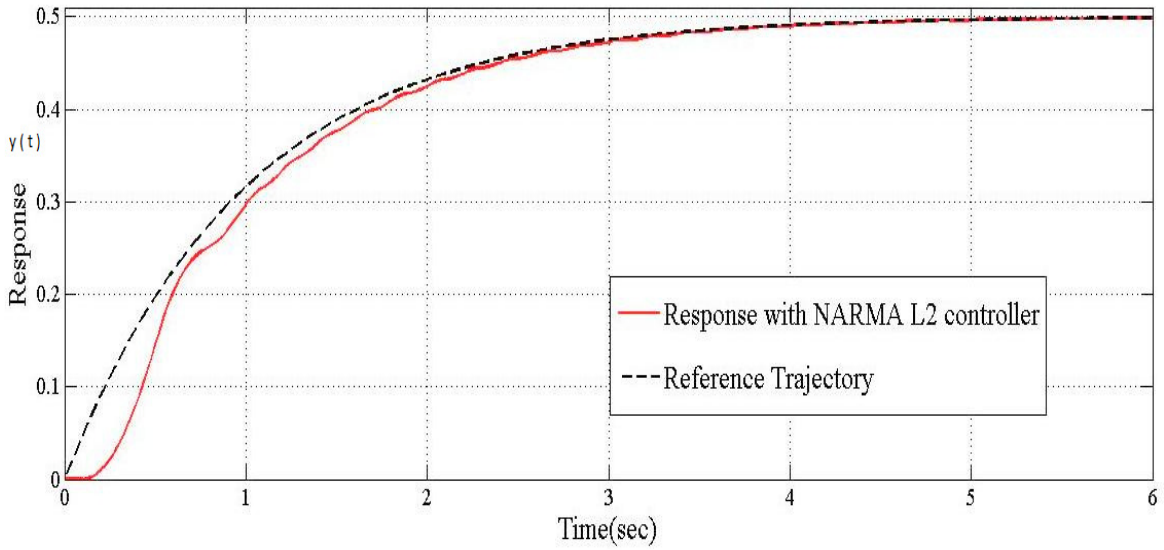

Figure 14. Response of NARMA L-2 Controlled NLDS

3.3 PSO Tuned PID Controller

Particle swarm optimization (PSO) is a metaheuristic optimization algorithm motivated by swarm intelligence of fish and bird schooling in nature. The multiple agents known as particles, swarm around the search space starting from some initial guess [19, 20]. PSO have some resemblances with genetic algorithms and ant colony algorithm but PSO is much modest because it uses real number randomness and global communication instead of mutation / crossover operators or pheromone. The PSO algorithm is initialized with a group of arbitrary particles in a search space and then the search for optima begins by updating generations. With each iteration the particles in the search space adjust their position by using two best values. The first best comes from the greatest fitness it has achieved so far (self-experience) which is stored as pbest (g^*) and the other best is tracked by any particle in the population (social experience) which is called the global best[19] or gbest (x_i^*). When the algorithm finds these two best values, it updates its velocity and position. Let x_i and v_i be the position vector and the velocity of particle 'i' respectively. The innovative velocity vector is determined by the equation (13)

$$v_i^{t+1} = C(v_i^t + \alpha\varepsilon_1 \odot [g^* - x_i^t] + \beta\varepsilon_2 \odot [x_i^* - x_i^t]) \quad (13)$$

Here 'ε_1' and 'ε_2' be two arbitrary vectors taking values between 0 and 1. The Hadamard product [21] of two matrices $u \Theta v$ is defined as entry wise product $[u \Theta v] = u_{ij}\, v_{ij}$. The parameters α and β are learning parameters heuristically taken as $\alpha \approx \beta \approx 2$. The initial locations of all the particles are uniformly distributed such that they can sample over most of the space. The initial velocity $v_i^t = 0$ at the new position can be updated using equation (14) and the v_i value is bounded in the range of $[0\ v_{max}]$. The flow chart of the proposed PSO tuned PID with NLDS is shown in figure.15.

$$x_i^{t+1} = x_i^t + v_i^{t+1} \quad (14)$$

The initial values for the PSO algorithm is as follows:

- Population size = 10
- Dimension = 3
- Learning parameter α =2.05
- Learning parameter β =2.05
- Constriction factor C= 2
- Maximum iterations = 50

The implementation of the PSO algorithm to tune the PID controller can broadcast the current best estimate and gives better and quicker convergence during optimal tracking of the specified desired signal. Here the swarm size, the number of iterations and the learning factors are taken as 20, 50 and 2.05 respectively. The PSO algorithm estimates the best K_p, K_i and K_d parameters based on the error signal e (t). The functional diagram of the PSO tuned PID controller with NLDS shown in figure 16. The PSO uses the NLDS output to search the optimal solution of the parameters ΔK_p, ΔK_i and ΔK_d for every discrete step. By knowing these states, the new optimal solution parameters would be added to the earlier PID parameters Kp (n-1), K_i (n-1) and K_d (n-1). The response of the NLDS with optimally tuned PID by PSO is shown in figure 17. The optimally tuned PID using PSO gives the parameters K_p= 167.7437, Ki =100.68827 and K_d =70.7849.

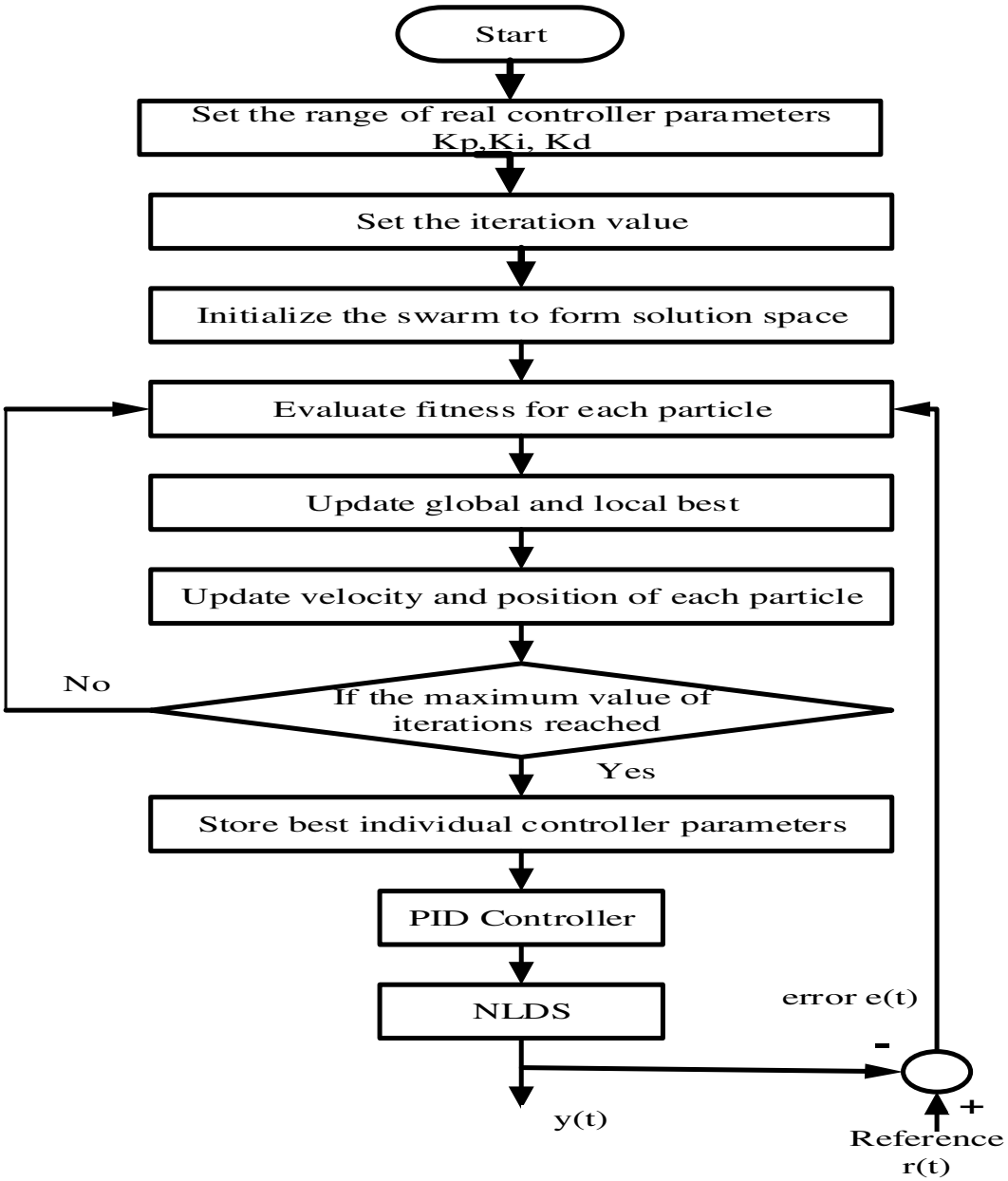

Figure 15. Flow chart of the PSO tuned PID with NLDS

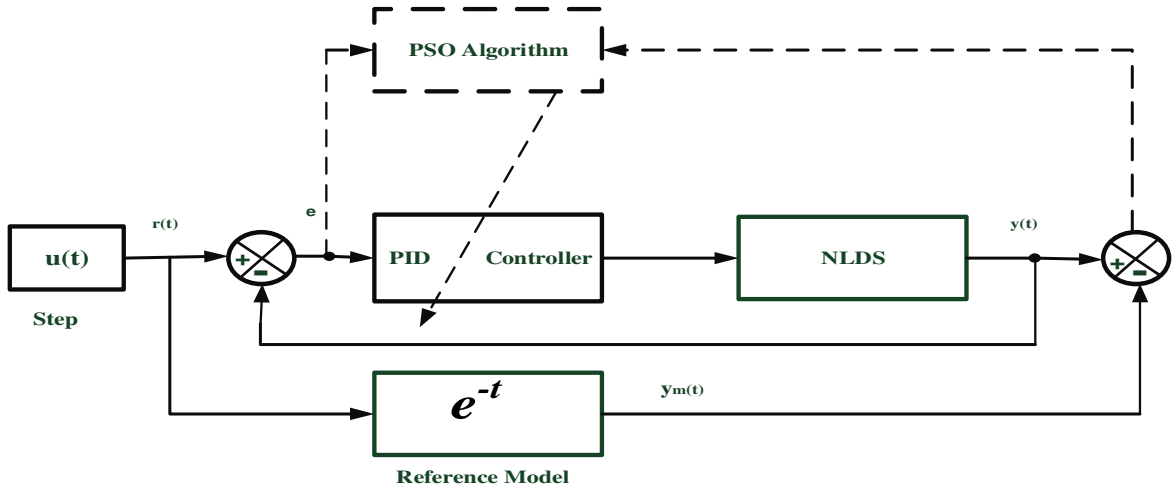

Figure 16. Functional diagram of PSO tuned PID controller with NLDS

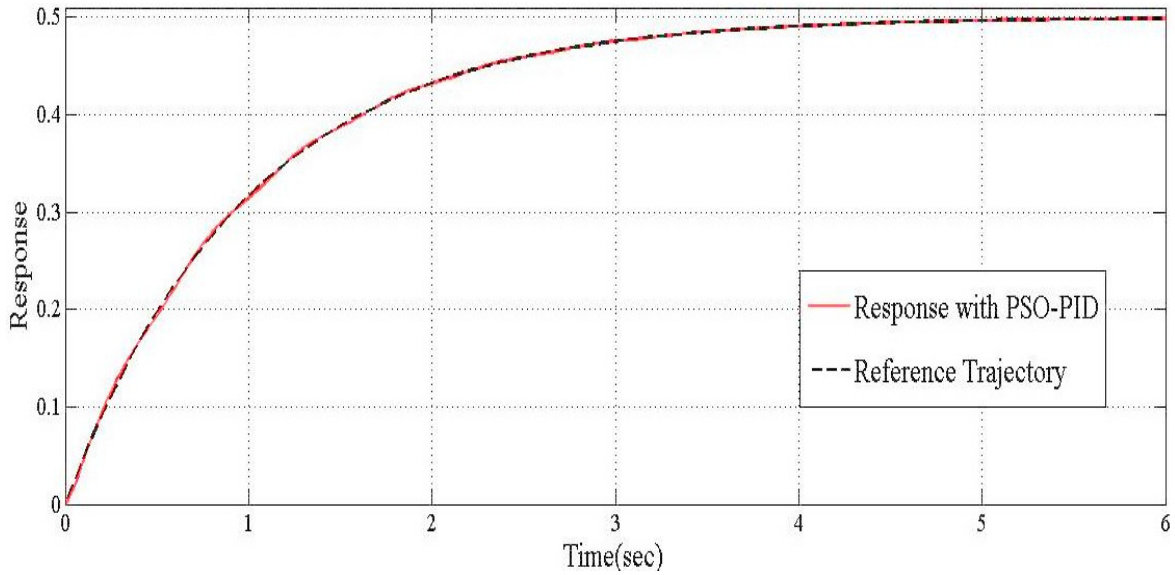

Figure 17. Response of NLDS with optimally tuned PID controller by PSO

4. COMPARISON OF SIMULATION RESULTS

Comparison of the NLDS responses using conventional PID, NARMA L-2 and optimally tuned PID by PSO is carried out through simulation study of NLDS. Since the reference trajectory taken is a model reference for a NLDS, both the error elimination and the transient behaviour of the system has been taken into account. The system is originally unstable due to the presence of disturbances, unmodelled dynamics and parametric variations. Figure 18 shows the system responses with the different types of controllers in respect of the various performance criteria like settling time, peak overshoot, and steady state error.

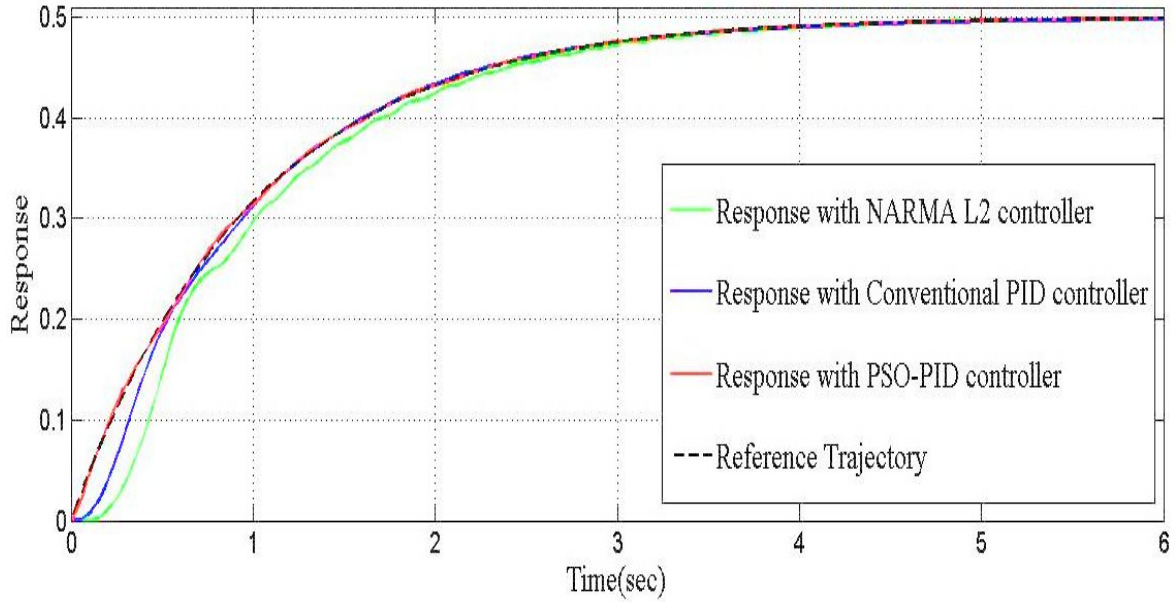

Figure 18. Comparison of response of NLDS with different controllers

The simulation results in figure 19 shows the trajectory tracking behaviour of the optimally tuned PID controller by PSO and it is observed from figure 19 that the PSO tuned PID operator of NLDS gives improved response than the either conventional PID and the NARMA L-2 controller for varying reference signal at t=10 sec.

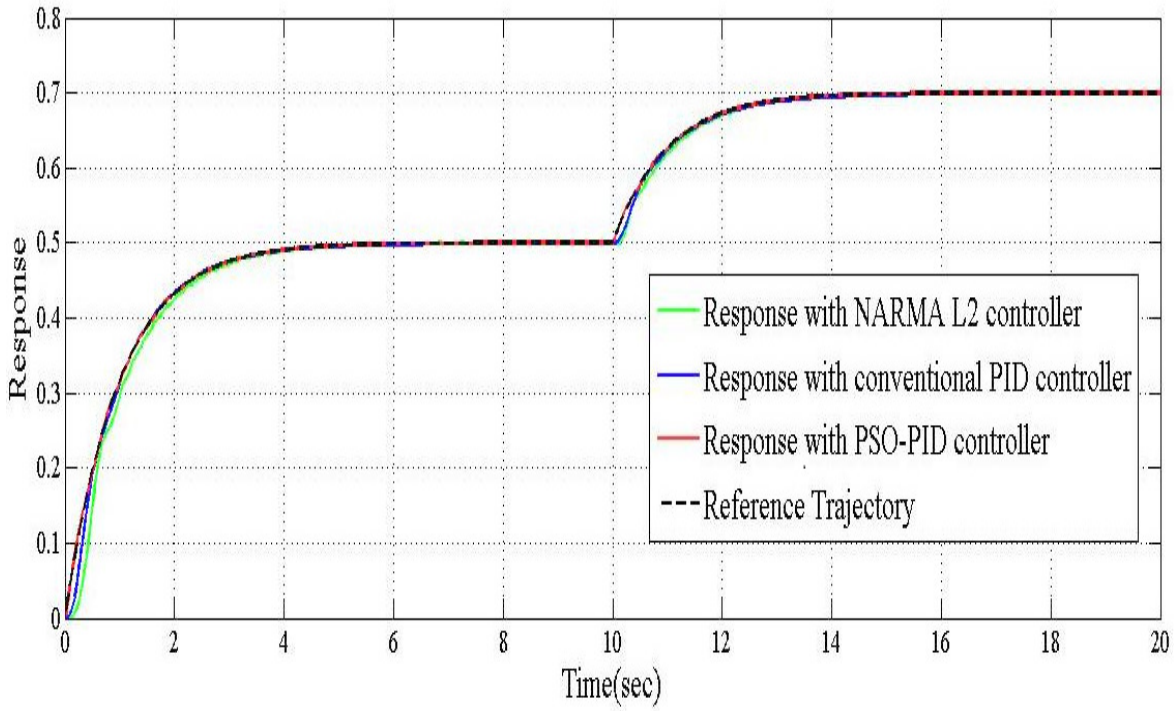

Figure 19. Comparison of response with varying reference trajectory

The following performance parameters through the dynamic response analysis of NLDS have been determined by using PID, NARMA L2 and PSO tuned PID controllers and the values are summarized in Table. I

Table. I Performance Parameters of NLDS using Different Controllers with r (t) =0.5

Controllers	Settling Time (Sec)	Peak Overshoot (%)	Steady state error
PID	3.975	0.0401	0.0002
NARMA-L2	4.000	-0.0375	0
PSO tuned PID	3.850	0.0002	0

5. CONCLUSION

The conventional PID, NARMA L-2 and optimally tuned PID controller by PSO have been successfully developed and tested for their performance in terms of settling time, peak overshoot and steady state error on a NLDS. Simulation results shows the effectiveness of these controllers for dealing with NLDS for widely varying operating conditions. In comparison with the conventional PID controller, the NARMA L-2 controller has the advantage of a no overshoot, zero steady state error but with the drawback of a higher settling time. On the other hand conventional PID controller tuned using PSO technique with model reference yields better performance as compared to these two controllers.

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Developing Global Engineering Competency Through Participation in "Engineers Without Borders"

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Developing Global Engineering Competency Through Participation in "Engineers Without Borders"

Abstract

With a growing need for globally competent engineers, global engineering educational experiences, such as *Engineers Without Borders* (EWB), have become an important potential avenue for teaching students global engineering competencies. The purpose of this qualitative case study was to better understand engineering students' learning experiences in a EWB project, looking specifically at how students participating on the project exhibit attributes of global engineering competencies. The case study investigates an EWB project with the mission of designing and implementing a solar-powered electricity system for a school in Uganda. We found that students do exhibit attributes of global engineering competencies, although attributes regarding engineering cultures and ethics were exhibited more strongly than attributes regarding global regulations and standards. We discuss implications of these findings for educational practice and future research.

Introduction

Providing engineering students opportunities to develop global competencies has become a pressing necessity for engineering programs given the highly global nature of engineering work that requires the ability to work productively with other cultures. Study abroad programs, virtual global courses, and courses and modules focused on engineering for a global society, are all pedagogical approaches to improving engineering students' global competencies. Although these formal education approaches can be highly effective, they are not always accessible to a wide population of students and largely engage students for only a single and short portion of students' academic experiences.[1] Increasingly, extracurricular activities, such as EWB, have emerged as another an alternative that offer students an opportunity to be immersed with global engineering challenges throughout their undergraduate careers.[2]

The purpose of this study was to better understand engineering students' learning experiences in an extracurricular activity focused on global engineering issues, specifically how participation in EWB influences the ways students exhibit global competency attributes. Understanding participating students' perspectives can help begin to identify the affordances and/or barriers of EWB that most influence students' development as global engineers. Research questions that guided our study were:

> **RQ1:** How do students describe their learning experiences with EWB?
> **RQ2:** What are the affordances and/or barriers of participating with EWB that most influence students' global competency development?

Our goal in exploring these particular research questions is to shed light how students participating in EWB exhibit global competency development. Specifically, we strive to understand the student perspective of the EWB educational experience with the goal of having a

more informed understanding of how such an experience might be assessed in the future as an accepted educational avenue for exposing students to authentic global engineering projects.

Global Competencies in Engineering Education

In the last 15 years, Engineering programs in the U.S. have been working towards improving engineering education, recognizing the necessity to enhance and modernize engineering education to better meet the demands of future engineering challenges.[3] Global competency is one of the important skills that has been identified by the engineering education community as essential and expected of all engineering graduates. Various curricular and non-curricular approaches have been implemented in engineering programs in the U.S. for the specific need of teaching and exposing engineering students to global engineering challenges.[1,4]

An important question to consider when developing, implementing, or evaluating any educational approach to teaching global competence is what it means to be a globally competent engineer. Having an inclusive, operational, and explicit definition for global competence that is agreed upon in the engineering education literature appears to be elusive, however there does appear to be an agreement for what the engineering education community has identified as general attributes of "global engineering competency". "Global engineering competency" refers to "those attributes uniquely or especially relevant for cross-national/cultural practice" (p. 660).[5] The attributes global engineering competency refers to include engineering ethics, engineering cultures, and regulations and standards. Table 1 lists how these attributes are further characterized in the literature.

Table 1. Attributes of Global Engineering Competency[5]

Attributes of Global Engineering Competency	**Definition**
Engineering Ethics	Capability of handling situations with ethical issues due to national/cultural differences
Engineering Cultures	Capability of understanding how engineering challenges and solutions are situated within national/cultural contexts
Regulations and Standards	Capability of understanding the national/cultural regulatory aspects influence engineering solution applications

The literature has also identified essential elements needed to produce global competency, specifically "coursework in international studies, second language proficiency and international experience" (p. 121).[4] Similarly, the literature has also identified specific learning outcomes to account for when examining global competency, such as: demonstrating "knowledge" of cultural differences in engineering work; demonstrating an "ability" to perform engineering work in global settings; having a "predisposition" to work effectively and respectfully with people of different cultural backgrounds; having an awareness of political/societal issues in global contexts; having an understanding of the globalization of engineering education; and having an understanding of international business, market, economy.[4,6,7]

Although these attributes and proposed learning outcomes are not concrete definitions of a globally competent engineer, they do provide insight into what is expected of globally competent engineers. A possible hindrance to explicitly stating a single definition and concise expected outcomes of educational global experiences for engineers might be the wide variety of strategies used to teach and expose engineering students to global engineering. What students experience in a course regarding engineering work with respect to international business and economy is not likely to be equivalent to what students experience in a study abroad program, or while working and traveling abroad for a global service learning project.[1] Such a complex skill is not likely to be fully captured by a single educational intervention. Engineering education research thus far has focused on the need for globally competent engineers and defining what that means, but research that investigates the possible educational avenues that might be used to accomplish these educational missions has been limited. This study aims to investigate students' learning experiences in a global service learning project, as a preliminary investigation into one possible educational avenue for teaching global engineering competency. More deeply understanding experiences of students working on global service projects can better inform engineering educators of the specific outcomes that might be expected of similar educational experiences.

Research Study

This study is a qualitative case-study of students working on a global service learning project at a large research intensive state institution in the U.S. We observed a team of 8 students working on a EWB sponsored project. We chose a EWB team because it is one of the more common and recognizable global service learning experiences available to engineering students in the U.S. The following sections will describe the research study design in more detail.

Research Site and Participants

This particular team of EWB students was working towards developing, implementing, and assessing a solar-powered electrical system for a school located in a remote area in Uganda. From here on, the team will be referred to as EWB-U. The study site and experience were non-mandatory for students to receive their degrees, and students self-selected to participate on the team. The team consisted of 8 students (3 senior/fifth-year students, 2 juniors, 1 sophomore, 2 freshmen), from various engineering majors including mechanical engineering, civil engineering, electrical engineering, and chemical engineering. The team was predominantly male, with only 2 female participants. The team was almost entirely student-run. The only non-student participant was an industry mentor who was a practicing electrical engineer from a local engineering company. The industry mentor would occasionally advise students on the electrical system design (via email, phone, or in-person meetings), and the industry mentor would also travel with the student team during the 3-week summer implementation/assessment trip to Uganda.

Methodology

This research employed a case study approach to examine the dynamics present within a service learning project team.[8] Qualitative methods were used to understand students' experiences of students regularly and actively participating in a EWB project. The primary purpose of this investigation was to understand students' experiences, rather than to measure learning outcomes, justifying a qualitative approach.[9,10]

A researcher with no affiliation with the EWB project conducted naturalistic observations, interview, and focus group discussions. Semi-structured interviews and focus groups were conducted with participating students. The eight student members participated in a one-hour focus group discussion, and the team leader participated in a 90-minute interview. The focus group protocol focused on students' decision to join the EWB, their experiences with EWB, their goals with EWB and professionally, and their general experiences and perceptions of their education as engineering students. The student leader was asked a couple of questions regarding their experience as a student leader, as well as questions regarding their educational and professional trajectory.

To supplement the interview and focus group data, observations of student meetings were conducted, detailed field notes were documented for all observations, and archival data was collected. The observer attempted to remain as an external observer as much as possible, with minimal interactions with participants. To ensure trustworthiness of observations and analysis, triangulation, reflexivity external audits, and peer examination were used.[11] Observation protocol focused primarily on conversation topics, student behavior, student actions, student interactions, and student-mentor interactions. Also, observation data from the research site somewhat informed the focus group protocol. For example, if a focus group participant discussed a particular event that the researchers had also observed, the focus group facilitator would bring up that observed instance as a clarifying example. EWB team observations included observations of typical team meetings. In addition to the observations, archival data from the research site was collected to further supplement the interview data. Specifically the team's website, team photos, and documents or reports written by the team were collected. This information was used to better familiarize and contextualize the type of environment that the team creates for students.

Data analysis was primarily guided by the global engineering competencies described earlier in Table 1. These attributes were used as constructs to guide the coding and analysis of the focus group and interview. More specifically, instances where students made a statement reflective of a global competency attribute ('engineering ethics', 'engineering cultures', or 'regulations and standards') were coded as such, and each instance was further analyzed to identify how the attribute was exhibited. It should be noted that this study is limited by being an examination of a single case. However, the scope of this study is that of a preliminary study, with the aim of beginning to characterize student experiences and identifying the potential affordances and barriers of similar global service learning projects. The results of this preliminary study will be used to inform a larger study examining a variety of learning environments that have missions to enhance engineering students' global competency. It should also be noted that this study is an IRB-approved study. For the sake of protecting the study participants' identities, no personal

identifiers will be used; names used to identify quotes from the data are pseudonyms. Quotes presented in the findings have been minimally edited to maintain grammatical clarity.

Research Findings

Recruitment issues, perceived time commitment, and gaps in knowledge transfer between outgoing and incoming student members were salient barriers to the sustainable success of EWB. However, once students commit to a EWB project, EWB serves as an example of how engineering students can be exposed to educational yet authentic global engineering experiences in ways that are meaningful and impactful to each student. Consistently active student members exhibited an awareness and capacity to work productively within the boundaries of an unfamiliar cultural context, successfully communicating and achieving the defined goals and tasks, as well as exhibiting a capacity to work across disciplinary and cultural boundaries to achieve a common goal. The following sections will discuss the findings with respect to the specific global engineering competency attributes exhibited by the students, as well as the affordances of participating in EWB and the barriers to participating in EWB.

Engineering Ethics

Students from the EWB-U team exhibited some attributes of engineering ethics (i.e., capability of handling situations with ethical issues due to national/cultural differences), particularly within the domain of recognizing a "[d]epth of concern for people in all parts of the world…moral responsibility to improve conditions and take action in diverse engineering settings" (p. 3).[12] Having an innate desire to help others around the world accounts for much of the students' motivation to participate in EWB-U. Even more specifically, the participating students often sited wanting to apply their engineering skills in knowledge in ways that could help improve the condition of the world, such as the following statement by Frank.

> [Frank]: "I wanted to help people and volunteer my time, and help out. I'm an electrical engineering student, so this very much lines up with what I want to do, cause I want to do power and alternate energies."

Working towards designing, developing, and assessing a solar-powered electrical system for a school in a remote location of Uganda, EWB-U students were able to feel as if they were making a difference on two fronts – sustainable energy systems and community service. Many of the students also stated that they initially considered engineering to be a relatively narrow profession. However, once they showed up to EWB interest meetings (held at the beginning of each academic term), they stated how that was when they realized that engineering can be applied in many diverse ways. Martin and Carmen, for example, both acknowledged that it is their goal to find engineering jobs where the priority is to make a difference rather than make money.

> [Martin]: "There's a lot stuff you can make, and you can get a job and have a professional career and all that. But there's a lot of other things you can do with an engineering degree [than just

> making money]… But I think using it, you know, for something like this is much more up my alley."
> [Carmen]: "I [feel] like it [is] my responsibility to serve others, and try to make the world a better place."

Overall, the students are very driven by a perceived necessity to do the work that they do for the Ugandan community.

> [Carmen]: "[I] [d]efinitely want to see the project move forward and continue. I've dealt with other projects that come to a stand still for whatever reason…When you have a connection, when you've traveled, you want this to happen. You want people to have electricity…if you don't do it, then no one else will."

However, they also recognize that they are limited in their ability to contribute given that they are engineering students, with limited experience, time, and resources to contribute. The students recognize that although they spend the academic year designing and preparing for the implementation trip, they are only on-site for about 3-weeks, which limits the amount of long-term impact they can have on the community. Even so, the students do not let the realities of the situation deter their willingness and motivation to pursue the engineering challenge, as demonstrated by Craig's statement below.

> [Craig]: "You know, you're not gonna save the world or anything like that. That doesn't mean you have to sit on your hands and not do anything."

Engineering Cultures

Students also exhibited attributes of understanding engineering cultures (i.e., capability of understanding how engineering challenges and solutions are situated within national/cultural contexts), with this particular attribute seemingly being the most strongly exhibited out of the three (i.e. engineering ethics, engineering cultures, and regulations and standards). The students demonstrated that they were very much aware of the constraints they were working under by keeping in mind the cultural context in which they were working. For instance, Craig, who had worked with EWB-U for nearly 3 years, noted how his first summer trip was focused on designing and implementing the system. The second year was focused on design changes, implementation, and initial assessment of the system. The upcoming trip was focused on implementing changes based on the 2nd year's assessment, and conducting further assessment of the system. When asked to give an example of how the design might change year to year, Craig stated:

> [Craig]: "I think every year the new system kind of reflects the results of the last monitoring. At [the school] we have the two-inverter system that we could switch back and forth, and that was definitely a new concept that we used. It should work a lot better **for their specific needs**."

Craig's example demonstrates how the students maintain an awareness of the specific needs of the community they are serving. Similarly, when describing to the newest team members the decision-making process for deciding where and how to place the solar-powered electrical systems, the students who had traveled earlier described that they wanted to look for places with

enough sunlight, but away from major roads, because "if [community members] don't know they're there, they can't steal them". This student interaction, which was observed during a team meeting, demonstrates how the EWB-U members are well aware of the realities of the cultural context of their project, and the students' recognition of the design constraints with which they are working. Carmen provides another example of how the students demonstrated an understanding of how implications of cultural differences might inform engineering solutions when she stated the following:

> [Carmen]: "[W]hen I traveled I learned a lot more about what actually works in sustainable development, and what you *can* do, and I saw a lot of different problems. Like, I know now I'm more interested in incinerating trash, because you see huge problems in Uganda. There's no trash pick-up, because you know all the money is focused on the roads and just keeping up basic infrastructure. But now that they're finding ways to use trash to create energy, that's what I'm really interested in, and hopefully one day I think there should be ways, incentives to not only clean up an area, but to use that to produce renewable energy"

Carmen also exhibited an understanding of the importance of needing to be fully educated about the general cultural context with which the students are working, in order to work productively, effectively, and respectfully.

> [Carmen]: "EWB made me realize that I wanted to be more than just an engineer. I picked up another major – sociology- because I was talking to everyone, and I realized - like I mean I want to do engineering, I want to help in that way - but I also realized that **I need to learn a lot about other people and culture because you know it's a completely different life over there**. And you don't even really understand - like things we do in the U.S., like standing up when you're eating is considered rude over there, and it's something we would never consider over here."

Other students recognized the value of the human relationships they make while participating abroad in EWB-U, understanding that those relationships might have a more lasting effect than the electrical systems that they design and implement.

> [Will]: "The first trip I went [on], I was very focused on being productive, and I just wanted to work all the time. But one of the things that I kind of learned from [industry mentor], when I went over there the second time, is your relationships that you build with people, they will last longer than the equipment that you'll bring. And that made a lot of sense to me looking back on the first trip."

Regulations and Standards

The remaining global competency attribute, regulations and standards (i.e., capability of understanding the national/cultural regulatory aspects influence engineering solution applications), was the attribute the students exhibited the least. The closest demonstration of this attribute was during an observation of student discussions during a team meeting. During this meeting, the team leader was discussing that a new task added to their upcoming trip to Uganda, in addition to assessing the current electrical system, was to build a safe welding laboratory for the school EWB-U was serving. In addition to building the facility, the students, along with their

industry mentor, were also going to host a workshop on safe welding for the students of the school EWB-U was serving.

The students' reasoning for building the welding facility and hosting a safe welding workshop was because of past observations, made by students who had traveled, of how unsafely welding work was currently done in this particular Ugandan community. Considering that their particular engineering solution involved quite a bit of welding work, finding welders who could work safely and with the appropriate equipment was very difficult for the EWB-U team. The EWB-U students recognized that regulations and standards regarding appropriate work conditions and procedures are very different in Uganda, as compared to the U.S., however they felt obligated to spread the awareness of proper welding techniques for the young Ugandan students that the EWB-U team was serving.

Affordances of Participation & Barriers to Participation

As illustrated in the previous section, the engineering students participating in EWB-U exhibited attributes of global engineering competency. Certain affordances offered by participating in EWB-U, that other educational experiences might not provide, might account for students exhibiting global competency attributes. For instance, the students frequently mentioned how much more meaningful participating in EWB-U has been, as compared to what they typically get out of a curricular course.

> [Shawn]: "I learn a lot more going on trips than I do in my classes and like doing all this work, you know like you're working for a purpose, you're doing something real."
>
> [Carmen]: "EWB has that cultural component that you're not going to get you know sitting here and doing this design work and you're not going to get uh you know in a classroom."
>
> [Craig]: "It forces you to meet people under the best possible circumstances. Which is nice."
>
> [Will]: "Here it's actual hands on…you gotta assess it, you analyze it, and then you implement it all the way through, like beginning to end. That's the best experience I'll probably get in my entire time here [in college]; a volunteer thing."

The students frequently indicated how the work they put into EWB-U had a greater meaning than just "getting a grade". This greater meaning fed the students' drive to be engaged in an engineering challenge that required them to understand and develop global competency attributes in order to succeed. Through EWB-U, the students were able to experience engineering working that benefited a community in need, all while experiencing engineering work in an authentic setting (i.e., financial constraints, timelines, client needs, demand for innovative solutions). Additionally, EWB-U provides students with an opportunity to be self-directed learners, by requiring them to manage their own schedules and tasks.

> [Will]: "It's kind of student-run, and that makes it fun as well. You just make your own schedule and everything like that. It's a good experience that way too."

> [Carmen]: "It's non-threatening because everyone is around the same age, doing the same classes…I get intimated talking to professors, but I feel like I can talk to all the people in our group, and I can talk to our mentor pretty easily."

Despite the positive affordances, there are substantial barriers to participation that prevent students from taking full advantage of the opportunities EWB, and similar extracurricular activities, have to offer. One barrier pointed out by the students was the general lack of student awareness that EWB exists, making recruitment for the team difficult.

> [Shawn]: "People don't really know about EWB. It's 10 years old, everyone assumes that it's Doctors Without Borders, and people on campus don't really have good ways of finding out about it unless they're part of some [email] listserv, or they happen to see some signs somewhere"

An even larger barrier that students identified was having the time to participate in EWB while completing rigorous engineering coursework. Although EWB offers a valuable educational experience, specifically with regard to global competency, students' academic achievement (i.e. grades and GPA) remains to be the priority.

> [Carmen]: "Sometimes it's hard balancing school and [EWB]. You know, for some people, it's more important to do well in their classes, where I guess, I kind of sometimes am one of those people who's like 'well… [forget about] differential equations, I don't really care anyways'. You know, I can do matrices, so I'm just going to work on [EWB project] instead. [S]ometimes balance is difficult. Staying interested [in EWB] with a heavy course load is hard to do"

> [Craig]: "You only have so many hours of productive work in a week, and when you try to throw that on top of coursework - there were definitely assignments that I didn't do while I was finishing paperwork for EWB. So that was uh, I don't know. I learned a lot from doing [the paperwork]."

Students participating in EWB-U do not receive any academic credit or acknowledgement for their participation, or for their success in implementing a functioning solar-powered electrical system for the community in need. While the students involved in this study appeared to prioritize the EWB-U project above their coursework, the students did acknowledge that, at the very least, they needed to be able to pass their classes in order to graduate. This time demand can be a significant barrier to participation for students focused on maintaining a high GPA, such as students needing to meet scholarship requirements.

Discussion

The purpose of this study was to investigate students' learning experiences with EWB, specifically identifying how students participating in EWB might exhibit global competency development. Overall, in our research study we found evidence that students who participated in this particular EWB exhibited attributes of global engineering competency, although the students exhibited certain attributes more than others. Specifically, and understanding of 'engineering cultures' was strongly exhibited by the students, whereas only some demonstration of understanding 'engineering ethics' and 'regulations and standards' was observed of the students.

While students showed a strong "moral responsibility to improve conditions and take action in diverse engineering settings" (p. 11)[12], the students never explicitly discussed the possibility of ethical issues that might arise from cultural differences[13], neither during focus group discussions nor during observations of team meetings. The students also did not discuss much in terms of the impact that international or global differences in workplace practices, regulations, or standards might have on their project.

The ways students exhibited global competency attributes could be due the nature of this particular engineering context, where students are voluntarily serving a community, rather than developing a product to be sold to a global market. Regulations and standards of the served community are important elements for students to consider, particularly regarding how cultural differences relate to product design, implementation, and use. However, having an understanding of intellectual property, business practices, and the international labor market is less relevant to students working on a global service learning project such as EWB-U. These elements of regulations and standards would be more relevant to students experiencing an engineering challenge sponsored by a global corporation. The students are primarily driven to learn enough to successfully meet the needs of the community they are serving. One possible strategy for ensuring students are exposed to all global competency attributes would be to offer students "skill sessions"[14], or similar workshop-style meetings, that could attempt to scaffold students' educational experience with global engineering work.

The EWB-U students did appear to have a strong understanding of the cultural implications and contexts of the community they were serving, which has been noted by previous similar studies[15,16]. Even more promising, the students demonstrated a willingness and desire to learn more about various international cultures, and the cultural implications to engineering, either through additional coursework or practical experiences. This could be attributed to the affordance of the EWB experience of exposing students to long-term authentic global engineering challenges. There are few research studies regarding the attributes of global engineering competency exhibited by engineering students participating in global service learning projects[5], so this study has contributed an examination of if and how attributes of global engineering competencies are exhibited by EWB student members. This study also identified a unique affordance that EWB provided students, which is to provide students with an authentic global engineering experience. Beyond needing engineers who can understand or be aware of global engineering competencies, engineers need to be able to apply and effectively work beyond global boundaries[17], which EWB offers students the experience to practice.

These findings appear to imply that global service learning projects, such as EWB team described by the study, are effective educational avenues for students to learn and be exposed to global engineering competencies. However, there are certain limitations of this study that should be considered. First, this study is a preliminary examination of the educational possibilities that global service learning projects might offer. More in-depth analyses of other similar global service learning projects, with additional cases available for comparison, can provide an examination that is wider in breadth regarding the affordances and barriers of global service learning projects. Second, the aim of this study was not to make claims of measured learning outcomes of students participating in global service learning projects, but rather was to describe and characterize the experiences of students participating in a global service learning project.

Previous studies have presented useful survey and assessment constructs regarding global competency[1,16,18], and the findings of this study do further inform future research regarding measured learning outcomes by providing specific constructs that can be expected of global service learning project students:

- In terms of engineering ethics, future studies aimed at measuring learning outcomes should focus on measuring students' awareness and understanding ethical issues pertaining to their project's cultural context. Engineering educators, industry professionals, or student leaders who mentor or lead related global service learning projects should consider having team members explicitly discuss and plan for potential ethical issues pertaining to the project's cultural context.

- With regard to engineering cultures, future studies aimed at measuring learning outcomes should focus on measuring students' awareness and understanding of cultural norms, and the implications these cultural contexts have on engineering solutions and applications. In terms of practice, team members should be tasked with learning and discussing expected cultural norms, as well as discussing and designing engineering solutions while considering the constraints and implications of the cultural context.

- Considering regulations and standards, future research aimed at measuring learning outcomes should focus on measuring students' understanding of the regulations and standards of the country and/or community they are visiting, as well as an understanding of how these regulations and standards might influence their project design and implementation. In practice, team members should be tasked with studying the relevant regulations and standards that would impact their engineering solution/application, as well as discuss possible approaches to handling unexpected situations regarding workplace practices or other economic/market issues.

The findings of this study indicate that expected learning outcomes of global educational experiences should be tailored to the mission of the educational experience. This recommendation has been previously expressed by other education literature on the alignment of curricular educational experiences and expected learning outcomes[18,20], and we believe it also applies in this non-curricular educational experience. Courses on engineering cultures or globalization of engineering cannot be expected to give students the same educational experience as global service learning projects, just as multi-national online courses will not have an identical educational influence as study abroad programs. While all global educational experiences share the characteristic of being avenues for teaching global competencies, they are all unique in terms of the specific global competency attributes that they can develop in students. Engineering educators, researchers, administrators, accreditors, and employers should account for these differences among global educational experiences when considering the global engineering competencies of engineering graduates. Future research should examine the comparison of various common global educational experiences with respect to their specific expected learning outcomes. With a greater understanding of how various global educational experience impact students' learning, opportunities such as EWB can be more strongly considered a *co*-curricular experience (i.e., an experience geared towards enhancing relevant curricular demands), rather

than an *extra*-curricular experience (i.e. additional experiences outside of curricular demands) within the grander context of engineering education.

Conclusion

Responding to the increased demand for engineers with global competencies, the engineering education community has implemented a variety of global educational interventions, such as courses focused on engineering cultures, global virtual classrooms, and global service learning projects. This study aimed to characterize the educational experiences of engineering students participating in a EWB project by using an accepted definition of global engineering competencies to guide the study analysis. This study also identified the affordances of participating and the barriers to participating in global service learning projects, as described by participating student members.

Students participating in EWB-U exhibited all attributes of global engineering competencies (engineering ethics, engineering cultures, and regulations and standards), however, regulations and standards was the weakest attribute exhibited by the students. We believe this was the weakest attribute demonstrated by students because of the inherent mission of EWB, which is more driven by global service needs rather than international corporate needs. Even so, we have detailed recommendations for how similar global service learning projects might enhance student members' development of global engineering competencies. Affordances of participating in EWB, as described by the students, includes having authentic and meaningful global engineering experiences, as well as providing an educational environment for students to behave as self-directed learners. The barriers to participation, however, are primarily the time constraints typical of engineering students working through rigorous engineering coursework, as well as a general lack of student awareness of EWB, which complicates the recruitment of new student members.

This study implies that global service learning projects are an effective educational approach to teaching engineering students global competencies. Research on specific educational experiences that influence students' development of global engineering competencies is relatively limited, so it is our hope that this study adds to this body of literature by providing a model for using existing literature on defined global engineering competencies to examine the role of various global engineering educational experiences. Being a preliminary exploratory study, we have described how our findings might inform future studies of other global service learning experiences, as well as other curricular and non-curricular educational experiences geared towards developing students' global engineering competencies.

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Enhanced electromagnetic shielding behaviour of multilayer graphene anchored luminescent TiO_2 in PPY matrix

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Enhanced electromagnetic shielding behaviour of Multilayer Graphene anchored luminescent TiO_2 in PPY matrix

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Abstract
Present research is focussed on the development of a novel composite material for highly-efficient absorption of electromagnetic interference (EMI) pollution. Herein, we report synthesis and characterization of polypyrrole (PPY) composite containing multi-layered graphene (MLG) anchored with titanium dioxide (TiO_2) via in-situ oxidative polymerization of pyrrole. The tuning of the microwave signals has achieved via composites with different weight ratios of MLG and TiO_2. The maximum Total shielding effectiveness (SE_T), 53 dB was observed for PPY/MLG/TiO_2 (5% composite) in the frequency range of 12.4 to 18 GHz. The observed results suggest that the composite material could be a new alternative for building block of electromagnetic shielding applications.

Keywords: Polymers, Nanocomposites, Luminescence, Multilayer Structure, Dielectrics

1. Introduction

Recent innovations in the field of electronic devices and our increased dependency on these products have amplified the need of error free electronic systems. These issues have encouraged scientists to develop materials that can shield the electronic devices against EM radiation [1,2]. Metal coated/plated polymers are the most widely used materials for EMI shielding because of their high conductivity. However, metal shields have poor flexibility, high weight, tendency to corrode, and limited tuning of the SE [3,4]. Literature survey shows that the conducting polymer composites offer various advantageous properties in the use of EMI shielding applications. PPY is a nitrogen based cyclic conducting polymer which offers good conductivity, environmental stability, and ease of synthesis [5,6]. However, conducting polymers lack in mechanical strength, it restricts their fabrication as an EMI shield for commercial applications. To overcome this, in the present work, dielectrics like TiO_2 are incorporated in the polymer matrix to enhance the absorption properties and thermal stability of these polymers (*See supporting information*) [3,7] and multi layered graphene (MLG) is incorporated as a conductive reinforcing material. Therefore, PPY composite incorporated with MLG decorated with TiO_2 constitutes a new generation material with great potential for EMI shielding applications.

2. Experimental

MLG was synthesized using chemical exfoliation graphite in the acidic medium[8]. The TiO_2 nano particles were synthesized by sol-gel method[9]. In-situ polymerization of pyrrole was carried out for the synthesis of the composite. Initially, The MLG and TiO_2 nanoparticles were ultra-homogenized in a 0.3 M aqueous solution of Sodium Lauryl Sulphate with distilled pyrrole (0.1 M) for 2 hours. The solution was polymerized using $FeCl_3$ (0.2 M). The solution is then filtered and the residue is dried at 60°C. Several compositions of PPY: MLG: TiO_2 having weight ratios 1:0.01:0.01, 1:0.05:0.05, 1:0:0.05 and 1:0.05:0 were prepared. The schematic of the synthesis of the composite is shown in Figure 1a.

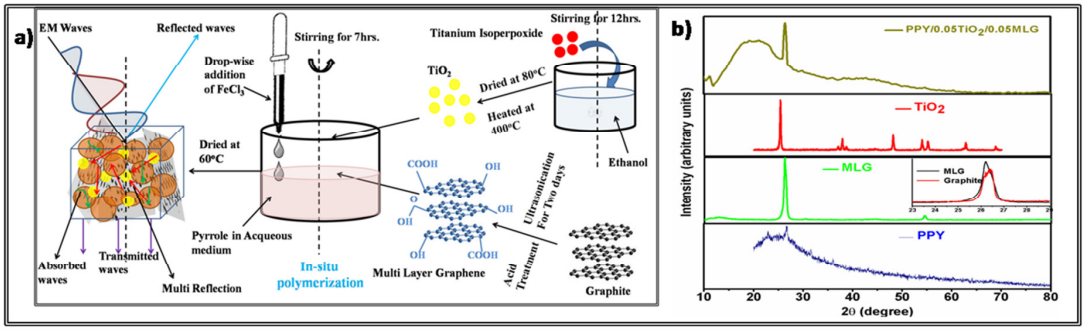

Figure 1 a) Schematic representation of the synthesis of composite b) X-Ray Diffraction (XRD) of different constituent materials

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3. Results and discussions

Figure 1b shows the XRD pattern of PPY, MLG, TiO_2 and PPY/TiO_2/MLG. TiO_2 nanoparticles show the characteristic peaks at 2θ 25.36°, 36.24°, 37.84°, 39.41°, 48.12°, 54.08°, which correspond to the (1 0 1), (1 0 3), (0 0 4), (1 1 2), (2 0 0) and (1 0 5) crystal planes, respectively confirming the anatase phase of TiO_2 [10]. The XRD spectrum of MLG, shows sharp peak at 26.22° and 54.51°. The peak at 26.22° is significantly broader than the corresponding peak of graphite, which verifies the good exfoliation of the graphite [11]. The neat PPY shows the characteristics broad hump from 17^0 to 27^0, with two low intensity peaks at 22.94° and 26.62° [7]. The composite (PPY/0.05TiO_2/0.05MLG), shows the characteristic peaks of TiO_2 and MLG. Additionally, the presence of broad diffraction pattern in the range of 11.8° to 25.34° is due to the polymer matrix. A slight shifting in the characteristic peaks was observed, which could be due to the synergistic interaction among the PPY, TiO_2 and MLG.

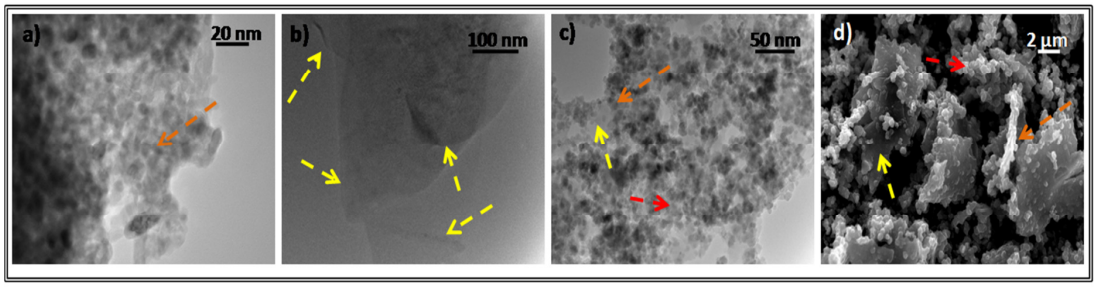

Figure 2: Transmission electron microscope (TEM) image of a) TiO_2 b) MLG c) PPY/0.05MLG/0.05TiO_2 & d) Scanning Electron Microscope (SEM) image of PPY/0.05MLG/0.05TiO_2

The TEM image of TiO_2 nanoparticles (Figure 2a) reveals the presence of fine particles (9 nm to 12 nm) having uniform morphology [12]. Fig. 2b shows the TEM image of the MLG sheets of few micrometers. The TEM and SEM images of the PPY/MLG/TiO_2 composite are shown in Figure 2c and d, respectively. The TEM image of the composite reveals the presence of MLG sheets decorated with TiO_2 nanoparticles and polyprrole. The SEM micrograph of the composite exhibits a MLG flakes are uniformly covered with polypyrrole and TiO_2 particles. The SEM & TEM interpretations are in accordance with the XRD results.

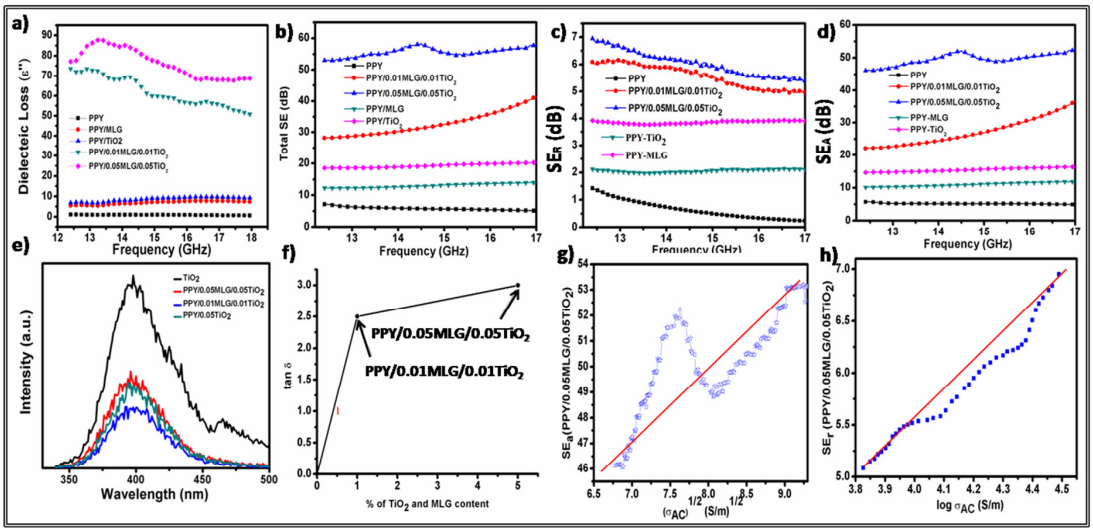

Figure 3 a) Dielectric loss of different composites b) SE_T versus frequency c) SE_R versus frequency d) SE_A versus Frequency e) PL emission spectra (excited at 254nm) f) Tangent loss g) SE_A versus $(\sigma_{AC})^{1/2}$ h) SE_R versus log σ_{AC}

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The shielding measurement has been done using scattering parameters by Nicolson Ross Weir method (*See supporting information*). Figure 3b, c and d show the variation of SE_T (Total Shielding Effectiveness), SE_R (Shielding Effectiveness Due To Reflection) and SE_A (Shielding Effectiveness Due To Absorption) with frequency in the 12.4-18 GHz range, respectively. SE_T of PPY, PPY/TiO_2, PPY/MLG, PPY/0.01MLG/0.01TiO_2 and PPY/0.05MLG/0.05TiO_2 is 7 dB, 13 dB, 19 dB, 28 dB and 53 dB, respectively. It is very evident from the mentioned data that with the addition of even small weight percentage of TiO_2 and MLG, the value of SE_T increases significantly. This is attributed to the combined effect of TiO_2 and MLG. Moreover, the SE_A of both the composites is more than 80% of the SE_T, which manifests the great microwave absorption properties of the synthesized composite.

SE_R can be expressed as:

$$SE_R\ (dB) \approx 10log\ (\sigma_{AC}/\mu_R f); \quad (1)$$

$$\sigma_{AC} \approx \omega\ \varepsilon_o\ \varepsilon'' ; \quad (2)$$

Where σ_{AC} is conductivity; μ_R is relative permeability; ω is angular frequency and f is Frequency. It can be inferred from the equation 1, that SE_R is directly proportion to the conductivity of the sample. Thus, high conductivity of MLG leads to higher value of PPY/MLG than PPY/TiO_2. Figure 3c also shows the gradual decrease in SE_R with the increase in frequency. The disturbance in the orientation of dipoles in a system due to increased frequency could be a possible reason for the retardation of SE_R. The validity of the above equations could be verified from the Figure 3c & 3h.

SE_A can be expressed as [13]

$$SE_A\ (dB) \approx k\ d\ (nf\ \mu\ \sigma)^{1/2} \quad (3)$$

Where K is constant; d is the thickness of the shield and other symbols describe the same variables which is described earlier.

Figure 3d & 3g verifies the above equation. A view of good measure of microwave absorption can also be indicated by the loss tangent, tan $\delta \approx \varepsilon''/\varepsilon'$. If tan δ is greater than 1, then the materials are considered to be "lossy" materials. This indicates strong absorption at a given frequency [14]. Figure 3f, clearly shows that the ratio of $\varepsilon''/\varepsilon'$ being more than 1 for all the composites. Further, the imminent increase in the microwave absorption properties of the PPY/0.05M/0.05/T can be related to the both complex and real part of permittivity of nano size of TiO_2 particles. Due to the small size, the anisotropic energy of the particles will be high and the increased anisotropy energy contributes to the enhancement of microwave absorption[15]. Besides the small size of TiO_2 particles, the efficient decoration of TiO_2 particles on MLG sheets lead to the increased polarization charges on the surface. The interaction of EM waves with the charges on these surfaces leads to the interfacial polarization and lags of polarization, which helps in the increase of high dielectric loss in the composite and high absorption effectiveness.

Photoluminescence study is carried out to evaluate the effect of the presence of TiO_2 in the PL properties of the polymer matrix. Figure 3e shows the typical PL spectra of TiO_2 nanoparticles, with a strong peak at 398 nm and other peaks observed within the wavelength range of 450-470 nm, which are attributed to the excitonic PL. This mainly results from the surface oxygen vacancies and defects[16, 17]. As compared to TiO_2 particles, the PL intensity of the PPY composites containing TiO_2 and MLG is significantly decreased. This is due to the fact that the PPY is a p-type narrow-bandgap semiconductor polymer and PPY has a quenching effect, which decreases the PL intensity with the increase of its concentration [17,18]. It is interesting to note that the PL intensity of PPY/0.05MLG/0.05TiO_2 composite is more than the PPY/0.05TiO_2 composite. The probable reason behind this result can be the higher interfacial area provided by Multi Layer Graphene sheets to TiO_2 particles. The remarkable increase in the PL intensity of PPY/0.05MLG/0.05TiO_2 composite in comparison to the PPY/0.01MLG/0.01TiO_2 reveals the potential use of the composite for the photoluminescence based device applications.

4. Conclusions

A facile method has been proposed to design a novel composite for EMI shielding effectiveness at 12.4-18 Hz frequency range. The XRD and morphological analysis of the composite justify the compatibility of MLG and TiO_2 particles with PPY matrix. The shielding effectiveness of the synthesized composite (MLG/PPY/TiO_2) is nearly 53dB with 46dB, the shielding effectiveness due to absorption. This intriguing effectiveness, high absorption properties and encouraging PL intensity results provide a platform for a multifunctional nano-composite for both shielding and photoluminescence based applications in next generation electronic devices.

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Highlights

- In-situ polymerization used to synthesize a composite of TiO_2 decorated with MLG in PPY.
- Total Shielding effectiveness in the 12.4-18 GHz range is 53dB for the composite.
- Potential photoluminescence properties were confirmed using luminescence spectrometer.
- Synergistic interactions among particles were verified using XRD, SEM and TEM.

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Flexible Sericin/Polyvinyl Alcohol/Clay Blend Films

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Abstract: This paper describes the preparation and characterization of flexible crosslinked Sericin/Polyvinyl alcohol (PVA)/ Clay blend films. Sericin/PVA (1:1 w/w) blend films are prepared by using glutaraldehyde as crosslinking agent, glycerol as plasticizer, Cloisite 30B and Sodium montmorillonite as nanoclays by solution casting method. The concentrations of glutaraldehyde, glycerol and nanoclays are optimized on the basis of mechanical properties of the blend films. It is observed that the tensile strength and elastic modulus of the crosslinked flexible Sericin/PVA film is enhanced on addition of clay. The blend films are characterized for structural, morphological and thermal properties. Fourier transform infrared spectra showed that gulteraldehyde chemically crossliked with PVA and Sericin. Scanning electron micrographs and tanδ thermograms revealed that the addition of gluteraldehyde is reduced the phase separation between Sericin and PVA in the blend films. The XRD spectra showed that clay is intercalated in Sericin/PVA matrix. Clays are completely dispersed in Sericin/PVA blend solution as observed in transmission electron microscopy (TEM).

Keywords: Sericin, Poly vinyl alcohol, Clay, Blend films

Introduction

The purpose of packaging is to preserve the quality and safety of the product it contains from the time of manufacture to the time it is used by the consumer [1]. Packaging materials provide physical protection and create proper physicochemical conditions for products that are essential for obtaining a satisfactory shelf life. The well-known packaging materials in the form of films that meet these criteria are petroleum based polymers such as polyethylene, polypropylene, polyester and polystyrene, which have been used by the industries for over 50 years. These materials are safe, inexpensive, versatile and flexible [2].

Environmental concerns caused by the solid waste after use of petrochemical-based plastic packaging materials have increased the interest in biodegradable packaging materials. These materials are often formulated with natural biopolymers, such as polysaccharides, proteins, and natural gums, capable of forming a cohesive and continuous matrix. However, relatively poor mechanical and water vapour barrier properties of these films are causing a major limitation for their industrial use [3]. Research efforts have been focused on the property modification of natural biopolymer-based films to improve their mechanical and water vapour barrier properties [4-6]. In the last two decades extensive research has been carried out in the area of polymer/layered silicate nanocomposite films. The layered silicate filled polymer nanocomposite films exhibit enhanced mechanical, thermal, barrier and other physiochemical properties at a low filler content when compared with pure polymer and conventional micro composites [7-9].

India is the second largest producer of silk and has the distinction of producing four variety of silk. The silk fibre is rich source of two different protein bio-macromolecules namely fibroin and Sericin. These two protein macromolecule are different in their amino acid composition structure and properties. Sericin is a glue-like protein which binds the fibroin fibre with successive sticky layers. It helps in the formation of the total cocoon and contributes about 20-30 % of the total cocoon weight. It contains many hydrophilic amino acids, which gives it high hydrophilicity and sensitivity to chemical modification. Sericin can be crosslinked, copolymerized and blended with other macromolecular materials to produce materials with improved properties. Sericin has attracted special attention among researchers because of its diverse physiological properties. Numerous studies have mentioned its edibleness and functional properties that it is oxidation resistant, antibacterial, and UV resistant, absorbs and releases moisture easily, with inhibitory activity of tyrosine and kinase and other medical applications [10-13].

To generate lusture and soft feel on silk textiles, the Sericin protein is removed through a process known as degumming, prior to dyeing and discarded into waste water stream which lead to high chemical oxygen demand and biological oxygen demand level [12]. Therefore, the waste water releases by silk industry leads to contamination of water and environment. The recovery of Sericin from waste water by various processes has been reported in the literature [14-16].

If Sericin can be used as packaging material, it will represent a natural biodegradable packaging material developed from waste. In addition to that the recovery of Sericin will reduce the pollution load in waste water. Despite the favourable characteristics of Sericin as a potential film forming material, films made of pure Sericin are found to be quite fragile, especially in dry state, probably due to its broad molecular weight distribution. In addition, because of strong hydrophilic characteristics, Sericin films readily swollen by aqueous solutions and can even be dissolved in aqueous solutions at elevated temperatures. Therefore, blended Sericin films have

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been produced along with whey protein [17], glucomannan [18] and PVA [19-31]. Chemical crosslinking has shown to be an effective approach to enhance the mechanical, thermal and chemical stabilities of films. Blended or crosslinked Sericin films found applications in the area of biomaterial for wound dressing, scaffold, filters and packaging films.

Polyvinyl alcohol (PVA) is synthetic, hot water soluble, nontoxic, biodegradable polymer with good film forming property which can be easily blended with Sericin [19-31]. Sericin and PVA has very good miscibility in hot water solution. However Sericin/PVA blend films show phase separation at high Sericin content (more than 30 %) [29]. Crosslinking reduces the phase separation of Sericin/PVA blend films. Gimens and Feng [26] have developed Sericin/PVA blend film along with dimethyl urea as cross linking agent for application in alcohol degradation by pervaporation. Siritientong *et al.* [27,28] have developed genipin cross-linked and glycerol plasticized Sericin/PVA films for wound dressing. The properties of Sericin/PVA blend films were enhanced by treatment with boric acid [29]. Non mulberry and mulberry Sericin/PVA blends have crosslinked with gluteraldehyde for wound dressing applications [26,31]. So far, Sericin/PVA blend films has not been exploited for packaging application. To enhance the mechanical properties of Sericin/PVA blend film using montmorillonite clay and quaternary ammonium modified montmorillonite (Cloistie 30B) has not been reported.

In the present study an attempt has been made to develop flexible Sericin/PVA blend films for packaging using glycerol (Gly) as plasticizer and glutaraldehyde (GA) as cross linking agent. The concentrations of glycerol and glutaraldehyde are optimized on the basis of mechanical properties of the films. Two different types of nanoclays namely Cloisite 30 B and Sodium montmorillonite are incorporated in optimized flexible crosslinked Sericin/PVA blend films. The concentrations of the nanoclays are optimized on the basis of mechanical properties. Sericin/PVA blend films are characterized.

Experimental

Materials

Bombyx mori silk cocoons were procured from Central Silk Research Board, Lucknow, India. Polyvinyl alcohol (MW 14000) was purchased from Central Drug House (P) Ltd. Reagent grade Glutaraldehyde (Central Drug House (P) Ltd.) and Glycerol (SRL) was used in this study. Cloisite 30 B and Sodium montmorillonite were procured from Southern Clay USA. Distilled water was used for all the experiments.

Methods

Preparation of Sericin

The silk cocoons were cut into small piece and Sericin was extracted using high temperature high pressure degumming technique [13]. Briefly, aqueous extraction of Sericin was carried out by boiling cut cocoons in autoclave at 120 ^{o}C for 1 hour keeping material to liquor ratio 1:15. The Sericin extracted aqueous solution then filtered with muslin cloth to remove fibroin and other suspended impurities. Solid Sericin was obtained by heating Sericin solution at 40 ^{o}C.

Preparation of Sericin/PVA Blend Films

Sericin/PVA (solid weight 10 wt.%) blend films were prepared by solution casting method. Aqueous solutions of Sericin/PVA in 1:1 (w/w) ratios were prepared in hot water with continuous stirring. Different concentrations of glycerol ranging from 20 % to 40 % (w/w) and glutaraldehyde from 2.5 % to 10 % (w/w) were added in Sericin/PVA solution. The solutions were poured in petri-dishes and dried at room temperature for at least 24 hours. After drying, the films were heat treated at 120 ^{o}C for 1 hour. The dry films were stored in plastic bags before all subsequent characterization. Films without glycerol and glutaraldehyde were also prepared and treated as control films. The thickness of the prepared films was in the range of 0.03-0.05 mm.

Preparation of Sericin/PVA/Clay Blend Films

Aqueous solutions containing Sericin/PVA (1:1w/w ratios), Glycerol 30 % (w/w) and glutaraldehyde 5 % (w/w) were prepared in hot water. Different concentrations of clays ranging from 0.5 to 1.5 % (w/w) were dispersed in the solution. The solutions were ultrasonicated for 30 min and poured in petridishes. After drying, the films were heat treated at 120 ^{o}C for 1 hour. The dry films were stored in plastic bags before all subsequent characterization.

Mechanical Testing

The mechanical properties of Sericin/PVA blend films were determined by using an Instron Universal Testing Machine (INSTRON model no. 3369) running at a crosshead speed of 5 mm/min and gauge length of 50 mm.

Characterization

Blended films with 0.03-0.05 mm thickness were analysed by FTIR spectrophotometer using transmittance Mode (Thermo Scientific Nicolet 380 Spectrophotometer, US). FTIR spectra were obtained in the range of wave number from 4000 to 650 cm^{-1}. X-ray diffraction intensity curves of blended films and nanoclay were obtained at a λ=1.5 Å for 2θ from 2 ^{o} to 60 ^{o} with a diffractometer Bruker D S Advanced (Germany) using CuKα radiation. Surface morphology of films was observed under scanning electron microscope (S-3700N SEM, Germany) at a voltage of 20 kV. Surface of film samples were coated with gold before analysis. Thermo gravimetric (TGA) analysis of films was performed under nitrogen atmosphere at 10 ^{o}C/min from ambient temperature up to 600 ^{o}C using Perkin Elmer pyris-6 thermal analysis system. The differential scanning calorimeter (DSC) of film samples was performed on Perkin Elmer DSC-7 data station with heating rate at 10 ^{o}/C from ambient to 300 ^{o}C under nitrogen atmosphere. TEM analysis was conducted on a H-7600 model machine (HITACHI, Ltd.) with an accelerating

voltage of 100 kV.

Results and Discussion

The aim of this study is to exploit Sericin protein as packaging material. Pure Sericin films do not show good mechanical properties and readily swollen by aqueous solution and can even be dissolved in aqueous solution at elevated temperatures. In this study Sericin protein is blended with the PVA as both are hot water soluble. PVA has good mechanical and film forming properties. Films prepared with weight ration of 1:1 Sericin/PVA have shown phase separation. To reduce the phase separation the films are crosslinked with gluteraldehyde. Crosslinking also enhanced mechanical and thermal properties of the films and reduced solubility in hot water so that we can use them for packaging purpose. However, after crosslinking the films have shown very high stiffness and became unsuitable for flexible packaging applications, therefore to generate flexibility in the blended films glycerol is used as plasticizer. The concentrations of glutaraldehyde and glycerol are optimized on the basis of mechanical properties of blended films. Further the mechanical properties of the blended films are enhanced by the incorporation of nanoclays. Two different types of nanoclays namely Cloisite 30 B and Sodium montmorillonite are incorporated in optimized flexible cross-linked Sericin/PVA blend films. The concentrations of the nanoclays are optimized on the basis of mechanical properties of blended films. Blended films are characterised for its structural, morphological and thermal properties.

Effect of Glutaraldehyde (GA)

The effect of glutaraldehyde on tensile strength, elastic modulus and elongation at break of Sericin/PVA films is shown Table 1. The tensile strength and young modulus of pure Sericin/PVA blend film are 16.08 MPa and 428.47 MPa respectively. However, visual phase separation observed in the control films (only Sericin/PVA). It is observed that with increase in GA concentration from 2.5 to 5 % the tensile strength and young modulus increases and further increase in concentration it decreases. Increase in tensile strength is due to the chemical crosslinking between GA, PVA and Sericin. Mandal *et al.* [25] studied the cross linking reaction

Table 1. Tensile properties of SS/PVA films with different GA content

GA content (%)	Tensile strength (MPa)	Elastic modulus (MPa)	Elongation at break (%)
0	16.08 (0.36)	428.47 (0.22)	13.77
2.5	18.08 (0.24)	1212.75 (0.67)	2.27
5	22.5 (0.56)	1291.6 (0.54)	2.59
10	16.42 (0.42)	878.41 (0.71)	4.2

Value given in the bracket shows coefficient of variation (CV %).

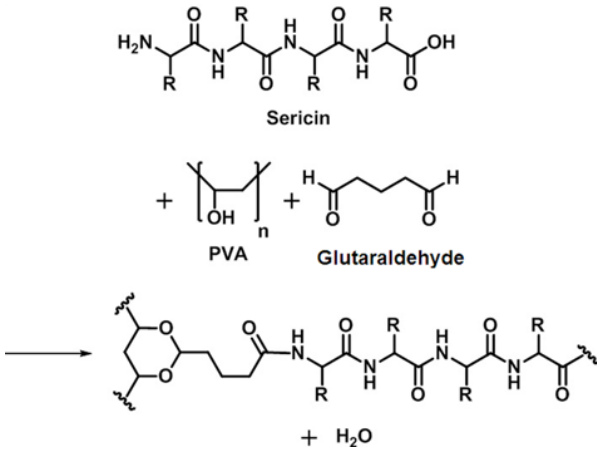

Figure 1. Proposed crosslinking reaction between Sericin and PVA with GA.

of PVA with GA. The cross linking reaction takes place between the -OH groups of PVA and the aldehyde groups of GA, results in formation of more ether linkages. GA can crosslink both amino and hydroxyl groups. So it may react with amine or/and -OH groups of polypeptide chains of Sericin and thus forms intense crosslinking in the blended films to provide optimum tensile strength. The proposed reaction of Sericin/PVA blend with GA is shown Figure 1. GA concentration 5 % (w/w) has taken as optimised concentration for further studies.

Effect of Glycerol (Gly)

The addition of crosslinking agent in the Sericin/PVA blend films make it very stiff. Incorporation of plasticizer generates flexibility in the blended films. In this study glycerol has been used as plasticizer. The effect of glycerol on mechanical properties of Sericin/PVA blend films is shown in Table 2. Addition of glycerol has drastically reduced the tensile strength and modulus of blended films. However opposite trend is observed for elongation at break which increases with increase in glycerol content. Decrease in tensile strength is due to the increase in amorphous structure in the blended films. The increase in elongation at break and reduced elastic modulus showed that flexibility of

Table 2. Tensile properties of cross-linked SS/PVA films with different Glycerol content

Glycerol content (%)	GA content (%)	Tensile strength (MPa)	Elastic modulus (MPa)	Elongation at break (%)
0	5	22.5 (0.56)	1291.6 (0.54)	2.59
20	5	6.71 (0.28)	16.7 (0.32)	131.23
30	5	7.39 (0.41)	10.34 (0.61)	224.34
40	5	6.70 (0.38)	4.51 (0.58)	388.88

Value given in the bracket shows coefficient of variation (CV %).

blended films. Similar results are observed by Sothornvit *et al.* [32] when Sericin/Glucomannan blend films plasticized with glycerol.

Effect of Nanoclays

The effect of Cloisite 30B on mechanical properties of flexible crosslinked Sericin/PVA films is shown in the Table 3. The addition of Cloisite 30B nanoclay up to 1 % enhances the tensile strength; elastic modulus and elongation at break (%) of Sericin/PVA blend films. Further increase in concentration of clay does not increase the tensile strength and elastic modulus. This may be due to high clay loading some agglomeration takes place in clay. The incorporation of Cloisite 30B not only increases strength but also stiffness, due to better dispersion of clay in Sericin/PVA matrix.

Table 3. Tensile properties of flexible crosslinked SS/PVA films with different Closite 30B content

Clay (%)	Tensile strength (MPa)	Elastic modulus (MPa)	Elongation at break (%)
0	7.39 (0.41)	10.34 (0.61)	224.34
0.5	6.62 (0.27)	37.58 (0.48)	346.35
1	11.62 (0.62)	36.29 (0.29)	386.47
1.5	11.11 (0.54)	20.19 (0.44)	200.21

Value given in the bracket shows coefficient of variation (CV %).

Table 4. Tensile properties of plasticised cross-linked SS/PVA films with different Na MMT content

Clay (%)	Tensile strength (MPa)	Elastic modulus (MPa)	Elongation at break (%)
0	7.39 (0.41)	10.34 (0.61)	224.34
0.5	7.34 (0.41)	11.26 (0.43)	140.22
1	8.69 (0.37)	24.54 (0.74)	283.54
1.5	8.52 (0.57)	23.37 (0.52)	260.48

Value given in the bracket shows coefficient of variation (CV %).

The effect of Sodium montmorillonite (Na MMT) on the mechanical properties of Sericin/PVA blend film is studied and results are presented in the Table 4. The addition of Na MMT from 0.5 to 1.5 % increases the tensile strength, elastic modulus and elongation at break properties of Sericin/PVA blend films. Due to the more hydrophilic nature of Na MMT as compared to Cloisite 30B higher clay loading is possible with Na MMT in Sericin/PVA blend films. The amount of Cloisite 30B (1.0 %) and Na MMT (1.5 %) is considered as optimized concentration for nanoclay as it enhanced the tensile strength, elastic modulus and elongation at break properties of flexible crosslinked Sericin/PVA blend films.

Characterization

Morphology

The surface morphology of Sericin/PVA films are analysed by scanning electron microscopy. The SEM images are shown in Figure 2. Figure 2(a) shows, SEM image of pure Sericin/PVA film. Pure Sericin/PVA blend film shows phase separation between PVA and Sericin. Wang and Qi [29] have also

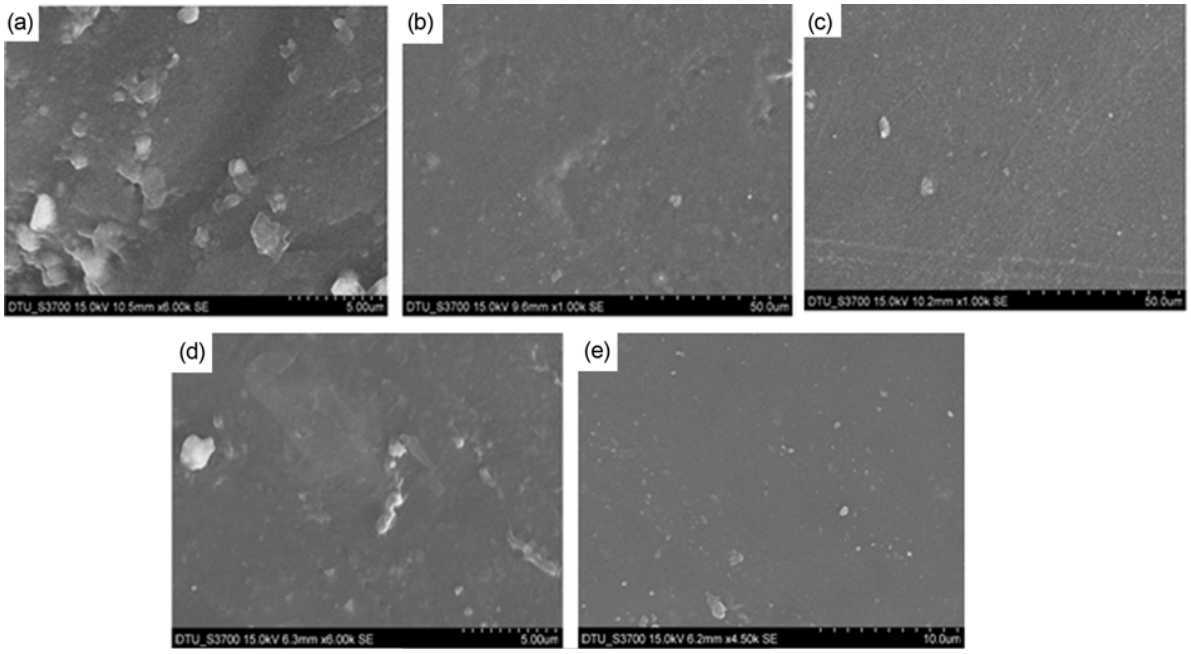

Figure 2. SEM images of various sericin films; (a) SS/PVA, (b) SS/PVA/GA, (c) SS/PVA/GA/GLY, (d) SS/PVA/GA/GLY/NaMMT, and (e) SS/PVA/GA/GLY/Cloisite 30B films.

observed the phase separation in Sericin/PVA blend films at blend ratio 6:4. Figure 2(b) and (c) shows the SEM photographs of cross-linked and flexible crosslinked Sericin/PVA blend film respectively. It is observed that phase separation is reduced by incorporating GA. Glutaraldehyde is acting as bridge between PVA & Sericin and reduces the phase separation. There is no change observed in surface morphology after addition of glycerol. The blend film showed smooth surface as shown in Figure 2(c) which implies that glycerol is homogenously distributes in the crosslinked Sericin/PVA films. Similar results were observed by Zhang *et al.* [33] when 10 % glycerol is incorporated in the pure Sericin films. The surface morphology of nanoclays incorporated Sericin/PVA films are shown in Figure 2(d) and (e). The surface of the film appeared to be smooth after incorporation of nanoclay which shows that nanoclay is completely dispersed in Sericin/PVA matrix.

FTIR Analysis

The structural properties of the blended film were studied using Fourier transform infrared spectroscopy. The FTIR spectra of films are shown in Figure 3. Figure 3(a) shows the FTIR spectra of SS/PVA films. Peak at 1648 cm^{-1} (amide I), 1545 cm^{-1}(amide II) and 1240 cm^{-1} (amide III) shows that the Sericin present in Sericin/PVA blend film has random coil structure. Broad peak at 3200 cm^{-1} showed the presence of hydroxyl groups. The peak of -NH_2 group is also merged in this broad peak. These -OH groups are also associated with alcoholic group of PVA and Carboxylic group of Sericin. Figure 3(b) shows the FTIR spectra of glutaraldehyde cross-linked Sericin/PVA film. It is observed that the intensity of -OH peak is reduced. Additional peaks at 1100 cm^{-1} is observed indicate the presence of ether. This confirms that gluteraldehyde chemically crosslinked with Sericin and PVA and hydroxyl group/amino group have taken part in crosslinking reaction. Mandal *et al.* [25] have also observed peak at 1140 cm^{-1} for FTIR spectra of non mulberry silk Sericin/PVA crosslinked with gluteraldehyde hydrogel matrix as a result of the reaction between -C=O of gluteraldehyde and -OH of PVA to form acetal. Figure 3(c) shows the FTIR spectra of glycerol modified cross-linked Sericin/PVA blend film. Again Broad peak at 3200 cm^{-1} is observed due the presence of -OH groups in glycerol.

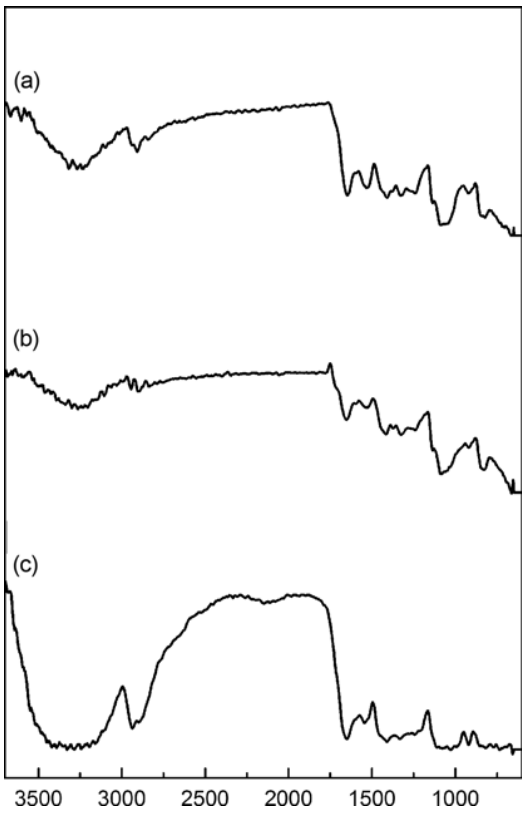

Figure 3. FTIR spectra of various sericin films; (a) SS/PVA, (b) SS/PVA/GA, and (c) SS/PVA/GLY films.

Thermal Properties

The thermal properties of Sericin/PVA films were analyzed by DSC, TGA and DMTA techniques. Figure 4 shows the TGA thermograms of Sericin/PVA and crosslinked Sericin/PVA. Sericin/PVA film showed multistep degradation. The initial weight loss up to 100 °C is due to presence of moisture in the Sericin/PVA films. The initial degradation temperature of blend film is 270 °C and the film is completely degraded at 600 °C, with overall weight loss of 97 %. Figure 4(b) shows the TGA thermogram of crosslinked Sericin/PVA films. Initial loss up to 100 °C is due the moisture. It is observed the crosslinked film showed the initial degradation temperature 300 °C and overall weight loss of 95 % at 600 °C. This shows that gluteraldehyde chemically crosslinked with Sericin/PVA and the thermal stability of film has enhanced by 30 °C after crosslinking.

Figure 5 shows the DSC thermogram of Sericin/PVA and crosslinked Sericin/PVA films. Sericin/PVA film showed two endothermic peaks at 85 °C and 217 °C (Figure 4(a)).

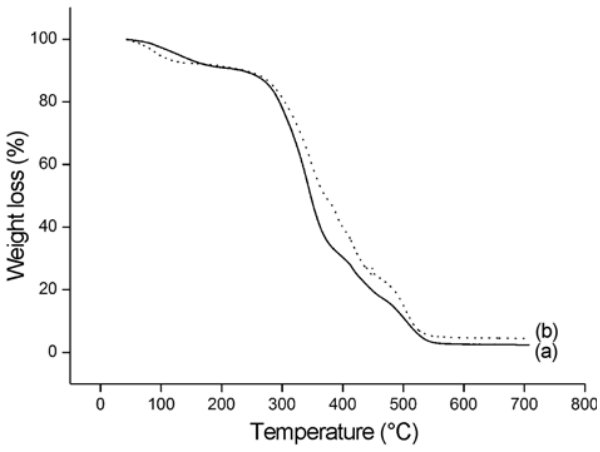

Figure 4. TGA thermograms of; (a) SS/PVA and (b) SS/PVA/GA films.

Bombyx mori Sericin shows two endothermic peak in the DSC thermogram at 212 °C and 319 °C, the former attributed to thermally induced molecular motion and melting of sericin peptides, while the latter to thermal decomposition [25,33]. On the other hand pure PVA shows glass transition temperature at 85 °C and melting temperature at 220 °C [25]. The broad endothermic peak at 217 °C may contain thermally induced molecular motion or T_g peak of Sericin and melting peak of PVA.

Figure 5(b) shows the DSC thermogram of crosslinked Sericin/PVA films. Two endothermic peaks at 85 °C and 199 °C are observed. The peak at 85 °C is associated with the glass transition temperature of the PVA. The shift in the endothermic peak from 217 °C to 199 °C suggested that presence of gluteraldehyde reduce the crystalline structure of PVA as some of the PVA chain chemically reacted with gluteraldehyde. Since the endothermic peak of glass transition temperature of Sericin merged with crystalline melting peak of PVA in DSC thermograms, to analyze the miscible/ immiscible nature of Sericin/PVA blend films, dynamic mechanical thermal analysis (DMTA) was performed.

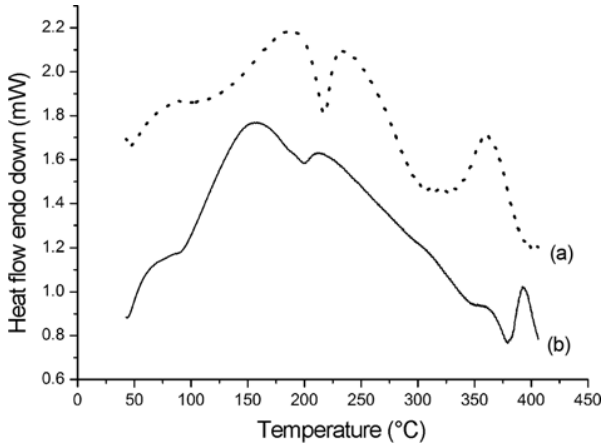

Figure 5. DSC thermograms of; (a) SS/PVA and (b) SS/PVA/GA films.

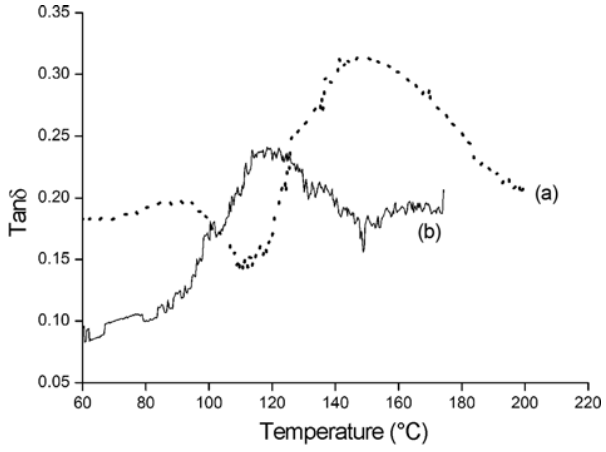

Figure 6. Tan δ of; (a) SS/PVA and (b) SS/PVA/GA films.

Figure 6 shows the tan δ thermogram of Sericin/PVA and crosslinked Sericin/PVA films. Sericin/PVA film shows two tan δ peaks at 90 °C and 150 °C, corresponding to glass transition temperature of PVA and Sericin, respectively. Two glass transition temperature peak suggested that at 1:1 blend ratio Sericin/PVA is non miscible in nature. Crosslinked Sericin/PVA/GA film shows one tan δ peak at 115 °C. Addition of gluteraldehyde enhanced the miscibility of Sericin and PVA.

X-ray Diffraction (XRD)

The crystallographic structures of Sericin/PVA films were analysed by XRD. Figure 7 shows the XRD diffractogram for (a) Sericin/PVA (b) Crosslinked Sericin/PVA (c) plasticized Sericin/PVA films. Sericin/PVA blend film (Figure 7(a)) shows a sharp peak of high intensity at 2θ=20 ° and shoulder peaks at 2θ 12 °, 23 ° and 42 °. X-ray diffractogram of pure PVA film shows intense peak at 2θ=19.8 ° and shoulder peak at 2θ=12 ° and 42 ° [31]. Pure Sericin shows a weak and wide pattern with a maximum 2θ around 20 ° [31]. This peak is due to presence of small amount of β-sheet structure in high molecular weight Sericin. In this study, peak of Sericin is shifted to 2θ=23 ° in the presence of PVA. Sericin/PVA

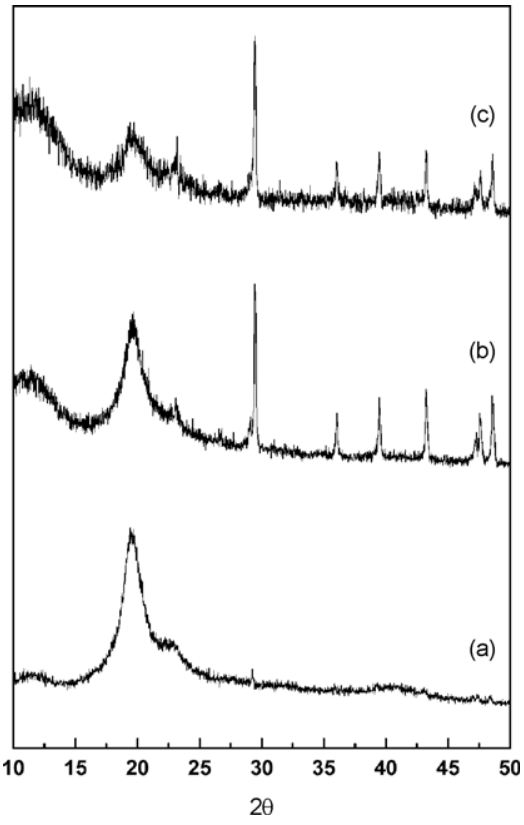

Figure 7. XRD diffractogram of; (a) Sericin/PVA, (b) Sericin/PVA/GA, and (c) Sericin/PVA/GA/GLY films.

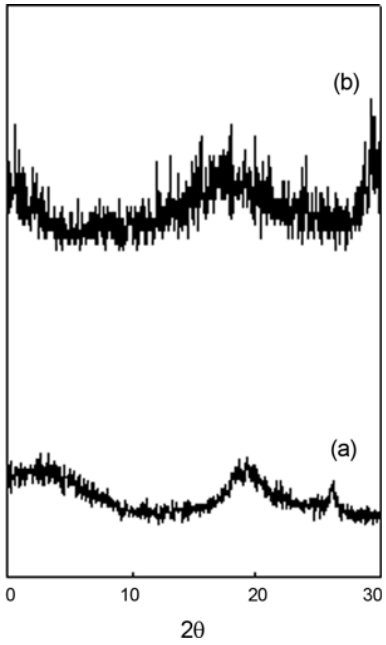

Figure 8. X-ray diffractogram of; (a) Sericin/PVA/Na MMT and (b) Sericin/PVA/Cloisite 30B nanocomposite films.

blend film shows characteristics peaks of Sericin and PVA. Due to the intense peak of PVA and small fraction of β-sheet content in Sericin, Sericin/PVA blend film is semi-crystalline in nature. The addition of crosslinking agent reduced the intensity of 2θ=20 ^{o} peak of PVA, peak at 2θ=23 ^{o} of Sericin is completely disappear by addition of crosslinking agent. This resulted in decrease in crystallinity of cross-linked Sericin/PVA film. In glycerol containing film diffraction intensity of peak at 2θ=20 ^{o} is further reduced. Broad peak depicts the amorphous nature of the glycerol containing film. The XRD results are in close agreement with DSC results.

Figure 8, shows the X-ray spectra of nanoclays and Sericin/PVA/clay nanocomposite films. X-ray diffractogram of Sodium montmorillonite shows a diffraction peak at 2θ=7.3, corresponding to basal spacing of 1.184 nm between the clay platelets [35]. X-ray diffractogram of Cloisite 30B shows a diffraction peak at 2θ=6.2 ^{o} corresponding to basal spacing 1.4 nm between the clay platelets [36]. Figure 8(a) and (b) show the X-ray diffractogram of Sericin/PVA/Na MMT and Sericin/PVA/Cloisite 30B nanocomposite films respectively. Nanocomposite films show similar diffractogram as plasticised cross-linked Sericin/PVA film (Figure 7(c)). By monitoring the position, shape and intensity of the basal reflections from dispersed clay particles, the structure (intercalated or exfoliated) of a nanocomposite can be identified. In an exfoliated nanocomposite, the extensive layer separation associated with the delamination of the original silicate layers in the polymer matrix results in the eventual disappearance of any coherent X-ray diffraction from the dispersed silicate layers. For intercalated nanocomposites the finite layer expansion

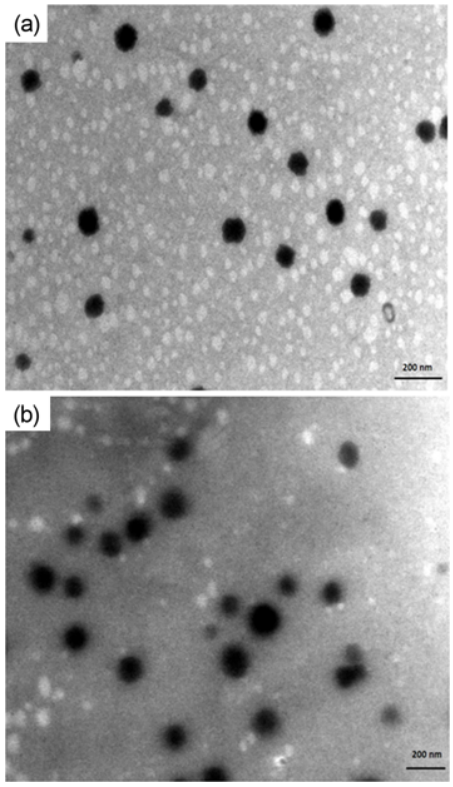

Figure 9. TEM images of SS/PVA solution with dispersed nanoclay (a) Cloisite 30B and (b) NaMMT.

associated with polymer intercalation results in the appearance of a new basal reflection, corresponding to a larger gallery height [31]. The shift in the diffraction peak towards the lower side in the 2θ range 4 ^{o} for nanocomposite film sample, indicates an intercalated structure. When clays were swollen in water and mixed with Sericin/PVA matrix, the polymer chains would be intercalated and substitute the solvent in the clay galleries resulting in the intercalation structure by a solution process [31]. We have also observed the peak near 2θ=2-4 ^{o} (Figure 8). This indicates that the Cloisite 30B and Na^{+} MMT intercalated in the Sericin/PVA blend films.

Transmission Electron Microscopy

The dispersion of clay in Sericin/PVA solution just before casting the film was analyzed by transmission electron microscopy. The TEM images of Sericin/PVA/clay solution are shown in Figure 9. The TEM image shows that the size of clay particles varies from 50 nm to 150 nm with circular structure. The clays are uniformly distributed in the polymer solution. The platelet structure of clay has not been observed in this study. Kim *et al.* [37] have observed the oval structure of clay [38].

Conclusion

Flexible crosslinked Sericin/PVA/Clay blend films are

prepared by using glutaraldehyde (5 % wt/wt), glycerol (30 % wt/wt), Cloisite 30B (1 % wt/wt) or sodium montmorillonite (1.5 %). Nano clay enhances the 57 % tensile strength and 250 % elastic modulus of plasticized Sericin/PVA blend films. Sericin/PVA at 1:1 blend ratio form immiscible blend. Addition of gluteraldehyde is enhanced the miscibility of the Sericin and PVA. FTIR study showed that glutaraldehyde has made crosslink with the hydroxyl group of Sericin and PVA. The XRD spectra suggested that clay is intercalated in the Sericin/PVA blend films. This study showed that Sericin/PVA/Clay films can be used as packaging material.

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Flexible Silk Fibroin Films for Wound Dressing

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Abstract: In the present study, an effort has been made to create dextrose incorporated (5-15 % w/w) flexible silk fibroin films for wound dressing applications. The flexibility of silk fibroin films increases with increase in dextrose content. The elongation at break properties of dextrose modified silk fibroin (DMSF) films increases from 3.2 % to 40 % with increase in dextrose content. The glass transition temperature (T_g) of the films decreases from 176 °C to 155 °C with increase in dextrose content. This shows that dextrose is acting as plasticizer for silk fibroin films. The structural and morphological properties of dextrose modified silk films (DMSF) are characterized by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) scanning electron microscopy (SEM) and atomic force microscopy (AFM). FTIR and XRD studies show that the dextrose content does not affect the crystalline structure of silk fibroin films. The surface roughness of the films also increases with increases in dextrose content in DMSF films. The addition of dextrose enhances the swelling and hydrophilicity of silk fibroin films. The adherence, proliferation and viability of L929 fibroblast cells cultured on DMSF films indicate that it has ability to support cell growth and proliferation as compared to SF film. The 15 % DMSF film showed significantly higher mass loss than SF film after 50 days of incubation in Protease XIV. Further, the data presented here constitute strong evidence that dextrose modified film has the great potential to be utilized as dermal wound dressing material.

Keywords: Silk fibroin, Wound dressing materials, Hydrophilicity, Cytocompatibility, Biodegradation

Introduction

The skin forms a self renewing and self repairing interface between the body and the environment. It provides an effective barrier against microbial invasion and has properties that can protect against mechanical, chemical, osmotic, thermal and photo damage [1]. Skin is composed of three structural layers, the epidermis, dermis and subcutis. Trauma to skin can be categorized into several degrees. The least damaging trauma relates to damage done at the epidermis layer and wound healing takes place via re-epithelialization. More serious trauma can lead to partial or complete damage of epidermis, dermis and subcutis layer of skin [2]. Wounds that extend partially through the dermis are capable of regeneration, but unfortunately the body can not heal deep dermal injuries adequately. With burn injuries arising from fire, accidents, terrorist attacks and an aging population (for chronic wound), there will always be a continual demand for skin regeneration products [3]. Many skin substitutes such as xenografts, allografts and autografts have been employed for wound healing. However, these approaches have many disadvantages such as higher cost, limited availability of skin grafts in severely burned patients, problems of disease transmission and immune response [2,4]. One strategy for dealing with serious skin damage is to develop tissue engineered skin substitute. Various synthetic and natural polymers such as chitosan, silk, collagen, poly(glycolic acid), poly(L-Lactic acid) and poly(lactic acid-co-glycolic acid) are currently being employed as tissue scaffolds for skin reconstruction [5,6].

Silk has been used in textile industries for centuries. The silk protein from silkworm *Bombyx mori* contains two fibroin proteins fibers held together by glue like protein called sericin. When sericin is presented to a body, it is detected as an antigenic factor by T-cells and causes immunologic reactions. Therefore, sericin is needed to be removed from cocoon fibers by a process called degumming. These degummed *Bombyx mori* silk fibroin exhibit unique properties as biomaterials. Fibroin was reported to be a perfect substrate for the proliferation and adhesion of large variety of cells. Silk fibroin has found diverse applications in the biomedical field, which can be attributed to its high tensile strength, controlled biodegradability, haemostatic properties, non-inflammatory characteristic [7-10]. To develop an ideal skin substitute, the performance of regenerated membranes from silk fibroin and its blends was examined by several researchers. Studies evaluated the biocompatibility of the membrane with fibroblasts and endothelial cells, which are the most important tissue repairing cells in healing. It was found that regenerated silk fibroin membrane does not show any toxicity [11] or genotoxicity [12]. Regenerated silk fibroin materials in the form of films, nano-fibrous membrane and woven textile have been employed as wound dressing for skin regeneration. Liu *et al*. [13] have explored the feasibility of using regenerated silk fibroin membrane to construct artificial skin substitute for wound healing. They observed that silk fibroin film does not have an adverse influence on the growth and biofunction of fibroblast and vascular endothelial cells. It also does not interfere with the secretion of angiogenesis

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growth factors such as VEGF, Ang-1, FGF2 and PDGF. Inpanya *et al.* [14] have studied the Aloe vera gel blended silk fibroin films and compared to aloe free fibroin films; the blended film enhanced the attachment and proliferation of skin fibroblasts. Vasconcelos *et al.* [15] have developed the silk fibroin and elastin scaffolds for treatment of burn wounds. Silk fibroin/keratin films incorporating a synthetic inhibitor of elastase to control the higher levels of this enzyme produced in a chronic wound environment [16]. Silk fibroin/alginate sponge demonstrates a higher healing effect than both components acting alone [17]. Karahaliloglu *et al.* [18] have modified the surface of silk fibroin film to obtain a biologically inspired nano-featured surface morphology, which enhanced the adhesion and proliferation of human epidermal keratinocytes and dermal fibroblasts.

Regenerated silk fibroin films are prepared by dissolving silk fibroin in suitable solvent, using solution casting method. These regenerated silk fibroin (SF) films contain α-helix or random coil structure and do not have enough intramolecular bonds to form stable structure [19]. Such films are water soluble and having low mechanical properties. To enhance the mechanical properties, films are crystallized in organic solvents such as methanol, in order to induce β-sheet structure. However, with methanol treatment silk fibroin films become brittle in the dry state and not suitable for wound dressing, particularly for load bearing application [20]. Therefore, there is a need to develop flexible fibroin films with good mechanical and biodegradable properties. The flexibility of the SF films can be improved by blending with natural polymers such as hyaluronic acid [21], chitosan [22] and alginate [23]. Plasticizers such as sorbitol, glycerol, glucose and PEG are commonly added to protein based films to enhance their flexibility [24-27]. The flexibility of silk fibroin films has been improved by incorporating glycerol [24] and glucose [25].

In present study, an attempt has been made to develop flexible silk fibroin films by incorporating dextrose. The mechanical, thermal and structural properties of dextrose modified films are characterized to understand the interaction between the silk fibroin and dextrose. The morphology, hydrophilicity, water absorption, biodegradation and cyto-compatibility of flexible silk fibroin are also studied.

Experimental

Materials and Methods

Multivoltine silk cocoons of *Bombyx mori* silkworm were purchased from silk development department, Kalpipara, Bahraich, India. All other chemicals used in this study were purchased from Merck, India. Distilled water was used throughout this study.

Preparation of Dextrose Modified Silk Fibroin Films

Degumming of silk cocoons was carried out according to standard procedures [28,29]. The *Bombyx mori* cocoons were cut in small pieces, vacuum dried, weighed, and placed in 1 liter boiling solution of Na_2CO_3 (0.02 M) for 1 hour to remove sericin. Subsequently, the silk fibers were rinsed three times in 1 liter hot water (90 ^oC) for 20 min and dried overnight. Degummed silk fibroin fibers were dissolved in a 2 % $CaCl_2$/formic acid solution (w/v) at room temperature by continuous stirring. The final concentration of silk fibroin solution was kept ~6 wt%. Different silk fibroin solutions were prepared by incorporating 0 to 15 % (w/w) dextrose. The solutions were poured onto polystyrene plates and dried at room temperature for formation of films. In order to induce crystallization, these air dried films were immersed in 80 % (v/v) methanol solution for 30 minutes.

Mechanical Properties

The tensile strength and elongation at break properties of the films were determined using Universal Testing Machine (Instron 3369) according to ASTM D 882-02. The pre-conditioned test samples (10×2.5 cm) were mounted between grips of the machine with span length 50 mm and pulled at cross head speed of 50 mm/min. Average tensile properties of five specimens were measured.

Thermal Properties

The thermal analysis of silk films was performed by Differential Scanning Calorimetry (DSC) instrument (TA Instruments Q100 DSC) under a dry nitrogen gas flow of 50 ml/min. The silk film of approximately 5 mg was filled in aluminium pan and heated at 2 ^oC/min from 0 ^oC to 400 ^oC.

The dynamic mechanical thermal analysis of silk films was carried out on a DM 8000 dynamic mechanical analyzer (Perkin Elmer) by using film testing fixture. Specimens of 40×10 mm were run at tensile mode at a frequency of 1 Hz with 0.125 % of strain and 3 ^oC/min of heating rate. The tan δ of specimens was determined as the function of temperature from 25-250 ^oC.

Morphological Characterizations

The surface morphology of SF and DMSF films was observed with a scanning electron microscope (SEM) (Hitachi S-3700N) at a voltage of 15 kV. Specimens were sputter-coated with gold before mounting on SEM machine.

Roughness measurements of SF and DMSF films were performed with atomic force microscope (Park) in contact mode with a tip mounted on V shaped silicon nitride cantilever with spring constant 40 N/m. Air dried SF and DMSF films were used for AFM measurement. All the measurements were carried out at room temperature with a scan area 2×2 μm. The roughness values were calculated as the root-mean-square (rms) deviation and arithmetic average height (Ra). The rms values represent the standard deviation of the height values within a given area and allows the surface roughness to be determined by statistical methods, whereas

Ra values gives average deviation of roughness irregularities from mean line over one sampling length [30,31].

Structural Characterization

As mechanical properties of silk is directly related to conformation of fibroin chain (β-sheet and random coil/ helix), attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) was performed to assess the secondary conformation of SF and DMSF films. ATR-FTIR measurements were performed using a Thermo Scientific Nicolet 380 Spectrometer, Japan, in reflection mode at 4 cm^{-1} resolution using 32 scans in the spectral range 4000 to 400 cm^{-1}.

The X-ray scans of SF and DMSF films were performed with a Seimens type-F, X-ray diffractometer (Bruker D S Advanced, Germany). The X-ray source was Cu Kα radiation (40 kV, 30 mA and λ=1.5 Å). The samples were mounted on aluminium frames and scanned from 5 to 50 ^{o} (2θ) at a speed of 2.0 ^{o}/min.

Hydrophilicity Measurements

Water Absorption (%)

The water absorption (%) of SF and DMSF films was calculated with the following equation:

$$\text{Water absorption (\%)} = (W_s - W_d)/W_d \times 100$$

where W_s is the weight of the swollen samples and W_d is the weight of the dry samples. The weight of the completely dried sample was measured directly. The weight of sample swollen in distilled water at 37 ^{o}C for 48 hours was measured after blotting the surface with filter paper.

Contact Angle Measurement

Hydrophilicity of SF and DMSF films was determined by analyzing water droplet angle formed between liquid/solid interfaces of different films by Sessile drop method. The volume of water droplet was kept at 4 μl. Contact angle value for each sample was taken as the average of three readings obtained at five different places of the sample.

Cell Viability Experiments

Cell Culture

The SF and DMSF films were assessed for their ability to support L929 fibroblast cells purchased from National Center for Cell Science, India, grown in Dulbecco's modified Eagle's medium (DMEM), supplemented with 10 % fetal bovine serum and 1 % UI ml^{-1} streptomycin-penicillin (Sigma-Aldrich).

Cell Seeding on Different Matrices

SF and DMSF films were cut into specific size (6.4 mm diameter) and sterile. The sterile samples were allowed to dip into DMEM media for 5 hours. The wells were treated with 0.2 % bovine serum albumin (BSA) in sterile phosphate-buffered saline (PBS≈pH 7.4) for 2 hours to prevent adhesion of cells on the vacant glass surface. Excess BSA was removed with sterile PBS (pH 7.4) washes. The films were placed into 96 well plates carefully with the help of forceps.

For the cell proliferation study, approximately 20,000 L929 fibroblast cells were seeded per well on SF and DMSF films at 37 ^{o}C in a humidified atmosphere containing 5 % CO_2, and were monitored at different time-intervals (1, 3 and 5 days).

Cell Morphology, Cytocompatibility and Viability

The L929 fibroblast cells seeded on different SF and DMSF films in 96-well tissue culture plate were visualized under an Inverted phase contrast microscope (Nikon ECLIPSE TS100) over 5 days. MTT assay was applied to determine the cytocompatibility of regenerated SF and DMSF films with L929 fibroblast cells. The MTT assay is a rapid calorimetric technique, in which yellow MTT is reduced to a purple formazan by mitochondrial dehydrogenase in cells to assess the cell proliferation. After 1, 3 and 5 day incubation in DMEM, the viability of L929 fibroblast cells were assessed. Briefly, L929 cells were washed three times with PBS to remove unattached cells. Then 100 μl serum free medium and 10 μl MTT stock solution (5 mg/m*l* in DMEM) were added in each well plate and incubated for 3 hours (37 ^{o}C) for MTT formazan formation. After 3 hours incubation at 37 ^{o}C, the reaction solution was carefully removed from each well and 100 μl dimethyl sulfoxide was added. The plates were gently agitated until the formazan precipitate was dissolved, followed by measurement of OD values by spectrophotometry at 595 nm with an ElX-800 Microelisa reader (Bio-Tek Inc., USA) with DMSO as a blank.

Trypan Blue exclusion assay is used to determine the number of viable cells present in 96 well plates with SF and DMSF films. This method is based on the fact that a viable cell will have a clear cytoplasm whereas a nonviable cell will have a blue cytoplasm.

***In vitro* Biodegradation**

For *in vitro* biodegradation study SF and DMSF films (20 cm in length) (N=4 per group and time point) were incubated at 37 ^{o}C in 3 m*l* solution of Protease XIV (1 mg/ m*l* in PBS) (from Streptomyces griseus, Sigma, 3.5 unit/mg activity) and in the PBS as a negative control over 50 days. Each solution contained an approximately equivalent (±2 mg) mass of silk films. Solutions were changed daily. At designated time points, samples were rinsed with distilled water, dried and weight.

Statistical Analysis

Numerical data are presented as mean±standard deviation. The data were analyzed using standard analysis of variance (ANOVA) techniques and statistical differences were considered at $p<0.05$. All experiments were completed in triplicate with three repeats for each experiment.

Results and Discussion

Regenerated silk fibroin films after methanol treatment have brittle nature. Due to this nature they are not suitable for dermal wound dressing application especially the load bearing areas such as knee joint, elbow joints etc., where the flexibility along with biocompatibility of the films are required. In this study we have chosen dextrose as plasticizer for silk films due its hygroscopic nature and its biocompatibility. The flexible silk fibroin films are prepared by incorporating different fractions of dextrose (5 to 15 % w/w). The effect of dextrose on physical, mechanical, structural, biodegradation and cytocompatibility of silk fibroin films are analyzed.

Mechanical Properties

The mechanical properties of different silk films were measured after conditioning at 65 % RH and 27 °C for one day. The results are shown in Table 1. It is observed from the Table 1, tensile strength of SF film was 28 MPa which is reduced significantly to 15.75 MPa due to addition of 5 % dextrose ($p<0.05$) but elongation at break increased from 3.2 to 3.7 % ($p>0.05$). With increase in dextrose content from 5 to 15 %, the tensile strength and elongation at break of films increases from 15.75 MPa to 17.64 MPa and 3.7 to 40 % ($p<0.05$), respectively. However, DMSF films have much higher elongation at break as compared to SF film. Similar trends were obtained when silk fibroin films modified with glucose in the study carried out by Baimark *et al.* [25]. Dextrose is intercalating between the polymer chains of silk fibroin and increase interchain space, which increases flexibility. Water has an important effect on the mechanical properties of SF and DMSF films. The presence of water enhances the flexibility and extensibility of silk films [32]. Since dextrose is highly hydrophilic molecule, when incorporated in silk fibroin films attract water from the environment and further helps in the enhancement of flexibility of silk films.

Thermal Properties

Differential Scanning Calorimetry (DSC) thermograms of regenerated SF and DMSF films are shown in the Figure 1. Endothermic peaks below 100 °C for different film samples are associated to water loss during heating cycle. The DSC curve of SF film (Figure 1a) shows an endothermic peak at 235 °C corresponds to second order transition and a prominent endothermic peak at 362 °C corresponds to degradation. It is observed that with increase in dextrose content from 0 to 15 %, the endothermic peak (second order transition) shifts from 235 °C to 186 °C. The incorporation of dextrose enhances the chain flexibility of fibroin films, therefore endothermic peak shifts from 235 °C to 186 °C.

Table 1. Mechanical properties of SF and DM-SF films

Silk films	Tensile strength (MPa)	Elongation at break (%)
SF	28±3.2 (0.03)	3.2±0.7 (0.09)
5 % DM-SF	15.75±1.4 (0.04)	3.7±0.1 (0.12)
10 % DM-SF	16.45±1.9 (0.05)	4.8±3.5 (0.06)
15 % DM-SF	17.64±2.5 (0.04)	40.1±2.5 (0.01)

*Values given in bracket are coefficient of variation (%).

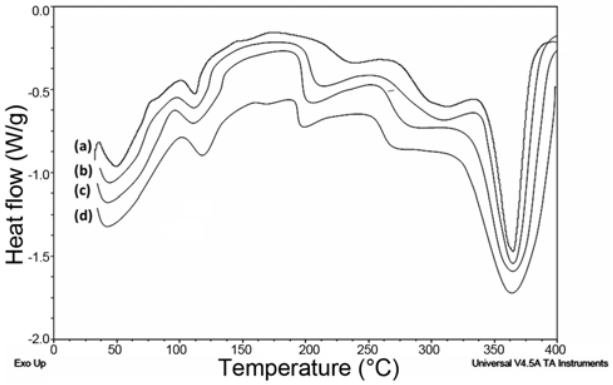

Figure 1. DSC thermograms of: (a) SF, (b) 5 % DMSF, (c) 10 % DMSF, and (d) 15 % DMSF films.

The thermal degradation peak is shifted from 362 °C to 372 °C by incorporating 0 to 15 % dextrose content. The shift in degradation peak to higher temperature is due to the formation of high ordered β-sheet structure. This enhancement of β-sheet structure of silk may be due to the thermal environment provided by DSC machine. The intrinsic morphological and physical properties with degree of molecular orientation are one of the most important parameters that influence decomposition of silk [33]. Highly oriented silk materials, such as films prepared in this study, normally exhibit a decomposition peaks located above 300 °C. Less oriented silk materials with β-sheet structure, usually decompose in the 290-295 °C and amorphous silk fibroin occurs at a lower temperature, normally less than 290 °C [34]. The SF and DMSF films showed decomposition peaks in the temperature range associated to well oriented β-sheet structure that is further conformed from XRD and FTIR results.

Dynamic loss tangent (Tan δ) curves of DMA are widely used to study molecular chain mobility of polymer & the resulted changes in structure [35,36]. Yuan *et al.* [37] studied correlation between dynamic mechanical behaviors of regenerated SF and its structural transitions. The tan curves of SF and DMSF films were obtained to identify segmental movement of silk fibroin molecules in the presence of dextrose molecules. The tan δ curve of SF and DMSF films are shown in the Figure 2. The temperature of tan δ peak was taken as the T_g of SF film [35,21]. Silk fibroin film shows tan δ peak at 176 °C. It was observed that with increase in dextrose content, the tan δ peak (T_g) was shifted from 176 °C to 155 °C. The shift of tan δ peak towards the lower temperature further supports that dextrose is acting as

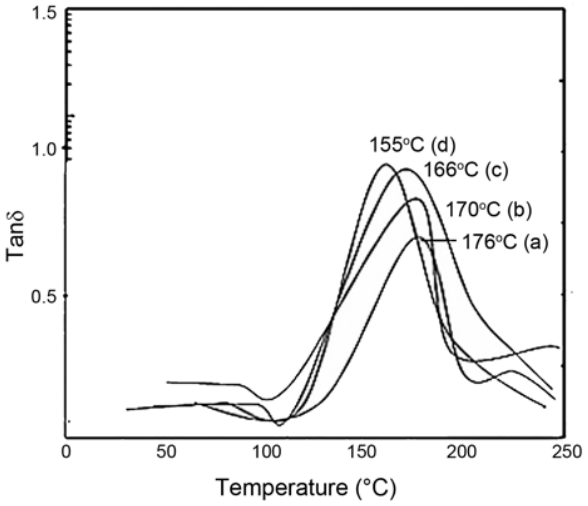

Figure 2. Representative tan δ curves of: (a) SF, (b) 5 % DMSF, (c) 10 % DMSF, and (d) 15 % DMSF films.

plasticizer for silk fibroin films. In silk fibroin films the mobility of polymer chains is limited due to strong inter chain hydrogen bonds formed by protein molecules. Incorporation of dextrose breaks this inter chain hydrogen bonding and increases the chain flexibility, therefore reduce the glass transition temperature.

Another factor which plays an important role in chain flexibility of silk fibroin films is water content. Due to hydrophilic nature of dextrose, it attracts water from the environment. With increase in dextrose content, the moisture content leads to increase in free volume. The increased free volume between polymeric chains results in decreased T_g [38-41]. The dextrose attract water molecules in DMSF films, so initial water content would promote secondary structural transition of DMSF films, because high ordered β-sheet crystallization only occurred when the crystallisable segments of silk fibroin obtain sufficient mobility by dextrose plasticization.

Morphological Characterization

Surface morphology of different silk film samples is characterized by scanning electron microscope (SEM). The SEM micrographs are presented in Figure 3. Regenerated silk fibroin film (SF) shows flat and smooth surface. The surface roughness increase with increase in dextrose content from 5 to 15 % and slight phase separation is noted in the case of 15 % DMSF film.

Nanophase topographies and surface roughness of SF and DMSF films were determined by atomic force microscopy (AFM). The roughness of SF and DMSF films are shown in Table 2. As demonstrated in Table 2, the SF film had the lowest nanophase roughness, which further increased by increasing dextrose content. The root mean square (Rq) value for SF, 5 % DMSF, 10 % DMSF and 15 % DMSF are 0.90, 1.18, 1.19 and 2.16, respectively. For average roughness (Ra), these values are 0.71, 0.94, 0.99 and 1.93 for SF, 5 % DMSF, 10 % DMSF and 15 % DMSF, respectively. The

Table 2. Surface roughness (RMS and Ra) for the SF and DMSF films

Samples	Rq (nm)	Ra (nm)
SF	0.90	0.71
5 % DMDF	1.18	0.94
10 % DMSF	1.19	0.99
15 % DMSF	2.16	1.93

RMS: root mean square; Ra Arithmetic average height.

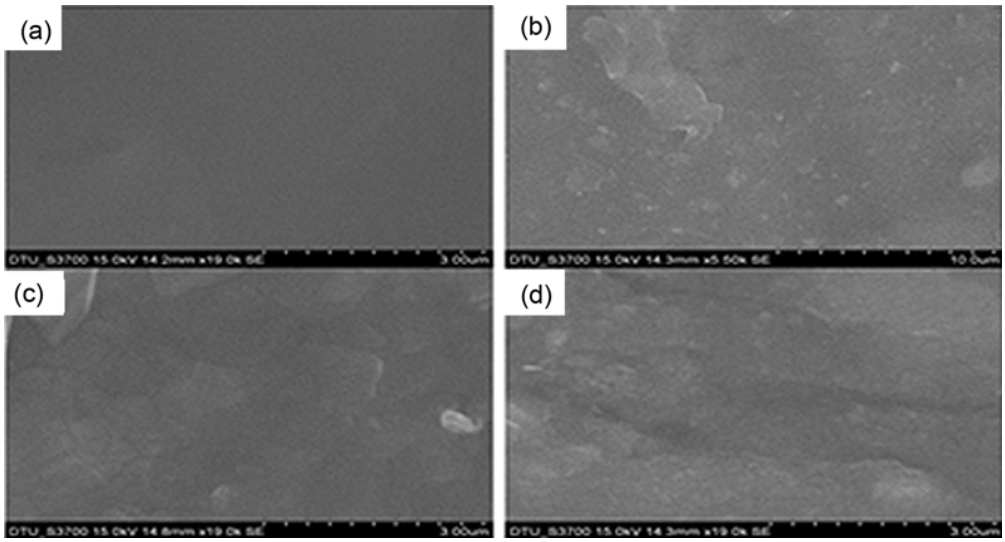

Figure 3. Scanning electron micrographs of: (a) SF, (b) 5 % DMSF, (c) 10 % DMSF, and (d) 15 % DMSF films.

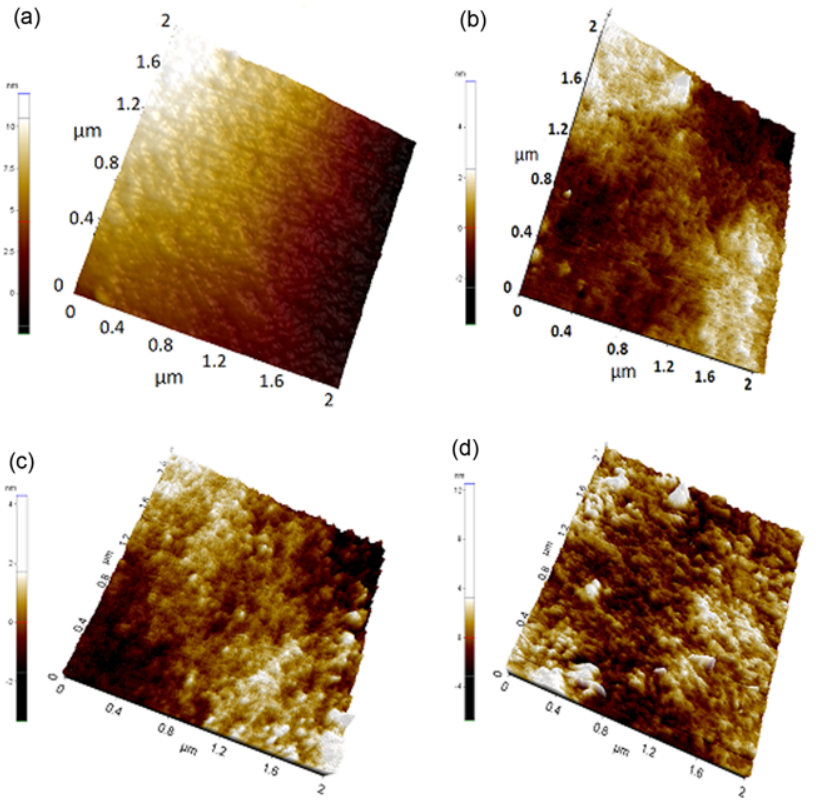

Figure 4. (a) Topographies of AFM images (tapping mode) for: SF, (b) 5 % DMSF, (c) 10 % DMSF, and (d) 15 % DMSF films.

untreated silk fibroin film showed relatively smooth surface as compared to dextrose modified silk fibroin films. The Rq and Ra values increased as the quantity of dextrose increased and statistical analysis indicates that there is significant difference between dextrose modified and unmodified silk fibroin films ($p<0.05$). This meant that in the absence of dextrose, fibroin molecules formed a very flat structure with good assembly, but when dextrose was added, it changes the interaction between silk fibroin molecules, that result in the increased Rq and Ra values, which causes appearance of more separate aggregation in the form of hill and valley morphology (Figure 4). The rough surface confers higher surface area and would help in adherence and proliferation of cells [30,31].

Structural Characterization

The infrared spectral region within 1700-1600 cm^{-1} is assigned to absorption by the peptide backbones of amide I, related to C=O stretching, 1600-1500 cm^{-1} region for amide II, due to N-H bending and C-H stretching vibration and (1200-1300 cm^{-1}) range for amide III, result from combination of C-N stretching and C=O bending [42-44], which have been commonly used for the analysis of different secondary structures of silk fibroin. The peaks at 1610-1640 cm^{-1} (amide I), 1510-1520 cm^{-1} (amide II) and 1220-1240 cm^{-1}

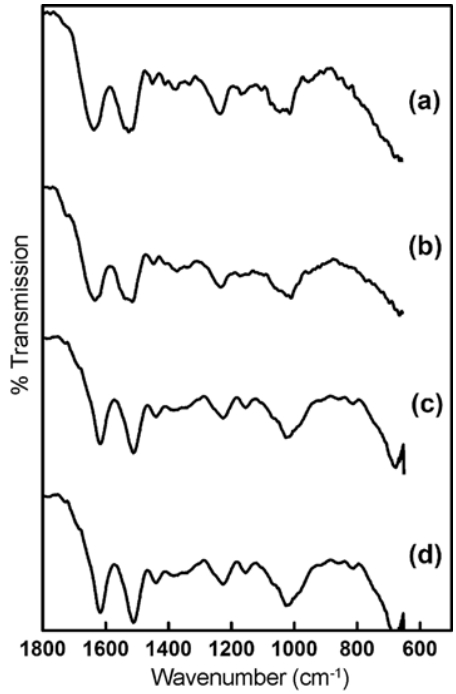

Figure 5. FTIR spectra of (a) SF, (b) 5 % DMSF, (c) 10 % DMSF, and (d) 15 % DMSF films.

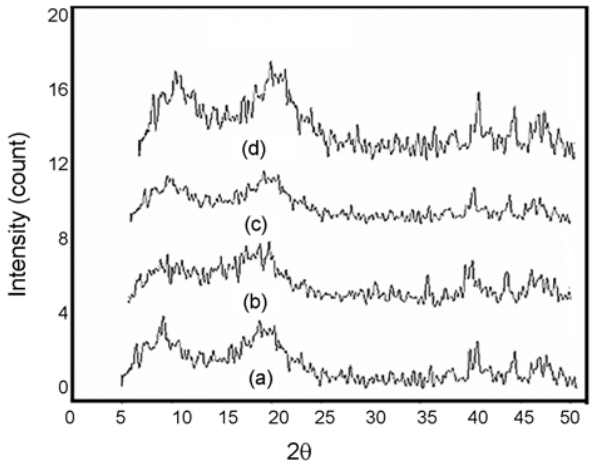

Figure 6. X-ray diffractogram of: (a) SF, (b) 5 % DMSF, (c) 10 % DMSF, and (d) 15 % DMSF films.

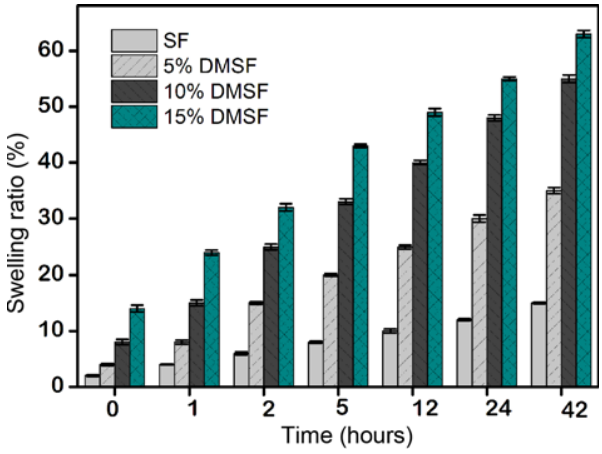

Figure 7. Water absorption (%) of: (a) SF, (b) 5 % DMSF, (c) 10 % DMSF, and (d) 15 % DMSF films.

(amide III) are characteristic of silk II structure (β-sheet) while the absorptions at 1648-1654 cm^{-1} (amide I), 1545-1560 cm^{-1} (amide II) and 1240-1260 cm^{-1} (amide III) are indicative of silk I structure (random coil/α-helix).

In order to see the effect of dextrose on conformation changes on silk fibroin secondary structure, FTIR spectroscopy was performed. Figure 5 shows the FTIR spectra of SF and DMSF films. SF film (Figure 5a) shows absorption bands at 1637 (amide I), 1526 (amide II) and 1237 cm^{-1} (amide III), corresponding to silk II β-sheet structure. Increase in dextrose content shift the amide I peak from 1637 cm^{-1} to 1617 cm^{-1}, amide II peak from 1526 cm^{-1} to 1511 cm^{-1} and amide III peak from 1237 cm^{-1} to 1226 cm^{-1}. Shifts in peaks are within prescribed range of amide I, amide II and amide III as discussed in previous paragraph. This shows that dextrose has very less effect on secondary structure of silk fibroin in crystalline region.

Secondary structures of SF and DMSF films were further analyzed by X-ray diffraction technique. X-ray diffractogram of silk fibroin film samples is shown in the Figure 6. SF film (Figure 6a) shows characteristic diffraction peaks at 8.9 °, 19.7 ° and 39.9 ° corresponding to d-spacing of 9.6, 4.3 and 2.19 A°, respectively. These d-spacing are attributed to a silk II structure (β-sheet). The diffraction peak values are consistent with literature [32]. The dextrose modified films also show the similar X-ray diffraction pattern. The results obtained from XRD support to FTIR results, which confirm that dextrose does not affect crystalline properties of silk fibroin films.

Hydrophilicity Measurements

Water Absorption

The absorption properties of wound dressing play an essential role in controlling the accumulation of wound exudates which create a feeding bed for bacteria. Considering the possible applications of dextrose modified silk fibroin films as biomaterials in skin regeneration, the water absorption of the films is determined (Figure 7). The absorption percentage of silk film is found to be 15 %. The water absorption increases significantly from 32 to 63 % with increase in dextrose content from 5 to 15 %. There is significant difference ($p<0.05$) between water absorption of SF and 15 % DMSF films. This increase in absorption is due to highly hygroscopic property of dextrose molecules. Wharram *et al.* [45] have studied the water absorption percentage of electrospun silk membrane for wound healing. A very high water absorption percentage (461-613 %) was observed in electrospun nonwoven matrix, which was primarily due to the network of interconnecting pore throughout the matrix.

Contact Angle

The hydrophilicity of the SF and DMSF films is further analyzed by water contact angle measurement. The water

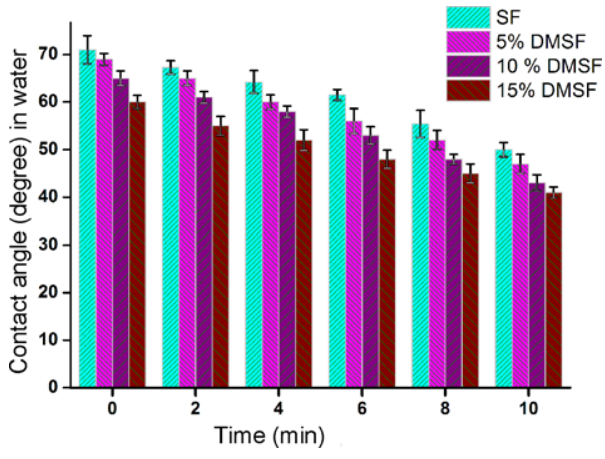

Figure 8. Water contact angle of (a) SF, (b) 5 % DMSF, (c) 10 % DMSF, and (d) 15 % DMSF films, bars represent mean±standard deviation (n=3).

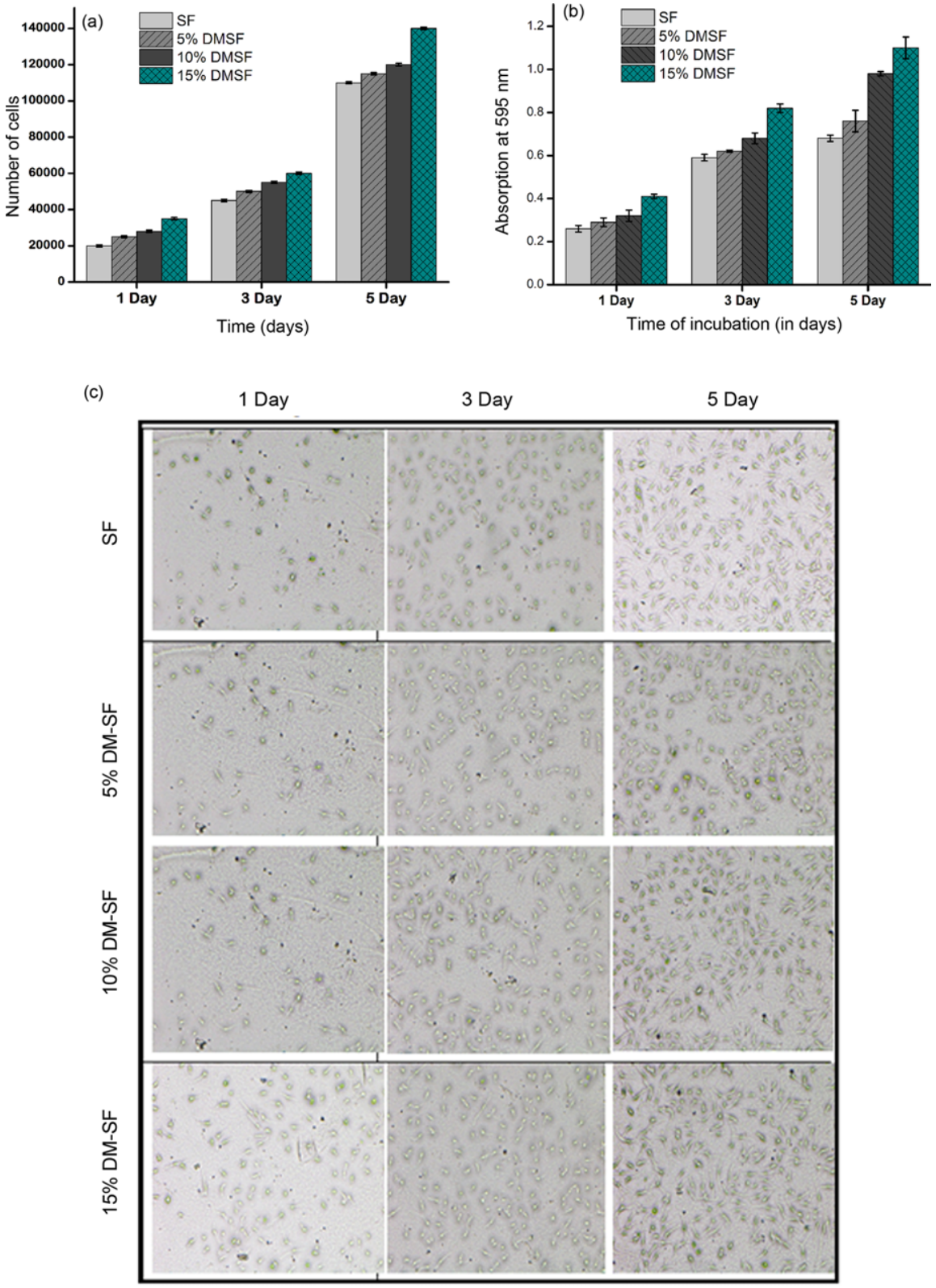

Figure 9. (a) Cell viability, (b) MTT assay, and (c) phase contrast microscopy of L929 fibroblast cells with silk fibroin and dextrose modified silk fibroin films over 5 days of incubation.

contact angle of SF and DMSF films are shown in the Figure 8. The SF film shows water contact angle of 71±2.8°. The 15 % DMSF films show the water contact angle of 60±1.2°. A significant reduction ($p<0.05$) in water contact angle shows that the dextrose modified films has more hydrophilic surface as compared to silk fibroin film. This is important, as scaffolds with hydrophilic surface are better suited for cell adhesion and growth [18,46].

Cell Viability, Cytocompatibility and Morphology

The viability of cells can be determined by counting total number of viable cells with Trypan Blue staining by using haemocytometer. The viability of cells on different films is shown in the Figure 9(a). After one day, viability of cells on DMSF films was observed to be significantly higher ($p<0.05$) than SF film. In next 3 and 5 days the viability of cells on SF and DMSF films increased but evidently more cells proliferate on DMSF films as compared to SF film ($p<0.05$). The viability of L929 cells cultured on the SF film was significantly different from that on DMSF at all time point after culture ($p<0.05$).

Result of MTT assay for fibroblasts seeded on SF and DMSF films is shown in the Figure 9(b). The optical density (OD) value of MTT formazan solution is proportional to the live cell numbers [29], so we can measure the OD values to evaluate the relative cell amount. For all the samples, cells continued to proliferate with the increase in culture time. As demonstrated in the cytocompatibility assay (Figure 9b), the OD value increases significantly with time up to 5 days and it was significantly higher for 15 % DMSF film as compared to SF film ($p<0.05$).

Cell morphology was observed at 1, 3, and 5 days from seeding on SF and DMSF films (Figure 9c) by phase contrast microscope, which showed that cell spread with time. Such comparison demonstrates that DMSF films are more favorable for cell proliferation (Figure 9c). The proliferation of cells on DMSF films is increased with increase in dextrose content. The density of cells on 15 % DMSF film is more as compared to SF film. This enhanced growth on DMSF films may be due to improved surface hydrophilicity and roughness. Cells viability and MTT assay suggested that dextrose modified silk fibroin films have good cytocompatibility with L929 fibroblast cells.

Higher cells adhesion and proliferation onto DMSF film as compared to SF films can be explained on the basis of combined effect of increased hydrophilicity and nanophase roughness. Dextrose being a hydrophilic molecules increase hydrophilicity and wettability. Increased hydrophilicity and wettability of DMSF films due to dextrose contributes higher adhesion and proliferation of cells as compared to SF film. In addition, due to dextrose, surface roughness of DMSF films also increased which will further help in anchoring and proliferation of cells. Various researchers have studied that nanophase roughness is responsible for higher adhesion and proliferation of cells.

Rajput *et al.* [47] showed that biocompatibility and

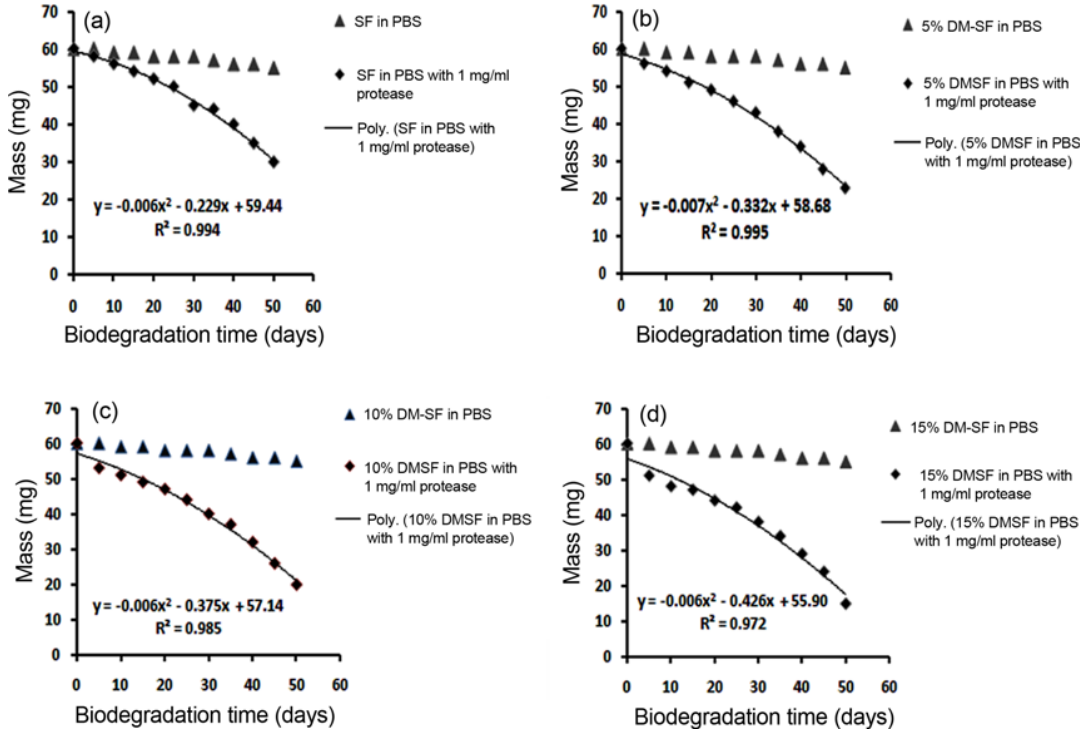

Figure 10. *In vitro* biodegradation study of: (a) SF, (b) 5 % DMSF, (c) 10 % DMSF, and (d) 15 % DMSF films.

cellular behavior such as adhesion, proliferation, spreading and interaction of 3T3 fibroblast cells were improved with a hydrophilic nano-patterned honey incorporated silk fibroin membrane as compared with native SF membranes. Karahaliloglu *et al.* [18] found that nanofeatured silk fibroin membrane promoted the adhesion and proliferation of fibroblast and keratinocytes. Dalby *et al.* [48] showed that adhesion and proliferation of fibroblast cells depend on size of nanometer islands which was created by a polymer demixing methods. Our findings were supported by these observations that surface roughness and hydrophilicity is responsible for greater cellular response.

In vitro Biodegradation

The *In vitro* biodegradation was performed by incubating various silk films in protease XIV. The mass loss of SF and DMSF films after incubation in PBS and protease enzyme are shown in the Figure 10. The mass loss of all types of films gradually increased from 0 to 50 days of incubation. The 15 % DMSF film showed significantly higher mass loss than SF film ($p<0.05$) after exposure to protease XIV for 50 days. After 50 days protease incubation, more than 75 % mass loss was noticed in 15 % DMSF film. The mass loss was consistent with second order polynomic trendline ($R^2=0.972$), while SF and 5, 10 % DMSF films showed comparatively less mass loss about 50 ($R^2=0.995$), 62 ($R^2=0.995$), and 67 % ($R^2=0.985$), respectively. No significant differences in mass loss were observed in PBS incubated samples for the same time ($p>0.05$) [49,50].

Conclusion

After evaluating various physicochemical aspects, we have found that the flexibility of silk fibroin films increases by addition of dextrose. Mechanical study indicates that dextrose is acting as a plasticizer for silk fibroin films. The glass transition temperature of dextrose modified films reduces from 176 to 155 °C further support that dextrose acts as plasticizer for silk fibroin films. The incorporated dextrose does not affect β-sheet content of silk fibroin films. Addition of dextrose has enhanced hydrophilicity and surface roughness of the silk fibroin films. Due to combine effect of increased hydrophilicity and nano-patterned roughness, dextrose modified silk fibroin films have exhibited improved cellular response as compared to pure silk fibroin film. This study shows that dextrose modification improves the flexibility and cell adhesion properties of silk fibroin films. Such modified films can be utilized as dermal wound dressing materials especially at those sites where flexibility of wound dressing material is required.

Acknowledgement

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Four wheel steering system for Automobile

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ABSTRACT

A Four wheel steering system also known as Quadra steering system. In this paper, both front wheel and rear wheels can be steered according to speed other vehicle and space available for turning. Quadra steer gives full size vehicle greater ease while driving at low speed, improves stability, handling and control at higher speed.

Production-built cars tend to under steer or, in few instances, overseer. If a car could automatically compensate for an under steer overseer problem, the driver would enjoy nearly neutral steering under varying conditions. Four wheel systems is a serious effort on the part of automotive design engineers to provide near-neutral steering.

This system finds application in off-highway vehicles such as forklifts, agricultural and construction equipment mining machinery also in Heavy Motor Vehicles. It is also useful in passenger cars.

It improves handling and helps the vehicle make tighter turns. This system is used to minimize the turning radius.

KEYWORDS: Quadra, turning radius, cornering, pure

INTRODUCTON:

What is Steering?

Steering is the term applied to the collection of components, linkages, etc. which will allow a vessel (ship or Boat) or vehicle to follow the desired course. An exception is the case of rail transport by which rail tracks combined together with railroad switches provide steering column, which may contain universal joints, to allow it to deviate somewhat from a straight line.

The steering function. The most conventional steering arrangement is to turn the front wheels using a hand–operated steering wheel which is positioned in front of the driver.

Types of Steering System:

CONVENTIONAL STEERING SYSTEM:

In that steering system, only the front wheels are steered towards right or left According to the requirement because of at rear their dead axle is present.

FOUR WHEEL STEERING SYSTEM:

In that steering system, the all four wheels are to be steered according to the steer perform to drive towards left or right. Four-wheel steering, 4WS, also called rear-wheel steering or all-wheel steering, provides a means to actively steer the rear wheels during turning maneuvers. It should not be confused with four-wheel drive in which all four wheels of a vehicle are powered. It improves handling and helps the vehicle make tighter turns. Production-built cars tend to under steer or, in few instances, over steer. If a car could automatically compensate for an under steer /over steer problem, the driver would enjoy nearly neutral steering under varying conditions.

In most active four wheel steering system, the rear wheels are steered by a computer and actuators, the rear wheels generally cannot turn as far as the front wheels. Some systems including Delphi's Quadra steer and the system in Honda's Prelude line allow the rear wheels to be steered in the opposite direction as the front wheels during low speeds. This allows the vehicle to turn in a significantly smaller radius sometimes critical for large tucks or tractors and vehicles with trailers.

Purpose of Automotive Steering System:

The purpose of the steering system allows the driver to control the direction of the vehicle by turning the front wheels. The steering system consists of the following component parts.

Components:

1. Steering wheel handles the steering operation.
2. Steering column joins the steering wheel and the steering gears.
3. Steering gears Convert the steering torque and rotational deflection from the steering wheel, transmit them to the wheel through the steering linkage, and make the vehicle turn.
4. Steering linkage a steering linkage is a combination of the rods and arms that transmit the movement of the steering gear to the left and right front wheels. Also, there are two types of steering.

Requirements of steering system:

The steering system has the following requirements.

1. Excellent manoeuvrability when the vehicle is cornering on a narrow, twisting road, the steering system must be able to turn the front wheels sharply yet easily and smoothly.
2. Proper steering effort if nothing is done to prevent it, steering effort will be greater when the vehicle is stopped and will decrease as the speed of the vehicle increase. Therefore, in order to obtain easier steering and better feel of the road, the steering should be made lighter at low speeds and heavier at high speeds.
3. Smooth recovery while the vehicle is turning, the driver must hold the steering wheel firmly. After the turn is completed, however, recovery – that is, the return of the wheels to the straight-ahead position – should occur smoothly as the driver relaxes the force with which he is turning the steering wheel.
4. Minimum transmission of shock from road surface Loss of steering wheel control and transmission of kickback due to road surface roughness must not occur.

Why Four-Wheel Steering System?

To understand the advantages of four-wheel steering, it is wise to review the dynamics of typical steering maneuvers with a conventional front -steered vehicle. The tires are subject to the forces of grip, momentum, and steering input when making a movement other than straight-ahead driving. These forces compete with each other during steering maneuvers. With a front-steered vehicle, the rear end is always trying to catch up to the directional changes of the front wheels. This causes the vehicle to sway. As a normal part of operating a vehicle, the driver learns to adjust to these forces without thinking about them.

When turning, the driver is putting into motion a complex series of forces. Each of these must be balanced against the others. The tires are subjected to road grip and slip angle. Grip holds the car's wheels to the road, and momentum moves the car straight ahead. Steering input causes the front wheels to turn. The car momentarily resists the turning motion, causing a tire slip angle to form. Once the vehicle begins to respond to the steering input, cornering forces are generated. The vehicle sways as the rear wheels attempt to keep up with the cornering forces already generated by the front tires. This is referred to as rear-end lag, because there is a time delay between steering input and vehicle reaction. When the front wheels are turned back to a straight -ahead position, the vehicle must again try to adjust by reversing the same forces developed by the turn. As the steering is turned, the vehicle body sways as the rear wheels again try to keep up with the cornering forces generated by the front wheels.

Types of Steering Mechanism:

1 Ackerman's Steering Mechanism
2 Davis Steering Mechanism

1 Ackerman's Steering Mechanism:

Ackermann steering geometry is a geometric arrangement of linkages in the steering of a car or other vehicle designed to solve the problem of wheels on the inside and outside of a turn needing to trace out circles of different radii. It was invented by the German Carriage Builder "Lankensperger" in 1817, then patented by his agent in England Rudolph Ackermann (1764–1834) in 1818 for horse drawn carriages. Erasmus Darwin may have a prior claim as the inventor dating from 1758.

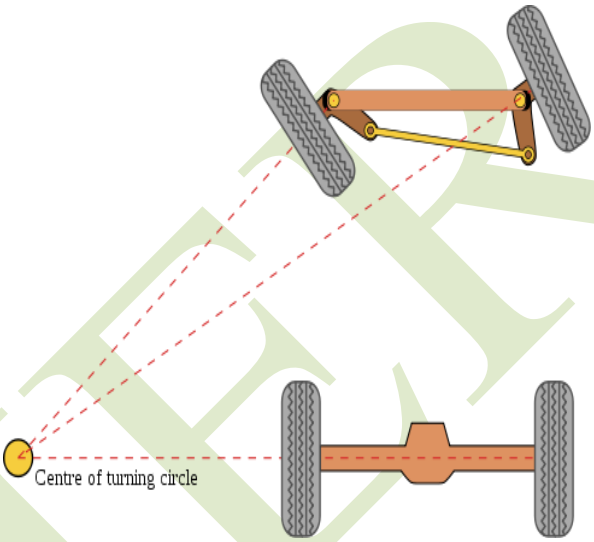


Fig 1.7 Ackerman's Steering Mechanism

The intention of Ackermann geometry is to avoid the need for tyres to slip sideways when following the path around a curve. The geometrical solution to this is for all wheels to have their axles arranged as radii of a circle with a common centre point. As the rear wheels are fixed, this centre point must be on a line extended from the rear axle. Intersecting the axes of the front wheels on this line as well requires that the inside front wheel is turned, when steering, through a greater angle than the outside wheel.

Rather than the preceding "turntable" steering, where both front wheels turned around a common pivot, each wheel gained its own pivot, close to its own hub. A linkage between these hubs moved the two wheels together, and by careful arrangement of the linkage dimensions the Ackermann geometry could be approximated. This was achieved by making the linkage *not* a simple parallelogram, but by making the length of the track rod (the moving link between the hubs) shorter than that of the axle, so that the steering arms of the hubs appeared to "toe out". As the steering moved, the wheels turned according to Ackermann, with the inner wheel turning

further. If the track rod is placed ahead of the axle, it should instead be longer in comparison, thus preserving this same "toe out".

A simple approximation to perfect Ackermann steering geometry may be generated by moving the steering pivot points inward so as to lie on a line drawn between the steering kingpins and the centre of the rear axle. The steering pivot points are joined by a rigid bar called the tie rod which can also be part of the steering mechanism, in the form of a rack and pinion for instance. With perfect Ackermann, at any angle of steering, the centre point of all of the circles traced by all wheels will lie at a common point. Note that this may be difficult to arrange in practice with simple linkages, and designers are advised to draw or analyze their steering systems over the full range of steering angles.

Modern cars do not use *pure* Ackermann steering, partly because it ignores important dynamic and compliant effects, but the principle is sound for low speed manoeuvres. Some race cars use *reverse* Ackermann geometry to compensate for the large difference in slip angle between the inner and outer front tyres while cornering at high speed. The use of such geometry helps reduce tyre temperatures during high-speed cornering but compromises performance in low speed maneuvers.

2 Davis Steering Mechanism

The Davis gear mechanism consists of a cross link KL sliding parallel to another link AB and is connected to the stub axles of the two front wheels by means of two similar bell crank levers ACK and DBK pivoted at A and B respectively. The cross link KL slides insides in the bearing and carries pins at its end K and L. The slide blocks are pivoted on these pins and move with the turning of bell crank levers as the steering wheel is When the vehicle is running straight, the gear said to in its mid-position. The short arms AK and BL are inclined an angle 90+α to their stub axles AC and BD. The correct steering depends upon a suitab1e selection of cross-arm angle α, and is given by

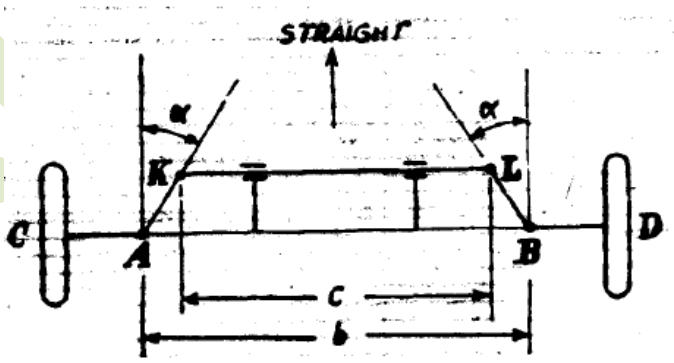


Fig 1.8 Davis Steering Mechanism

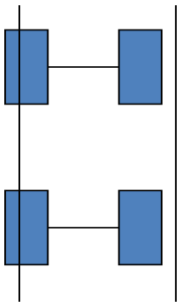
$$\tan \alpha = b / 2l$$

Where b=AB=distance between the pivots of front axles.
l=wheel base.

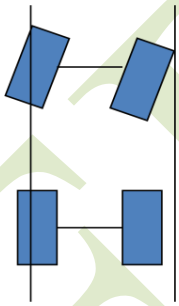
The range of b / l is 0.4 to 0.5 hence angle α lies between 11.3 and 14.10.

STEERING CONDITIONS:

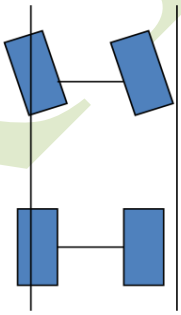
1 Normal steering



Idle position

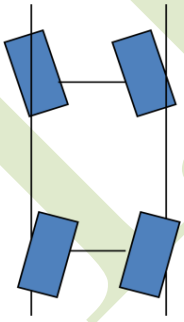


Right turn

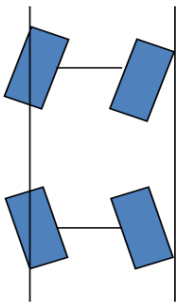


Left turn

2 Four wheel steering:



Extreme left



Extreme right

3 Comparison Of Four Wheel Steering System With Two Wheel Steering Conventional System

1. Car more efficient and stable on cornering.
2. Improved steering responsiveness and precision.
3. High speed straight line stability.
4. Notable improvement in rapid, easier, safer lane changing maneuvers.
5. Smaller turning radius and tight space manoeuvrability at low speed.
6. Relative Wheel Angles and their Control.
7. Risk of hitting an obstacle is greatly reduced

COMPARISION OF FOUR WHEEL AND TWO WHEEL STEERING SYSTEM

TURNING RADIUS	FOUR WHEEL STEER	TWO WHEEL STEER
By experiment	5.14 ft	14.70 ft

Fabrication model of four wheel steering system of Maruti 800.

Advantages

1. Superior cornering stability.
2. Improved steering responsiveness and precision.
3. High speed straight line stability.
4. Notable improvement in rapid lane changing manoeuvres.
5. Smaller turning radius and tight space manoeuvrability at low speed.
6. Relative wheel angles and their control.

APPLICATIONS:

1. Parallel parking: Due to smaller turning radius the parking and un parking of vehicle is easily performed towards the right or left side.
2. High speed lane changing: In this is less steering sensitive this does require a lot of concentration from driver since he has to judge the space and vehicles behind them.
3. Slippery road surfaces: Due to the rear wheel steering operation on low friction surfaces occurs hence vehicle direction easier to control.
4. Narrow Roads: Due to rear wheel steering on narrow roads with tight bends, counter phase steering reduces the turning radius.
5. U-Turns: By minimizing the vehicle's turning radius and counter phase steering of rear wheels enables U-Turns to be performed on narrow roads.

CONCLUSION:

It is observed that when Maruti 800 during turning actual turning radius is 14.70ft. But after making modification in the four wheel steering system it is measured as 5.14ft. hence we conclude that after making modification the turning radius is reduced more than half.

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RESEARCH ARTICLE

Green Quotient Evaluation of Existing Buildings : A Case Study

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Abstract

The construction, characteristics, operation, and demolition of buildings are increasingly recognized as a major source of adverse environmental impact. Without significant transformation of building construction and operations, such impacts are expected to increase with population growth and changes in other demographic and economic factors. One strategy for achieving that transformation is most widely known by the term Green Building[3]. We have gone past the point where going 'green' is an option. It has now become an absolute necessity to not only mandatorily construct green but rate Green Quotient of our existing buildings also according to LEED-EB. Existing buildings in Delhi-NCR form the main bulk of the building stock, and they are a significant consumer of energy and water resources, and thus negatively affecting the environment. The International Energy Agency released a publication that estimated that existing buildings are responsible for more than 40% of the world's total primary energy consumption and for 24% of global carbon dioxide emissions [5]. Undertaking a green retrofit of an existing building brings about both tangible and intangible benefits- reduce the energy and water consumption, improve the building's indoor environment quality and reduces 'sick building' syndrome. In this paper, a case study on an existing building in Delhi-NCR has been presented to inspire all stakeholders in the industry to make a concerted effort to improve the performance of our existing buildings in every sense and ensure a better built environment for our future. Regulations have to be framed by the Govt. for every building to evaluate their green status and thus minimize the negative effects of building industry on the environment.

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INTRODUCTION

The National Capital Territory of Delhi, has a population of about 11 million and a metropolitan population of about 16.3 million, making it the second most populous city and second most populous urban agglomeration in India[11]. The urban expansion in Delhi has expanded beyond the NCT to incorporate towns in neighboring states and at its largest extent can count a population of about 25 million residents as of 2014 [2]. Buildings in Delhi-NCR are an integral part of the city's heritage, skyline and a valuable asset but they also consume significant energy and

resources. Built up area in Delhi has been on a rise and using Green Building concept for new construction can definitely reduce the environmental impact of buildings in Delhi. But the area in and around Delhi was probably inhabited before the second millennium BC, and there is evidence of continuous inhabitation since at least the 6th century B.C.[1]. Thus, besides the new constructions, there is quite a huge potential of existing buildings to adversely affect the environment unless their operation and maintenance methods checked and evaluated. Mandatory restrictions will have to be imposed in the Govt. Policies regarding energy/water use and CO_2 emissions[4]. Aside from energy/water efficiency, many other significant sustainability improvements can be made in existing buildings in terms of resource use, waste reduction via recycling programs[6] as also, sustainable purchasing policies, procurement, and ongoing operations & maintenance procedures which will improve a buildings' performance[7,8]. In addition to the tangible benefits, there are other 'intangible' benefits associated with green buildings such as Employee comfort and indoor environmental quality that are hard to quantify but are equally important to address[5]. 'Indoor Environmental Quality (IEQ)', encompasses items like access to natural daylight, air quality, views, thermal and physical comfort, and the ability to control one's environment (i.e. temperature, air flow and lighting) which have positive psychological and physical effects and contribute to happier, healthier occupants. Good IEQ has been shown to increase productivity, decrease absenteeism due to sickness and improved morale of the employees. Thus good IEQ will also contribute towards economic benefits in the same manner as energy or water efficiency[9]. A well designed and well operated building will have enhanced value, demand and lower operating costs. The need to build, operate and maintain our buildings in a more sustainable way will only increase as energy costs rise, potable water and material resources become increasingly scarce and the impact of Govt. legislation increases.

Green Building Rating Schemes like LEED by IGBC or GRIHA[10] by TERI can be used to assess the environmental performance of buildings in India. Leadership in Energy and Environmental Design (LEED) is an internationally adopted program of the U.S. Green Building Council (USGBC,1998) and later adopted by Indian Green Building Council(IGBC). The system covers the majority of certified projects as New Construction, or LEED-NC. But, adverse effects on environment, sustainability and potential cost savings do not stop once a building is constructed. To address this, the USGBC developed LEED for Existing Buildings, or LEED-EB[12] which includes 14 prerequisites and 85 distinct credits.

LEED for Existing Buildings: Operations & Maintenance ("LEED EBOM" or "LEED EB") establishes uniform standards for existing buildings that focus on environment sensitive operations and maintenance. An existing building that applies and achieves LEED certification, whether at the Certified, Silver, Gold, or Platinum level, demonstrates high performance as "green building" in five major categories: Sustainable Sites, Water Efficiency, Energy and Atmosphere, Materials and Resources, and Indoor Environmental Quality (USGBC,2009)[12]. LEED EBOM certification is highly achievable for a number of different building types, and is becoming increasingly popular as building owners and managers exhibit their environment responsibility and seek to distinguish their spaces from among those of their competitors. Evaluating your building for its green status sets a target level of achievement against these tools, and can be used to track the progress[13]. Here, the existing building is in Delhi-NCR which has been evaluated for green status using LEED-EB rating tool, de facto green building standard. The case study presented here documents the sustainability approach taken in the specific organization and building. It also offers insights on getting an organizational commitment to pursue LEED-EB certification, managing a environmentally responsible project, the problems that may arise, and the solutions that can be used to address those problems.

2. METHODOLOGY

This case study details the actions the organization took to improve the building's performance, and offers guidance to further improve its LEED-EBOM rating. It also facilitates other campuses to complete a successful LEED-EB project. The organisation under study is an integrated global pharmaceutical and life sciences company engaged in manufacturing and supplying of APIs, Solid Dosage Formulations, Radiopharmaceuticals, Allergy Therapy Products and Life Science Ingredients. The following issues were evaluated against the standards laid out in LEED-EBOM.

2.1 ENERGY

An energy audit was undertaken to find out which areas of the building are consuming large amounts of energy. Then these areas were targeted for improvement. The energy audit included electricity, gas use and any other energy source used. Also, energy bills were reviewed to discover any abnormal variation in consumption. There are incentive schemes available to help fund the cost of an energy audit. Efficient Equipment, Renewable Energy, Energy Efficient Transportation facilities were also recorded.

2.2 WATER

A water audit was performed to establish the areas of the building that are consuming large amounts of water and targeted for improvement. This was done in conjunction with a review of water bills to determine any variation in consumption that may be abnormal. Also, there are incentive schemes available to help fund the cost of a water audit. The type of water fittings (i.e. sinks, toilets, urinals and showers) that were installed were catalogued or reviewed in order to evaluate their individual water consumption (i.e. flow rates). Some or all of the water fittings needed to be replaced. All new premises and existing premises undergoing renovation are required to only be installed with water fittings and products (i.e. taps, dual flush Low Capacity Flushing Cisterns (LCFCs), urinals and urinal flush valves) that are labeled with at least one or more ticks under WELS (Water Efficiency Labeling Scheme). Water Treatment, Alternate Sources, Metering, Irrigation measures of green areas etc was recorded.

2.3 WASTE

A waste audit was undertaken to find out the total amount of solid waste the building generated and also how much of it was being recycled and how much was sent to incineration and landfill. This knowledge helped us find opportunities to increase recycling efforts and reduce the amount of waste sent to incineration and landfill.

2.4 CONDITION AUDIT

A condition audit was undertaken intended to determine the current condition and expected remaining economic life of building's components. It produced a complete inventory of building (including equipment) that identifies deficiencies. Typical areas to be examined included the structure, external walls and roof, mechanical, electrical and IT systems, hazardous materials (asbestos, lead, etc), security and safety issues were reviewed.

2.5 INDOOR ENVIRONMENTAL QUALITY

Many existing buildings have a poor indoor environmental and/or air quality (IEQ/IAQ). IEQ encompasses thermal comfort, air quality, lighting levels and noise levels. Each of these were audited to find out how they currently perform and where improvements can be made.

2.6 OCCUPANT SATISFACTION

Occupant surveys were conducted to judge the current performance of building. After all, the occupants are the people who spend the most time in the building. The occupant survey highlighted any day-to-day building performance that falls below employees' expectations and also highlighted thermal comfort, noise, glare, transport and other operational issues. To be effective, the audit was carried out in a highly structured manner so that the results can allow comparison with a well-established, benchmarked database of criteria.

2.7 FACILITIES MANAGEMENT

Facilities management providers contribute significantly to the success of an organization. Ineffective providers can lead to occupant dissatisfaction and premature failure of major building systems. A review of the facilities management was conducted which included- Management process used in the property, Maintenance schedules and Operations & Maintenance manuals (O&M), Building Management System for its calibration and correct use.

Based on the observations of the building and points awarded for different categories under LEED-EBOM, assessment of the building was done. Points earned and suggestions for each category are tabulated as under-

Table No 1. Site & Facility Management (Maximum 18 Points)

Intent: Environmentally sensitive site maintenance practices to be followed to reduce site maintenance costs while creating and maintaining an outdoor space that is healthy for occupants and local plant and wildlife, support alternative transportation, protect and/or restore natural sites.

IGBC Category	Criterion to be followed	Max. Point	Present Scenario	Present Points	Our Suggestions	Scope of Points
Site & Facility Management (Maximum 18 Points)	Green Policy	Mandatory	In place	Mandatory	Nil	Mandatory
	Waste collection & Disposal	Mandatory	Waste segregation and disposal of non-hazardous waste not in place	Mandatory	Recycling and reusing of the non-hazardous waste	Mandatory
	Eco-friendly Commuting Practice: 25%, 50%	4	Provide shuttle services to nearest public transportation facility	2	Encourage car pools for people by setting up forums where people could discuss their daily route and club in with others travelling on the same route	4
	Eco-friendly	2	Less than 15% of	2	Usage of organic	2

	Landscaping Practice: 25%, 75%		immediate area is landscaped, however maintaining a green belt in front of the office building		fertilizers majorly is a thumbs up; can increase the overall landscaped area in the building premises	
	Heat Island Reduction, Non-roof: 50%, 75%	4	Less than 50% of shaded non-roof hardscape area	0	Shade from solar panels/ structured surface parking	4
	Heat Island Reduction, Roof: 50%, 75%	4	Wing C and wing B's roof is covered with reflective coating having a high SRI and accounts 70.04% of total roof area	2	Adopting similar practices with roofs of Wing A	4
	Outdoor Light Pollution Reduction	2	No external Lighting is upward looking	2	Nil	2
	Building Operations & Maintenance	2	Have in place O&M plan for HVAC systems, power back-up systems, elevators and building management systems	1	Carry-out energy and water audit, once in 3 years and explore opportunities for improvement	2
	Total (A)	18		7		18

Table No 2. Water Efficiency (Maximum 26 Points)

Intent: Maximize the use of strategies and technologies that reduce the amount of potable water consumed in buildings and reduce municipal water supply and treatment burden.

IGBC Category	Criterion to be followed	Max. Point	Present Scenario	Present Points	Our Suggestions	Scope of Points
Water Efficiency (Maximum 26 Points)	Water Efficient Fixtures	Mandatory	Yearly water consumption is double of the consumption as guided by IGBC	Mandatory	Immediate action should be taken to install water smart devices in the building premises	Mandatory
	Water Efficient Fixtures: 20%,30%,40%	6	Yearly water consumption is double of the consumption as guided by IGBC	0	Immediate action should be taken to install water smart devices in the building premises	2
	Rain Water Harvesting: 25%, 50%	4	No system installed yet	0	Install a rain water harvesting system that stores 50% of the runoff	4
	Waste Water Treatment, 100%	4	No system installed yet	0	Concept of zero discharge can be used.	4
	Waste Water Reuse, 75%, 100%	4	Not in use	0	The reused water can be sent to the already installed water softening unit and used for cooling towers and flushes.	4
	Water Metering	4	Only 2 water meters	0	Install water meters on	4

			installed; one for measuring the total extraction of ground water and other for soft water demand		each floor, water meters for flushing, irrigation requirements	
	Turf Area: 50%, 25%	4	Less than 15% of immediate area is landscaped.	0	Increase the green cover of the site to at least 15%	4
	Total (B)	26		0		22

Table No 3. Energy Efficiency (Maximum 30 Points)

Intent: Verify that fundamental building systems and assemblies are performing as intended to meet current needs and sustainability requirements. Also, the goal is to establish energy efficiency and system performance, encourage renewable and alternative energy sources to support ozone protection protocols.

IGBC Category	Criterion to be followed	Max. Point	Present Scenario	Present Points	Our Suggestions	Scope of Points
Energy Efficiency (Maximum 30 Points)	Eco-friendly Refrigerants &Halons	Mandatory	R134a refrigerant is used	Mandatory	Change the refrigerant of stand by chillers from R22 to R134a	Mandatory
	Minimum Energy Performance	Mandatory	Check	Mandatory	Nil	Mandatory
	Improved Energy Performance : 10%, 12.5%, 15%, 17.5%, 20%, 22.5%, 25%	14	EPI calculated was 172.34kWh/year/m2	0	Use improved energy and rated appliances	6
	On site Renewable Energy: 2.5%, 5%, 7.5%	6	No on-site Renewable Energy systems in use	0	Installation of Solar panels for energy generation is the most apt renewable source of energy at the location and for the type of building	4
	Off Site Renewable Energy: 25%, 50%, 75%	6	Nil	0	Installation of Solar panels, biogas plants in the production units under the company	4
	Energy Metering	4	Only 1 energy meter installed for the building	0	Installation of energy meters for central HVAC, lightening consumption, power back-up systems, etc	4
	Total (C)	30		0		18

Table No 4. Health & Comfort (Maximum 14 Points)

Establish good indoor air quality- eliminate, reduce and manage the sources of indoor air pollution, ensure thermal comfort and systems controllability. Provision for occupant connection to the outdoor environment should be there.

IGBC Category	Criterion to be followed	Max. Point	Present Scenario	Present Points	Our Suggestions	Scope of Points
Health & Comfort (Maximum 14 Points)	Tobacco Smoke Control	Mandatory	No Smoking Area	Mandatory	Setting up a smoking area with proper exhaust and ventilation or designate a space 7.6 m from all outdoor intakes (doors, windows, etc)	Mandatory
	Fresh Air Ventilation	Mandatory	Check	Mandatory	Nil	Mandatory
	Carbon dioxide Monitoring & Control	2	Nil	0	Install CO_2 sensors and maintain a differential CO_2 level of 530 ppm	2
	Isolation of Polluting Equipment & Systems	2	Check	2	Isolate printer rooms and install an exhaust fan	2
	Eco-friendly Housekeeping Chemicals	2	Check	2	Nil	2
	Thermal Comfort, Indoor Temperature & RH	2	The comfort condition maintained is 26+ 2 degree C and RH in the range of 30 to 70 %	2	Conduct a survey once in 6 months and show that 80% of the building occupants are satisfied with the temperatures maintained.	2
	Facilities for Differently Abled People	4	Ramps with raining, uniformity in floors an car spaces having easy access to lift lobby	0	Braille and Auto assistance in lifts to be worked upon; restrooms for differently abled people	4
	Occupant Well-being Facilities	2	The building has a gymnasium and indoor games facility for at least 10%	2	Meditation/ Outdoor games	2
	Total (D)	14		8		14

Table No 5. **Innovation Category (Maximum 12 Points)**

Intent: Recognize exemplary performance in any achieved LEED-EB credit and innovation in green building not addressed by current standards.

IGBC Category	Criterion to be followed	Max. Point	Present Scenario	Present Points	Our Suggestions	Scope of Points
Innovation Category (Maximum 12 Points)	Innovation Credits	10	Maintenance of the park in front of the building	2	Apply innovations as suggested in the report	10
	IGBC AP	2		0	Involve an IGBC AP as a principal participant of the project	2
	Total (E)	12		2		12

Total (A+B+C+D+E)		**100**		**17**		**84**

3. DISCUSSION

The company uncompromisingly has adopted an approach which defines sustainability as 'Business as usual'. Their promise of Caring, Sharing, and Growing along with their stakeholders is the essence of all their activities that are directed towards sustainable growth. To further augment their promise, the following policies have been framed and implemented:

- Sustainability Mission
- Climate Change Mitigation Policy
- Environment, Health & Safety Policy
- Green Supply Chain Policy
- Business Code of Conduct
- Whistle-blower Policy
- Quality Policy

The policies are in place but the company scores just 17 points when assessed against LEED criteria which do not enable it to earn even a certification, for which minimum 50 points are required. But the company can incorporate the suggestions made in the report, major ones being installing solar panels, smart water devices, rain water harvesting, other water efficiency measures, recycling non-hazardous waste, encouraging car pools, smoking areas etc. All this will not incur larger costs than the benefits accrued. If the company is able to score greater than 70 points, it qualifies for Gold or a Platinum certification which gives it a Global Leadership as also exhibition of greater corporate social responsibility towards environment protection.

4. CONCLUSION

Existing buildings in Delhi-NCR comprise the larger segment of the built environment. Their operation and maintenance protocols contribute majorly towards negative effects on environment. We need to assess the performance of each major building according to the green building standard for existing buildings-LEED-EBOM. Depending on the points earned as per this scheme, major renovations and retrofits can be designed to include sustainability initiatives and have a good LEED-EBOM Green Building Rating. This will reduce operation and maintenance costs and environmental impacts, and can increase building adaptability, durability, and resiliency. Conserving energy is not the only reason for retrofitting existing buildings; rather the goal should be to create a high-performance building by applying the integrated, whole-building design process. The integrated project team may discover a single design strategy that will meet multiple design objectives so that the building will be less costly to operate, will increase in value, last longer, and contribute to a better, healthier, more comfortable environment for people. In an era of LEED-certified construction and growing concern for sustainability, it may also be observed that constructing new, energy-efficient buildings can be less eco-friendly than renovating old ones. Mandatory Regulations have to be imposed by the Govt to enforce Greener built environment and also incentives be given to those who implement.

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1. Introduction

Increased industrialization and ever growing consumerism has led to a situation where industrial pursuits of mankind have started to cast an unfavourable impact on environment that may prove self-destructive for the former. Developed countries, in their pursuit of economic development and progression to their current economic status, showed little respect for environmental concerns, earlier. But as on today, there is an increased awareness on part of their industries, governments and even consumers for conserving environment and cutting down on pollution. Conversely, industries in developing nations are not so sensitive towards the cause of conserving the environment, and thus there is greater need of adoption of GSCM practices. They are in a race for faster economic growth and their economies are booming owing to rapid industrial expansion. This has led to a situation where they are emerging as top polluters of the world for tomorrow. China has been at forefront amongst developing countries, when it comes to harm caused to environment for the sake of industrial growth. India also has shown little respect towards environmental conservation while pursuing for economic growth. But there is now a glimmer of hope, as India, like other developing nations, is slowly waking up to the necessity and gains of GSCM practices. Nevertheless, it is just a beginning and there is a long, long way to go. In the wake of this, it is required to introduce environmental friendly practices in industrial supply chains to ensure that that there is no degradation of environment; coupled with materialization of economic gains. The growing awareness for environmental concerns led to adoption of GSCM, which though of relatively recent origin has gained worldwide popularity and recognition in a brief time period. In Indian context, during the last few years, hundreds of studies have been carried out on the subject, addressing the various facets of the concept. This has led to establishment of various generic /specific laws, identification of previously unknown parameters associated with its implications and the possibilities that GSCM holds for future improvements in manufacturing and supply chain execution.

2. Literature Review

There is relative dearth of unanimity in defining the nature and scope of Green supply chain Management as its building blocks i.e. Corporate Environmental Management and Supply Chain Management are themselves in their nascent stages of evolution. Nevertheless, in general, Green Supply Chain Management deals with adoption and implementation of environmental friendly means while executing various actions in the progression of a supply chain. GSCM is a holistic terms that involves within itself concepts like Green Purchasing, Green Manufacturing/Materials Management, Green Distribution, Green Marketing, Waste Management and Reverse logistics.

2.1 Green Supply Chain Management in Developed Countries

Srivastava (2007) defined GSCM as integrating environmental thinking into supply chain management, including product design, material sourcing and selection, manufacturing processes, delivery of the final products to the consumers, and end-of-life management of the products after its useful life. GSCM covers activities such as Green Design, Green Sourcing/Procurement, Green Operations or Green Manufacturing, Green Distribution, Logistics/Marketing and Reverse Logistics.

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The origin and extensive spread of GSCM is relatively more associated with developed economies, rather than developing/non-developed ones. Developed Countries are characterised by high level of economic growth, industrialization and Human Development Index (HDI). Various researchers conducted their study in developed countries to examine the integration of environmental concept and supply chain management. One study from Germany conducted by Large and Thomsen (2011) identified five potential drivers of GSCM performance viz. Green Supply Management capabilities, strategic level of purchasing department, level of environmental commitment, degree of green supplier assessment, and degree of green collaboration with suppliers. Azevedoet.al. (2011) examined the links between green practices featuring in a supply chain, and the subsequent effect on the latter's performance in context of Portuguese Automotive Supply Chain. The study of Chiou et al. (2011) in Taiwan concluded that greening the supplier through green innovation leads to significant benefits to the environmental performance and competitive advantage of the firm. A study in Italy carried out by Cagno et al. (2011) examined Green Supply Chain Practices (GSCP) adopted by Third Party Logistics (3PLs) Service Providers, such as specific practices implemented and level of adoption of each practice by examining the potential effects of GSCP on company performance. In a study carried out in Japan by Arimura et al. (2011), the influence of ISO 14001certification on the GSCM was determined by using Japanese facility level data. The study proved that ISO 14001 and voluntary Environment Management System (EMS) government program significantly influence GSCM practices. These programs help in evaluating suppliers environmental performances and ask them to undertake specific environmental practices. Another study from Japan by Zhu et al. (2010) sought to introduce environmental, GSCM experiences of large Japanese manufactures. The study showed that large companies by greening their supply chains, can create win-win relationships with their partners, and hence realize sustainable growth for across their supply chains. Besides, it also indicates that suitable regulations and policies set by government can help GSCM circulation from larger leading companies to smaller companies. Hsu and Hu (2008) investigated the consistency approaches by factor analysis that determine adoption and implementation of GSCM in Taiwanese electronic industry. The fuzzy Analytic Hierarchy Process method was applied to prioritize the relative importance of four dimensions and 20 approaches among nine firms in electronic industry. Meanwhile, Shang et al. (2010) explored key GSCM capability dimensions and firm performance based on electronics-related manufacturing firms in Taiwan. On the basis of factor analysis, six GSCM dimensions were identified: green manufacturing and packaging, environmental participation, green marketing, green suppliers, green stock, and green eco-design. Holt and Ghobadian (2009) investigated the level and nature of greening the supply chain in manufacturing sector of UK. In this study, the work explores the driving forces behind environmental management, the specific practices accruing from them, and the relationships between them. The study by Nawrocka et al. (2009) in Sweden, has concentrated on the role of ISO 14001in environmental supply management practices in Swedish companies. The study described the existing and potential role of ISO 14001 for three key operational tasks of environmental supply chain management: communicating the requirements to the supplier, to motivate and enable the supplier, and to verify that the supplier follows the requirements. A study from South Korea carried out by Lee (2008) identified the drivers of participation in GSC initiatives by considering small and medium-sized suppliers and their most important stakeholders, including buyers and the government. Raymond et al. (2008) examined the relationship between supply chains and environmental performance of Small and Medium- sized Enterprises (SMEs) in Canada. This study proved that time and financial resources to deal with solid waste and energy issues are the most limiting factors. In addition, Chen (2008) looked into the relationship between green innovation and green image of companies in

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Taiwan. The study proposed a new concept of Green Core Competence. Chien and Shih (2007) examined adoption of GSCM practices among electrical and electronic industry in Taiwan. The relationship between GSCM practices and environmental performance, as well as financial performance has been studied. One study from Australia, conducted by Simpson et al. (2007) explored the moderating impact of relationship conditions existing between a customer and its suppliers and effectiveness of the customer's environmental performance requirements. Practically no research exists on the actual effectiveness of green supply requirements when placed in context with the realities of inter-organizational dynamics.

2.2 Green Supply Chain Management in Developing Countries

GSCM, in general, is believed to represent the environment-friendly image of products, process, systems, technologies and conduct of business. Most companies especially in developing countries adopted the green solutions into their business to reduce the negative environmental effects rather than adopting a proactive approach to reduce the sources of waste or pollution. These adopted green solutions continue to be traditional "command-and control" or "end-of-the-pipe" solutions (Anbumozhi and Kanada, 2005).Not enough literature has been devoted to the concern of GSCM in developing countries. The GSCM concept is relatively new concept in South East Asian Region and probably only a few companies are actually able to implement it (Rao 2002). However, as claimed by Rao (2002) in his study on green supply chain in South East Asian Region (Philippines, Indonesia, Malaysia, Thailand, and Singapore), GSCM practices have started to take firm roots. Thus, the findings from those researches in Asian Region can be useful for manufacturing in developing countries in order to develop the appropriate GSCM practices and help to reduce the environmental problems. Recent literature showed that a number of researchers have started investigating the spread of GSCM in East Asian Region, such as China, that is identified with complex GSCM issues being a major manufacturing country. Zhu et al. (2011) investigated that whether different Chinese manufacturer clusters vary in their extent of implementing GSCM from the ecological modernization perspective or not. The study also examined Chinese manufacturer's awareness of local and international environmental ESPR-oriented (Enhancing Energy Savings and Pollution Reduction) compliance related to GSCM implementation. He also deduced that mediating effect of regulatory pressure plays a major role in adoption of GSCM practices. It is concluded that the varying pace of Chinese manufacturers to ecological modernize with GSCM practices and the significance of regulatory pressure to distribute the practices adoption by Chinese manufacturing industry. The study by Liu et al. (2011) in China has analysed the relationship between GSCM level and the classified determinant factors. The study confirmed that a company's environmental management capacities will be strongly enhanced by frequent internal training of employees to increase its involvement in GSCM practices. Another research from China, studied by Yan Li (2011), examined the adoption levels of GSCM practices in China and explored the performance measurement for GSCM. The findings demonstrated that GSCM was strongly balancing to other advanced management practices, and contributed to improving environmental performance. Zhu et al. (2008) evaluated GSCM practices relating GSCM to closing the supply chain loop for four Chinese industries (power generating, chemical/petroleum, electrical/electronics and automobile). They concluded that adoption of GSCM practices in different industrial contexts is not uniform across the four industries. Another study also by Zhu et al. (2005) in China has evaluated and explained GSCM drivers, practices and performance among diverse Chinese manufacturing firms. Concern about the environmental issues has also augmented the interest of researchers to investigate the adoption and implementation of GSCM practices in another Asian Countries such as

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Thailand, India and Malaysia. A study of Ninlawan et al. (2011) in Thailand analysed recent green activities in computer parts manufacturers and also measured the level of GSCM. The in-depth interview regarding green procurement, green manufacturing, green distribution, and reverse logistic has been conducted. The study conducted in India by Diabat and Govindan (2011) identified the drivers influencing the implementation of GSCM using an Interpretive Structural Modelling (ISM) methodology and extracted 11 drivers collected through literature. One study from Malaysia by El Tayeb and Zailani (2009) has identified the four key drivers or motivators to GSC initiatives: Regulations, customer requirements, expected business gains, and social responsibility. Eltayeb et al. (2011) analysed the relationship between GSC initiatives and performance outcomes and identified the key initiatives (eco-design) that have positive effect on the four types of outcomes (environmental, economic, cost reductions, and intangible outcomes).

2.3 *Green Supply Chain Management in India*

In India, industrial waste accounts for over 50% of total pollution caused in the country. The government itself has classified 17 industries as highly polluting and 24 industries as environmentally problematic in nature. Chemical and Engineering industries are the major culprits, causing bulk of industrial pollution in the country. Other notable industries include integrated iron and steel plants, non-ferrous metallurgical units, pharmaceutical and petrochemical complexes, fertilizers and pesticide plants, thermal power plants, textiles, pulp and paper, tanneries and chloralkali units. In 2006, Small and Medium Enterprises (SMEs) which accounted for 40 percent of industrial production, deployed limited pollution control technologies and were responsible for an estimated 70 percent of the total industrial pollution caused nationwide. (OECD Report 2006).

Being the fourth largest economy in the world, there are no surprises that the country is also the fifth–largest global Green House Gasses (GHG) emitter. Between 1990 and 2008, India's carbon dioxide emissions increased more than 1.5 times, which is second-highest globally after China. Rapid industrialization is putting strain on resources and generating tremendous waste, to the tune of 4 million tonnes. Only 3% of E-waste, that is a hazardous class in itself, is recycled in authorized recycling facilities. The status of pollution and wastage calls for adoption of GSCM measures on an immediate basis across the Indian industrial sector (Bhattacharyaetal.2011).

The relevance of adopting green supply chain practices is greater in India than anywhere else. Manufacturing sector which accounts for 16% of GDP is poised for growth and its share as percentage growth of GDP will go up to 25% by 2022, propelled by SME sector. The record of SME sector on the front of efficiency is not that encouraging. SMEs are challenged by rising input costs, including energy costs, unavailability of resources (especially power, fossil based fuels, etc.), poor logistics management and lack of skilled labour force. To counter these, cost rationalizations by greening of supply chains in SME sector needs to be taken more seriously in India, than ever before. The Indian SME scene is identified with lack of willingness to move away from traditional practices which is a hindrance to the spread of GSCM measures in a significant way. The phenomenon is equally applicable to larger corporate houses, as well. Coupled with willingness, the knowledge of green technologies, practices and methodologies also play a crucial role in making the supply chain green. There is considerable lack of knowledge on the part of top management that retards the proliferation of GSCM in India. (TERI 2013).

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Apart from SMEs, the other focus area is agriculture, that being central to Indian socio-economic set up, cannot be neglected. Agriculture is a big guzzler of power in India, and knowledge about Renewable Energy technologies can help the sector to go green substantially. Modern technologies such as sprinkler, drip and micro-irrigation are crucial not only in reducing the water-requirement for irrigation purposes, but also electricity or diesel requirement for running the pump sets. Energy efficient motors account for a very small percentage of motor sales in India. Retrofitting of even 10% of the existing inefficient pump sets (~15.35 million as on March 2007) annually would translate into a savings of ~ 4 billion kWh (kilowatt-hour) per year at the user's end and ~900 MW of equivalent generation capacity. On a similar note, green measures need to be undertaken with respect to crop residue management, nutrient management, irrigation water management, precision agriculture, pesticide management etc.(Govindan and Bhanot, 2012).The "National Mission on Sustainable Agriculture "calls for measures for to secure improved crop seeds, livestock and fish culture, improved water efficiency; pest management, improved farm practices; nutrient management; agriculture insurance and credit support; creation of new market infrastructure and alignment of R&D with market needs and livelihood diversification (NMSA Report, 2010).

On an optimistic note, certain sections in Indian SME sector have taken lead in adoption of GSCM practices owing to the advantages offered by it in terms of increased efficiency. Cutting & hand tools, auto parts, spare parts, industrial equipment's, machinery manufacturer etc. seem to be quite advanced in the implementation of green warehousing and distribution initiatives. But such instances are more of an exception, rather than a norm. In 2012, India's Environmental Performance Index (EPI) rank stood at a dismal 125 out of 132 countries ranked. EPI measures effectiveness of national environmental protection efforts, on the count of measurable outcomes such as emissions or deforestation rates rather than policy inputs, such as program budget expenditures etc. India's poor rank indicates the miserable status of country's awareness of green supply chain management practices (Nimawat and Namdev, 2012). Despite that, it can safely be said that environmental consciousness, if not optimally significant, is still on the increase across various stakeholders of supply chains in India. The concept of "Green Products" like organic food, solar heaters, electrical cars etc., are gaining wider acceptance with both Indian companies and consumers. Indian manufacturing is catching up with the long term benefits of green processes to improve corporate brands, reduce costs, and achieve compliance simultaneously. Energy intensive companies are implementing lean processes to minimize waste and enhance energy efficiency (CII 2011). In India, though the number of companies embracing GSCM is increasing, yet it can safely be said that there is limited awareness about the concept amongst suppliers, consumers and employees, in general. The notion of Reverse Logistics is also absent in majority of companies, whereby waste can be retrieved from the end consumer for capturing its remaining value or for its environment-friendly disposal (Dutta and Vaibhavanand 2012).

Indian government, realizing the importance of eco-friendly industrial practices and the gains that accrue from them, is serious about enforcing measures that can curb environmental degradation. As per the Manufacturing Plan of the Planning Commission of India 'being green' should be the primary focus of businesses, and should not be treated as an obligation by the manufacturers. On the other hand, it is important that government must come out with institutional support for the Micro, Small and Medium Enterprises (MSMEs) because of their outdated and incompetent technologies will find obligatory imposition of standards on them as challenging. The government may come out with initiatives like regulations encouraging disclosure by firms of their environmental sustainability performance, low-interest loans for

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manufacturing to invest in new plans to produce clean /green technology or invest in new plants to produce green products; creation of a central fund for supporting research in the area of green manufacturing and making it mandatory to get a certain percentage of its electricity mix from renewable sources(Planning Commission).In nutshell, the process of greening the MSME sector is a two way process, wherein both the manufacturers and government should make efforts to address the challenges in the way of augmenting GSCM adoption across the industrial sector of India

Sarkis (2011), in his study has stated that there are enormous opportunities for researches to find new dimensions of the concept of GSCM, as still much of its possible facets remain unexplored. Furthermore, much of the literature on the subject is of recent origin, which points to the fact that the concept is still in its nascent stage, and more surprises are waiting to manifest, as our knowledge on the subject will progress towards its growth and maturity. Sarkis has made his statement in global context. Sarkis is of the view that despite in primary stages of development even in Western World; GSCM has delivered substantial gains– both economic and environmental, for the practising firms. That being true, the gains awaiting for developing countries like India are immense, given the fact that the percolation of GSCM, even in its existing status of infancy, has been limited. This offers not only opportunities, but also poses challenges in the shape of dissemination of information and know how; as well as developing the capacities to the required level of achieving its threshold level of acceptance, adoption and implementation. Major causes for the mentioned challenges are specific to developing countries like India because of many reasons viz. weak information-sharing channels, limited exchange of technology between enterprises, lack of capital, limited enthusiasm to switch over to more environment-friendly technology etc.

3. Research Methods and Directions

The study is aimed at exploring the various facets of GSCM in Indian context; which makes it exploratory in nature. It has purposely focused on addressing common aspects of GSCM; and thus refrained from laying emphasis on any peculiar aspect of any particular industry. The approach of undertaking a survey would have been more suitable, if the study was aimed at eliciting responses from a small target group. A case study could have been ideal, if the subject had revolved around a certain small operational domain. That not being the case, literature review was undertaken to gather a holistic view of the most accurate and most reliable facts on the subject. The research approach encompasses the study of the most rudimentary aspects of the main theme of research. Major drivers of GSCM were identified, and their present status was traced in context of Indian settings and those of other important industrial nations across the globe. The status of India's adoption and implementation of GSCM was juxtaposed with those of Chinese and US Firms; and parallels as well as commonalities, were drawn.

On the basis of review of literature on GSCM – the concept, its dimensions, its applications and its ensuing evolution; sufficient information to introduce the concept was gathered, to shape the preliminary/introductory part of the research. Though the implementation of GSCM may reflect variations on case to case basis, based on peculiarities inherent to the studied case; yet there are broad commonalities that define the concept in its generalized form. Accordingly, certain drivers were identified that are integral to nearly all the GSCM implemented systems. They were subjected to study in context of India and one developed nation and one developing nation; to draw parallels between them. The comparative analysis

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helped in ascertaining the depth of penetration of GSCM in industrial sector, vis a vis what is being practiced in other significant transnational industrialized domains. Thereafter, various aspects of the concept in study were like Inter-relation between Economic Growth & Environmental Degradation, Managing Growth with Environmental Concerns, Relation between Environmental Pollution and Development Status of an Economy, Chasing Growth and Environmental Concerns simultaneously, Government Regulations, Top Technologies, Barriers etc. were studied. An attempt was made to study the GSCM Initiatives taken by Indian firms and leading companies to adopt and implement GSCM in their operational systems; to understand the most significant and relevant developments in eco-friendly industrial processes in Indian context.

3.1 Status of Important Drivers of GSCM of India vis a vis other Developed/Developing Countries:

Although GSCM, in itself is not of very late origin; the concept has seen tremendous acceptability and practice across the globe – amongst the developed as well as developing nations. Obviously, the developed nations have made bigger leaps in embracing it, putting it to practical usage. The developing nations, on the other hand, are characterized by mixed responses to the environment friendly management technique. It is enlightening to see the progress of GSCM India vis a vis some developed nation; and also in comparison to a leading developing economy. USA is an optimal example of a developed economy with substantial lead in practicing GSCM by its industrial set up. China, on the other hand, presents an ideal choice as a developing country to compare its advances on the front of GSCM in comparison with India.

A brief analysis of the status of few selected drivers of GSCM in case of India, China and USA has been done to assess the relative positioning of India with respect to other global manufacturing giants. The findings have been enumerated driver-wise to gauge the relative strengths and weakness of the same in Indian context.

Green Procurement

UNEP(United Nation Environment Programme) in its report titled "Sustainable Public Procurement: A Global Review" (2013) states that Green Public Procurement (GPP) is a relatively new concept in Indian context, which can be used as a policy instrument to further the cause of environment conservation across the industrial scenario of the country. The fact that public procurement sums up to 30% of the total GDP in case of India, the concept of GPP offers bright prospects to promote GSCM in a big way by leveraging its sheer strength to make supply chains across various industries eco-friendly. As of now, there is no procurement law in place, and the public purchases are materialized on the basis of government policies only. Hence, there is room to streamline purchases made by Public sector enterprises and contribute towards greening the environment. The government has also woken up to the need of developing a framework to execute green purchases and Public Procurement Bill is on the anvil. Nevertheless, Eco labels and Environment Standards are in place since long. ISO14001 was introduced in 1996 to depict a firm's commitment to environmental management, as well as Eco mark- the Eco label for Indian products in 1991, but that has not been embraced by the suppliers to the extent, it was originally intended.

In its report titled "Procurement, Innovation and Green Growth" (2012) by International Institute for Sustainable Development, Canada; the efforts of Chinese Government have been highlighted in ensuring GPP across its various levels of functioning. Local government

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accrue 90% of the government expenditure on procurement, and that shows the potential of GPP that China has at its hands. In context of purchasing, the government has released a list of Energy Saving products which enlists more than 30,000 products. However, the purchase of these products is voluntary on the basis of the local governments, which leaves the effectiveness of GPP in case of China, an open ended issue. One of the peculiar issues affecting GPP in China is the inability of new products getting visibility in the said list. Innovation is happening fast in China and innovators are coming with ever-improved products. But the authorities, already overburdened with the task of evaluating the huge number of new products coming for appraisal, find it hard to evaluate and assess all the emerging innovative inventions. Nevertheless, the intention of Chinese Government in promoting GPP cannot be doubted, as is evident from the national dialogue, backed by a national questionnaire, initiated by it to promote the culture of green purchasing in the country.

In USA, the concept of GPP is being promoted by a number of organizations acting independently towards securing the goals of green procurement. In fact, Organization for Economic Cooperation and Development (OECD) of which USA is a prominent member, has been carrying out extensive research, work shop programs and policy analysis on the issue of GPP since 1996. North American Green Purchasing Initiative (NAGPI) is an inter government body which apart from USA, has Canada and Mexico as its members; working together to ensure that environmental conservation should be considered duly while making purchases by the government. On the end of private endeavours, Responsible Purchasing Network (RPN) is another network of buyers that aims to encourage the culture of Green Purchasing on translational basis in North America. Hence, it can be concluded that GPP is backed not only by the state players, but by non-state actors as well; pointing to the maturity of the concept in American markets.

Green Technology:

India and China, because of their cheap labour markets and being profitable markets for the west, are emerging as investment and production hotspots for established companies of the developed world. Furthermore, because of increased technological capacity and suitable human resources to carry out innovations, many MNCs are shifting their R&D facilities in these countries; by which of virtue Green Technology is receiving a fillip on its own. So, in a sense, Green Technology in India and China can be considered to be closely related with the concept of Technology Transfer from relatively more developed countries. But at the same time, it needs to be accepted that that technology is transferred in a narrow sense of the word and alterations and innovations in the acquired technology determines the shape of final technology that is developed and deployed. Having mentioned that, the governments in two countries are also striving to invest in development of Green Technology. Chinese Govt. in the last decade has extended a support of 2 billion Yuans for R&D works, and has plans for tenfold increase in that amount for the coming decade. The emergence of China is the largest producer of Rechargeable Batteries used in vehicles in the world. Similarly, in India expenditure in R&D activities to develop Green Technology is manifested in many examples. For ex. Bharat Heavy Electricals Limited has started manufacturing electric buses, vans & Special Purpose Vehicles through indigenous technology only (Lema and Lema, 2012). As per Watson (2013) 57% of business houses based in USA, use green technologies aimed at securing energy efficiency while more than 50% deploy green technology to cut down on wastages. Evidently, this is an appreciable number, which points to awareness and acceptability of environment friendly technology amongst the Americans.

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Green Energy

The fact that Industrial sector is dependent upon power for sustenance and growth; the concept of Green Energy acquires significance in the wake of another fact that generation of energy by conventional means is synonymous with environmental pollution. Any effort to make industrial operations green and conserve the environment is closely related with availability of green power. It is in this background, that the green energy should be considered integral to any of the GSCM study undertaken.

Indian Renewable Energy Status Report IRESR (2010) point towards India's seriousness towards development of Green Energy towards meeting the domestic energy needs, which owes largely to curtail its ever growing expenditure on fuels. In fact, India was the first country in the word to constitute a ministry dedicated to the cause of development of green energy, when in 1992 it constituted Ministry of New & Renewable Energy aimed at generating eco-friendly power/energy. By the mid of 2010, the country had an installed capacity of 17.5 GW of installed renewable energy capacity, amounting to 10% of India's net installed power generating capacity. Apart from that, the government has set up dedicated centres of studies like Solar Energy Centre and the Centre for Wind Energy Technology to tap the potential of renewable energy sources in the country. Furthermore, the Indian Renewable Energy Development Agency (IREDA) has been set up to provide financial assistance to green power projects of the country. The Electricity Act 2003 enacted by the government mandates that that each State Electricity Regulatory Commission (SERC) establishes minimum renewable power purchases and National Electricity Policy 2005: Allows SERCs to establish preferential tariffs for electricity generated from renewable sources. India has made an appreciable beginning in tapping its green energy potential, but it is still in its infancy.

On similar grounds, China has also been an enthusiast of Green Energy with its focus not just on hydro power but other non-renewable sources of energy, as well. Most predominantly, after hydro power, China has made big strides in development of its wind power generating capacity with an ambitious target of 100 GW by 2020. Riding high on its Renewable Energy Law 2005, China offers subsidies to companies managing grids, who buy power from Renewable Energy producers. USA on the other hand does not have a comprehensive national policy on promotion of green energy, owing to the fact that higher initial cost of generating green energy is in conflict with the "Market Economy" principle to which the US relates itself with. However, Bio Fuels have emerged as a popular form of renewable energy, mostly due to substantial support extended to their development by the Federal Government in the shape of RFS (Renewable Fuel Standards). RFS mandates the blending of specified quantities of renewable fuels with gasoline/diesel etc. The policies on renewable energy, howsoever little may be, have their roots in the erratic changes in global energy prices during the last quarter of last century, prompting the US authorities to look at Renewable Energy as an alternative and cheap source of power (Campbell 2010).

Green Legislations:

In India, as per the report of High Level Committee of Ministry of Environment, Forest & Climate Change, Government of India (2014) on "Review of Various Acts administered by the Ministry", environment related legislations received attention only after Bhopal Gas Leak Disaster of December 1984; following which EP Act 1986 was enacted. The law empowered Central Government to regulate emissions and effluent standards, restricts sites for industrial use, handling of hazardous waste, investigate and research pollution issues. The EP Act in

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1986 further gave way to amendments in Air Act 1987 and Air Act 1988, which play a significant role in the ensuring regulating industrial undertakings on the count of environment protection. Other laws relating with environmental protection include Handling of Management of Hazardous Waste Rules in 1989 and 2008, Public Liability Insurance Act 1991, EIA Notification 1994 and 2006, CRZ Notification 1991 and Bio Diversity Act 2002, National Green Tribunal 2010 etc. Significantly, informal regulations propelled by NGOs, civil society and social media have furthered the cause of promulgating environment related legislations in the country. Nevertheless, the enforcement of legislations pertaining to environment conservation on the part of industrial establishments is an area of concern, with little or no punitive action against the offenders in general.

In China, laws pertaining to environmental conservation were initiated in 1979 as a result of rapid environment deterioration resulting from industrialization of the country in early 1970s. There are as many as thirty laws pertaining to the issue are environment conservation, with relevance to industrial sectors of the country too. Environmental Protection Law (EPL) is the axial environmental legislative provision for enforcing environment friendly operations at the end of industry, organizations and individuals in general. Nevertheless, there are lots of limitations in the same, and attempts have been made to bring about amendments in it. Though effectiveness in enforcement of green legislations is an issue open to debate in the case of China, it is encouraging to see that the legislations have evolved over a period of time, due to learning from the experiences of relatively developed nations.

At the moment there are no set procedures or legislation regulating e-waste in India. The e-waste is mostly taken by scrap dealers, either collected from various users and scavengers or bought at auctions from large companies. The re-usable parts are sold as spares and the rest is used to recover various metals. The biggest environmental and health hazards come from the recovery of metals such as gold, silver, copper etc. The residues which contain heavy metals and toxic organic traces are often dumped in the open.

Customer Involvement

Presumably, there seems to be greater awareness in developed countries amongst the consumers pertaining to environmental issues, which is reflected in their buying behaviour patterns as well. In a studied carried out by Kumar et al. (2013) , nearly 75% of consumers based in USA stated that their buying decisions get affected by the environment friendly reputation of the company; and nearly 80% stated that they had no reluctance in paying an extra amount for a commodity, with environment friendly attributes. This shows that customers are more aware and more responsive towards environmental aspects of products/commodities they use, in case of a developed nation like USA.

In India there is relative limited awareness amongst the end users of the green nature of the products of the users. This further limits the customer's involvement in the greening the supply chain. However the manufacturers can take initiatives in ensuring that the consumers play an active part in the GSCM; for example, green labelling of products will help in disseminating information about the green aspects about the product; that will effectively help the consumers to make choices among the options available to them. Companies can also use their marketing & advertising channels to push with green products and can calibrate their marketing campaign to launch pad for greener products. Such moves will trigger consumer awareness about GSCM practices, which will snowball into greater spread of the same across a wider spread of customer base. This will eventually result in increased quantum of customers' commitment towards conserving the environment.

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Chinese firm being more export oriented, have a larger broader based customer base. Exports and overseas sales hinge upon the preferences of overseas customers, who exhibit a more profound concern towards green products. This means the Chinese firms have to look at GSCM more as a requirement than an option while manufacturing their products. Subsequently, the Chinese consumers are also getting exposed to the concept of green manufacturing and green products, which is now becoming more conspicuous in their buying behaviour patterns across various product categories, most predominantly in automobile industry. Nevertheless, there are companies (mostly in Electronics/ electrical commodities), which are not willing to embrace GSCM that effectively, as they already have long term relationship with the customer base, and need no green-make over to win or retain their customers.

Reverse Logistics

It is strange that developing nations act as dumping grounds of products used and discarded by the developed countries, and yet they fail to execute the concept of Reverse Logistics to its optimum, when it comes to indigenous products. Sharma at al. (2011) in their study on Reverse Logistics (RL) in Indian context, state that though India has both the technology and manpower to execute RL, the latter find limited application in Indian industrial scenario because of various reasons viz. lack of RL structure, unresponsive management, financial limitations, company's policy-frameworks etc. Top managements see RL as a measure that relates with financial and operational facets of the company's undertakings and may affect company's performance in an unfavourable manner. It is a risky endeavour for the top management as it involves financial and operational aspects which determine the performance of the company in long run. The barriers mentioned not only affect the operations of reverse logistics but also influences one another. Thus, it is very essential to understand the mutual relationship among the barriers. The study revealed that in Indian perspective, limited awareness about the concept of RL, monetary constraints and legal issues affect the deployment of RL, in a predominant way. Some of the legal provisions also act as a hindrance in executing RL. For example Goods for which excise tax has been paid, cannot be brought back again by the manufacturing enterprise, unless consent is secured from the excise department, regarding the same. In an effort to the avoid Red Tapeism, the manufacturer simply does not go for execution of Reverse Logistics at his end. Financial constraints too form a significant hurdle in carrying out recycling by Indian firms, on a significant scale. Deployment of IT based systems to track/trace the reclamation of products is a cost intensive proposition; along with the cost associated with aligning and training human resources towards executing RL exercises. Moreover, unawareness on the part of stake holders regarding the concept of RL, its prospective gains and the methodology to implement it; retard its adoption and spread on a massive scale.

In context of Chinese companies, (Abdulrahman and Subramanian, 2012) stated that the economic boom in the country has led to enormous consumption by the Chinese, resulting in voluminous generation of waste. Pollution spurt in the country can be gauged from the fact that contaminated water and solid waste per unit of China is much higher than many of the developed countries. Electrical & Electronics waste are particularly more prominent with them accounting for thrice the volume of the conventional waste. The Chinese have woken up to need of RL, but Chinese forms are still way behind the US ones as far as spread and status of RL is concerned across the Chinese industrial scenes. Lack of capital to initiate RL operations and setting up monitoring systems to execute its returns is the single most important reason for the relative lesser spread of RL implementation. Furthermore, low levels

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of commitment on the part of Chinese firms to the concept and lack of expertise also contributes to less than desired penetration of RL Culture in China.

The culture of RL is comparatively more broad-based and advanced in USA, where the market for RL was pegged at $58 billion in 2004, comprising 0.5% of the US gross domestic product; as per a study conducted by Olorunniwo and Li (2011), and was poised for an upswing with progression of time. But despite that, it cannot be stated that RL has reached desirably high levels in USA, as a significantly high number of companies don't spend even 5% of their total logistic cost on Reverse Logistics, and many managers don't see it as integral part of their operations citing their none or little contribution to company's profits. In fact, some see RL as a "Cost" to the company, rather than a "Gain". But, there are firms which while evaluating RL doesn't consider only the monetary gains, but also non-monetary gains while evaluating RL applications and hold an appreciable view of the concept.

3.2 Inter-relation between Economic Growth &Environmental Degradation

The relationship between the environment and pollution is the subject of intense public debate. Pollution& GHG emissions are often used as indicators for environmental quality with the obvious intuition that more emissions imply worse environmental quality. One's intuition may lead to the belief that emissions simply increase linearly as an area's economy grows through time. An examination of the empirical relationship between economic growth and emissions, however, reveals different results. Grossman and Krueger (1991) proposed that emissions followed an inverse-U shaped path as a country's economy grew over time. The authors defined this relationship as the Environmental Kuznets Curve (EKC) hypothesis named after the Kuznets Curve hypothesis developed by Kuznets in 1955. Since the proposal of the EKC hypothesis, several other studies have been conducted to examine the validity of the hypothesis. Till date, no comprehensive theoretical model has been developed to explain the relationship between environmental quality and economic growth from which an empirical EKC can be explicitly derived. Since no comprehensive theory exists researchers have only used regression models to examine the relationship. The potential problem with numerous studies is that the emissions-data from some countries may not reflect the actual facts (particularly countries with little environmental regulatory oversight) and could present potential problems of measurement error. Examining the data at a national level may also be doubtful because valuable information is potentially lost as the emissions data is aggregated to a national level. Nevertheless, it can be said with certainty that economic growth has a "potential" by-product in the shape of environmental degradation. The word "potential" should be noted, signifying that it is not necessary that the economic growth is achieved at the cost of healthy environment. There are ways by which we can scale economic prosperity by giving due consideration to environmental concerns. GSCM is an effective tool, that if practiced sincerely could significantly minimise, if not eliminate the chances of environmental deterioration.

3.3 Green Supply Chain Management: Managing Growth with Environmental Concerns

GSCM is an emerging concept, which has evolved tremendously over the last few years. This idea covers every stage in manufacturing from the first to the last stage of life cycle of the product to its recycling. Industries in every sector are feeling the pressure to reduce their impact on the environment. The aim is to change the traditional open-loop supply chain structures into the GSC to minimize the negative impact of the environment, increase the recycling link, to achieve material and energy recovery in order to eventually

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achieve economic and environmental benefits for the most optimized sustainable economic development by examining the companies who have already made progress at the front of GSCM, that will help others to begin their own transition.

3.4 Exploring the relation between Environmental Pollution and Development Status of a Country:

Major economies of the world, in general, also rank highly in term of environment pollution caused by them. The same is depicted in Figure-1

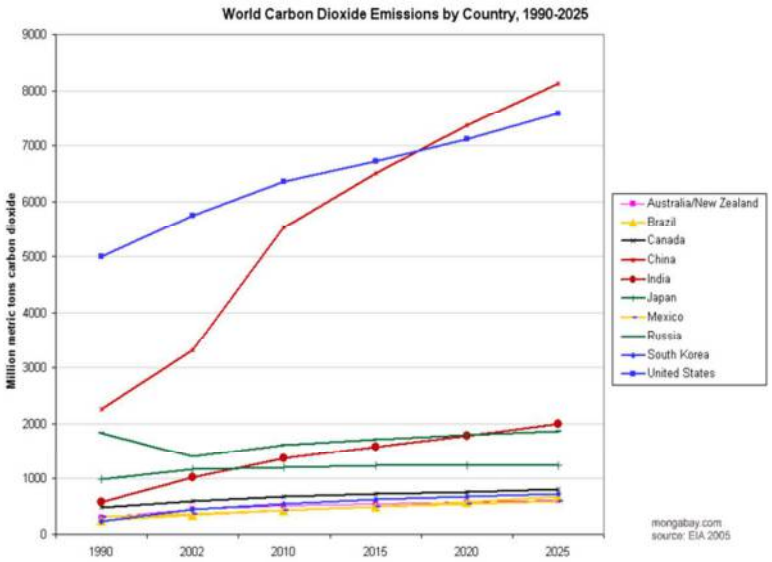

Figure-1

Source: Energy Information Administration." of the US Department of Energy (DOE), http://www.eia.doe.gov/neic/aboutEIA/copy_right.html

Conversely, there are nations as well, that are doing pretty well on the count of environmental conservation. All such countries belong to the category of developed nations; that shows that industrial progress and environmental conservation are not mutually exclusive. GSCM practices make it possible for a country to be industrially developed and eco-friendly at the same time. The topmost eco-friendly nations of the world (EPI Report, 2014) are depicted in List-I.

1. Switzerland
2. Luxembourg
3. Australia
4. Singapore
5. Czech Republic
6. Germany
7. Spain
8. Austria
9. Sweden
10. Norway

List-I: Top Most eco-friendly nations of the world

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List I and Figure-I clearly signify that it is a myth that adoption of GSCM practices has any bearing on the development status of any country. There are developed countries like USA, Japan and Russia in the list of polluting nations, and also developing countries like India, China and Mexico. Similarly, the list of eco-friendly countries has host of developed nations, and also finds the mention of Spain and Austria, that are certainly not economic power houses. It can be inferred that economic growth may or may not lead to environmental degradation, depending upon adoption of certain practices that ensure that the latter does not take place. For sure, the countries that show greater commitment towards conservation of environment are adopting a good measure of GSCM practices. Nevertheless, a substantially detailed status of GSCM adoption in developed and developing countries are discussed in the following sections.

3.5 The Indian Story: Chasing growth and environmental concerns simultaneously

India is one of the fastest growing economies in the world today. Projections from the Indian government, global financial institutions and international economic bodies indicate that India's GDP will double in the next 20 years from current levels. And so will the demand for energy, to fuel this growth, and the consequent per capita carbon emission levels. The need for India is to embark on a path of sustainable growth that will maintain the economic growth momentum while addressing the need for reducing carbon emissions through the use of green technologies. Over the next five years, it is expected to see a flurry of sustainability initiative and programmes being introduced that will lay the foundation for sustainable growth in the future. This will lead to India's spending on sustainability initiatives that impact various spheres of economy, industries and the society at large, doubling from the current levels through 2015.

3.6 GSCM: Government Regulations and Level of Adoption by Indian Corporate:

India has a lot of regulations pertaining to environmental conservation, starting from energy ratings standards by Bureau of Energy Efficiency for all kinds of IT hardware equipment's and consumer electronic equipment's to the mandatory reporting and spending on corporate social responsibility for Indian organisations. The government has set a target to increase energy efficiency by 20 per cent by 2016, and to achieve a 20 per cent to 25 percent reduction (from 2005 levels) in emission intensity by 2020. Moreover a chapter on Sustainable Development and Climate Change was introduced in the government's annual Indian Economic Survey, 2011-2012. The survey has suggested making lower- carbon sustainable growth a central element of India's 12th Five Year Plan that commenced in April 2012. This will certainly have a bearing on the adoption levels of GSCM practices by Indian firms.

3.7 Top Technologies at the forefront of Green Operations in India:

There are many existing technologies and applications that are applied to improving the sustainable performance of Indian enterprises — technologies that are mature and simply need repurposing. In addition to this, there is an emergence of a plethora of new exciting and interesting technologies and applications that will help enterprises to make both incremental and substantial improvements in sustainable performance. While there is much excitement around many of these technologies, it is important to recognise their relative maturity or immaturity and how apt they are for your organisation's critical business issues. Innovation is happening on two fronts - IT based technologies& New-age innovative technologies front. IT

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based technologies help in lowering power consumption and cooling requirements. These technologies including virtualisation, cloud computing etc. are very popular among companies. Adoption of these technologies helps to save power and reduce carbon emission. These could help industrial units for whom electricity bills constitute a large part of their operational cost. By using energy monitoring devices, various companies have successfully reduced the electricity bill by 3-4 percentage points. At the forefront are the Information technologies that are pushing ahead with GSCM practices are Environmental Health and Safety (EHS) applications, sustainability/CSR performance management systems, enterprise wide carbon and energy management, sustainable design and product lifecycle management tools, and sustainability business operations etc. On the front of New-age innovative technologies are advanced metering infrastructure, carbon capture and sequestration, intelligent transportation system, solar energy technology, building integrated PV systems, Eco labels and footprints, combined heat and power technology, e-waste, distributed power generation, and water management are very essential to usher in low carbon sustainable growth, and a variety of pilot projects funded by private organizations and government bodies are underway in many of these technology areas currently.

Major Hindrances in the adoption of GSCM Practices in India:

Prohibitive Cost:

The biggest perceived barrier to adopting GSCM is Prohibitive Costs .The biggest perceived barrier [26% of respondents] to adopting GSCM practices is that it is cost prohibitive, followed closely by it being too complicated to implement [25% of respondents]. Almost a third of the companies surveyed [17%] felt that there were no financial incentives to justify adopting GSCM. Lack of executive support was not felt to be a significant barrier. Insufficient technology was only perceived by one in five respondents as a barrier. The message seems clear that if GSCM makes financial sense and is easy to implement, chances for adoption are much higher.

Lack of Awareness:

According to the individuals surveyed, the most important issue facing manufacturing sectors in India is the lack of awareness about environmental issues [51%] followed by waste disposal [40%]. Others issues such as conserving natural resources and green buying preferences were also in concern. The challenge of complying with government regulations came out as the least important issue, although it was still cited by one in five respondents as important. Open ended responses raised additional pertinent issues. For example, there is a strong need to ensure that the standards and protocols of retail customers in the Indian market are clearly communicated in India with partner factories and their management. Other concerns included overproduction of goods, green packaging, green energy and complying with chemical & hazardous materials regulations. The bright side to a lack of awareness about environmental issues is that it can easily be addressed through education. The general signs are optimistic that Indian manufacturing sector is moving in the direction of making its operations more eco-friendly. 51% of manufacturing industries feel that lack of awareness of environmental issues is the biggest issue facing manufacturing sectors in India.

Dithering with Implementing Green Initiatives:

On an approximate basis, one in six of the industries surveyed state they would be implementing GSCM initiatives in the next six months. Another one-third plan to implement green initiatives within the next six months to two years. More than one in five [24% of industries have no initiatives planned and another one in five [24%] are not sure about their

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company's plans. 36 % of manufacturing industries have plans to implement GSCM initiatives within 2 years.

3.8 GSCM Initiatives taken by Indian firms:

Green sourcing & procurement focused initiatives using electronic processes:
Leveraging the might of IT based tools, Indian firms are creating efficiencies in sourcing and procurement, that was top initiative cited to majority of industries. Other initiatives such as employing environment friendly design and product lifecycle management and working with suppliers on sustainability and GSCM guidelines were almost equally planned and implemented initiatives in manufacturing sectors of India. Training and development of internal staff, suppliers and clients were also cited as important initiatives. Reducing use of paper in contract and auditing suppliers were the least commonly implemented initiatives (both cited by less than a 3rd of respondents). The indicators here are positive and suggest that as technology improves and supply chains become more efficient, green practices will become more prevalent. Nearly half of Indian companies use electronic processes to create efficiencies in sourcing & procurement.

Green productions & manufacturing focused initiatives
Given that recycling is a concept that has time and support to be success should be adopted by consumers and the broader society, even in Indian manufacturing sector, it's not surprising that utilization of fuel efficient tools & machine initiatives are a priority for companies. Recycling programs for raw materials and for reusable component parts were the most common green production and manufacturing focused initiatives. Applying carbon off-setting was a distant priority. Carbon offsetting is a relatively new and abstract concept that will take time to adopt. Other green production and manufacturing initiatives that Indian manufacturing companies are implementing include the introduction of "returnable and reusable packaging, reducing the usage of solvent based chemicals and choosing compliant factory and supplier partners.

Green warehousing & distribution focused initiatives
Most companies seem to be quite advanced in the implementation of green warehousing and distribution initiatives, most likely because these initiatives often mean improved efficiency. Companies appear to be most ahead in green practices in their inventory reduction and product handling [53%] have already implemented initiatives; and their ability to consolidate orders [44%] have already implemented these initiatives; and usage of reusable containers and storage equipment , where [57%] have already implemented these initiatives. When it comes to reducing energy consumption through the use of solar panels or green roofing options, surprisingly [14 %] of companies have already adopted such initiatives. Similarly around [22%] of companies report that they have already optimized the location of their distribution hubs. While these types of initiatives show direct cost and efficiency benefits, the up-front cost associated with them may be the reason why other companies have not adopted them.

Green transportation focused initiatives
Manufacturing Companies in India are also fairly well advanced in the types of green transportation. Similar to their production and warehousing initiatives, there is a crossover between implementation of green and levels of efficiency. Almost half of companies

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surveyed are already periodically services of the vehicles at service stations along reducing empty miles, truck idle time and increasing cube utilization to create efficiency. Adoption of more sophisticated green transportation measures which have less direct relation to efficiency and cost savings are not in wide practice. These more advanced green transportation measure such as using more aerodynamic trucks [9%] and more alternative fuel powered trucks are all adopted by [11%] or less of companies.

4. Conclusion

As Indian economy expands to new frontiers, the industrial activity in the country braces itself for manifold growth, fuelling fears of adverse impact on environment. The industrial growth of the country cannot be compromised at any cost; and this causes genuine concerns for the conservation of environment in the midst of all ensuing industrial growth. Nevertheless, in contrary to the general belief that economic development has a direct correlation with the environmental degradation, GSCM offers a glimmer of hope on the front of developing eco-friendly supply chains across various industrial sectors.

There are many developed countries that have been very eco-friendly in their industrial undertakings, and have made tremendous strides at the front of green industrial operations, without affecting their profits and other organisational objectives in a negative way. Rather, GSCM has helped them to save on resources and streamlining their supply chains for better. Developing countries, in contrast, have not fared equally well on environment conservation front while achieving their industrial and economic growth. The distinguishing factor between the developed and developing economies that accounts for the difference in pollution and environmental degradation caused by them is the extent of adoption of GSCM by them. China, a developing nation, despite its dismal record on environmental pollution caused by rapid industrialisation, is making quick strides on the issue of GSCM as its government has realised the gains that the management tool can extend to its industrial sector. India despite it substantial progress on the front, still remains in transition stage with respect to adoption of GSCM. The spread of GSCM is not uniform across the Indian industrial horizon, and there are only few players who have realised that GSCM is more of a necessity rather than an option for them, in the new order of global industrial scene.

Till now the interest shown by Indian companies in adoption of GSCM in their respective organisations is not much enthusiastic; as is evident from the pollution caused by its industrial units. Nevertheless, the future of GSCM adoption in the country is not bleak, as a number of companies have shown increased interest in saying yes to eco-friendly practices. As India becomes R&D destination because of adequate skilled manpower, available at cheap costs, there is optimism of emergence of innovative green technologies fuelled by research works and technology transfer. These technologies will percolate in industrial undertakings of the country making them more environment friendly. There is enormous potential for promoting GPP in the country, but that will require providing of adequate number of legislations governing the issue of green procurement, and their strict enforcement on ground. The legislations on the issue of securing eco-friendly industrial operations are in place, but are not adequately enforced resulting in gross damage to environment by erring industries. There is a need to revise them to give them more sinew, and should be enforced strictly to set exemplary precedence for various stake holders of supply chains. Customer awareness with respect to their part in greening the supply chain is negligible, which is largely due to lack of their knowledge regarding their roles and involvement in GSCM. This results in slow progress made by country on the front of adoption and implementation of GSCM. Furthermore, in India major of stakeholders of supply chains are unaware of the value of

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waste generated, and are thus oblivious of the concept of Reverse Logistics. Though RL is visible in a crude form across Indian industrial scene, yet there is general absence of a systematic structure to recycle waste and generate value out of it.

Nevertheless India has witnessed appreciable endeavours by various corporate houses and successive governments in making serious attempts to embrace environment friendly industrial practices. This auger well for the spread of GSCM in India, in coming times. It is hoped that in near future, there will be immense escalation in awareness and adoption levels of GSCM amongst various stakeholders of supply chains of various industries in the country. Hopefully, Indian manufacturers, industrialists and corporate houses will exhibit greater responsibility towards safeguarding environment for a healthy future for coming generations, which will be manifested by greater and more comprehensive adoption of GSCM practices at their end.

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Impact of device parameter variation on RF performance of gate electrode workfunction engineered (GEWE)-silicon nanowire (SiNW) MOSFET

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Abstract In this paper, we explore the quantitative investigation of the high-frequency performance of gate electrode workfunction engineered (GEWE) silicon nanowire (SiNW) MOSFET and compared with silicon nanowire MOSFET(SiNW MOSFET) using device simulators: ATLAS and DEVEDIT 3D. Simulation results demonstrate the improved RF performance exhibited by GEWE-SiNW MOSFET over SiNW MOSFET in terms of transconductance (g_m), cut-off frequency (f_T), maximum oscillator frequency (f_{MAX}), power gains (Gma, G_{MT}) parasitic capacitances, stern's stability factor and intrinsic delay. Further, using three-dimensional device simulations, we have also examined the efficacy of parameter variations in terms of oxide thickness, radius of silicon nanowire, channel length and gate metal workfunction engineering on RF/microwave figure of merits of GEWE-SiNW MOSFET. Simulation result reveals significant enhancement in f_T and f_{MAX}; and a reduction in switching time in GEWE-SiNW MOSFET due to alleviated short channel effects, improved drain current and smaller parasitic capacitance, thus providing detailed knowledge about the device's RF performance at such aggressively scaled dimensions.

Keywords Power gains · GEWE · RF · Silicon nanowire MOSFET · Parasitic capacitance · f_T and f_{MAX}

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1 Introduction

Silicon based transistors have become an appealing low cost solution for many low power and high frequency applications such as mobile telecommunication. The relentless scaling of CMOS toward nanometer-scale gate lengths has produced MOSFETs with digital and RF performance that is suitable for mixed signal applications [1–4]. However, scaling down arises the so-called SCEs such as mobility degradation, hot carrier effects, drain induced barrier lowering, parasitic capacitances etc. making the scaled devices inapt for RF/wireless applications [5]. To surpass these hindrances, new device architectures with 3-D gate structures have been intensively studied. Among them, cylindrical gate MOSFET [6] has emerged as a most promising candidate in recent years. Recently, many theoretical and experimental studies on cylindrical gate MOSFET have been reported in literature to eliminate SCEs, to achieve high transconductance and nearly ideal subthreshold slope (60 mV/decade) [7,8]. It allows excellent electrostatic control of the gate over the channel hence overcoming the scaling limitations caused due to the SCEs, thereby improving the device performance. Further, Silicon nanowire emerged as a most promising in electronic devices due to the fact that its properties such as concentration, dopant type can be changed during synthesis. Also, its mobility is higher than bulk silicon due to stronger quantum confinement. The body thickness (diameter) of the nanowire can readily be reduced to a few nanometers in size scale that is challenging to obtain using bulk silicon. Therefore, to get further improvement against SCEs the concept of silicon nanowire MOSFET was put forward by Cui et al. [9] in 2003 concluded that silicon nanowires MOSFET as building blocks for future nano-electronics. Also, the small volume and low leakage current of nanowire MOSFETs make them attractive for high density memory arrays

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and logic chips [10,11]. Yang et al. [12] fabricated vertical gate-all-around silicon nanowire MOSFET and showed excellent transistor characteristics compared to conventional devices. Also it was proven that it has a merit of outstanding maximum oscillation frequency (f_{MAX}) [13].

In 1989, Shur introduced the notion of split gate which escalate the carrier transport efficiency of device [14]. But the misalignment of two gates during fabrication and fringing capacitances between the gates limits the device speed. Hence, to overcome this drawback, gate electrode workfunction engineering scheme was proposed by Zhou and Long [15] in 1999. With this scheme, there is appreciable reduction in the SCEs, improvement in current capabilities due to two dissimilar metal gates and reduction in electric field at the drain end thus providing hot-carrier reliability [16]. Pal et al. [17] reported a 2-D analytical drain current model of DMG-GAA MOSFET which employs gate material engineering scheme to reduce SCEs. To incorporate the advantage of gate electrode engineering scheme, combined with silicon nanowire MOSFET, a novel device structure called gate electrode workfunction engineered (GEWE) silicon nanowire (SiNW) MOSFET is proposed [18]. Recently, we have reported the hot-carrier performance and [19] and analog behaviour of GEWE-SiNW MOSFET [20].

However, the reported work mentioned above not discuss about the Quantum RF behaviour of GEWE-SiNW MOSFET and the impact of device parameter variation especially radius, length and oxide thickness. Moreover, due to the increased demand for high-speed electronics products, the accurate analysis of MOSFET at high frequencies (HF) is necessary to represent the behavior of device in microwave circuits and systems [21]. Therefore, in this paper, for the first time we carried out the quantum 3D-numerical simulation of GEWE-SiNW MOSFET in terms of RF FOMs to study the effect of HF (GHz) on the performance of GEWE-SiNW MOSFET and simulations results so obtained are compared with the conventional SiNW MOSFET. Further, Sect. 2 describes the device structure and its default parameters followed by simulation methodology. Section 3 contains the results obtained by device variation and also explores the dependency of GEWE-SiNW MOSFET's performance on metal workfunction at the drain end, gate oxide thickness, channel length and radius of silicon nanowire which would be indispensable for optimizing the device designs at millimeter range frequency.

2 Device structure and its description

Figure 1a, b shows the simulated device structure of SiNW MOSFET and GEWE SiNW MOSFET respectively. All simulations have been performed using ATLAS and DEVEDIT 3D device simulator. The Source/Drain region is highly

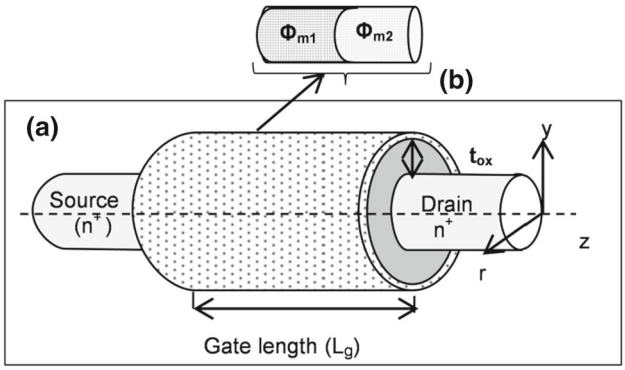

Fig. 1 Schematic cross-sectional view of **a** SiNW MOSFET and **b** GEWE-SiNW MOSFET

doped with n-type impurity of a length of 5 nm. The silicon nanowire is doped with a p-type impurity and t_{ox} thick oxide layer is embodied in it as shown in Fig. 1. In order to fairly analyze the device performances, both the devices are optimized to have the same threshold voltage, i.e., 0.4 V. In this simulation, all the junctions of the structure are assumed to be abrupt and the biasing conditions are considered at room temperature (T = 300 K) with the doping profiles being uniform. The detailed description of default parameters used in the simulations is shown in Table 1. Further, two numerical techniques Gummel and Newton have been considered to obtain the solutions [22]. To obtain the convergence in the inversion region, the DIRECT parameter is added for more robust solution.

2.1 Simulation methodology and calibration

All the simulations have been performed using following models as shown in Table 2.

It is important to define the carrier transport with proper models to characterize the device performance accurately. The most popular one is drift-diffusion (DD) model, which is widely used in engineering field. For deep submicron device simulation, the hydrodynamic transport model is commonly used to examine in detail the carrier energy in the carrier transport. It is argued that hydrodynamic model produces the carrier velocity overshoot even in the ballistic regime, which overestimates the drain current level [23]. Furthermore, the quantum confinement effect in the deep scaled device may not be negligible [24]. This is because the inversion charge layer thickness in the conducting silicon nanowire channel is comparable to the nanowire dimension. Therefore, the quantization effect model is included in the device simulation. Bohr Quantum Potential (BQP) Model [25] with alpha = 0.5 and gamma = 1.2 was used to take quantum mechanical effects into consideration.

The calibration of model parameters used in simulation has been performed according to the published results

Table 1 Default design parameters used in the analysis

Design parameters of SiNW and GEWE-SiNW MOSFET device design	
Channel length (L_g)	30 nm
Substrate doping (N_A)	1×10^{16} cm^{-3}
Radius of Nanowire (R)	5 nm
Source/drain doping (N_D^+)	1×10^{19} cm^{-3}
Physical oxide thickness (t_{ox})	1.5 nm
Permittivity of SiO_2 (ε_{ox})	3.9
Gate to source voltage (V_{gs})	0.7 V
Drain to source voltage (V_{ds})	0.2 V
Work function for SiNW-MOSET (Φ_m)	4.8 eV
Work function for GEWE-SiNW MOSFET	Φ_{m1} = 4.8 eV (Gold)
	Φ_{m2} = 4.4 eV (Titanium)

The design parameters as discussed above are the default parameters used in the analysis, unless otherwise stated

Table 2 Simulations model

S. No.	Physical models	Description
1.	Mobility models	*Lombardi CVT and Constant Low Field Mobility Model*
2.	Recombination model	*Shockley Read Hall (SRH)* Recombination is included to incorporate minority recombination effects with carrier lifetime = 1×10^{7} s
3.	Statistics	*Boltzmann Transport model*, The use of Boltzmann statistics is normally justified in semiconductor device theory, but Fermi-Dirac statistics are necessary to account for certain properties of very highly doped (degenerate) materials
4.	Impact ionization and tunneling model	No such model is used in current work as we are not interested in evaluating hot-carrier performance
5.	Energy transport model	*Hydrodynamic Model* is used as it includes all nonlocal effects and is more accurate than the drift-diffusion method [22]. Drift diffusion Model show short comings as channel length scales down to 50 nm
6.	Quantum mechanical model	*Quantum Mechanical Model* plays an important role in determining the performance of surrounding gate MOSFET In this paper we take into account QMEs

obtained by Gnani et al. [26], using above models and calibrated results are shown in Fig. 2a in order to validate the simulations. Figure 2b shows the drain current and gate transconductance characteristics of GEWE-SiNW MOSFET at drain bias 0.2 V. As it is shown in Fig. 2b, the current driving capability of nano-scale GEWE-SiNW MOSFET is enhanced by 20 % in comparison to SiNW MOSFET. This enhancement

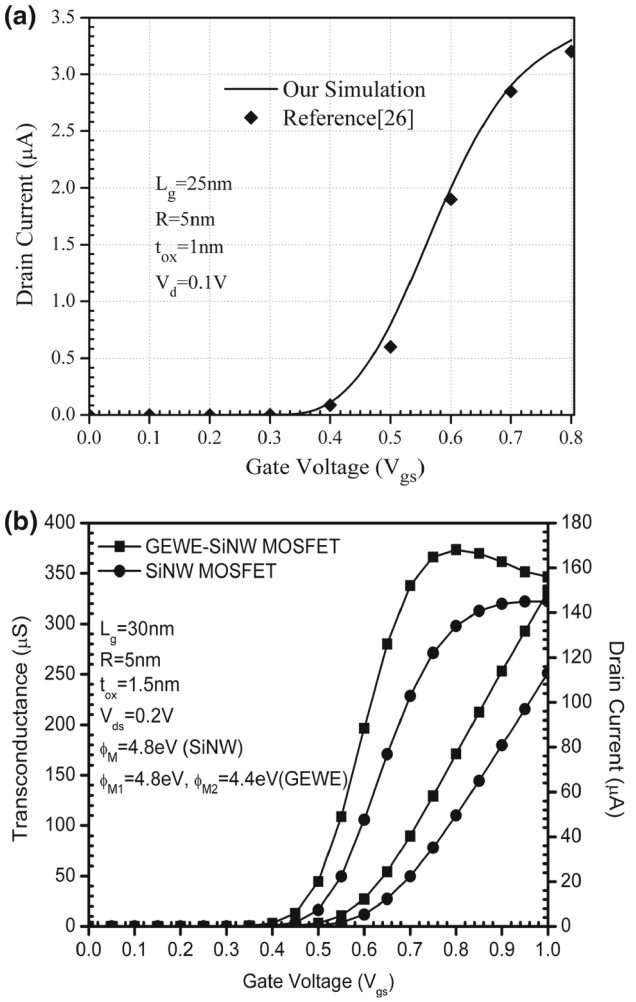

Fig. 2 **a** Calibration with the published result, $I_{ds}-V_{gs}$ characteristics of silicon nanowire MOSFET, **b** transfer and transconductance characteristics of silicon nanowire and GEWE-silicon nanowire MOSFET at V_{ds} = 0.2 V respectively

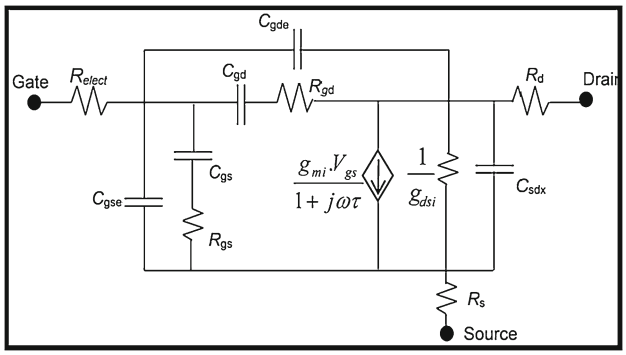

Fig. 3 Non-quasi-static (NQS) equivalent circuit model of SiNW MOSFET at RF region operating in the strong inversion region

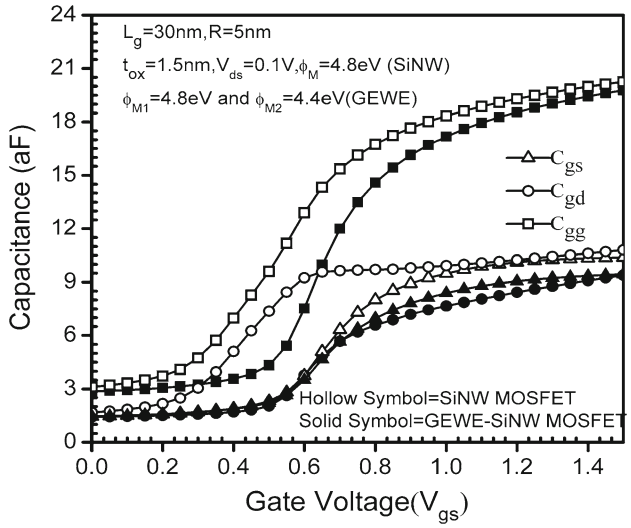

Fig. 4 Intrinsic capacitances of SiNW MOSFET and GEWE-SiNW MOSFET as a function of Vgs

is due to incorporation of gate-metal engineering scheme which causes gradual step change of surface potential at the interface of two metals and hence increases gate efficiency of device. The MOSFET transconductance ($g_m = \partial I_{ds}/\partial V_{gs}$) is typically measured in the linear regime and is used as an indirect monitor of inversion carrier mobility. Transconductance is useful in designing linear amplifiers and does not have any significance in switching power supplies. In general, the larger the transconductance of a device, the greater the gain (amplification) it is capable of delivering, when all other factors are held constant. It is clearly evident from Fig. 2b that transconductance of GEWE-SiNW is higher in comparison to conventional SiNW MOSFET due to enhanced on-current. Also, significant enhancement in g_m of our device is obtained as compared to previously reported work [27].

3 RF performance metrics inquisition

In deep sub micrometer regime, it is very challenging to design RF devices for ultra-low power applications due to aggressive scaling of MOSFETs. In this section, we investigate the comparison of conventional SiNW and our device in which we incorporated GEWE scheme onto conventional SiNW MOSFETs to examine the efficacy of high frequency in terms of RF metrics. Further, the impact of device parameters variation of GEWE-SiNW MOSFET on the same has been studied.

Figure 3 shows the non-quasi-static equivalent circuit of a MOSFET to extract small signal parameters of GEWE-SiNW MOSFET and conventional silicon nanowire MOSFET that is based on conventional MOSFET's small signal microwave modeling. Here, R_s and R_d are source and drain resistances respectively. R_{gs} and R_{gd} are distributed channel resistance and C_{gde} and C_{gse} are extrinsic gate-to-drain and gate-to-source capacitances respectively. g_{dsi} and g_{mi} are intrinsic gate-to-drain conductance and transconductance. C_{ds} and C_{gs} are intrinsic gate-to-drain and gate-to-source capacitances respectively [28]. The capacitances between each pair of electrodes are calculated through AC small signal analysis after post processing operation of DC solution.

Parasitic capacitance in RF amplifiers may cause these amplifiers to have low gain due to parasitic loss. In some cases, it may cause these amplifiers to oscillate. In digital switching circuits, the rise time and fall time of the digital signal greatly affect the maximum speeds achievable [29]. The intrinsic parasitic capacitances are extracted from small signal analysis after post processing operation of DC solution at an operating frequency of 1 MHz. The parasitic capacitance on the inputs and outputs of the digital devices increases the rise and fall times. Thus, it is required to investigate the parasitic capacitances at high frequency. Figure 4 shows the variation of bias-dependent parasitic capacitances such as gate–source (C_{gs}), gate–drain (C_{gd}) and gate-gate (C_{gg}) capacitance as a function of gate voltage for GEWE-SiNW MOSFET and SiNW MOSFET. The capacitance value changes depending on the voltage that appears across the drain source and also across the gate source of the device. It is evident from Fig. 4 that GEWE-SiNW exhibits smaller C_{gs}, C_{gd} in comparison to its conventional SiNW MOSFET due to metal gate workfunction difference which results in improved screening of conducting channel from drain bias variations. A similar kind of behaviour is also observed in Ref. [30].

A parameter generally described when comparing transistors for RF applications is the cut-off frequency, f_T [31,32]. f_T is a specification for high-speed digital applications (speed and high swing) and can be defined as follow:

$$f_T = \frac{g_m}{2\pi\left(C_{gs} + C_{gd}\right)} \tag{1}$$

where g_m is the transconductance, C_{gs} and C_{gd} are parasitic capacitances.

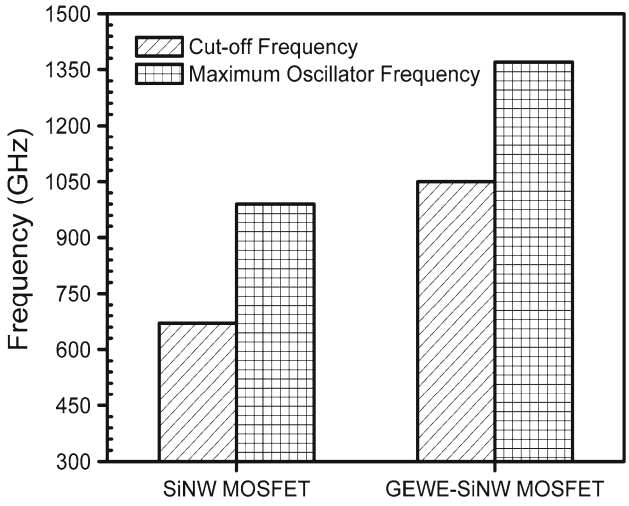

Fig. 5 Cut-off and maximum oscillator frequency of SiNW MOSFET and GEWE-SiNW MOSFET at $V_{gs} = 0.7$ V and $V_{ds} = 0.2$ V

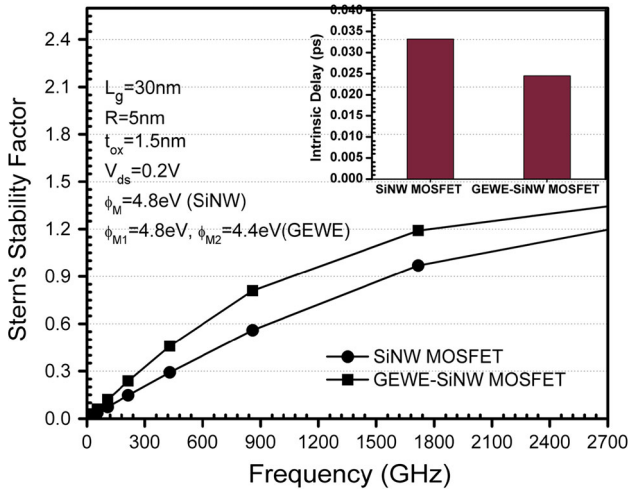

Fig. 6 Stern's stability factor of SiNW and GEWE-silicon nanowire MOSFET. *Inset* intrinsic delay of SiNW and GEWE-silicon nanowire MOSFET at $V_{ds} = 0.2$ V

Also, the incorporation of GEWE design enhances the carrier mobility of a device, leading to increase in cut-off frequency as is evident from Fig. 5. For characterizing a device for tuned RF amplifiers and oscillators, maximum oscillation frequency is an important parameter to consider. f_{MAX} is the maximum oscillation frequency which is defined as the frequency where the maximum unilateral power gain falls to unity (0 dB) [33].

$$f_{MAX} = \frac{f_T}{\sqrt{4R_g\left(g_{ds} + 2\pi f_T C_{gd}\right)}} \tag{2}$$

Further, f_{MAX}, as is seen from Fig. 5, is higher for GEWE-SiNW MOSFET than SiNW MOSFET, which is due to higher parasitic capacitance in the conventional SiNW MOSFET, thereby giving the GEWE-SiNW design a new strength for switching applications and wireless communication.

Intrinsic Delay is another important measure for switching application. The increasing capacitance between the gate and the overlapped S/D region deteriorates the intrinsic gate delay [34]. Intrinsic delay metric is defined as:

$$\tau = \frac{C_{gg}.V_d}{I_{ON}} \tag{3}$$

where C_{gg} is the parasitic gate capacitance, V_d is the bias voltage applied to drain and I_{ON} is the on-current.

Inset of Fig. 6 shows the comparison of GEWE-SiNW with SiNW MOSFET in terms of intrinsic delay parameter. As is evident from the figure, there is notable reduction in intrinsic delay of GEWE-SiNW MOSFET than its conventional counterpart due to incorporation of two dissimilar metal gates and cylindrical silicon nanowire which increases on-current, reduces parasitic capacitances and which leads to considerable reduction of intrinsic delay. Power gains play an important role in designing RF amplifiers. For low noise amplifier (LNA) design, maximum available power gain and stability are two important criterions. Stability measures the ability of LNA to oscillate at high frequencies. When designing an amplifier for RF frequency range, our aim is to get void of any oscillations. The standard way to scrutinize stability is by so-called stern stability factor. The stern's stability factor (K) is usually less than 1 at low frequency and greater than 1 at high frequency [35,36]. The factor K is defined as in the following equation:

$$K = \frac{1 + |\Delta|^2 - |S_{11}|^2 - |S_{22}|^2}{2.|S_{12.} \cdot S_{21}|} \tag{4a}$$

where, S_{11} and S_{22} are the reflection coefficients and S_{12} and S_{21} are transmission coefficients and s-matrix Δ is defined as

$$\Delta = S_{11} \times S_{22} - S_{12} \times S_{21} \tag{4b}$$

Figure 6 shows the variation of stability factor as a function of frequency. As is clear from the figure, at high frequency K is significantly higher for GEWE-SiNW in comparison to SiNW MOSFET. This is due to increased gate control, which causes maximum power transfer from source to load. Figure 7 shows the improvement of HF maximum available power gain (Gma) of GEWE-SiNW MOSFET over SiNW MOSFET. This is due to better gate controllability and higher silicon nanowire mobility which results in enhanced transconductance and reduced parasitic capacitances. Also, Maximum transducer power gain (G_{MT}) of a two port network is defined as the ratio of average power delivered to the load by a source to a maximum available power from the

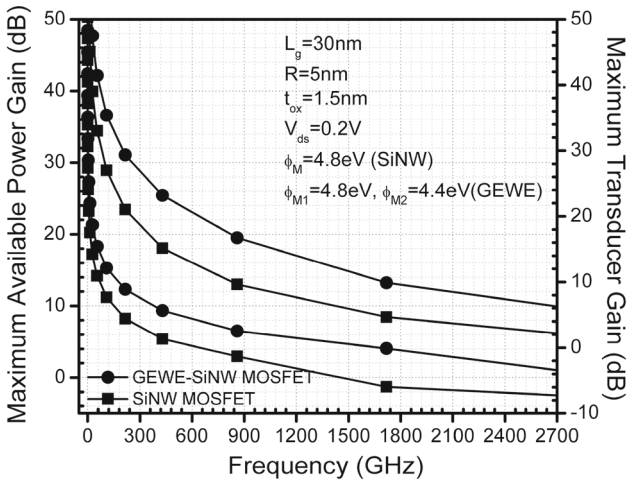

Fig. 7 Maximum available power gain and maximum transducer power gain of SiNW and GEWE-silicon nanowire MOSFET at $V_{ds} = 0.2\,V$ and $V_{gs} = 1.0\,V$

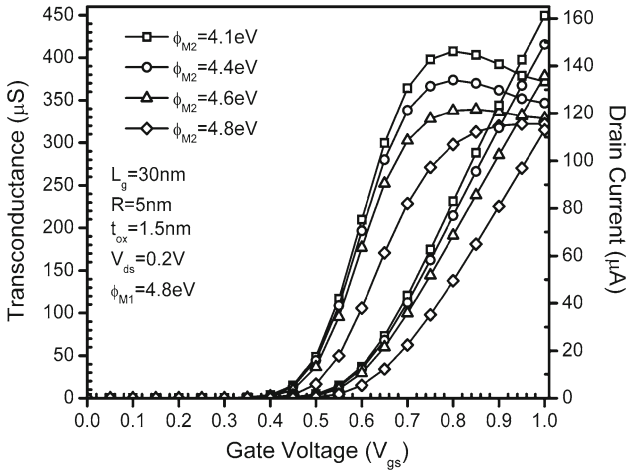

Fig. 8 Transfer and transconductance characteristics of GEWE-silicon nanowire MOSFET at $V_{ds} = 0.2\,V$

source. This is a measure of efficacy of the two ports [37,38]. Figure 7 evaluates the device performance in terms of maximum transducer gain. As it clear from the graph that G_{MT} is improved in GEWE-SiNW in comparison to SiNW. This enhancement is due to integration of GEWE design onto silicon nanowire which augments current driving capability and results in higher power at the load end i.e. at drain end, hence suitable for RF/wireless applications.

3.1 Effect of gate metal engineering

In this sub-section, we examine the effect of metal workfunction engineering on the RF metrics of GEWE-SiNW MOSFET by keeping the workfunction at the source side constant and varying the workfunction of metal gate at the drain end.

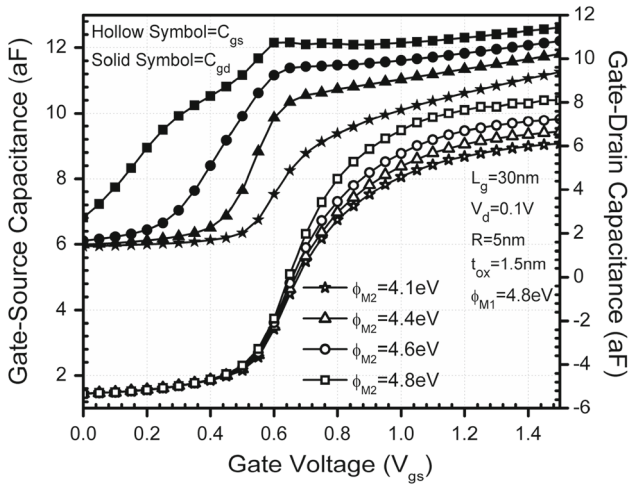

Fig. 9 Gate-source and gate-drain capacitance of GEWE-silicon nanowire MOSFET as a function of gate voltage for various metal workfunction values at $V_{ds} = 0.2\,V$

Figure 8 indicates the transfer and transconductance characteristics of GEWE-SiNW MOSFET for different values of metal workfunction at drain side (Φ_{M2}). As is evident from Fig. 8 that as we increase the workfunction difference from 0 to 0.2 eV, the on current increased by 10.13 % and further increment in workfunction difference to 0.7 eV, results in 20 % enhancement in drain current. Also, significant enhancement in transconductance is observed as we decrease the metal workfunction at the drain end due to better improvement of carrier transport efficiency with increase in workfunction difference as stated in [39], thus, signifying the suppression of short channel effects.

Figure 9 depicts that there is prominent degradation of parasitic capacitances as we increase the metal gate workfunction difference. Capacitance decreases due to enhanced screening of channel region from drain bias variations thus, reducing the turn-on delay time.

Figure 10 compares the cut off and maximum oscillator frequency of GEWE-SiNW MOSFET for different metal workfunction. It is clearly evident from Fig. 10 that as the metal work function at the drain end decreases, the cut off frequency increases which leads to higher switching speed. Further, with increase in metal workfunction difference, the cut-off frequency increases as is shown in Fig. 10. This is due to enhanced gate control over channel and screening of potential from the drain side, which increases the transconductance, leading to increase in cut-off frequency and device packaging density, thereby making the device suitable for CMOS wireless applications. Also, the use of metal gates results in reduced gate resistance, and hence increases f_{MAX}. An appreciable accretion of maximum oscillation frequency is observed by increasing gate metal workfunction difference due to reduced parasitic capacitances as is shown in Fig. 9.

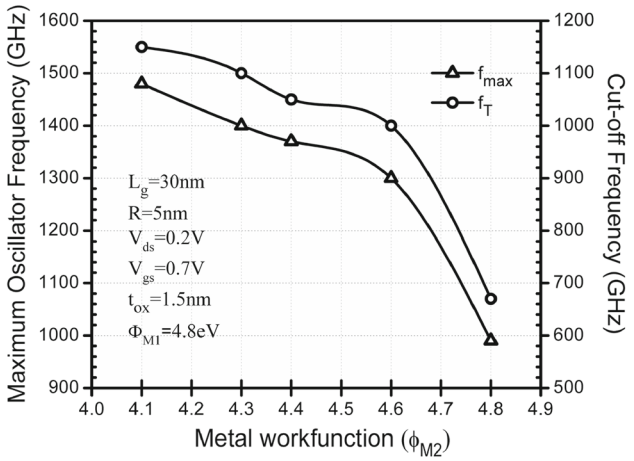

Fig. 10 Cut-off and maximum oscillator frequency of GEWE-SiNW MOSFET for various metal workfunction values

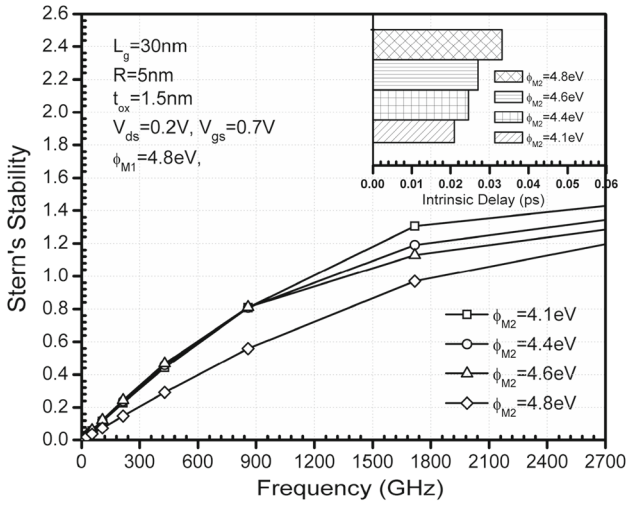

Fig. 11 Stern's Stability factor of GEWE-SiNW MOSFET for various metal workfunction values. *Inset* intrinsic delay of GEWE-SiNW MOSFET for various metal workfunction values

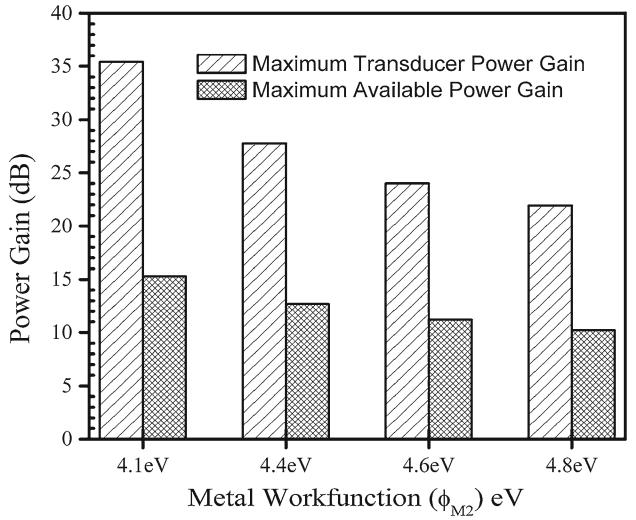

Fig. 12 Maximum available power gain and maximum transducer power gain of GEWE-SiNW MOSFET as a function of Φ_{M2}

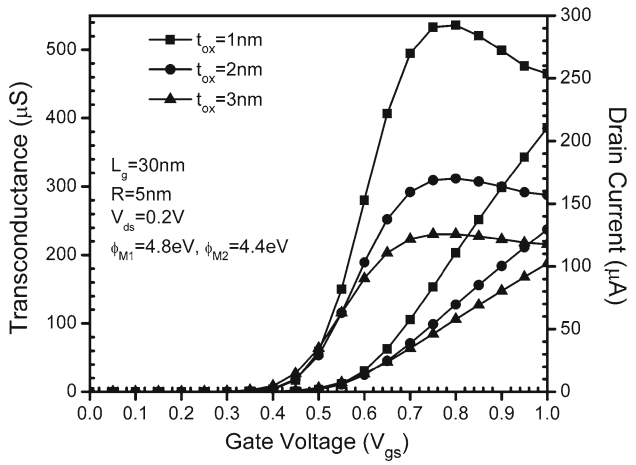

Fig. 13 Transfer and transconductance characteristics of GEWE-silicon nanowire MOSFET at $V_{ds} = 0.2$ V for different oxide thickness

Further, increasing the metal workfunction difference increases the K-factor as shown in Fig. 11. This is due to improvement of screening effect and I_{on} thus, maximizing power transfer from source to load. Hence, GEWE-SiNW is suitable for low noise amplifier and RF applications. Also, with increase in metal workfunction difference, delay reduces due to enhanced gate control and redistribution of electric field in the channel which results in higher mobility leading to improvement in carrier transport efficiency as shown in inset of Fig. 11.

G_{MT} also improves with the tuning of metal gate workfunction at drain end. Since, higher the metal gate workfunction difference, higher the electric field in the channel due to which mobility increases and hence significantly enhances the power gain. Further, tuning of structural parameters of GEWE-SiNW in terms of increased metal workfunction difference can enhance Gma as is evident from Fig. 12 due to enhanced transconductance owing to improved carrier efficiency and alleviated SCEs. Thus, GEWE-SiNW MOSFET proves to be a promising candidate for RF amplifiers and high speed applications.

3.2 Effect of oxide thickness

This section studies the impact of oxide thickness on RF metrics. It is clearly evident from Fig. 13 that scaling down the gate oxide thickness from 3 to 1 nm results in a better gate controllability over the channel which significantly enhances the driving current capability and improves the transconductance. This overcomes the drawback of mobility degradation due to increased channel doping. When oxide thickness

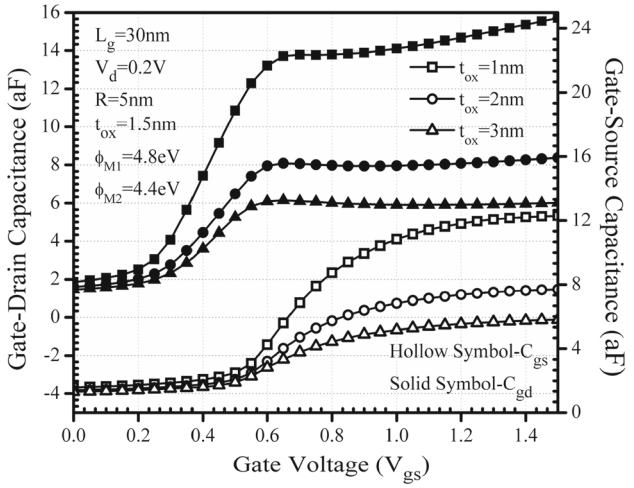

Fig. 14 Gate-drain and gate-source capacitance of GEWE-silicon nanowire MOSFET as a function of gate voltage for different oxide thickness

scales down from 3 to 1 nm, the on-current increases by 77 % and transconductance by approximately 100 % thereby, reflecting significant improvement in SCEs at sub-nm range.

However, at high frequencies the picture is completely reversed, where the efficacy of the gate oxide capacitance dominates the RF behavior of devices. Figure 14 reflects the intrinsic parasitic gate-source and gate-drain capacitances as a function of gate voltage. It can be seen that as oxide thickness increases, parasitic capacitances decreases due to reduction in inversion charge. The same trend is shown by Pati et al. and Dastjerdy et al. [40,41]

The enhancement of transconductance due to better gate control on the channel for oxide thickness 1 nm compared to 3 nm does not counter balance the effect of the gate capacitances. As a result, $t_{ox} = 3$nm has better cut-off frequency and maximum oscillator frequency as can be clearly shown in Fig. 15 a, b. Further, current gain and unilateral power gains are extracted for determining the values of cut off frequency and maximum oscillation frequency respectively.

In addition, the Stern's stability factor also significantly improves as oxide thickness scale down from 3 to 1 nm as shown in Fig. 16. This enhancement is due to higher value of transconductance and better gate controllability.

Inset of Fig. 16 shows the intrinsic delay ratio of GEWE-SiNW MOSFET for three different oxide thickness. Since, delay depends upon gate capacitance and transconductance, therefore, intrinsic delay reduces as oxide thickness increases. Hence, scaling of oxide thickness significantly degrades the speed and the matching of the device in RF circuits.

Moreover, power gains such as maximum available power gain and maximum transducer gain also increseses with thinning of gate oxide as clearly is evident from Fig. 17, thus, providing maximum voltage gain.

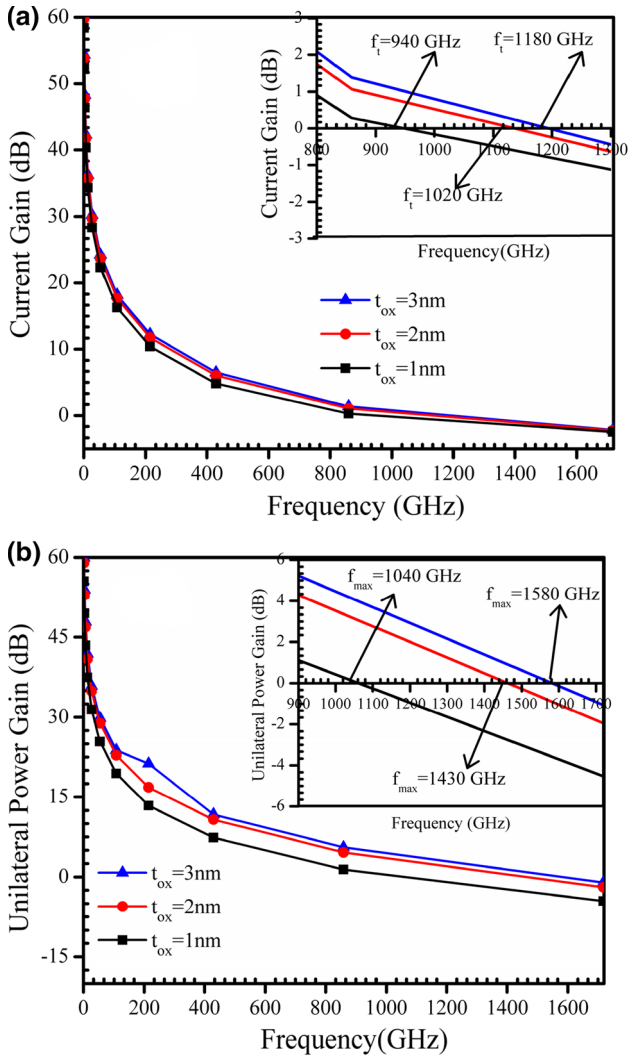

Fig. 15 **a** Cut-off frequency of GEWE-SiNW MOSFET at $V_{ds} = 0.2$ V for different oxide thickness as a function of gate voltage, **b** Current Gain of GEWE-SiNW MOSFET for different oxide thickness

3.3 Effect of channel length (L_g)

In this section, the impact of channel length is studied on various parameters.

Figure 18 shows as we scale down the channel length of silicon nanowire, the transfer characteristics improves due to better gate controllability and incorporation of dissimilar metal gates. This enhances the transconductance of device, and hence overcomes the SCEs associated due to scaling of channel length. Further, Fig. 19 depicts that there is a prominent degradation of gate-source and gate-drain capacitances. Since, as we reduce the channel length the inversion charge density of nanowire increases which results improvement in mobility across the channel due to reduction in scattering from nearby atoms and hence results in reduction in C_{gs} and C_{gd}.

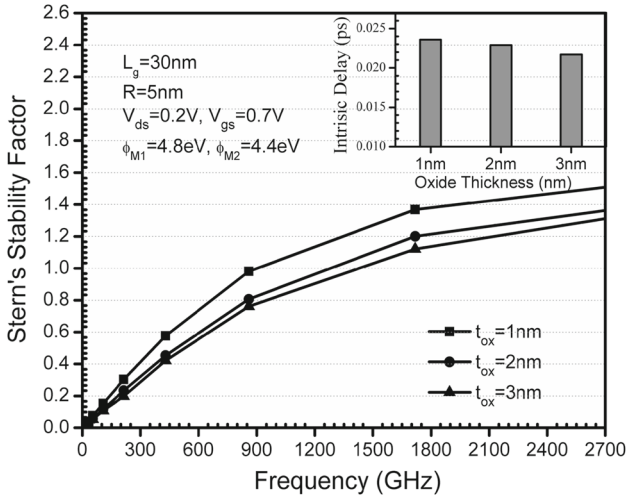

Fig. 16 Stern's stability factor of GEWE-SiNW MOSFET for various metal workfunction values. *Inset* intrinsic delay of GEWE-SiNW MOSFET at $V_{ds} = 0.2$ V for different oxide thickness

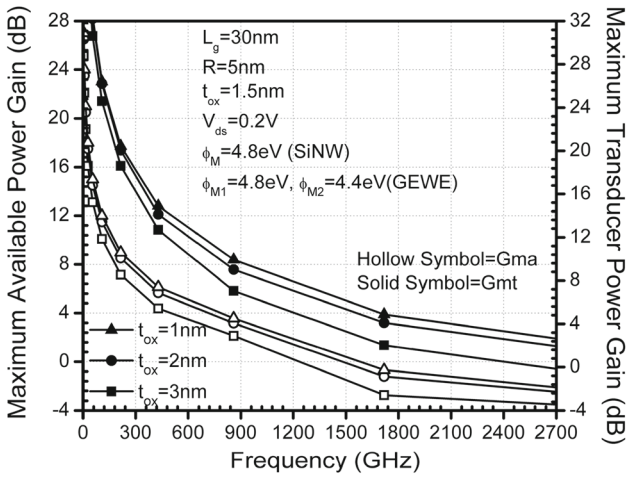

Fig. 17 Maximum available and maximum transducer power gain of GEWE-SiNW MOSFET for different oxide thickness

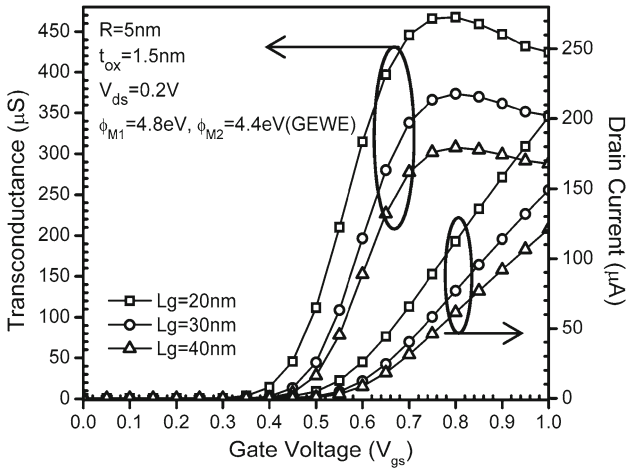

Fig. 18 Transfer and Transconductance characteristics of GEWE-silicon nanowire MOSFET for different channel lengths

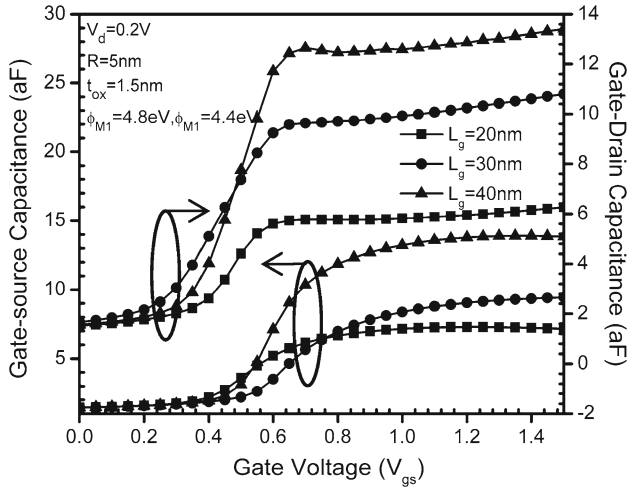

Fig. 19 Gate-source and gate-drain capacitance of GEWE-silicon nanowire MOSFET as a function of gate voltage for different channel lengths

Figure 20a, b shows the current gain and unilateral power gain as a function of frequency. As we have already mentioned that f_T and f_{MAX} are extracted from current gain and unilateral power gain respectively, it is clearly evident that as channel length scales down, both cut-off and maximum oscillator frequency increases due to increase in transconductance and reduction in parasitic capacitance as is shown in Eq. (1) and (2).

Moreover, stern's stability factor which determines the stability of a device at high frequency decreases as we scale down the channel length due to overlapping of source and drain fields which results in a commuted gate control in scaled devices, thus causing instability as is shown in Fig. 21.

Intrinsic Delay of GEWE-SiNW improves further as we scale down the channel length from 40 to 20 nm as shown in inset of Fig. 21. This improvement is due to reduction in gate parasitic capacitance. Figure 22 shows the Maximum Available and Maximum Transducer power gain as a function of frequency for different gate lengths. The Power gain of GEWE-SiNW improves further as channel length of nanowire scales down to 20 nm due to enhancement in current gain.

3.4 Effect of radius of silicon nanowire (R)

In this section, we examine the efficacy of silicon nanowire radius on RF performance of GEWE-SiNW MOSFET. Figure 23 shows that as radius of nanowire decreases drain current decreases due to the decrement in inversion charge density which increases the threshold voltage as a result of which the on-state current decreases and hence the transconductance.

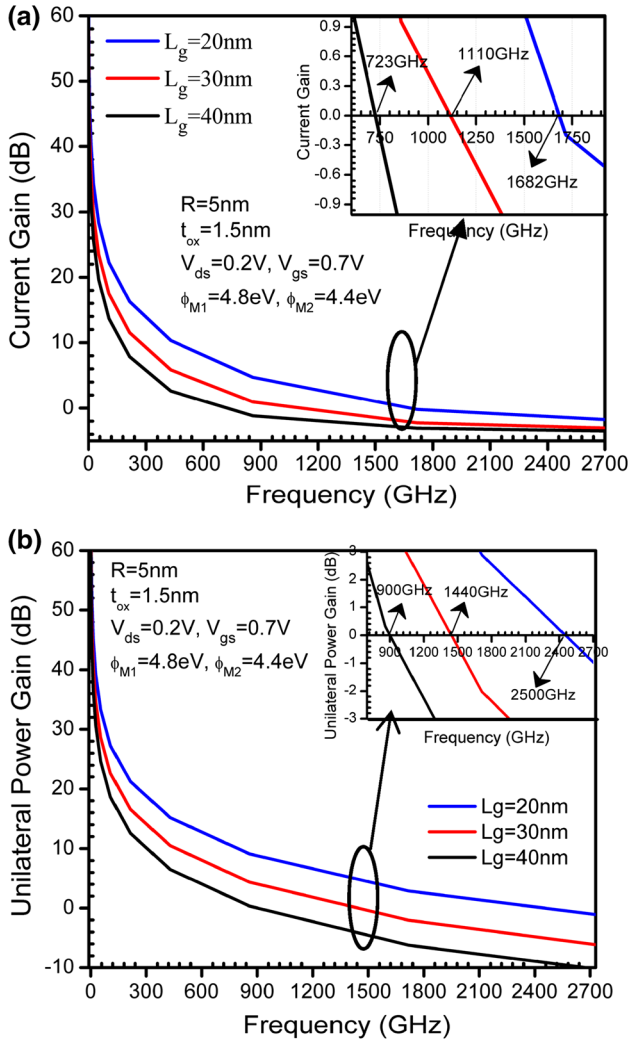

Fig. 20 **a** Current gain and **b** Maximum Unilateral Power Gain of GEWE-SiNW MOSFET $V_{ds} = 0.2$ V for different channel lengths

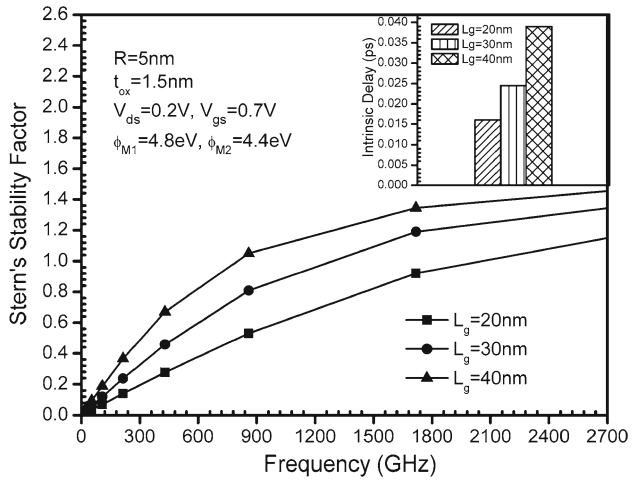

Fig. 21 Stern's stability factor of GEWE-SiNW MOSFET for different channel lengths. *Inset* intrinsic delay of GEWE-SiNW MOSFET at $V_{ds} = 0.2$ V for different channel lengths

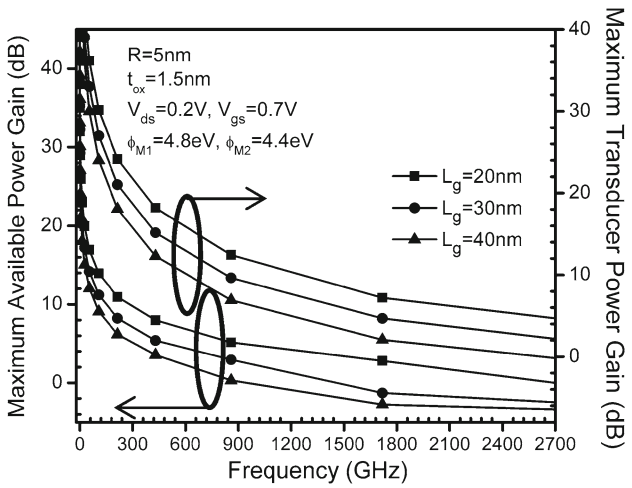

Fig. 22 Maximum available and maximum transducer power gain of GEWE-SiNW MOSFET at $V_{ds} = 0.2$ V for different channel lengths

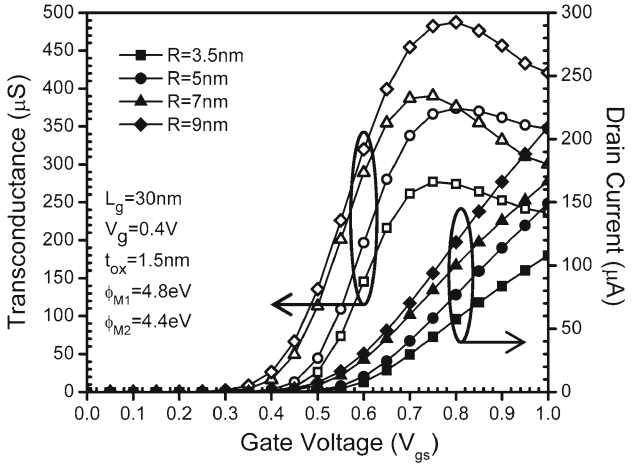

Fig. 23 Transfer and transconductance characteristics of GEWE-Silicon Nanowire MOSFET for different radius of silicon nanowire

On the other hand, parasitic gate capacitance which is sum of the gate-source and the gate-drain capacitance degrade as radius of silicon nanowire decreases. Smaller values of these capacitances play an important role in device switching performance due to reduction in the turn-on delay time. Figure 24 shows the behaviour of C_{gd} and C_{gs} as a function of gate voltage as is also predicted by Li et al. [42].

Figure 25 depicts the cut-off and maximum oscillator frequency of GEWE-SiNW MOSFET as a function of silicon nanowire radius. As is shown, ft increases as radius decreases due to degradation in parasitic gate capacitance. But fmax decreases as we reduce the radius of nanowire. So we have to choose optimal value of radius so that we can achieve desirable cut-off and maximum oscillator frequency for CMOS wireless applications.

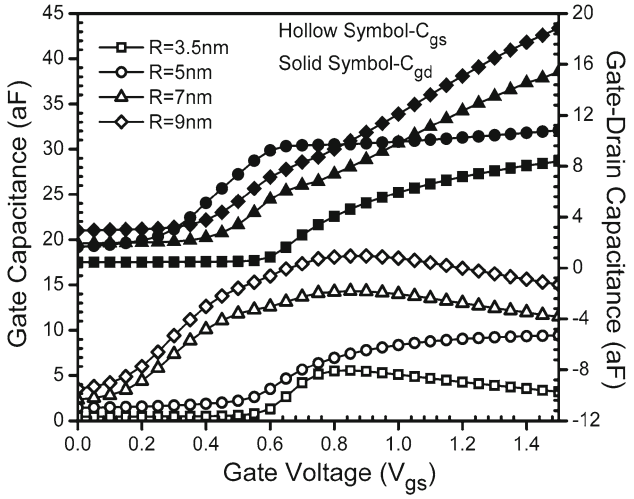

Fig. 24 Gate-drain and gate-source capacitance of GEWE-silicon nanowire MOSFET as a function of gate voltage for different radius of silicon nanowire

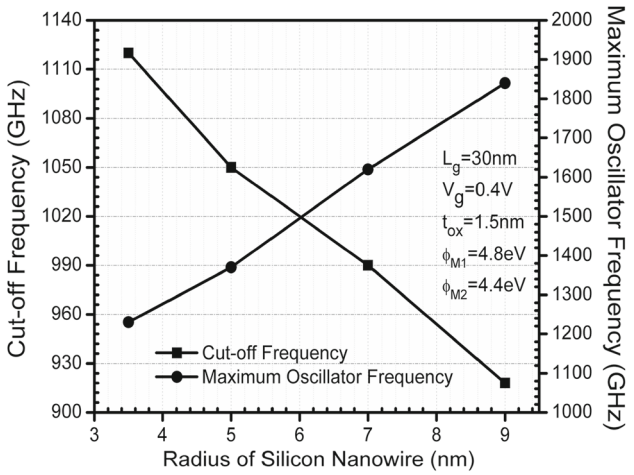

Fig. 25 Cut-off and maximum oscillatory frequency of GEWE-silicon nanowire MOSFET for different radius of silicon nanowire

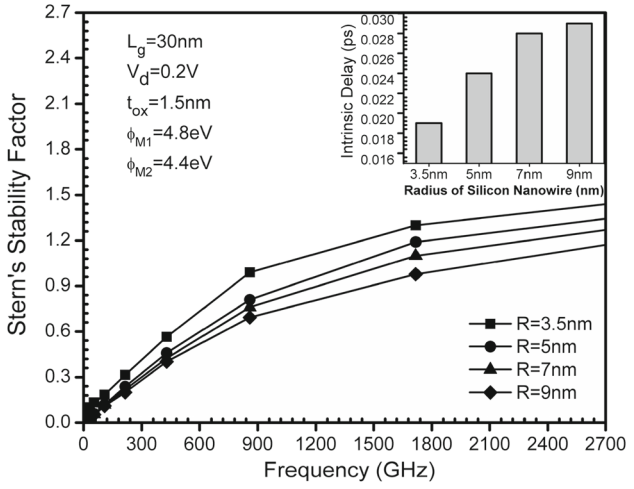

Fig. 26 Stern's stability factor of GEWE-SiNW MOSFET for different channel radius. *Inset* intrinsic delay of GEWE-SiNW MOSFET

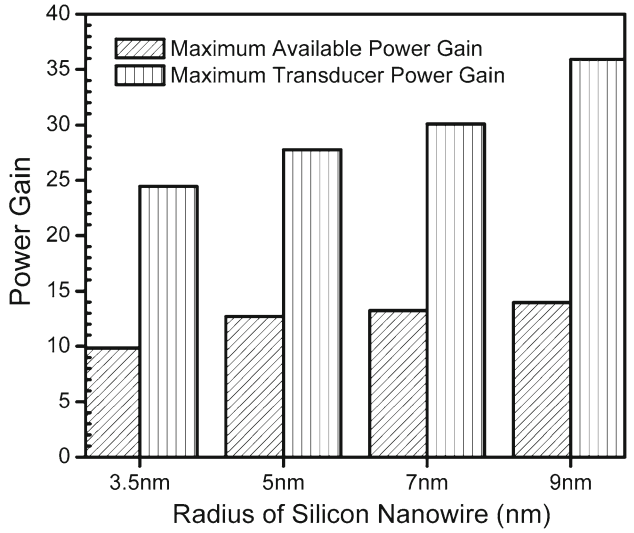

Fig. 27 Maximum available power gain and maximum transducer power gain of GEWE-SiNW MOSFET at $V_{ds} = 0.2$ V for different silicon nanowire radius

Figure 26 shows the stern's stability factor as a function of frequency and its inset shows the intrinsic delay of GEWE-SiNW as s function of radius of nanowire. It is clearly evident that at high frequency, $K > 1$ for GEWE-SiNW but its value enhances as radius scales down, hence make it suitable for low noise amplifiers. Also, intrinsic delay reduces to 50 % as we scale down the radii of nanowire due to degradation of parasitic capacitance as shown in Fig. 24.

In addition, power gains degrade as we reduce the radius of nanowire. Both maximum available power gain and maximum transducer power gain reduces 1.5 times as clearly shown in Fig. 27. Hence, for millimeter wave applications, we have to optimize the value of silicon nanowire radius.

4 Conclusion

The present work focuses on RF performance investigation of Conventional SiNW and GEWE-SiNW MOSFET in terms of parasitic capacitance, power gains, maximum and cut-off frequency, stability and intrinsic delay at high frequency. It has been found that due to improved transconductance, gate controllability and carrier mobility, GEWE-SiNW MOSFET exhibit superior performance in all RF metrics compared to its counterpart, thus providing its use in high frequency amplifier and microwave applications. Further, noticeable improvement in RF performance is observed by varying the device parameters such as metal workfunction at the drain end, channel length of nanowire, hence, giving a new opening for HF wireless and switching applications. Moreover, thinning of oxide thickness degrades the RF performance of GEWE-SiNW MOSFET and reduction in radii of nanowire also leads to degradation of RF metrics but improves as

compared to conventional SiNW. Thus, we have to choose optimum values of device parameters for better device performance at RF/Wireless applications.

Acknowledgments The authors would like to thank the Microelectronics Research Lab, Department of Engineering Physics, Delhi Technological University (formerly DCE) and one of the authors (Neha Gupta) is grateful to the University Grant Commission (UGC) for providing the necessary financial assistance to carry out this research work.

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Indian Energy Crises and Biodiesel as Renewable Alternative Fuel

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***Abstract*--In this research paper we found that in order to meet the growing energy needs as a consequence of spiraling demand and diminishing supply, in today's world renewable energy and biomass sources mostly bio-fuels are receiving more attention. The demand for energy has been phenomenon due to the rapid development of certain growing economies, especially in developing countries. Also because of the environmental pollution from internal combustion engines, the increasing global concern has compelled the researcher's worldwide to focus on the renewable alternative fuels. Various research studies to replace petroleum based diesel fuel with the vegetable oils or their derivations suggested that biodiesel can be produced from various vegetable oils, waste cooking oils and animal fats.**

***Keywords*-- Energy crises, Biodiesel, Diesel engine, Pollution, Environment**

I. Introduction

Energy is one of the most significant inputs for growth of all sectors including agricultural, industrial service and transport sectors. Energy has been at the centre stage of national & global economic development for several decades. The demand for energy, around the world is increasing exponentially, specifically the demand for petroleum-based energy. Petroleum derived fuels, actually, exceeds the demand of any other fuels or energy resources. The world consumption for petroleum and other liquid fuel will grow from 85 million barrels/day in 2006 to 107 million barrels/day in 2030. Under these growth assumptions, approximately half of the world's total resources would be exhausted by 2030. Also, as per many studies, the world oil production would peak sometime between 2007 and 2030 [1]. Therefore, the future energy availability is a serious global. Another, major global concern is environmental degradation or climate change such as global warming. Global warming is related with the greenhouse gases which are mostly emitted from the combustion of petroleum fuels. In order to control the emissions of greenhouse gases, Kyoto Protocol targets to reduce the greenhouse gas emission by a collective average of 5% below 1990 level of respective countries.

The Intergovernmental Panel on Climate Change (IPCC) concludes in the Climate Change 2007 that, because of global warming effect the global surface temperatures are likely to increase by 1.1°C to 6.4°C between 1990 and 2100 [1].

II. Energy Crisis

There is a realization throughout the world that the petroleum resources which are non-renewable, are limited and are being consumed at an alarming rate. The growing demand for energy and gradual extinction of fossil fuels has lead to an energy crisis. Most of the power in industries and transportation is derived from oil and coal. Special mention is needed for automobiles where almost all of the fuels for combustion engine today are derived from petroleum, a nonrenewable source of energy, which is nearing its end at an unprecedented pace. The grave name of the energy problem was sharply brought into focus by the oil crisis of 1973. Since then, several price hikes have taken place, upsetting economy of most of the nation. The globe today uses about 147 trillion kWh of energy which is expected to rise in the coming future [2]. A major chunk of this rise will be due to the developing countries, which are bound to grow by leaps and bounds.

Energy Scenario: Indian Context

India had experienced robust growth for the past few years, and after an impressive 9.6 per cent gross domestic product (GDP) growth in 2006-07 the Indian economy is headed towards 8.7 per cent growth in the current fiscal [3]. The energy needs of India are also rising to cope up the growth rate Of the 156.1 million tonnes of crude oil that India consumed in 2007-08; it produced only 34.12 million tonnes [4]. Indian economy is mainly agriculture based and modern agriculture system is heavily dependent upon internal combustion engines for running farm machinery, irrigation pump sets, and other equipments. Indian growth is mainly based on energy, produced by "oil-burning" in IC engines. It is very difficult to find clear blue sky in Indian metropolis. Petroleum fuels are major contributor to ecological imbalance in India.

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As Indian economy is heavily based upon IC engines, it is not possible in any case to discard them and some other, easily available renewable fuels in India. These renewable fuels must be sought to lease new life to existing engines in order to curb the twin problems of fuel scarcity and air pollution. Various national emission standards have been set by the Government of India through which the fleets are facing greater pressures to switch to cleaner alternative fuels. The alternative fuels are desirable from the fact that they are the only fuels used with recent engine developments, which can meet the stringent EURO-IV emission norms, which are expected to be enforced in India from 2010. India being richer in flora and fauna can look forward to use fuels from bio origin as the suitable alternatives. The prominent bio fuels from Indian perspective are ethanol and biodiesel. India, the world's second most populous nation, has seen its population exploding from 300 million in 1947 to around 1.2 billion today. This rapidly growing population has placed a strain not only on India's infrastructure, but also on its environment. According to the World Health Organization, New Delhi is one of the top ten most polluted cities in the world. Two primary sources of air pollution in India are vehicular emissions and untreated industrial smoke. The number of vehicles has registered a sharp increase more so, during the last decade. In Delhi alone, the vehicle number has crossed about 4.6 million. Today, the vehicular pollution contributes roughly 64 % of total air pollution in Delhi, followed closely by Mumbai at 52% and somewhat controlled figure of 30% for Kolkata. About 50% of the total petroleum products consumed in the country go into the transport sector mainly in the form of high-speed diesel and gasoline [5]. India's per capita energy use and carbon emissions, while lower than the world average, result in a substantial percentage of world energy use and carbon emissions, due to the country's large population and heavy reliance on fossil fuels. Increased use of renewable energy is one means of reducing carbon emissions.

III. Energy Demand And Supply

Energy Security is driven by the demand and supply behaviour. India ranks sixth in the world in terms of energy demand accounting for 3.64% of world commercial energy demand in 2007. Although India ranks fifth in total energy consumption in the world (404.4 MTOE (million tones of oil equivalent), this is only 17.12% of the energy consumed by the largest consumer, i.e. USA (2361.4 MTOE). In per capita terms, its consumption is only about 20% of the global average. Rapid Industrialization and Globalization have pushed the demand of energy to new heights.

In the year 2011, India will have a total population of about 1.3 billion people of which 68% will be living in rural areas. Since diesel constitutes 37 % of total petroleum consumption mainly for transportation and other purposes, its demand is integrally related to economic growth and is seen as a growth inducing factor. Stress of the over-burdening population will augment the strain in terms of the volume of fuel required, but the picture of proven oil reserves distribution doesn't reflect the pleasant sight at all. The share with respect to the energy distribution of the remaining oil reserves across the world is shown in Figure 1.

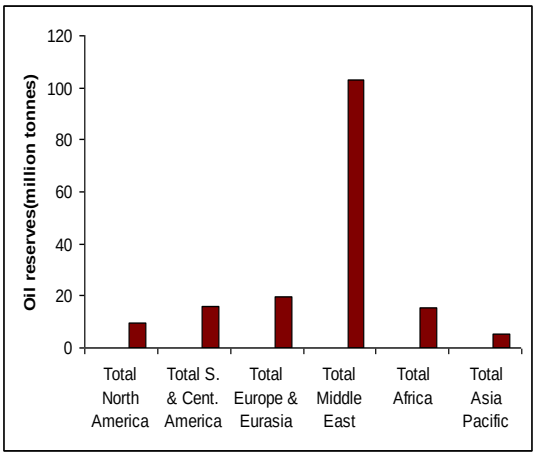

Figure 1: World Oil Reserves, 2008 [6]

It can be observed, that bulk of the reserves are with Middle East. The condition of the Asia Pacific countries presents a dismal trend, presently, only 3.3%of the total share is in their buckets. Therefore, it is apparent that the Asian countries have to change their fuel strategy or live with the escalating burdens of oil imports or with joint venture abroad with the hope to meet their requirement. At present, India imports about 77.94 % of its crude oil required. Net import of crude oil has increased from 74.10 MMT in 2000-01 to 121.67 MMT in 2007-08. India paid Rs.272,699 Crores for importing crude oil in 2007-08. This import comprised about 30 % of the total value of Indian imports in 2007-08 [4]. Heavy dependence on import of crude oil is a subject of serious concern. As per The World Energy out Look, India's dependence on oil import would grow to 91.6 % by the year 2020. The trend of import of crude oil in India is shown in table 1.

As already evident from above discussion that the self reliance of our country is declining and has reached to a very low figure of 21.86% in year 2007-08 as shown in table 2.

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Although, India has invested considerable resources in petroleum sector, the crude oil production has stagnated around 32-33 million metric tonnes per year over the past decade. The majority of India's roughly 5.4 billion barrels in oil reserves are located in the Bombay High, Upper Assam, Cambay, Krishna-Godavari, and Cauvery basins. India's average oil production level for 2007 was 801000 barrels per day [4]. But the consumption continues to outstrip production. Over the years, the domestic availability of the crude oil has not kept pace with the demand. Table 2 summarises the trends of demand and supply of crude petroleum in the preceding years.

Table 1
Import of Crude Oil in India [4]

Year	Crude Oil	
	Qty MMT	Value (Rs. In Crores)
1996-97	33.91	18538
1997-98	34.49	15897
1999-99	39.81	14876
1999-00	57.80	30695
2000-01	74.10	65932
2001-02	78.70	60397
2002-03	85.81	62876
2003-04	90.43	83528
2004-05	95.86	117003
2005-06	99.41	171702
2006-07	110.86	219991
2007-08	121.67	272699

Table 2
Consumption and Domestic Availability of Crude Oil [4]

Year	Domestic Production (Mt)	Demand (Mt)	(%)Self Reliance
1990-91	33.02	53.72	61.4
1995-96	35.17	62.51	56.2
2000-01	32.43	106.523	30.4
2001-02	32.03	110.738	28.92
2002-03	33.04	115.031	28.72
2003-04	33.38	123.815	26.96
2004-05	33.98	129.84	26.17
2005-06	32.19	131.6	24.4
2006-07	33.99	144.85	23.46
2007-08	34.12	156.1	21.86

IV. Alternate Fuels

To solve dual problems of fossil fuel depletion and environmental degradation, the renewable fuels with lower environmental impact are necessary. Nowadays, many new fuels have been used and biomass derived fuels are among them. Some of the well known biomass derived fuels are ethanol for gasoline engines and bio-diesel for compression ignition engines. Biodiesel is a renewable and environmental friendly alternative fuel for diesel engine which is produced from variety of vegetable oils and animal fats by the trans-esterification process. Transesterification is a chemical reaction in which vegetable oils and animal fats are reacted with alcohol in the presence of a catalyst. The products of reaction are fatty acid alkyl ester and glycerine, and the fatty acid alkyl ester is known as biodiesel. Bio-diesel is an oxygenated fuel containing 10% to 11% oxygen by weight. Also it is a sulphur-free fuel. These lead biodiesel to more complete combustion and less harmful exhaust emissions. However, biodiesel fuel has higher viscosity, density, pour point, flash point and cetane number than diesel fuel. Also the energy content or net calorific value of biodiesel is about 12% lower than that of diesel fuel on a mass basis. Using biodiesel can help in reducing the world's dependence on fossil fuels and also has significant environmental benefits. Using biodiesel instead of the conventional diesel fuel reduces exhaust emissions such as the overall life circle carbon dioxide (CO_2), particulate matter (PM), carbon monoxide (CO), sulphur oxides (SO_x), volatile organic compounds (VOCs), and unburned hydrocarbons (UBHC). However, most of the biodiesels give 10% to 15% higher oxides of nitrogen (NO_x) when fuelling with 100% biodiesel [7]. Depending on the abundantly availability of feedstock in local region, the different feedstocks are tried for the biodiesel production. In the United States, the primary sources for biodiesel production is soy bean oil, while EU nations prefer to utilize rapeseed oil, and in South East Asia regions, palm oil, coconut oil and Jatropha oil are used for biodiesel productions. Growing the production of biodiesel in many countries around the world has been accompanied by the development of standards to ensure high fuel quality. The biodiesel standards are ASTM D6751 in the United States and EN 14214 in EU Nations. The properties of biodiesel are mainly determined by the structure of fatty acids alkyl esters which constitutes it, particularly, the combustion characteristics such as ignition quality, and the fuel properties such as density, viscosity, pour point and oxidation stability of biodiesel are mostly affected by the structure of fatty acids alkyl esters [8].

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V. Alternative Fuel Attributes

There are some very important parameters which should be considered before adaptation of an alternative fuel in an existing engine. These include:

- No or minimum engine modification
- Use of same storage and transportation infrastructure.
- Biodegradable and non-toxic assuring safe handling and transportation.
- Capability of being produced locally and low investment cost. [2, 3].

The economic benefits of the fuels like vegetable oils, compressed natural gas, ethanol, and methanol etc. compared to the traditional petroleum resources are marginal but the environmental benefits are enormous, thus public policies need to be revised to encourage the development of these resources for which:

- Land for production need to be explored
- An efficient extraction of oil from oil seeds and transesterification plant would be required
- Distribution and storage facilities constructed
- Monitoring of major users for detection of problems
- Large scale use are needed before the technology can be recommended for general use
- The magnitude of our energy needs provides an inexhaustible market of our total agriculture production capacity at the highest possible level
- Farm back to work providing for our food needs and also growing crops and livestock for energy. Energy is the only crop that we could never grow in surplus [4,9].

VI. Biodiesel As An Alternative

Biodiesel is an organic, non-toxic and biodegradable fuel made from everyday renewable resources, like vegetable oils or animal fats. It can power your car's engine and help the environment at the same time. It doesn't contain any petroleum, so forget about escalating gas prices. Biodiesel cuts down on CO2 emissions; in fact, it's the only alternative fuel to have fully completed the health effects testing requirements of the US Clean Air Act. Biodiesel can be purchased at a growing number of fuelling stations around the world but you can also make it in your own backyard. Even if you don't like chemistry, you can brew your own.

Use of Biodiesel in Railways

Indian Railways has set up a biodiesel production unit at Loco Workshops Perambur in Chennai which is successfully manufacturing biodiesel for the past 8 years. Similar plants are being established at Raipur in Chattisgarh and Tondiarpet near Chennai. Biodiesel is being used in blends of B5, B10 and B20 for diesel engines of transport vehicles and locomotives. These locomotives have 2600 hp diesel engines and are mostly underutilized. Similarly both these workshops invariably use diesel engine operated fork lift trucks as the components handled are quite heavy. As already Biodiesel is successfully introduced it can also be tried out in both of these workshops in days to come. [10-11]

Waste Vegetable Oil

Restaurants use many different oils for frying foods. These oils are subjected to very high temperatures as well as fats and water from various foods. The process of frying food changes the physical and chemical make-up of the oil increasing the acidity and water content. This affects the Transesterification Process - the chemical process of making of biodiesel. Higher FFA's require more catalyst and alcohol, which in turn increases production costs. Other problems may arise from oils high in water or FFA's, such as poor fuel from incomplete reaction and the formation of emulsions from a water washing process due to excess soap formation or shortened life of ION exchange resins. WVO with the least amount of water ("under 1%") and low FFA'S (fewer than 5%") are desirable. Biodiesel Chemically known as Fatty Acid Methyl Ester (FAME) refers to any vegetable oil or animal fat that has been altered through a process called transesterification, a process in which oil, (an ester) gets converted to biodiesel, (another ester) and glycerin a byproduct. Biodiesel is a clean burning renewable fuel that mimics the properties of petroleum diesel, but with increased lubricity and lower emissions. Biodiesel can be mixed in any ratio with petroleum diesel to create a blend. Common blends are B2 and B20.

Places to look for high quality oil would be restaurants that fry low fat foods, vegetables, fish, chicken, and potato chips. Example: Oriental restaurants and shrimp boats etc. The types of WVO to look for are Canola, Soy, Sunflower and Corn Oil in this order from thin to thick. The thickness or viscosity of the oil becomes a concern in cold climates as biodiesel made from heavier oil has "higher viscosity" and poor cold weather performance.

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Thinner oils will have better cold flow properties and better cold weather performance. Biodiesel made from WVO will usually have a higher viscosity than biodiesel made from virgin oil due to the physical and chemical changes made to WVO in the frying process. This will not be a large temperature difference, but you should expect a few degrees difference. Hotels and restaurants use many different oils for frying foods. These oils are subjected to very high temperatures as well as fats and water from various foods. The process of frying food changes the physical and chemical make-up of the oil increasing the acidity and water content. This affects the Transesterification Process - the chemical process of making of biodiesel. Higher FFA's require more catalyst and alcohol, which in turn increases production costs. Other problems may arise from oils high in water or FFA's, such as poor fuel from incomplete reaction and the formation of emulsions from a water washing process due to excess soap formation or shortened life of ION exchange resins. WVO with the least amount of water ("under 1%") and low FFA'S (fewer than 5%") are desirable look for high quality oil would be restaurants that fry low fat foods, vegetables, fish, chicken, and potato chips. Example: Oriental restaurants and shrimp boats etc. The types of WVO to look for are Canola, Soy, Sunflower and Corn Oil in this order from thin to thick. The thickness or viscosity of the oil becomes a concern in cold climates as biodiesel made from heavier oil has "higher viscosity" and poor cold weather performance. Thinner oils will have better cold flow properties and better cold weather performance. Biodiesel made from WVO will usually have a higher viscosity than biodiesel made from virgin oil due to the physical and chemical changes made to WVO in the frying process. This will not be a large temperature difference, but you should expect a few degrees difference.

Non-hydrogenated or partially hydrogenated oils will be the most common type of oils used in restaurants. Some will use completely hydrogenated oil that is solid at room temperature and should be avoided. Non-hydrogenated oil will have better cold flow properties, but will not store as well without adding stabilizers.

Partially hydrogenated oil has a higher "cloud point" but will not oxidize as fast. The difference between non-hydrogenated and partially hydrogenated oil is small and both are treated the same when making biodiesel. Hydrogenation results in the conversion of liquid vegetable oils to solid or semi-solid fats. Complete hydrogenation converts unsaturated fatty acids to saturated ones. Changing the degree of saturation of the fat changes some important physical properties such as the melting point, which is why liquid oils become semi-solid. Since partially hydrogenated vegetable oils are cheaper than animal source fats and are available in a wide range of consistencies, and have other desirable characteristics (e.g., increased oxidative stability). Table 3 gives the summary of proposed BIS (Bureau of Indian Standards) standards for biodiesel.

Most restaurants tend to use partially hydrogenated oil due to cost and longer life of Non-hydrogenated or partially hydrogenated oils will be the most common type of oils used in restaurants. Some will use completely hydrogenated oil that is solid at room temperature and should be avoided. Non-hydrogenated oil will have better cold flow properties, but will not store as well without adding stabilizers. Partially hydrogenated oil has a higher "cloud point" but will not oxidize as fast. The difference between non-hydrogenated and partially hydrogenated oil is small and both are treated the same when making biodiesel. Hydrogenation results in the conversion of liquid vegetable oils to solid or semi-solid fats. Complete hydrogenation converts unsaturated fatty acids to saturated ones.

Changing the degree of saturation of the fat changes some important physical properties such as the melting point, which is why liquid oils become semi-solid. Since partially hydrogenated vegetable oils are cheaper than animal source fats and are available in a wide range of consistencies, and have other desirable characteristics (e.g., increased oxidative stability. Most restaurants tend to use partially hydrogenated oil due to cost and longer life of oil. Table 4 gives the Properties of biodiesel from different oils.

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Table 3
summary of proposed BIS(Bureau of Indian Standards) standards for biodiesel [9]

Standard / specification	Unit	Proposed BIS
Density @ 15°C	g/cm^3	0.87 –
Viscosity @ 40°C	mm^2/s	3.5 -
Flash point	°C	>=100
Sulphur, max.	%mass	0.035
CCR,100%distilation	%mass	0.05
Sulphated ash,max,	%mass	0.02
Water.max	mg/kg	500
Total contamination,	mg/kg	20
Cetane no	-	>=51
Acid no	mg	<=0.8
Methanol	%mass	<=0.02
Ester content	%mass	>=96.5
Diglyceride	%mass	<=0.2
Triglyceride	%mass	<=0.2
Free glycerol	%mass	<=0.02
Total glycerol	%mass	<=0.25
Iodine no		<=115
Phosphorus	ppm	<=10
Alkaline matter(Na,K)		<=10
Distillation, T 95%	°C	<=360

Table 4
Properties of biodiesel from different feedstocks [9]

Vegetable oil methyl esters	Kinematic viscosity mm^2/s	Cetane no.	LHV MJ /kg	Cloud point (°C)	Pour point (°C)	Flash point °C	Density (kg/l)
Peanut	4.9	54	33.6	5	–	176	0.883
Soya bean	4.5	45	33.5	1	-7	178	0.885
Babassu	3.6	63	31.8	4	–	127	0.875
Palm	5.7	62	33.5	13	–	164	0.880
Sunflower	4.6	49	33.5	1	–	183	0.860
Tallow	–	–	–	12	9	96	–
Diesel	3.06	50	43.8	–	-16	76	0.855
20% Bid-d blend	3.2	51	43.2	–	-16		0.859

VII. CONCLUSIONS

In this work it is observed that the fuel properties of biodiesel need to be monitored when different feedstocks are used. If the fuel properties of biodiesel are compared to petroleum diesel fuel, it can be seen that biodiesel has higher viscosity, density, pour point, flash point and cetane number, near-zero aromatic compound, and no sulphur link make it more suitable than petro-diesel. Keeping the large wasteland available in India a tangible planning is needed to use the vegetable oil biodiesel as a supplement/ substitute for the petro-diesel.

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Investigation of Strength of Concrete Containing Locally Available Industrial and Agriculture Waste

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Abstract: ***This paper presents the experimental study undertaken to investigate the influence of partial replacement of cement with Fly Ash (FA), Rice Husk Ash (RHA) and Sand with Stone Dust (SD). Fly ash is a by-product of burned coal from power station, stone dust is a by-product of crushed aggregate and rice husk ash is a by –product of burned rice husk at higher temperature from paper plant and other industries. Waste disposal is an important issue in the present time and utilization of Industrial waste Fly Ash, Stone Dust and Agricultural waste -Rice Husk Ash in concrete making is being researched. Considerable efforts are being taken worldwide to utilize natural waste and by –product as additional cementing materials to improve the properties of cement concrete. Stone Dust (SD), Rice Husk Ash (RHA) and Fly Ash (FA) are such materials. This study is carried out by keeping 20% replacement of cement by FA in all the mixes and then replacing cement and sand by RHA and SD respectively by different percentages. This study shows that 10% RHA+20% FA and 30% SD in concrete gives maximum strength.***

Keywords: Concrete, Compressive Strength, Fly Ash, Rice husk Ash and Stone dust.

1. Introduction

Concrete is well known as a heterogeneous mix of cement, water and aggregates. The characteristic of the concrete is determined by quality of the paste. Various materials are added such as fly ash, rice husk, stone dust to obtain concrete of desired property. The investigation is done to study the effect of partial replacement of cement with RHA, FA and sand with SD. The compressive test done for concrete cube size (150 x 150 x 150) mm.

(Kumar Sushil, 1992) represented that only small percentage that is 3% to 5% of fly ash is being used in India while in other countries the percentage of utilization is 30% to 80%, whatever be the type of fly ash, it causes types of pollution and air born diseases such as silicoses, fibrosis of lungs, bronchitis etc. As per the estimation of Government of India, power plants are going to use 1800 million tons of coal that may result 600 million tons of fly ash by 2031-2032 (Ujjwal Bhattachar, 2002). Author also enlightened the areas in which fly ash usage has potential in India. He pointed out that despite quite optimistic levels of utilization of fly ash in India; only less than 25% of the total fly ash produced is being utilized. (Chandrasekhar, 2006) rice husk is an agricultural residue which accounts for 20% of the 649.7 million tons of rice produced annually worldwide (World paddy production, 2008). The produced partially burnt husk from the milling plants when used as a fuel also contributes to pollution and efforts are being made to overcome this environmental issue by utilizing this material as a supplementary cementing material. (Dashan and Kamang, 1999) carried out an extensive work on some characteristics of Rice husk ash/ordinary Portland cement concrete. Test results indicate that the compressive strength for all the mixes containing RHA increases with age up to the 14-day hydration period but decreases to the 28-days hydration period while the conventional concrete increases steadily up to 28-day hydration period. (Nagabhusana and Bai, 2011) crushed stone powder can be effectively used to replace natural sand without reduction in the strength of concrete at replacement level up to 40%. (Pofale and Quadori, 2013) compressive strength of concrete (M25, M30) made using crusher dust increased at all the replacement level between 30-60% at an interval of 10%. However, maximum increased strength is observed at a replacement level of 40%**.** The work presented in this paper reports an investigation on the behavior of concrete produced from blending cement with FA and RHA.

2. Materials and Methods

The work presented in this paper reports an investigation on the behavior of concrete produced from blending cement with Rice Husk Ash (RHA), Fly Ash (FA), natural sand with Stone Dust (SD) and coarse aggregate. The physical and chemical properties of RHA, FA, SD and OPC were first investigated. Mixture proportioning was performed to produce high workability concrete for the control mixture. The effect of RHA, FA and SD on concrete properties was studied by means of the fresh properties of concrete and the mechanical properties. I.e. Compressive strength test was studied.

A. Cement

Table 1: Chemical properties of cement (OPC), Fly ash and Rice husk ash

Materials	SiO2	Al2O3	Fe2O3	CaO	MgO	LOI	SO3	K2O	Na2O3
Cement	19.71	5.20	3.73	62.91	2.54	0.96	2.72	0.90	0.25
Fly ash	60.20	18.45	16.20	2.00	1.02	--------	1.00	--------	---------
Rice husk	93.80	(SiO2+ Al2O3+ Fe2O3)		0.89	0.32	3.37	-----	0.12	---------
ash		=82.64							

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The cement used was Ordinary Portland cement (43 Grade). OPC 43 grade cement is used for this whole experimental work. The physical test results on OPC are as follows.

1) Normal consistency = 28%
2) Initial Setting time = 47 min.
3) Final Setting Time = 405 min.
4) Specific Gravity = 3.22

B. Rice Husk Ash

Rice husk ash used was obtained from Nova. Industries, Malanpur, Gwalior .The Specific gravity of rice husk ash is 2.08 and produced after burning of Rice husk (RH) has high reactivity and pozzolonic property. Indian Standard code of practice for plain and reinforced concrete, IS 456- 2000, recommends use of RHA in concrete but does not specify quantities. Chemical compositions of RHA are affected due to burning process and temperature. Silica content in the ash increases with higher the burning temperature.

C. Fly Ash

Fly ash used was obtained from Parichha thermal power plant, JHANSI (U.P.), INDIA. Fly ash is one of the residues generated in the combustion of coal.
Specific gravity of fly ash 1.95.

D. Aggregate

Good quality river sand was used as a fine aggregate. Coarse aggregate passing through 20mm and retained 10mm sieve.

a) Fine Aggregate
- Specific gravity = 2.57
- Fineness modulus = 3.58

b) Coarse Aggregate
- Specific gravity = 2.68
- Fineness modulus = 6.8

E. Stone Dust

Stone dust used was obtained from Stone Crusher plant located in Deen Dayal Nagar Gwalior (M.P.).The fineness modulus and specific gravity are 3.13 and 2.62 respectively.

3. Experimental Programme

Experimental programme comprises of tests on cement, RHA, FA and SD. Cement Concrete with partial replacement of cement with RHA, FA and natural sand by SD.

A. Mix Design

M20 mix is designed as per guidelines in IS 10262, 1982 based on the preliminary studies conducted in the constituent materials. Tests on fresh concrete are obtained as follows.

(1). Slump Test=55mm

Table 2: The quantities of ingredients per cubic meter

Water (liters)	Cement (kg)	Fine Aggregate (kg)	Coarse Aggregate (kg)
0.50	1	1.63	2.97
191.61	383	627.92	1138.06

B. Mixture Proportioning

The control design was done as per IS 10262-1982. The total mixing time was 5 minutes, the samples were then casted and left for 24 hrs before demoulding. They were then placed in the curing tank until the day of testing Cement, sand, Fly ash, Rice husk ash, Stone dust and fine and coarse aggregate were properly mixed together. Replacement levels of cement and sand by different waste materials are given in Table. Coarse aggregate were same in all concrete.

Table 3: Percentage of ingredients

S. No.	Designation	Mix Type	Binder			Water kg	Aggregate		
			Cement kg	FA kg	RHA kg		Coarse Agg. kg	Fine Agg. kg	
								Sand kg	SD kg
1.	C	Control	100%	-----	-----	0.64	100%	100%	-----
2.	M1	10%RHA+20% FA	70%	20%	10%	0.64	100%	60%	40%
3.	M2	10%RHA+20% FA	70%	20%	10%	0.64	100%	70%	30%
4.	M3	5%RHA+ 20% FA	75%	20%	5%	0.64	100%	60%	40%

4. Results and Discussion

The cube samples were tested are 2000 KN Compressive Testing machine at the curing ages of 3,7,14 and 28 days. The results are given in table-

S. No.	Mix Type	Compressive strength															
		3 Days strength of Cubes in KN			AVG. Str. N/mm^2	7 Days strength Of Cubes in KN			AVG. Str. N/mm^2	14Days strength of Cubes in KN			AVG. Str. N/mm^2	28Days strength of Cubes in KN			AVG. Str. N/mm^2
		1	2	3		1	2	3		1	2	3		1	2	3	
1.	C	150	180	150	7.11	250	240	200	10.22	300	420	310	15.25	600	650	590	27.25
2.	M1	150	170	180	7.40	360	310	350	15.11	380	350	360	16.14	450	400	400	18.22
3.	M2	210	160	280	9.63	360	400	350	16.44	400	390	450	18.37	500	530	490	22.51
4.	M3	210	150	170	7.85	200	250	230	10.07	280	280	320	13.03	450	460	400	19.40

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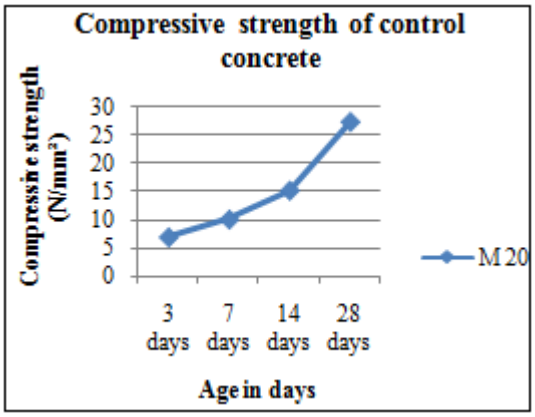

Figure: Compressive Strength of control concrete at different curing ages.

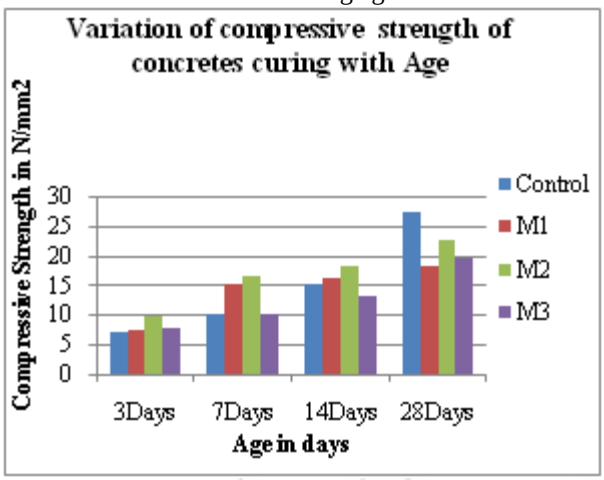

Figure: Variation of Compressive Strength of concrete at different curing ages.

5. Conclusions

Based on the results presented above, the following conclusions can be drawn:

1) Strength of M2 mix containing (70%C,10% RHA,20% FA and30% SD) was only 100% less than the control mix.

2) Strength of Mixes of M1 and M3 were (70%C, 10%RHA, 20%FA, 40%SD), (75%C, 5% RHA, 20% FA, 40% SD) and 100% less than the control mix respectively.
3) The durability properties are not checked.
4) Rice Husk Ash can be used as admixture as a partial replacement of cement.

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Lean Six Sigma Implementation: An Analytic Hierarchy Process Approach

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Abstract - 'Reduction of waste' has been key theme of 'lean' concept implementation in manufacturing, process and up to some extent in service sectors of industries; however, 'six-sigma' concept implementation focuses upon 'quality improvement techniques' in production and delivery of products/services. 'Lean six-sigma (LSS)' concept combines tools and techniques of 'lean' and 'six-sigma' towards achieving enhanced benefits to gain competitive advantage. Implementation of LSS concept has been emphasized in this paper by addressing identification of appropriate enablers and ranking of these enablers. Literature review and subsequent discussions with experts enabled to: identify; sort and combine; and finalize twelve enablers important to implement 'lean six-sigma' concept. Analytical hierarchy process (AHP) has been used to rank identified LSS enablers by utilizing experts' opinions. 'Management involvement and funds allocation' has been rated as top ranked enabler to implement LSS concept. Decision making authorities may be benefitted in dealing with planning and implementation of 'lean six-sigma' concept in manufacturing and service sectors.

Keywords – Analytical Hierarchy Process (AHP); Enablers important to implement LSS; Lean Six Sigma (LSS); Manufacturing and Service Sectors.

1. Introduction

Today's dynamic and competitive environment, which has been globalized in nature, demands for high quality and cost effective products and services to be offered to prospective customers; and hence, emphasizes the need for implementation of lean and six-sigma; however, the more recent concepts of lean and six-sigma have mainly replaced – but not necessarily added to – the concepts of 'Just in Time (JIT)' and 'Total Quality Management (TQM)' (Näslund, 2008).

In fact, combination of lean and six-sigma as 'Lean Six-Sigma (LSS)' may become truly useful in achieving business goals of manufacturing sector as well as service industry. Important concepts of lean, six-sigma and lean six-sigma have been summarized in Table 1 providing information about core objectives, tools/techniques, outcomes, limitations and application areas.

Table 1: Concepts of Lean, Six Sigma and Lean Six Sigma (Adapted from Kumar et al, 2013)

Factor for Conceptualization	Lean Concept	Six-Sigma Concept	Lean Six-Sigma (LSS) Concept
Objective/s	To identify, sort and eliminate 'waste' or 'non value adding activities'	Continuous quality improvement of processes and products with use of appropriate statistical	To optimize value by continuous improvement in processes and quality and reduce cost by eliminating

		techniques (Buyukozkan and Ozturkcan, 2010)	wastes and non value adding activities
Focus	Waste elimination	Quality improvement	Quality improvement and waste elimination
Concepts Involved	Continuous flow, pull system, leveling of workload, defect-free processes, standard tasks, visual control, technology (McKone et al., 1999; Swink et al., 2005; Linderman et al., 2006; Nahmens and Mullens, 2009)	DMAIC principle: define; measure; analyze; improve; control	Merger of lean and six sigma principles
Tools and Techniques Involved	Value process mapping and problem solving (Piercy and Rich, 2009)	Use of statistical tools/techniques and various software, Project planning and management tools, Pareto analysis, Measurement system analysis etc.	Combination of tools and techniques of lean and six sigma
Benefits of Implementation	Cost reduction and increase in speed of the process	Quality enhancement, reduction in rejection rate, process excellence (Antony et al., 2007; Buyukozkan and Ozturkcan, 2010)	Cost reduction, value addition, reduction in process variation customer satisfaction, financial performance, learning and growth
Limitations of Concepts	Large investment in facilities, equipment, and manpower, employees' willing (Magrab et al. 2009)	Time, manpower, funds, Structured implementation, expensive projects (Magrab et al. 2009)	Total employee commitment, structured plan for implementation, man power motivation (Magrab et al. 2009)
Areas of Applications	Product development and design, manufacturing system, supply chain, service sector and others (Liker and Morgan, 2006; Taj, 2008)	Product development, manufacturing system (Gremyr and Fouquet,2012)	New product development, product design, manufacturing system, supply chain, numerous applications in various sectors

1.1 Organization of the Paper

In a case study, in order to reduce operational cost, original equipment manufacturing (OEM) industries opted for outsourcing their products with proposal of LSS implementation success model; and a practical guide of the LSS program was implemented and this practical guide helped the LSS practitioners to focus on certain enablers/'Critical Success Factors (CSFs)' and it prevents the LSS execution from losing momentum when faces roadblock (Jeyaraman and Teo, 2010). Therefore, it is important to identify, sort, analyze and rank enablers/CSFs of LSS implementation.

1.2 Organization of the Paper

Section 2 deals with identification of important enablers of lean six-sigma (LSS) concept implementation from literature review and discussions with experts from academia and industry. Methodology (Brief about Analytical Hierarchy) to rank enablers of LSS implementation have been given in Section 3. Section 4 deals with results and discussions followed by conclusions as Section 5. In last section, limitations of the study with future research have been provided.

2. Identification of Enablers of LSS

Enablers of 'lean six-sigma (LSS)' concept implementation have been identified from literature review and subsequent detailed discussions with experts from academia and industry. These identified enablers are: Management involvement and funds allocation; Culture with Effective communication; Training and change management; Project management and LSS techniques (Statistical Thinking); Linking LSS to business strategies; Customer Integration; HRM, employees' motivation and team management practices; Supplier involvement (quality of raw material); Manufacturing facilities, standardization and scheduling; Visual control; Floor layout and optimization of transportation & material Handling; Reliable data collection and retrieval system.

2.1 Management involvement and funds allocation

Management initiative, vision, support and continuous involvement may be required to carry out the process of lean six-sigma concept in the organization (Bhuiyan and Baghel, 2005); however, management involvement is a must to agree upon allocate suitable funds for then LSS implementation (Snee, 2010).

2.2 Culture with Effective communication

Conducive environment with cooperative culture; and open and effective communication may lead to easy, efficient and productive lean six-sigma process implementation (Zu et al., 2010).

2.3 Training and change management

'Lean six-sigma' concept implementation has to be supported by appropriately designed training programs to manage change towards seeking complete involvement of all the employees (Näslund, 2008; Smith, 2010).

2.4 Project management and LSS techniques (Statistical Thinking)

Lean six-sigma implementation requires project management skills and a specific mind-set with statistical thinking and analytical abilities in employees of the organization (Hilton and Sohal, 2012).

2.5 Linking LSS to business strategies

Lean six-sigma program need to be linked to business strategies to achieve goals of organization through appropriate 'policy decisions' by top and middle management (Antony, 2014).

2.6 Customer Integration

Lean six-sigma implementation process may not be successful in true sense without integration of customer with appropriate feedback mechanism and channels (Albliwi et al., 2014).

2.7 HRM, employees' motivation and team management practices

Appropriate human resource management practices may foster complete employees' motivation and involvement towards coming up as a team for lean six-sigma implementation in an efficient and fruitful manner (Kerzner, 2013).

2.8 Supplier involvement (quality of raw material)

Quality of raw material has been found important towards ensuring high quality goods/services (Snee, 2010); however, overall supplier involvement is quite important in successful implementation of lean six-sigma process (Pope, 2012).

2.9 Manufacturing facilities, standardization and scheduling

Good quality, precise and accurate manufacturing facilities may help in producing cost effective and high quality goods to satisfy customers (Antony et al., 2012). Standardization may help in reducing inventory, whereas, efficient scheduling in reducing waiting/idle time involved in production (Maleyeff et al., 2012).

2.10 Visual control

There are various tools and techniques of lean six-sigma implementation; visual control may be considered as one important factor out of those many helping in identifying areas for improvement in terms of better quality and waste reduction/elimination (Akbulut-Bailey et al., 2012).

2.11 Floor layout and optimization of transportation & material Handling

Well designed and optimized floor layout may contribute in to mitigation of unnecessary transportation and material handling towards reduction of cost (Al-Aomar, 2012; Barbosa and Carvalho, 2014).

2.12 Reliable data collection and retrieval system

Decision making may be made effective and efficient with the help of appropriately designed data collection and retrieval system to support implementation process of lean six-sigma (Antony et al., 2012; Evans and Lindsay, 2014).

3. Methodology

Analytic Hierarchy Process (AHP) methodology has been utilized to achieve the objectives of present research work i.e. ranking of enablers of LSS.

3.1 Interpretive Structural Modeling

The AHP methodology describes alternatives with respect to a criterion to solve a Multi-Criteria-Decision-Making (MCDM) problem by using pair wise comparison mode resulting in to ranking of the alternatives/enablers towards assisting the decision maker to make a choice of alternative; and it has the following three steps (Saaty, 1990; Saaty, 2000; Saaty, 2008; Kumar et al., 2009; Luthra et al., 2013; Luthra et al., 2015):

- Establishing the hierarchical structure: Construct the hierarchical structure with decision elements and make pair-wise comparisons between alternatives using suitable scale that is a nine-point scale.
- Making pair wise comparison matrix: Make set of pair wise comparison matrices.
- Calculating the consistency: To ensure the consistency of the priority of elements, the maximum eigenvector, consistency index (CI) and consistency ratio (CR) are calculated for each matrix order n using Eq. (1) and Eq. (2.

$$\mathbf{CI = (\lambda_{max} - n)/(n-1)} \quad \ldots\ldots \quad \textbf{Eq. (1)}$$

$$\mathbf{CR = CI/RI} \quad \ldots\ldots \quad \textbf{Eq. (2)}$$

The value of RI (Random Index) depends upon the size matrix. Tables 2 shows the value of the RI for matrix of order (N) 1 to 12 obtained by approximating random indices using a sample size of 500 (Saaty, 2000).

Table 2: Random index (RI) for matrix of order N (Saaty, 2000)

N	1	2	3	4	5	6	7	8	9	10	11	12
RI	0	0	0.58	0.90	1.12	1.24	1.32	1.41	1.45	1.49	1.51	1.48

The acceptable consistency ratio range varies according to the size of matrix i.e. 0.05 for a 3 by 3 matrix, 0.08 for a 4 by 4 matrix and 0.1 for all larger matrices, 'N' equal to or greater than 5 (Saaty, 2000). If the value of consistency ratio is equal to or less than the acceptable value, it implies that the evaluation within the matrix is acceptable or indicates a good level of consistency in the comparative judgments represented in that matrix. An acceptable consistency ratio helps to ensure decision-maker reliability in determining the priorities of a set of criteria (Kumar et al., 2009; Luthra et al., 2015).

4. Results and Discussions

The results and discussions of adopted methodology (AHP approach) have been presented and discussed as follows:

Two experts, one each from academia and Indian industry, were contacted for the purpose of getting the enablers of 'Lean Six Sigma' implementation rated. Analytical Hierarchy Process (AHP) methodology was used to rank these enablers.

Based on the ratings obtained during workshop by experts, matrix is formed and the priorities are synthesized using the methodology of AHP. AHP framework to evaluate ranking of enablers of lean six-sigma is structured as a hierarchy and pair wise comparison matrix is formed as shown in Table 3, which clearly describes weights given by experts to these enablers of lean six-sigma.

Table 3: Pair wise comparison matrix of enablers of lean six-sigma

Enablers to LSS	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
1	1	3.00	2.00	3.00	2.00	2.00	2.00	3.00	3.00	5.00	5.00	3.00
2	0.33	1	1.00	0.50	0.33	0.50	1.00	1.00	0.25	0.33	0.33	2.00
3	0.50	1.00	1	0.50	0.25	2.00	1.00	1.00	0.50	1.00	0.33	0.50
4	0.33	2.00	2.00	1	1.00	1.00	1.00	1.00	1.00	2.00	1.00	1.00
5	0.50	3.00	4.00	1.00	1	1.00	1.00	1.00	1.00	3.00	1.00	1.00
6	0.50	2.00	0.50	1.00	1.00	1	1.00	1.00	0.33	0.50	0.25	0.50
7	0.50	1.00	1.00	1.00	1.00	1.00	1	1.00	0.50	2.00	0.50	1.00
8	0.33	1.00	1.00	1.00	1.00	1.00	1.00	1	1.00	2.00	1.00	1.00
9	0.33	4.00	2.00	1.00	1.00	3.00	2.00	1.00	1	1.00	1.00	1.00
10	0.20	3.00	1.00	0.50	0.33	2.00	0.50	0.50	1.00	1	0.25	2.00
11	0.20	3.00	3.00	1.00	1.00	4.00	2.00	1.00	1.00	4.00	1	1.00
12	0.33	0.50	2.00	1.00	1.00	2.00	1.00	1.00	1.00	0.50	1.00	1

Table 4 describes priority of each enabler of lean six-sigma. Based upon the priority weight values, enablers of LSS have been ranked and presented in Table 4.

Table 4: Rank of enablers of lean six-sigma

S. N.	**Enabler of lean six-sigma**	**Priority**	**Rank**
1	Management involvement and funds allocation;	20.3%	**I**
2	Culture with Effective communication	4.7%	**XII**
3	Training and change management	5.2%	**XI**
4	Project management and LSS techniques (Statistical Thinking)	7.8%	**V**
5	Linking LSS to business strategies	9.7%	**III**
6	Customer Integration	5.4%	**X**
7	HRM, employees' motivation and team management practices	6.5%	**VIII**
8	Supplier involvement (quality of raw material)	7.0%	**VI**
9	Manufacturing facilities, standardization and scheduling	9.4%	**IV**
10	Visual control	6.1%	**IX**
11	Floor layout and optimization of transportation & material Handling	11.0%	**II**
12	Reliable data collection and retrieval system	7.0%	**VII**
Consistency Ratio (CR) = 0.069			

From the analytical results shown in Table 4, "Management involvement and funds allocation (20.3%)" has been identified the most important enabler of "lean six-sigma" concept implementation followed by "Floor layout and optimization of transportation & material Handling (11.0%)", "Linking LSS to business strategies (9.7%)", "Manufacturing facilities, standardization and scheduling (9.4%)", "Project management and LSS techniques (Statistical Thinking) (7.8%)", "Supplier involvement (quality of raw material) (7.0%)", "Reliable data collection and retrieval system (7.0%)", "HRM, employees' motivation and team management practices (6.5%)", "Visual control (6.1%)", "Customer Integration (5.4%)", "Training and change management (5.2%)" and "Culture with Effective communication (4.7%)" being ranked at twelfth position.

Analysis of key findings of one of the questionnaire based survey of companies, geographically dispersed, from both the manufacturing and service industry to present the CSFs for the effective implementation of Lean Six Sigma and to analyze the implementation of Lean Six Sigma, focusing on the CSFs identified in the literature, highlighted

that the most important factors are: management commitment, cultural change, linking Lean Six Sigma to business strategy and leadership styles (Laureani and Antony, 2012). The literature offers fairly similar and rather general CSF for 'lean and six-sigma' e.g. top management support and the importance of communication and information; and what seems to be missing, however, is the need for a systemic approach to organizational change and improvement (Näslund, 2008).

5. Conclusions

Many businesses have initiated a process improvement program to improve quality and productivity, with the goal of increased profitability. In recent years, two of the more popular programs of this type are Lean and Six Sigma (Maleyeff, 2014). 'Lean six-sigma (LSS)' concept combines fundamentals, principles, tools and techniques of 'lean' and 'six-sigma' to gain competitive edge over competitor organizations/supply chains by achieving 'reduction of waste' by implementing 'lean' concept in manufacturing, process and service sectors and 'quality improvement' by implementing 'six-sigma' concept. Therefore, 'Lean six-sigma (LSS)' concept has been used to achieve enhanced benefits to gain competitive advantage.

Identification of appropriate enablers (Management involvement and funds allocation; Culture with Effective communication; Training and change management; Project management and LSS techniques (Statistical Thinking); Linking LSS to business strategies; Customer Integration; HRM, employees' motivation and team management practices; Supplier involvement; Manufacturing facilities, standardization and scheduling; Visual control; Floor layout and optimization of transportation & material Handling; Reliable data collection and retrieval system) of 'lean six-sigma', twelve in numbers, has been carried out by reviewing suitable literature and followed by ranking of these enablers using analytical hierarchy approach utilizing experts' opinions. "Management involvement and funds allocation", "Floor layout and optimization of transportation & material handling", "Linking LSS to business strategies" and "Manufacturing facilities, standardization and scheduling" have been rated top four ranked enabler towards implementation of 'lean six-sigma' philosophy in Indian manufacturing industry.

This paper may help quality and production engineers/managers to identify and analyze enablers of 'lean six-sigma' implementation in their manufacturing/service organization. Ranking of the relevant enablers may be found useful in prioritizing so as enablers may be managed according to the importance. It may also help decision making authorities in formulating policies and decision making related to planning and implementation of 'lean six-sigma' concept in manufacturing and service sectors.

6. Limitations and Scope of Future Work

In AHP approach, all pair comparisons have been made on the basis on the experts' opinions (selected from academia and industry). As it is natural, opinions of experts may be biased.

From the literature review and expert opinions in detail, various enablers to implement LSS have been identified and ranked. Further, Interpretive Structural Modeling (ISM) technique or Analytical Network Process (ANP) or some other suitable technique may also be used to determine ranking among these enablers considered in our study and results may be compared with this study. Interpretive Ranking Process (IRP) may also be used to rank these enablers with respect to performance measures to implement LSS.

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LOW COST X BAND RADAR SYSTEM FOR MULTIPLE TARGET DETECTION

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Abstract

Radar based object detection systems have been in place for about a century serving various purposes like detection of ships aircrafts, spacecraft, navigation, reading weather formations and terrain mapping. With the advent of better packing technologies and signal conditioning circuits radars have become compact and affordable thus offering comparatively low cost solutions than other systems based on imaging. This paper describes an X band Radar System for multiple target detection that can work as an effective solution for obstacle detection and collision avoidance system to be used in automated braking systems. This radar system is capable of detecting multiple targets from the clutter encountered by the radar signals within a range of 20 metres. The paper discusses various moving target indicator techniques employed for multiple target detection and speed of the object in real time. This is particularly useful in automotive industries where the low cost motion sensors are needed in variety of applications which are necessary to ensure the safety of the passengers. To ensure a good signal to noise ratio we have used non coherent integration so that the radar signal is recognizable among the clutter. Moving Target Indicator techniques are used primarily to detect the number of objects in the range of the radar. This is carried out along with adaptive constant false alarm thresholding technique so that the object can be detected among the clutter and noise accurately. An Arduino Uno is used for detecting the objects and speed after processing on the non-coherently integrated pulse.

Keywords: *Radar, Clutter. CFAR, MTI*

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1. INTRODUCTION

The term RADAR, introduced as an acronym for Radio Detection And Ranging is now a specially coined term referring to systems employing radio waves for object and target detection. Radar detects objects using radio waves to determine the range, altitude, direction, or speed of objects. Radars have wide-ranging applications such as detecting aircrafts, ships, space crafts, guided missiles, motor vehicles and mapping terrain. The radar transmitter transmits radio waves through the radar transmitting antenna which are electromagnetic in nature. These waves travel through the medium to the object incurring losses on the way. The object, generally metal interacts with the radio waves producing electromagnetic field of its own so that no net electric field is formed inside the metal. This electromagnetic field that is produced to oppose the incident electromagnetic field then travels to the receiver antenna.

The existing implementations employing HB 100 Doppler radars have developed systems that are capable of detecting single targets using continuous wave operation[1]. This paper discusses Doppler radar for detecting multiple targets using Moving Target Indicator techniques in pulse Doppler mode.

1.1 Received Energy of X band Signals

Radar systems are classified on the basis of frequency of operation in S band (3 GHz), C band (5 GHz), X band (10 GHz), and other higher frequency bands. X band radars are imaging radars that offer a comparatively reliable low cost solution than other motion sensors. The received signal energy from the radar is given by the equation:

$$\text{Received Signal Energy} = \underbrace{P_T}_{\text{Transmit Power}} \underbrace{\left(\frac{4\pi A}{\lambda^2}\right)}_{\text{Transmit Gain}} \underbrace{\left(\frac{1}{4\pi R^2}\right)}_{\text{Spread Factor}} \underbrace{\left(\frac{1}{L}\right)}_{\text{Losses}} \underbrace{(\sigma)}_{\text{Target RCS}} \underbrace{\left(\frac{1}{4\pi R^2}\right)}_{\text{Spread Factor}} \underbrace{(A)}_{\text{Receive Aperture}} \underbrace{(\tau)}_{\text{Dwell Time}}$$

Fig 1: Received Signal Energy Formula[2]

This received energy at the receiver is mixed with noise. Noise are of following types galactic, solar, manmade interference noise, atmospheric, ground, transmitter, receiver, waveguide and duplexer noise.

1.2 Detection of Radar Pulses in Noise

The detection of radar pulses involves two parameters namely probability of detection and probability of false alarm. On a fixed threshold, higher the Signal to Noise Ratio higher would be the probability of detection. The Signal to Noise Ratio of Radar is given by following equation.

$$SNR = 10 \log_{10} [\text{signal power/noise power}]$$

Signal Power reflected from target and received by radar $P_r = \frac{P_t G_t}{4\pi R^2} \frac{\sigma A_e}{4\pi R^2}$

Average Noise Power $N = k T_s B_n$

Signal to Noise Ratio $\frac{S}{N} = \frac{P_r}{N}$

Fig 2: Signal Power and Avg. Noise Power Formulas[2]

$$\frac{S}{N} = \frac{P_t G^2 \lambda^2 \sigma}{(4\pi)^3 R^4 K T_s B_n L}$$

Fig 3: Signal to Noise Ratio Formula[2]

•The System Noise Temperature Ts , is divided into 3 components :

$$Ts = Ta + Tr + LrTe$$

•Ta is the contribution from the antenna
- Apparent temperature of sky (from graph)
- Loss within antenna
•Tr is the contribution from the RF components between the antenna and the receiver
- Tempe`rature of RF components
• Lr is the loss of input RF components
•Te is the temperature of the receiver
- Noise factor of receiver

The detection of target echoes in noise involves integration of pulses, fluctuating target issues and adaptive thresholding techniques. The integration of pulses can be done using coherent and non-coherent techniques. Coherent integration involves addition of in phase and quadrature quantities of complex radar return signal. These voltages are then computed, averaged and matched with a threshold. In general non-coherent integration, the pulse magnitude is calculated which is then averaged so that it can be compared with a threshold. In coherent techniques no information is lost while in non-coherent techniques phase information is lost. Coherent techniques are more efficient than non-coherent integration techniques.

2. MULTIPLE TARGET DETECTION USING MTI TECHNIQUES

Targets can be distinguished from the clutter using Moving Target Indicator technique and Pulse Doppler technique. Moving target Indicator techniques use low pulse repetition frequency and short waveforms to separate targets and clutter. Pulse Doppler technique classifies targets into different velocity regimes providing velocity data along with separation of targets from clutter. This technique uses long waveforms for their operation.

A two pulse MTI canceller can be used to illustrate the principal of multiple object detection. The amplitude of return signal from the moving objects changes in consecutive pulses owing to the Doppler shift while the fixed clutter returns fixed echoes. The subtraction of subsequent pulses eliminates the clutter from the return signal and gives the multiple moving objects at different range cells. The following block diagram depicts method deployed for multiple target detection.

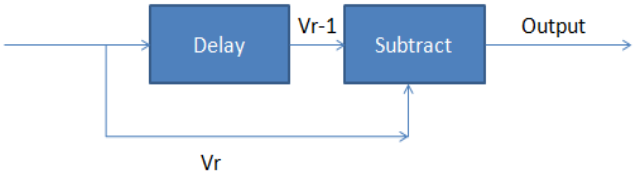

Fig 4: 2 Pulse MTI Canceller Block Diagram[2]

For 2 pulse MTI canceller,

$$V_{output} = V_{i+1} - V_i$$

For 3 pulse MTI canceller,

$$V_{output} = V_i - 2V_{i-1} + V_{i-2}$$

2.1 Adaptive Thresholding Technique for Radar Signals

Constant false alarm rate (CFAR) thresholding can be used to adaptively threshold the radar signals. For adaptive thresholding the noise floor of the non-coherently integrated signal should be computed using adaptive thresholding. In mean level CFAR technique we process the range cells in window slides. The cell under test is matched to a threshold using mean value of other range cells in the window. This process can detect false targets in sharp clutters and interference. To avoid this Greatest of Mean level CFAR technique is used in which the surrounding range cells are divided into left and right halves which are then averaged. The greatest noise level range half is used to determine the threshold.

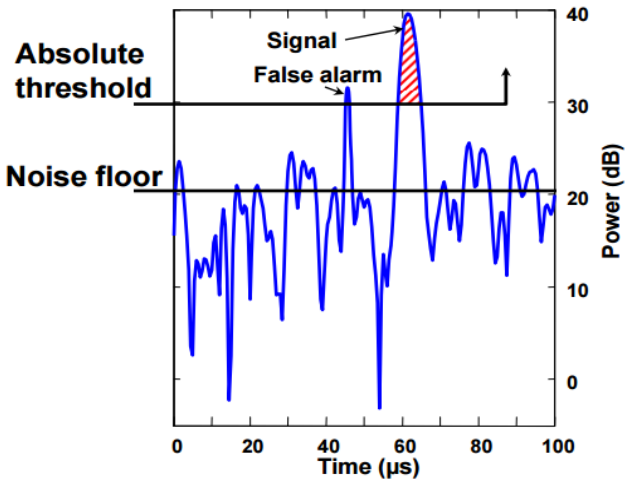

Fig 5: Disadvantage of Absolute Thresholding Technique[2]

3. PRACTICAL IMPLEMENTATION

The radar system is designed using the HB-100[3] pulsed microwave Doppler sensor module. The range of the module is up to 20 meters which is enough for automatic braking systems. Doppler shift output is observed from IF terminal when movement is detected in the field of detection. The magnitude of the Doppler Shift is in proportions to reflection of transmitted energy and is in microvolts. A high gain low frequency bandwidth amplifier is connected to the IF pin to amplify the Doppler shift to a level that can be read by development platform like Arduino Uno. Frequency of Doppler shift is calculated using the algorithm to determine the velocity of targets. Doppler frequency is related to velocity of motion through:

$$F_d = 2V\left(\frac{F_t}{C}\right)\text{Cos}\theta$$

Fig 6: Doppler Frequency Formula [3]

Where
F_d = Doppler Frequency
V = Velocity of the target
F_t = Transmit frequency
C = Speed of light ($3x10^8$ m/sec)
Θ =the angle between the target moving direction and the axis of the module.

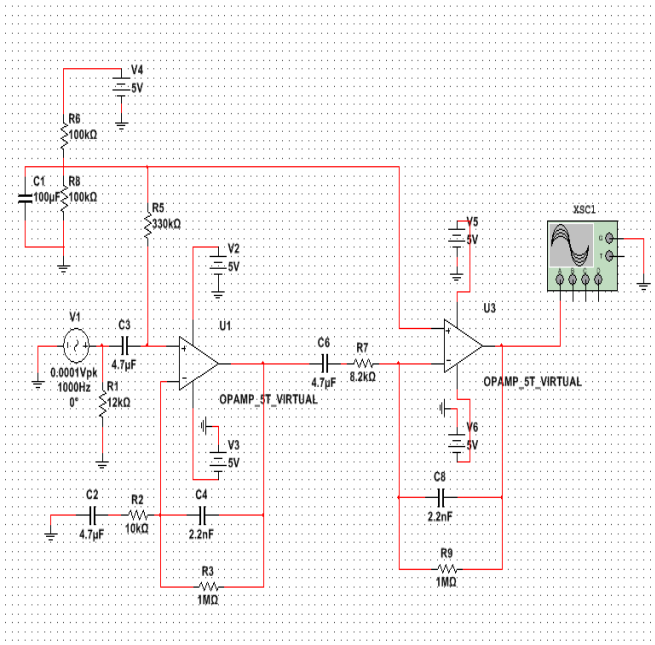

Fig 7: Radar Amplifier Circuit Diagram

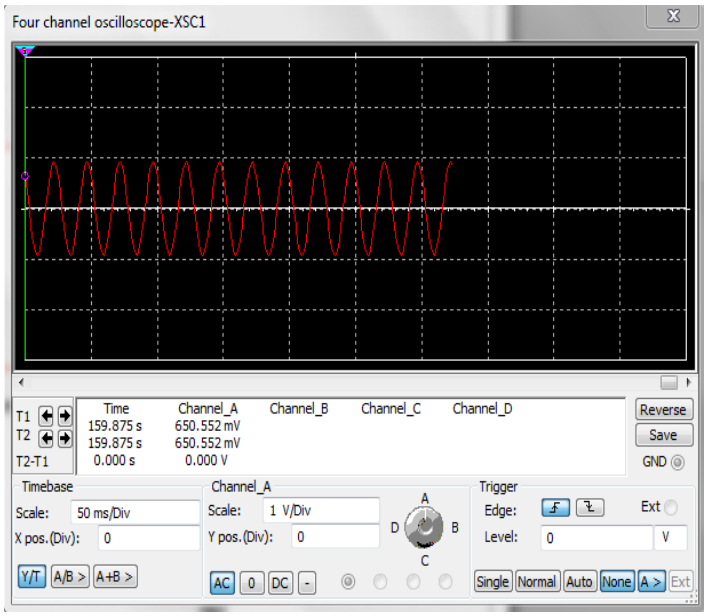

Fig 8: Simulation Of Amplifier Circuit in MultiSim

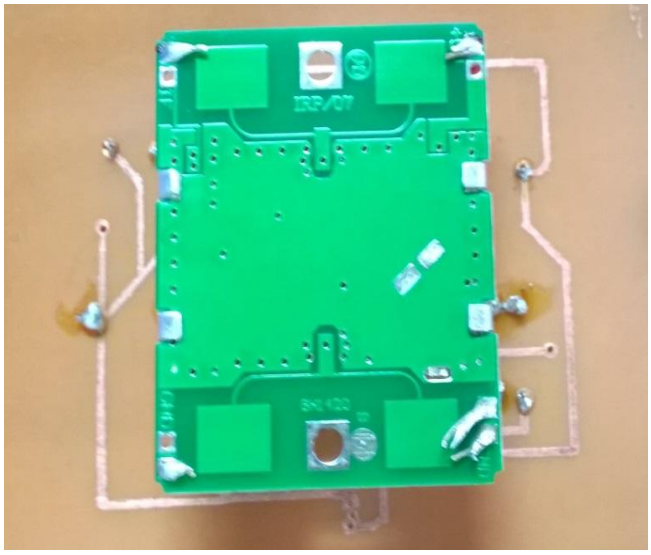

Fig 9: Finally assembly of Radar on a PCB

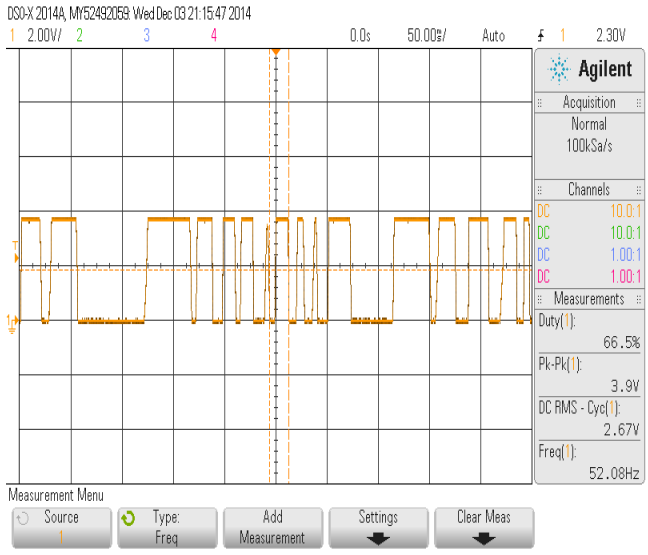

Fig 10: Output of the Amplifier Stage

3.1 Algorithm

The Arduino Uno is initialized with Pin 11 as Pulse generator. A PWM of 2 kHz pulse repetition frequency is generated with a pulse width of 10 microseconds high time using the delay Microseconds() function and giving 240 microseconds low time for the digital pin. The pulse received is converted from analog to digital and this is sent to non-coherent integrator wherein the consecutive pulses are simply added and averaged to increase SNR. These integrated pulses are then differenced from subsequent pulses to get the number of objects. The objects in the path are detected using Greatest of Mean level CFAR technique adaptive thresholding with the Arduino storing the range gates in an array and then thresholding each range point with the greater of the mean of the next and previous ten range points. The non-coherently integrated pulses are passed through a zero crossing detector [4] or comparator to get a square wave. The frequency counter library of Arduino is then used to compute the frequency and hence the speed.

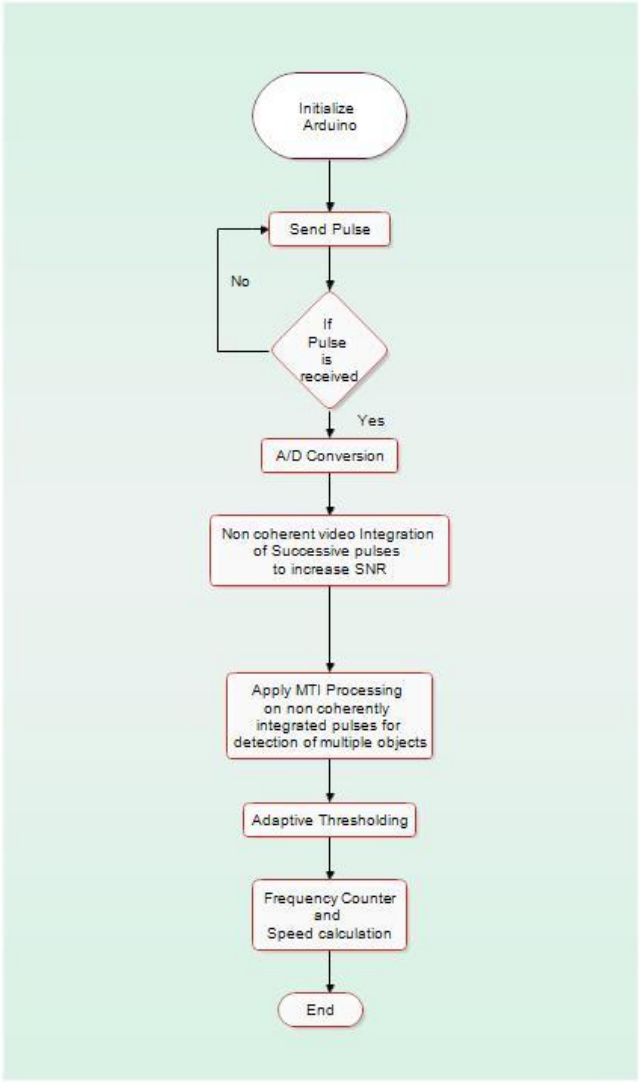

Fig 11: Flowchart of the whole Algorithm

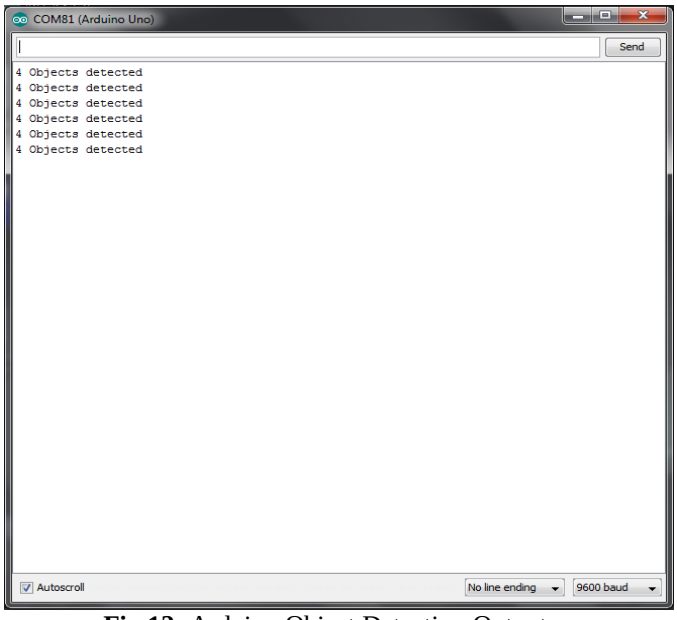

Fig 12: Arduino Object Detection Output

4. CONCLUSION

The radar system is promising but constitutes a lot of irregularities and clutter which can be eliminated using Doppler filter banks. So instead of MTI processing, pulse Doppler filter techniques would be our future research work.

As the automotive industry is flourishing day by day, we need more and more cost effective solutions to accommodate all economic classes of the society. The cutting edge technologies of the generation are necessary.

Table -1: Test results of radar system

S.No	Doppler Frequency (Hz)	Speed (km/hr)
1.	20.0	1.026
2.	52.08	2.672
3.	66.2	3.396
4.	101.53	5.209
5.	305.78	15.688

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BIOGRAPHIES

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Optimal Solution of a Fully Fuzzy Linear Fractional Programming Problem by Using Graded Mean Integration Representation Method

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Abstract

In the present paper, the study of fully fuzzy linear fractional programming problem (FFLFPP) using graded mean integration representation method is discussed where all the parameters and variables are characterized by trapezoidal fuzzy numbers. A computational algorithm has been presented to obtain an optimal solution by applying simplex method. To demonstrate the applicability of the proposed approach, one numerical example is solved. Also to check the efficiency and feasibility of the proposed approach, we compare the results of examples by applying crisp numbers, triangular fuzzy numbers and trapezoidal fuzzy numbers.

Keywords: Fully fuzzy linear fractional programming problem; Trapezoidal fuzzy number; Graded mean integration representation

MSC 2010 No.: 90C32, 90C70, 97N60

1. Introduction

Fractional programming (FP) was studied extensively in the middle of 1960s and early 1970s of the last century in the literature (1962, 1970). In many practical applications like stock problems, ore blending problems, shipping schedules problems, optimal policy for a Markovian chains, sensitivity of linear programming problem (LPP), optimization of ratios of criterion gives more insight into the situations than the optimization of each criterion (1988).

To study the efficiency in different fields such as education, hospital administration, court systems, air force maintenance units, bank branches, etc., fractional programming solves more efficiently the above type of problems (1978). FP problem, which has been used as an

important planning tool for the past decades, is applied to different disciplines such as engineering, business, finance, economics, etc. FP is generally used for modelling real life problems with one or more objective(s) such as profit/cost, inventory/sales, actual cost/standard cost, output/employee, etc.

Charnes and Cooper (1962) showed that the linear fractional programming problem (LFPP) can be optimized by solving a LPP. Bellman and Zadeh (1970) has proposed decision making in a fuzzy environment. S. H. Chen (1985) has discussed operations of fuzzy numbers with function principle. Chen and Hsieh (1999) has studied the graded mean integration representation (GMIR) of generalized fuzzy numbers while Chen et al. (2006) has used some concepts of GMIR of L-R type fuzzy numbers. Nachammi et al. (2012) have studied fuzzy linear fractional programming problem (FLFPP) by metric distance ranking. The present authors (2013) have discussed FLFPP by signed distance ranking where variables and parameters are characterized by triangular fuzzy numbers (TFN).

The objective of this paper is to deal with a kind of FLFPP where all the variables and parameters are trapezoidal fuzzy numbers (TrFN). In this paper an attempt has been made to develop an algorithm for solving FLFPP based on GMIR of fuzzy numbers.

The paper is organized as follows: Section 2 outlines the definitions and preliminaries of TrFN and its arithmetic operations. In section 3 we have discussed the methodology of GMIR of TrFN based on fuzzy set theory. In section 4, we first recall some basic notions about FLPP and FLFPP in which a theorem based on conditions of fuzzy optimality is presented.

An algorithm is developed which gives the computational procedure for optimal solution of FLFPP. Section 5 demonstrates two numerical examples to illustrate the above algorithm. Section 6 discusses the main results and conclusions of this paper.

2. Definitions and Preliminaries

We review the fundamental notation of fuzzy set theory initiated by Bellman and Zadeh (1970). Below, we give definitions and notations taken from Zimmerman (1983).

Definition 2.1.

If X is a collection of objects denoted generally by x, then a fuzzy set $\tilde{A}$ in X is defined as a set of ordered pairs:

$$\tilde{A}=\{(x,\mu_{\tilde{A}}(x)):x\in X\},$$

where $\mu_{\tilde{A}}(x)$ is called the membership function of x in $\tilde{A}$. The membership function maps each element of X to a membership grade (or membership value) between 0 and 1.

Definition 2.2.

A fuzzy number $\tilde{A}$ is a convex normalized fuzzy set on the real line **R** such that:

(i) it exists at least one x_0 in **R** with $\mu_{\tilde{A}}(x_0)=1$, and

(ii) $\mu_{\tilde{A}}(x)$ is piecewise continuous.

Definition 2.3. Trapezoidal Fuzzy Number

A fuzzy number $\tilde{A}= (a, b, c, d)$, $a \le b \le c \le d$ $(a, b, c, d > 0)$ is said to be a trapezoidal fuzzy number if its membership function is given by:

$$\mu_{\tilde{A}}(x)=\begin{cases} 0, & x < a, \\ \frac{x-a}{b-a}, & a < x \le b, \\ 1, & b < x < c, \\ \frac{d-x}{d-c}, & c \le x < d, \\ 0, & x > d. \end{cases}$$

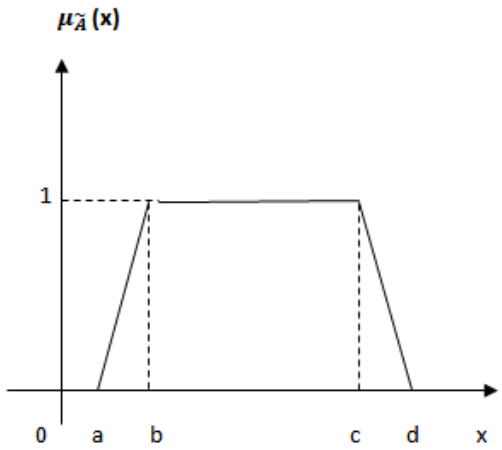

Figure1: Trapezoidal Fuzzy Number $\tilde{A} = (a, b, c, d)$

***Remark**:*

If $b = c$, the trapezoidal fuzzy number reduces to a triangular fuzzy number as shown in Figure 2. It can be written by a triplet (a, b, d).

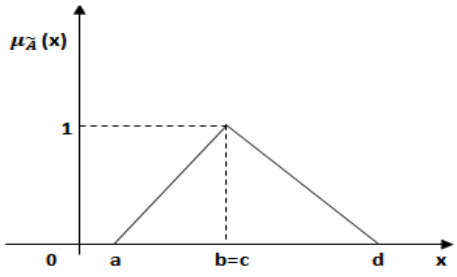

Figure2: Triangular Fuzzy Number $\tilde{A}$=(a,b,d)

3. Methodology

3.1. Graded Mean Integration Representation Method

Chen and Hsieh (1999) introduced graded mean integration representation method based on the integral value of graded mean α-level of generalized fuzzy number.
First, we describe generalized fuzzy number as follows:

Suppose, $\tilde{A} = (a_1, a_2, a_3, a_4; w_A)$ is a generalized fuzzy number. It is described as any fuzzy subset of the real line **R**, whose membership function $\mu_{\tilde{A}}(x)$ satisfies the following conditions:

(a) $\mu_{\tilde{A}}(x)$ is a continuous mapping from **R** to the closed interval [0,1],

(b) $\mu_{\tilde{A}}(x) = 0, \quad -\infty < x \leq a_1$,

(c) $\mu_{\tilde{A}}(x) = L(x)$, is strictly increasing on $[a_1, a_2]$,

(d) $\mu_{\tilde{A}}(x) = w_A, \ a_2 \leq x \leq a_3$,

(e) $\mu_{\tilde{A}}(x) = R(x)$, is strictly decreasing on $[a_3, a_4]$,

(f) $\mu_{\tilde{A}}(x)$=0, $a_4 \leq x < \infty$,

where $0 < w_A \leq 1$ and a_1, a_2, a_3 and a_4 are real number. Also this type of generalized fuzzy number be denoted as $\tilde{A} = (a_1, a_2, a_3, a_4; w_A)_{LR}$.

When w_A=1, it can be written as $\tilde{A} = (a_1, a_2, a_3, a_4)_{LR}$.

Secondly, by graded mean integration representation method L^{-1} and $R^{-1}$are the inverse functions of L and R, respectively and the graded mean α-level value of generalized fuzzy number $\tilde{A} = (a_1, a_2, a_3, a_4; w_A)_{LR}$:

$$\frac{\alpha\left(L^{-1}(\alpha)+R^{-1}(\alpha)\right)}{2}.$$

Then the graded mean integration representation of $\tilde{A}$ is $P(\tilde{A})$ with grade w_A , where

$$P(\tilde{A}) = \frac{\int_0^{w_A} \frac{\alpha(L^{-1}(\alpha)+R^{-1}(\alpha))}{2} d\alpha}{\int_0^{w_A} \alpha \, d\alpha} \quad \text{with } 0 < \alpha \leq w_A \text{ and } 0 < w_A \leq 1.$$

When $w_A = 1$, the above generalized fuzzy number $\tilde{A}$ is considered as trapezoidal fuzzy number and is written as $\tilde{A} = (a_1, a_2, a_3, a_4)_{LR}$.

Therefore,

$$P(\tilde{A}) = \frac{a_1+2a_2+2a_3+a_4}{6}.$$

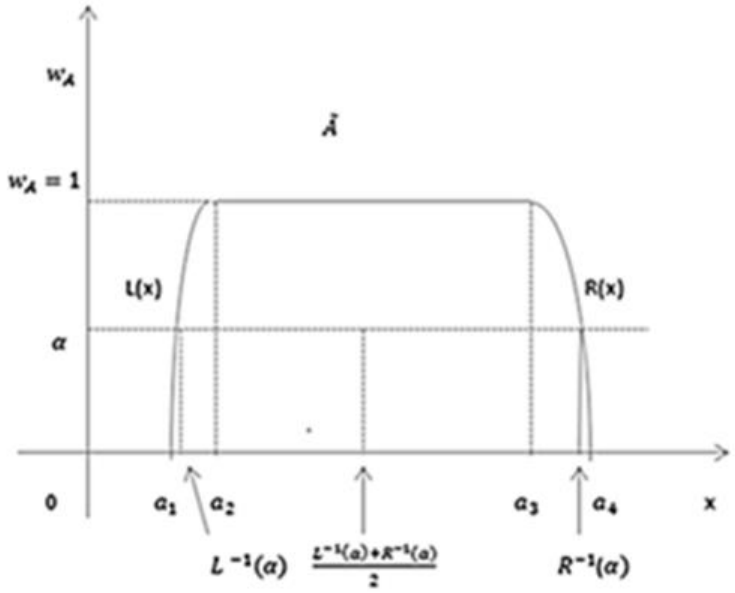

Figure 3. The graded mean $\alpha - level$ value of generalized fuzzy number $\tilde{A} = (a_1, a_2, a_3, a_4; w_A)_{LR}$

3.2. The fuzzy mathematical operations under function principle

Function principle is proposed by Chen (1985) to be as the fuzzy arithmetical operations by trapezoidal fuzzy numbers. This method is more useful than the extension principle (1999, 2006) for the fuzzy numbers with the trapezoidal membership functions.

We describe some fuzzy arithmetical operations under function principle as follows:

Suppose, $\tilde{A} = (a_1, a_2, a_3, a_4)$ and $\tilde{B} = (b_1, b_2, b_3, b_4)$ are two trapezoidal fuzzy numbers. Then,

1. $\tilde{A} \oplus \tilde{B} = \left(a_1 + b_1, a_2 + b_2, a_3 + b_3, a_4 + b_4\right)$.
2. $\tilde{A} \otimes \tilde{B} = \left(a_1 b_1, a_2 b_2, a_3 b_3, a_4 b_4\right)$.
3. $-\tilde{B} = -(b_1, b_2, b_3, b_4) = (-b_4, -b_3, -b_2, -b_1)$.
4. $\tilde{A} \ominus \tilde{B} = (a_1 - b_4, a_2 - b_3, a_4 - b_2, a_4 - b_1)$.
5. $\frac{1}{\tilde{B}} = \widetilde{B^{-1}} = \left(\frac{1}{b_4}, \frac{1}{b_3}, \frac{1}{b_2}, \frac{1}{b_1}\right)$.
6. $\tilde{A} \oslash \tilde{B} == (\frac{a_1}{b_4}, \frac{a_2}{b_3}, \frac{a_3}{b_2}, \frac{a_4}{b_1})$.
7. Let, $\lambda \in R$,

For > 0, $\lambda \otimes \tilde{A} = (\lambda a_1, \lambda a_2, \lambda a_3, \lambda a_4)$,

For < 0, $\lambda \otimes \tilde{A} = (\lambda a_4, \lambda a_3, \lambda a_2, \lambda a_1)$,

where $a_1, a_2, a_3, a_4, b_1, b_2, b_3$ and b_4 are all non-zero positive real numbers.

3.3. Signed distance ranking of Triangular fuzzy number

Yao and Wu (2000) proposed a signed distance ranking to rank fuzzy numbers.

Let, $\tilde{A}$=(a_1, a_2, a_3) be a triangular fuzzy number of L-R type then

$$R(\tilde{A}) = \frac{a_1+2a_2+a_3}{4}.$$

4. Fuzzy linear fractional programming problem

4.1. Definition

Fuzzy linear fractional programming: The general format of fuzzy linear fractional programming problem (FLFPP) may be written as:

$$\text{Max } \tilde{Z}(x) = \frac{\tilde{c}x+\tilde{\alpha}}{\tilde{d}x+\tilde{\beta}},$$

subject to the constraints:

$$\tilde{A}x = \tilde{b}, x \geq 0,$$

where x$\in R^n, \tilde{c}, \tilde{d} \in R^n, \tilde{A} \in R^{m\times n}, \tilde{b} \in R^m, \tilde{\alpha}, \tilde{\beta} \in R$.

With the additional assumption that the denominator is positive for all feasible solution.

4.2. Definition

Initial basic feasible solution:

Let $x_{\tilde{B}}$ be the initial basic feasible solution such that

$$\tilde{B}x_{\tilde{B}} = \tilde{b} \Rightarrow x_{\tilde{B}} = \tilde{B}^{-1}\tilde{b}, \qquad x_{\tilde{B}} \geq 0,$$

$$\text{where } \tilde{B} = (\widetilde{b_1}, \widetilde{b_2}, \dots, \widetilde{b_m}).$$

Further let $\tilde{z}^1 = \tilde{c}_B x_{\tilde{B}} + \tilde{\alpha}$ and $\tilde{z}^2 = \tilde{d}_B x_{\tilde{B}} + \tilde{\beta}$,

where $\tilde{c}_B$ and $\tilde{d}_B$ are the vectors having their components as the coefficients associated with the basic variables in numerator and denominator of the objective function respectively.

4.1. Theorem (Conditions of optimality). [Swarup et al. (1997) and De and Deb (2013)]

A sufficient condition for a feasible solution to a fully fuzzy linear fractional programming problem (FFLFPP) to be fuzzy optimum is that $\widetilde{u}_{ij} \geq \widetilde{0}$ for all *j* which the column vector $\widetilde{a}_j$ in $\widetilde{A}$ is not in the basis $\widetilde{B}$.

Proof:

Let the fully fuzzy linear fractional programming be stated as follows-

$$\text{Max } \tilde{Z}(x) = \frac{\tilde{c}x+\tilde{\alpha}}{\tilde{d}x+\tilde{\beta}},$$

subject to the constraints:

$$\tilde{A}x = \tilde{b} \text{ and } \tilde{x} \geq \tilde{0},$$

where x$\in R^n$, $\tilde{c}, \tilde{d} \in R^n, \tilde{A} \in R^{m\times n}$, $\tilde{b} \in R^m$, $\tilde{\alpha}, \tilde{\beta} \in R$.

Here we show that for any $\tilde{a}_j$ and $\tilde{A}$ not in $\tilde{B}$ at least one $\tilde{u}_{ij} > \tilde{0}$. If possible let all $\tilde{u}_{ij} \leq \tilde{0}$, ($i$=1,2, ..., m). We have the fuzzy basic feasible solution to this FLFPP is

$$\sum_{i=1}^{m} \tilde{x}_{Bj}\tilde{b}_i = \tilde{b}. \tag{1}$$

Suppose that we add and subtract $\bar{\theta}\tilde{a}_j$ ($\bar{\theta}$ is any scalar), then we get

$$\sum_{i=1}^{m} \tilde{x}_{Bi}\tilde{b}_i - \bar{\theta}\tilde{a}_j + \bar{\theta}\tilde{a}_j = \tilde{b}. \tag{2}$$

Since

$$-\bar{\theta}\tilde{a}_j = -\theta\sum_{i=1}^{m}\tilde{u}_{ij}\tilde{b}_i, \tag{3}$$

we have ,

$$\sum_{i=1}^{m}\tilde{x}_{Bi}\tilde{b}_i - \bar{\theta}\sum_{i=1}^{m}\tilde{u}_{ij}\tilde{b}_i + \tilde{\theta}\tilde{a}_j = \tilde{b},$$

$$\sum_{i=1}^{m}(\tilde{x}_{Bi} - \bar{\theta}\tilde{u}_{ij})\tilde{b}_i + \bar{\theta}\tilde{a}_j = \tilde{b}.$$

When $\bar{\theta} > \tilde{0}$, we have $\tilde{x}_{Bi} - \bar{\theta}\tilde{u}_{ij} \geq \tilde{0}$. Since by assumption, $\tilde{u}_{ij} \leq \tilde{0}$, (i =1,2, ..., m). Therefore, $(\tilde{x}_{Bi} - \bar{\theta}\tilde{u}_{ij}),\cdots,(\tilde{x}_{Bm} - \bar{\theta}u_{mj})$ and $\bar{\theta}$ is a fuzzy feasible solution for all $\bar{\theta} > \tilde{0}$. Thus, the set S is unbounded, which is contrary to our hypothesis of regularity. Hence, $\tilde{u}_{ij} > \tilde{0}$.

4.6. Definition

A fuzzy basic feasible solution $\tilde{x}_B$ to fuzzy linear fractional programming problem is called fuzzy unbounded solution if for at least one j, for which $\tilde{u}_{ij} \leq 0$ (i =1, 2,..., m), $\tilde{z}_j - \tilde{c}_j$ and $\tilde{z}_j - \tilde{d}_j$ are negative, then there does not exist any optimum solution to this FLFPP.

Algorithm for solving fully fuzzy linear fractional programming problem by simplex method:

The steps for the computation of a fuzzy optimum solution are as follows:

Step 1:

First consider the variables and parameters of the example as fuzzy number like trapezoidal fuzzy number.

Step 2:

Check whether the objective function of the given fully fuzzy linear fractional programming problem (FLFPP) is to be maximized or minimized. If it minimized then we convert it into a problem of maximizing it by using the result,

$$\text{Min } \tilde{z} = -\text{Max } (-\tilde{z}).$$

Step 3:

Check whether all $\tilde{b}_i$ (i = 1, 2, ..., m) are non-negative . If any one of $\tilde{b}_i$ is negative then multiply the corresponding in equation of the constraints by -1, so as to get all $\tilde{b}_i$ (i =1, 2, ..., m) non-negative.

Step 4:

Convert all the in equations of the constraints into equations by introducing slack and /or surplus variables in the constraints. The costs of these variables equal to zero.

Step 5:

Obtain an initial basic feasible solution to the given problem in the form $\tilde{x}_B = \tilde{B}^{-1}\tilde{b}$ and put it in the third column of the simplex table.

Step 6:

Compute $\tilde{z} = \dfrac{\tilde{z}^1}{\tilde{z}^2}$, where $\tilde{z}^1 = \tilde{c}_B x_{\tilde{B}} + \tilde{\alpha}$ and $\tilde{z}^2 = \tilde{d}_B x_{\tilde{B}} + \tilde{\beta}$.

Step 7:

Compute the net evaluation $\tilde{\Delta}_j$ (j =1, 2, ..., m), where

$$\tilde{\Delta}_j = \tilde{z}^2(\tilde{z}_j^{\,1} - \tilde{c}_j) - \tilde{z}^1(\tilde{z}_j^{\,2} - \tilde{d}_j).$$

Here, $(\tilde{z}_j^{\,1} - \tilde{c}_j)$ and $(\tilde{z}_j^{\,2} - \tilde{d}_j)$ are calculated by using the relation $\tilde{z}_j^{\,1} - \tilde{c}_j = \tilde{c}_{\tilde{B}} \tilde{y}_j - \tilde{c}_j$ and $\tilde{z}_j^{\,2} - \tilde{d}_j = \tilde{d}_{\tilde{B}} \tilde{y}_j - \tilde{d}_j$.

Step 8:

Examine the sign $\tilde{\Delta}_j$ (using the method of GMIR method):

(i) If all $(\tilde{z}_j - \tilde{c}_j) \geq \tilde{0}$, then the initial basic feasible solution $x_{\tilde{B}}$ is a fuzzy optimum basic feasible solution.

(ii) If at least one $(\tilde{z}_j - \tilde{c}_j) < \tilde{0}$, proceed to the next step.

Step 9:

If there are more than one negative $\tilde{\Delta}_j$, then choose the most negative of them. Let it be $\tilde{\Delta}_r$ for some $j = r$.

(i) If all $\tilde{y}_{ir} \leq \tilde{0}$, ($i$ =1, 2, ..., m) then there is an unbounded solution to the given problem.

(ii) If at least one $\tilde{y}_{ir} > \tilde{0}$ (i=1, 2, ..., m), then the corresponding vector $\tilde{y}_r$ enters the basis $\tilde{y}_B$.

Step 10:

Compute the ratios

$$\left\{ \frac{\tilde{x}_{Bi}}{\tilde{y}_{ir}}, \tilde{y}_{ir} > \tilde{0}, i = 1, 2, \cdots, m \right\}$$

and choose the minimum of them. Let the minimum of these ratios be $\frac{\tilde{x}_{Bk}}{\tilde{y}_{kr}}$. Then, the vector $\tilde{y}_k$ will leave the basis $\tilde{y}_B$. The common element $\tilde{y}_{kr}$ which is in the k^{th} row and r^{th} column is known as leading or (pivotal) element of the table.

Step 11:

Convert the leading element to unit TrFN by dividing its row by the leading TrFN itself and all other elements in its column to zero TrFN by making the use of the relations:

$$\hat{\tilde{y}}_{ij} = \tilde{y}_{ij} - \frac{\tilde{y}_{kj}}{\tilde{y}_{kr}} \tilde{y}_{ir}, \; i = 1, 2, ..., m+1; i \neq k, \text{ and}$$

$$\hat{\tilde{y}}_{kj} = \frac{\tilde{y}_{kj}}{\tilde{y}_{kr}}, \; j = 0, 1, 2, \cdots, n.$$

Step 12:

Go to **step 6** and repeat the computational procedure until either an optimum solution is obtained or there is an indication of an unbounded solution.

5. Numerical Example

Example 1.

Solve the following linear fractional programming problem:

$$\text{Max } z = \frac{6x_1+5x_2}{2x_1+7}$$

subject to the constraints:

$$x_1 + 2x_2 \leq 3,$$
$$3x_1 + 2x_2 \leq 6,$$
$$x_1, x_2 \geq 0.$$

Solution:

Table1: Initial Iteration:

		c_j	6	5	0	0	
		d_j	2	0	0	0	
c_B	d_B	x_B	y_1	y_2	y_3	y_4	$\frac{x_{Bi}}{y_{ij}}$
0	0	$x_3 = 3$	1	2	1	0	3
0	0	$x_4 = 6$	3^*	2	0	1	$2 \longrightarrow$
$z^1 = 0$	$z^2 = 7$	$z_j^1 - c_j$	-6	-5	0	0	
$z = 0$		$z_j^2 - d_j$	-2	0	0	0	
		Δ_j	-42 $\uparrow$	-35	0	0	

Here $\Delta_j \leq 0$, so x_4 leaves the basis and x_1 enters the basis.

Table 2: The next iterated simplex table is:

		c_j	6	5	0	0	
		d_j	2	0	0	0	
c_B	d_B	x_B	y_1	y_2	y_3	y_4	$\frac{x_{Bi}}{y_{ij}}$
0	0	$x_3 = 1$	0	$\frac{4}{3}^*$	1	$\frac{-1}{3}$	$\frac{3}{4} \longrightarrow$
6	2	$x_1 = 2$	1	$\frac{2}{3}$	0	$\frac{1}{3}$	3
$z^1 = 12$	$z^2 = 11$	$z_j^1 - c_j$	0	-1	0	2	
$z = \frac{12}{11}$		$z_j^2 - d_j$	0	$\frac{4}{3}$	0	$\frac{2}{2}$	
		Δ_j	0	$-27 \uparrow$	0	14	

Here $\Delta_j \leq 0$, so x_3 leaves the basis and x_2 enters the basis.

Table 3: The optimum iterated simplex table is:

		c_j	6	5	0	0	
		d_j	2	0	0	0	
c_B	d_B	x_B	y_1	y_2	y_3	y_4	$\frac{x_{Bi}}{y_{ij}}$
5	0	$x_2 = \frac{3}{4}$	0	1	$\frac{3}{4}$	$\frac{-1}{4}$	
6	2	$x_1 = \frac{3}{2}$	1	0	$\frac{-2}{3}$	$\frac{1}{2}$	
$z^1 = \frac{51}{4}$	$z^2 = 10$	$z_j^1 - c_j$	0	0	$\frac{-1}{4}$	$\frac{7}{4}$	
$z = \frac{51}{40}$		$z_j^2 - d_j$	0	0	$\frac{-4}{3}$	1	
		Δ_j	0	0	$\frac{29}{2}$	$\frac{19}{4}$	

In the optimum iterated table, all $\Delta_j \geq 0$ and the problem reaches its optimality. Hence, the optimal solution is $x_1 = \frac{3}{2}$=1.5, $x_2 = \frac{3}{4} = 0.75$ and

$$\text{Max } Z^* = \frac{51}{40} = 1.28.$$

Now the above problem can be solve by fuzzified version as followed: By taking triangular fuzzy number:

$$\text{Max } \tilde{z} = \frac{(5,6,7)\tilde{x}_1+(3,5,6)\tilde{x}_2}{(1,2,3)\tilde{x}_1+(5.5,7,8.5)}$$

subject to the constraints:

$$(0.5, 1, 1.5)\tilde{x}_1 + (1.5, 2, 2.5)\tilde{x}_2 \leq (2, 3, 5),$$
$$(2, 3, 4)\,\tilde{x}_1 + (1, 2, 3)\tilde{x}_2 \leq (5, 6, 7),$$
$$\tilde{x}_1, \tilde{x}_2 \geq 0.$$

Solution: The initial iteration table is given below:

Table 4:Initial Iteration:

		$\tilde{c}_j$:	(5,6,7)	(3,5,6)	(0,0,0)	(0,0,0)	
		$\tilde{d}_j$:	(1,2,3)	(0,0,0)	(0,0,0)	(0,0,0)	
$\tilde{c}_B$	$\tilde{d}_B$	$\tilde{x}_B$	$\tilde{y}_1$	$\tilde{y}_2$	$\tilde{y}_3$	$\tilde{y}_4$	$\frac{\tilde{x}_{Bi}}{\tilde{y}_{ij}}$
0	0	$\tilde{x}_3 = (2,3,5)$	(0.5,1,1.5)	(1.5,2,2.5)	(0,1,0)	(0,0,0)	(8,3,7)
0	0	$\tilde{x}_4 = (5,6,7)$	(2,3,4)*	(1,2,3)	(0,0,0)	(0,1,0)	(4.6,2,3.8)
$\tilde{z}^1$ =(0,0,0)	$\tilde{z}^2$ =(5.5,7,8.5)	$\tilde{z}_j^1 - \tilde{c}_j$:	(-7,-6,-5)	(-6,-5,-3)	(0,0,0)	(0,0,0)	
$\tilde{z}$ =(0,0,0)		$\tilde{z}_j^2 - \tilde{d}_j$:	(-3,-2,-1)	(0,0,0)	(0,0,0)	(0,0,0)	
		$\tilde{\Delta}_j$:	(-82,-42,-86)	(-69.5,-35,-63.5)	(0,0,0)	(0,0,0)	

In Table 4, $\tilde{\Delta}_j \leq 0$, so $\tilde{x}_1$ enters the basis and $\tilde{x}_4$ leaves the basis by using

$$\text{Min } [\text{d}(\tilde{\Delta}_{j1}, \tilde{\Delta}_{j2})] = \text{d}(\tilde{\Delta}_{j1}) = \tilde{y}_1,$$

$$\text{Min } [\text{d}(\frac{\tilde{x}_{B1}}{\tilde{y}_{12}}, \frac{\tilde{x}_{B2}}{\tilde{y}_{22}})] = \text{d}(\frac{\tilde{x}_{B2}}{\tilde{y}_{22}}) = \tilde{x}_4.$$

Therefore, $(2,3,4)^*$ is the leading element. Now convert this element as unit triangular fuzzy number and all other elements in the column as zero. The new iterated simplex table is given below:

Table5: Iterated Simplex Table:

		$\tilde{c}_j$:	(5,6,7)	(3,5,6)	(0,0,0)	(0,0,0)	
		$\tilde{d}_j$:	(1,2,3)	(0,0,0)	(0,0,0)	(0,0,0)	
$\tilde{c}_B$	$\tilde{d}_B$	$\tilde{x}_B$	$\tilde{y}_1$	$\tilde{y}_2$	$\tilde{y}_3$	$\tilde{y}_4$	$\frac{\tilde{x}_{Bi}}{\tilde{y}_{ij}}$
0	0	$\tilde{x}_3 = (5.8,1,9.6)$	(2.55,0,3.6)	(4,1.3,4.3)*	(0,1,0)	(0.25, -0.3, 0.5)	(4.71,0.77, 7.61)
(5,6,7)	(1,2,3)	$\tilde{x}_1 = (4.6,2,3.8)$	(2.1,1,2.05)	(1.8,0.7,1.5)	(0,0,0)	(0.5,0.3 ,0.25)	(7.68,2.85, 6.76)
$\tilde{z}^1$ =(37.6,12, 36.8)	$\tilde{z}^2$ =(16.7, 11,22.1)	$\tilde{z}_j^{\,1} - \tilde{c}_j$:	(24.6,0, 24.3)	(20.3, -0.8, 16.9)	(0,0,0)	(4.5,1.8 ,3.6)	
$\tilde{z}$ =		$\tilde{z}_j^{\,2} - \tilde{d}_j$:	(8.2,0,8.1)	(4.3,1.4,5.1)	(0,0,0)	(1.30.6, 1.4)	
		$\tilde{\Delta}_j$:	(367.8,0, 365.7)	(97.22, -25.6, 272.46)	(0,0,0)	(118.44 ,12.6, 117.54)	

In Table 5, $\tilde{\Delta}_j \leq 0$, so $\tilde{x}_2$ enters the basis and $\tilde{x}_3$ leaves the basis by using

$$\text{Min}[\text{d}\,(\tilde{\Delta}_{j1}, \tilde{\Delta}_{j2})] = \text{d}\,(\tilde{\Delta}_{j1}) = \tilde{y}_2,$$

$$\text{Min}[\text{d}\,(\frac{\tilde{x}_{B1}}{\tilde{y}_{21}}, \frac{\tilde{x}_{B2}}{\tilde{y}_{22}})] = \text{d}(\frac{\tilde{x}_{B1}}{\tilde{y}_{21}}) = \tilde{x}_3.$$

Therefore, $(4, 1.3, 4.3)^*$ is the leading element. Now convert this element as unit triangular fuzzy number and all other elements in the column as zero. The optimum iterated simplex table is given below

Table 6: Optimal iteration:

		$\tilde{c}_j$:	(5,6,7)	(3,5,6)	(0,0,0)	(0,0,0)	
		$\tilde{d}_j$:	(1,2,3)	(0,0,0)	(0,0,0)	(0,0,0)	
$\tilde{c}_B$	$\tilde{d}_B$	$\tilde{x}_B$	$\tilde{y}_1$	$\tilde{y}_2$	$\tilde{y}_3$	$\tilde{y}_4$	$\frac{\tilde{x}_{Bi}}{\tilde{y}_{ij}}$
(3,5,6)	(0,0,0)	$\tilde{x}_2 = (4.71,$ 0.77,7.61)	(1.96,0, 2.77)	(3.39,1, 3.61)	(0.25,0.77, 0.23)	(0.12, -0.23,0.31)	
(5,6,7)	(1,2,3)	$\tilde{x}_1$=(9.93,1.46, 7.09)	(4.04,1, 3.42)	(4.33,0,3.87)	(0.16, -0.54,0.18)	(0.72,0.46, 0.33)	
$\tilde{z}^1$ =(92.74, 12.61, 95.43)	$\tilde{z}^2$ =(26.82, 9.92, 26.06)	$\tilde{z}_j^{\,1} - \tilde{c}_j$:	(46.04,0, 46.37)	(51.93, 0, 50.27)	(1.82, 0.61, 3.07)	(6.53,1.61, 5.37)	
$\tilde{z}$ =(9.82, 1.27,10.09)		$\tilde{z}_j^{\,2} - \tilde{d}_j$:	(12.08, 0, 10.84)	(8.66,0,7.44)	(-0.22,- 1.08,-1.26)	(1.9,0.92, 2.04)	
		$\tilde{\Delta}_j$:	(593.41,0, 612.32)	(608.97,0, 607.88)	(153.36, 19.67, 198.36)	(221.48, 4.37,206.12)	

In Table 6, $\widetilde{\Delta_j} > 0$ and, hence, $d(\widetilde{\Delta_j}) > 0$. Therefore, the problem reaches its optimality. Hence, the optimal solution is

$$\widetilde{x_1} = (9.93, 1.46, 7.09) \text{ and } \widetilde{x_2} = (4.71, 0.77, 7.61).$$

Therefore, Max $\widetilde{z^*}_1 = (9.82, 1.27, 10.09)$. By taking trapezoidal fuzzy number:

$$\text{Max } \tilde{z} = \frac{(5,6,7,8)\tilde{x}_1 + (3,5,6,7)\tilde{x}_2}{(1,2,3,4)\tilde{x}_1 + (5.5,7,8.5,9)}$$

subject to the constraints:

$$(0.5,\ 1,\ 1.5,\ 2)\tilde{x}_1 + (1.5,\ 2,\ 2.5,\ 3)\tilde{x}_2 \leq (2, 3, 5, 7),$$
$$(2,3,4,5)\ \tilde{x}_1 + (1, 2, 3, 4)\tilde{x}_2 \leq (5, 6, 7, 8),$$
$$\tilde{x}_1, \tilde{x}_2 \geq 0.$$

Solution: The initial iteration table is given below:

Table7: Initial Iteration:

		$\tilde{c}_j$:	(5,6,7,8)	(3,5,6,7)	(0,0,0,0)	(0,0,0,0)	
		$\tilde{d}_j$:	(1,2,3,4)	(0,0,0,0)	(0,0,0,0)	(0,0,0,0)	
$\tilde{c}_B$	$\tilde{d}_B$	$\tilde{x}_B$	$\tilde{y}_1$	$\tilde{y}_2$	$\tilde{y}_3$	$\tilde{y}_4$	$\frac{\tilde{x}_{Bi}}{\tilde{y}_{ij}}$
(0,0,0,0)	(0,0,0,0)	$\tilde{x}_3 = (2,3,5,7)$	(0.5,1,1.5,2)	(1.5,2,2.5,3)	(1,0,0,0)	(0,0,0,0)	(1,2,5,14)
(0,0,0,0)	(0,0,0,0)	$\tilde{x}_4 = (5,6,7,8)$	$(2,3,4,5)^*$	(1,2,3,4)	(0,0,0,0)	(0,1,0,0)	(1,1.5,2.3,4) →
$\tilde{z}^1$ =(0,0,0,0)	$\tilde{z}^2$ =(5.5,7, 8.5, 9)	$\tilde{z}_j^1 - \tilde{c}_j$:	(-8,-7,-6, -5)	(-7,-6,-5,-3)	(0,0,0,0)	(0,0,0,0)	
$\tilde{z}$ =(0,0,0,0)		$\tilde{z}_j^2 - \tilde{d}_j$:	(-4,-3,-2, -1)	(0,0,0,0)	(0,0,0,0)	(0,0,0,0)	
		$\tilde{\Delta}_j$:	(-44,-49, -51,-45) ↑	(-38.5,-42, -42.5,-27)	(0,0,0,0)	(0,0,0,0)	

In Table 7, $\widetilde{\Delta_j} \leq 0$, so $\tilde{x}_1$ enters the basis and $\tilde{x}_4$ leaves the basis by using

$$\text{Min } [P(\widetilde{\Delta}_{j1}, \widetilde{\Delta}_{j2})] = P(\widetilde{\Delta}_{j1}) = \tilde{y}_1,$$

$$\text{Min } [P(\frac{\tilde{x}_{B1}}{\tilde{y}_{11}}), P(\frac{\tilde{x}_{B2}}{\tilde{y}_{12}})] = P(\frac{\tilde{x}_{B2}}{\tilde{y}_{12}}) = \tilde{x}_4 \ .$$

Therefore, $(2,3,4,5)^*$ is the leading element. Now convert this element as unit trapezoidal fuzzy number and all other elements in the column as zero.
The new iterated simplex table is given below:

Table8:Iterated Simplex Table:

		$\tilde{c}_j$:	(5,6,7,8)	(3,5,6,7)	(0,0,0,0)	(0,0,0,0)	
		$\tilde{d}_j$:	(1,2,3,4)	(0,0,0,0)	(0,0,0,0)	(0,0,0,0)	
$\tilde{c}_B$	$\tilde{d}_B$	$\tilde{x}_B$	$\tilde{y}_1$	$\tilde{y}_2$	$\tilde{y}_3$	$\tilde{y}_4$	$\frac{\tilde{x}_{Bi}}{\tilde{y}_{ij}}$
(0,0,0,0)	(0,0,0,0)	$\tilde{x}_3 = (21,35.2, 61,86.5)$	(0, 9.3, 16.9, 24)	(16.75,24, 30.75,37.3)*	(12.5,0,0, 0)	(0,0, -0.25,0)	(0.56,2.08, 2.54,5.16)
(5,6,7,8)	(1,2,3,4)	$\tilde{x}_1$ = (1,1.5,2.3,4)	(1,1.8,3.2, 6.25)	(0.2,0.5,1,2)	(0,0,0,0)	(0,0.25,0,0)	(0.5,1.5, 4.6,20)
$\tilde{z}^1$=(5,9, 16.1, 32)	$\tilde{z}^2$ =(6.5,10, 15.4,25)	$\tilde{z}_j^1 - \tilde{c}_j$:	(-3,3.8, 16.4,45)	(-6,-3,2,13)	(0,0,0,0)	(0,1.5,0,0)	
$\tilde{z}$ =(0.2,0.58, 1.61,4.92)		$\tilde{z}_j^2 - \tilde{d}_j$:	(-3,0.6, 7.6,24)	(0.2,1,3,8)	(0,0,0,0)	(0,0.5,0,0)	
		$\tilde{\Delta}_j$:	(-787.5, -84.36, 247.16, 1140)	(-295, -78.3,21.8,324)	(0,0,0,0)	(0,15, -4.5,0)	

In Table 8, $\tilde{\Delta}_j \leq 0$, so $\tilde{x}_2$ enters the basis and $\tilde{x}_3$ leaves the basis by using

$$\text{Min } [P(\tilde{\Delta}_{j1}, \tilde{\Delta}_{j2})] = P(\tilde{\Delta}_{j1}) = \tilde{y}_2,$$

$$\text{Min } [P(\frac{\tilde{x}_{B1}}{\tilde{y}_{21}}), P(\frac{\tilde{x}_{B2}}{\tilde{y}_{22}})] = P(\frac{\tilde{x}_{B1}}{\tilde{y}_{21}}) = \tilde{x}_3 \ .$$

Therefore, $(16.75, 24, 30.75, 37.3)^*$ is the leading element. Now convert this element as unit trapezoidal fuzzy number and all other elements in the column as zero. The new iterated simplex table is given below:

Table9: Optimum Iteration:

		$\tilde{c}_j$:	(5,6,7,8)	(3,5,6,7)	(0,0,0,0)	(0,0,0,0)	
		$\tilde{d}_j$:	(1,2,3,4)	(0,0,0,0)	(0,0,0,0)	(0,0,0,0)	
$\tilde{c}_B$	$\tilde{d}_B$	$\tilde{x}_B$	$\tilde{y}_1$	$\tilde{y}_2$	$\tilde{y}_3$	$\tilde{y}_4$	$\frac{\tilde{x}_{Bi}}{\tilde{y}_{ij}}$
(3,5,6,7)	(0,0,0,0)	$\tilde{x}_2 = (1.3,2.5, 5.7,11.5)$	(0, 0.67,1.57, 3.2)	(1,1.7,2.9,5)	(0.75,0,0,0)	(0,0, -0.02,0)	
(5,6,7,8)	(1,2,3,4)	$\tilde{x}_1$ = (0.5,1.27,2.2,4)	(1, 1.7, 3.2, 6.25)	(0, 0.4, 0.9, 2)	(0,0,0, -0.03)	(0,0.25,0,0)	
$\tilde{z}^1$=(6.4, 20.12,49.6, 112.5)	$\tilde{z}^2$ =(6,9.54, 15.1,25)	$\tilde{z}_j^1 - \tilde{c}_j$:	(-3,6.55, 25.82, 125.5)	(-4,4.9, 18.7,48)	(2.25,0,0, -0.24)	(0,1.5, -0.12,0)	
$\tilde{z}$ =(0.26,1.33, 5.19,18.75)		$\tilde{z}_j^2 - \tilde{d}_j$:	(-3,0.4,7.6, 24)	(0,0.8,2.7,8)	(0,0,0, -0.12)	(0,0.5,0,0)	
		$\tilde{\Delta}_j$:	(-2718, -340,382, 3144.2)	(-924,-85,269, 1200)	(27,0,0,-6)	(0,15, -11.86,0)	

In the optimum iteration table, all $\tilde{\Delta}_j > 0$ and hence $P(\tilde{\Delta}_j) > 0$. Therefore the problem reaches its optimality. Hence the optimal solution is $\widetilde{x_1} = (0.5, 1.27, 2.2, 4)$ and $\widetilde{x_2} = (1.3, 2.5, 5.7, 11.5)$. Therefore,

$$\text{Max } \tilde{z}^*_2 = (0.26, 1.33, 5.19, 18.75).$$

Example 2.

Solve the following FLFPP (2013):

$$\text{Max } z = \frac{2x_1+3x_2}{x_1+x_2+7}$$
$$\text{subject to the constraints:}$$
$$3x_1 + 5x_2 \leq 15,$$
$$4x_1 + 3x_2 \leq 12,$$
$$x_1, x_2 \geq 0.$$

Solution:

The solutions of crisp number and triangular fuzzy number are taken from (2013) and that of trapezoidal fuzzy number are solved like above example 1. After solving above example, the results are given below:

By crisp number, the optimal solution is $x_1 = 0, x_2 = 3$ and Max $z^{**} = 0.9$
By triangular fuzzy number, the optimal solution is:

$$\tilde{x}_1 = (0,0,0), \tilde{x}_2 = (5.95, 3, 6.5) \text{ and}$$
$$\text{Max } \widetilde{z_1}^{**} = (3.655, 0.9, 3.9).$$

By trapezoidal fuzzy number, the optimal solution is:

$$\tilde{x}_1=(0,0,0,0),\ \tilde{x}_2= (2.8,4.2,6.8,10) \text{ and}$$
$$\text{Max } \widetilde{z_2}^{**}=(0.07,0.70,3.04,8.29).$$

The results of crisp number, triangular fuzzy number and trapezoidal fuzzy number are given in Table10.

Table 10: Comparison of optimal solution of the numerical examples

Observation	Crisp number	Triangular fuzzy number	Trapezoidal fuzzy number
Example 1	Optimal solution is $x_1 = 1.5$, $x_2 = 0.75$ and $Max\ Z^* = 1.28$	Fuzzy optimal solution is $\widetilde{x_1} = (9.93,1.46,7.09)$, $\widetilde{x_2} = (4.71, 0.77, 7.61)$ and Max $\widetilde{z^*}_1 = (9.82, 1.27, 10.09)$.	Fuzzy optimal solution is $\widetilde{x_1} = (0.5, 1.27, 2.2, 4)$, $\widetilde{x_2} = (1.3, 2.5, 5.7, 11.5)$ and Max $\widetilde{z^*}_2 = (0.26, 1.33, 5.19, 18.75)$.
Example 2	Optimal solution is $x_1 = 0$, $x_2 = 3$ and Max $Z^{**} = 0.9$	Fuzzy optimal solution is $\tilde{x}_1 = (0,0,0), \tilde{x}_2 = (5.95, 3, 6.5)$ and Max $\widetilde{z_1}^{**} = (3.655, 0.9, 3.9)$	Fuzzy optimal solution is $\tilde{x}_1$=(0,0,0,0), $\tilde{x}_2$ = (2.8,4.2,6.8,10) and Max $\widetilde{z_2}^{**}$=(0.07,0.70,3.04,8.29).

5. Conclusions

In this paper, we have solved fully fuzzy linear fractional programming problem (FFLFPP) by using graded mean integration representation (GMIR) method where the parameters and

variables are characterized by trapezoidal fuzzy number. To check the efficiency of the proposed approach one numerical example has been solved by taking parameters and variables are in crisp number, TFN and TrFN. Example 2 has been solved in paper (2013). From Table 10, the optimal solution of both the examples has been presented. From that, the optimal solutions obtained by different numbers are nearly equal. The above method can be applied to solve FLFPP to reduce the complexity in problem solving like agriculture, production planning, inventory problems, transportation problems, etc.

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Reduced graphene oxide modified smart conducting paper for cancer biosensor

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ABSTRACT

We report results of the studies relating to the fabrication of a paper based sensor comprising of poly (3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) and reduced graphene oxide (RGO) composite. The effect of various solvents like methanol, ethylene glycol and H_2SO_4 on the electrical conductivity of PEDOT:PSS coated Whatman paper has been investigated. The conductivity of this solution processed conducting paper significantly increases from $\sim 1.16 \times 10^{-4}$ S cm^{-1} up to $\sim 3.57 \times 10^{-2}$ S cm^{-1} ($\sim$300 times) on treatment with ethylene glycol. The observed significant increase in electrical conductivity is due to conformational rearrangement in the polymer and is due to strong non-covalent cooperative interaction between PEDOT and the cellulose molecules. Further, incorporation of RGO into the conducting paper results in improved electrochemical performance and signal stability. This paper electrode is a promising alternative over the expensive conventional electrodes (ITO, gold and glassy carbon), that are known to have limited application in smart point-of-care (POC) devices. This low cost, flexible and environment friendly conducting paper based biosensor utilized for cancer biomarker (carcinoembryonic antigen, CEA) detection reveals high sensitivity of 25.8 μA ng^{-1} mL cm^{-2} in the physiological range, 1–10 ng mL^{-1}.

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1. Introduction

Paper based point-of-care (POC) devices are rapidly evolving for desired analytical and clinical applications since these are predicted to be simple, cost-effective, portable, consume low power and are disposable. These devices have potential applications in healthcare, detection of toxicants, explosives and environmental studies. Compared to conventional laboratory assays, these devices are found to be very helpful for making speedy decision for therapeutics. Besides this, the testing can be performed near the vicinity of a patient and hence these devices have recently gained considerable attention in health care (Gervais et al., 2011; Kumar et al., 2013a, 2013b; Luppa et al., 2011).

Electrochemical sensors are known to play an important role in on-going transition towards the paper based POC diagnostic devices. The electrochemical techniques offer high sensitivity, high signal-to-noise ratio, portability and fast response time (Wang, 2006). Therefore, its integration with the paper may be advantageous. To ensure the application of paper in an electrochemical sensor, it is essential to make it conducting. In this context, many methods such as screen printing, inkjet printing etc. have been used to incorporate conducting ink on a paper substrate (Jagadeesan et al., 2012; Tobjörk and Österbacka, 2011). These methods require complex fabrication steps, additional instrumentation, skilled personnel and are time-consuming. Conducting polymers (CPs) have been considered a promising candidate to obtain conducting paper due to delocalization of π electrons since they are known to facilitate rapid electron transfer, mechanical flexibility and solution processability. Doping of a conducting polymer has been found to enhance its electronic, optical, physical, chemical and electrochemical properties (Dhand et al., 2011). CPs have been predicted to have enough potential for the development of a low cost and high performance biosensor materials that offer high permeability biocompatibility, and rapid electron transfer (Li et al., 2015; Zhai et al., 2013). Among the various conducting polymers, poly(3,4ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) has been considered to be a interesting candidate for development of a conducting paper due to its homogeneous entrapment in/on a paper using a simple dip coating method with

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enhanced stability. Moreover, the conductivity of PEDOT:PSS based paper can be significantly enhanced and tuned by treatment with a desired solvent. Further, doping with a nanomaterial may modulate the performance of paper in terms of electrochemical kinetics or signal stability and sensitivity. The reduced graphene oxide (RGO) has recently aroused much interest for development of electrochemical sensors. This is due to excellent electrochemical properties and large 2D surface area. Its abundant defects and chemical groups facilitate charge transfer and thus ensure increased electrochemical activity (Pumera, 2011). Hence incorporation of RGO in the PEDOT:PSS matrix may further improve electrochemical performance of a desired paper sensor (Gao et al., 2014; Zhang et al., 2014).

Cancer is currently a serious concern and a medical threat to the contemporary world. An estimated 14.1 million new cases of cancer and 8.2 million deaths were reported in 2012 necessitating early diagnosis of this dreaded disease (Cancer, 2012). Carcinoembryonic antigen (CEA) is known to be a tumor marker associated with colon, lung, ovarian and breast cancer that are responsible for more than half of all cancer deaths each year (Kulpa et al., 2002; Myers et al., 1978; Pepe et al., 2001; Wanebo et al., 1978). Determination of CEA in serum may be an interesting alternative for clinical diagnosis and monitoring of a cancer.

We report a facile method to obtain enhanced conductivity (~300 times) of PEDOT:PSS coated paper on treatment with ethylene glycol. Further, incorporation of RGO into the solution processed conducting paper results in improved electrochemical characteristics. This low cost, flexible and environment friendly conducting paper platform reveals high sensitivity towards a cancer biomarker (carcinoembryonic antigen, CEA) detection in the physiological range.

2. Materials and methods

2.1. Fabrication of PEDOT:PSS based conducting paper

The conducting paper (1 cm × 3 cm) was prepared using a simple dip coating method. The PEDOT:PSS aqueous solution (1.3 wt%, PEDOT content 0.5 wt%, PSS content 0.8 wt%) purchased from SigmaAldrich was ultrasonicated prior to use after which 3% ethylene glycol (EG) was added to the aqueous suspension of PEDOT:PSS. This solution was used to dip coat the Whatman filter paper #1 (procured from GE healthcare UK) rendering it conductive. It was then dried in a hot air oven at 100 °C and was termed as conducting paper.

2.2. Fabrication of PEDOT:PSS/RGO based electroactive paper

Preparation of the reduced graphene oxide (RGO) and PEDOT:PSS/RGO composite is given in Supporting information. The Whatman paper (1 cm × 1 cm) was dipped in PEDOT:PSS/RGO aqueous suspension (PEDOT:PSS content 1.3 wt%, RGO content 0.035 wt%) containing 3% EG for 1 h and then dried at 100 °C in a hot air oven. Thereafter it was treated with EG by dipping in the EG solution for 20 min. The EG treated conducting paper is finally dried at 100 °C for about 1 h. A Schematic of the experiment has been demonstrated in Fig. 1.

2.3. Characterization

The conductivity of the conducting paper was measured using the four points probe technique with a low current source (LCS-02), digital microvoltmeter (DMV-001) and PID controlled oven (PID-200), SES Instruments, India. The surface morphology was investigated by the high-resolution field emission scanning electron microscopy (Nova Nano Sem450, FEI). The transmission electron microscopy (TEM) was carried out with a JEM-2200 FS (JEOL, Japan). X-ray photoelectron spectroscopy (XPS) studies were performed using Axis-Nova, Kratos Analytical Ltd., Manchester, UK. The electrochemical studies were carried out by an Autolab Potentiostat/Galvanostat (Metrohm, Netherlands) using a conventional three-electrode cell with the electroactive paper as working electrode, platinum as auxiliary electrode and Ag/AgCl as the reference electrode in phosphate buffer saline (PBS, 50 mM, pH 7.4) containing 5 mM $[Fe(CN)_6]^{3-/4-}$.

3. Results and discussion

3.1. Electron microscopy and elemental analysis

Transmission electron micrograph of the RGO exhibits curved sheet like structure with a fairly smooth surface (Fig. 2A). The observed lighter and darker regions indicate the presence of RGO. The lighter region pertains to a few layered graphene whereas the darker region corresponds to the multilayerd graphene. The wrinkles and folds pertaining to the graphene sheet (sub-microns in size) are clearly visible. The selected area electron diffraction (SAED) pattern of RGO reveals hexagonal atomic structure and crystalline nature of the RGO sheets (Fig. 2B). The inner six member ring represents the [1100] plane. The visible six diffraction spots corresponding to [0001] indicate hexagonal symmetry

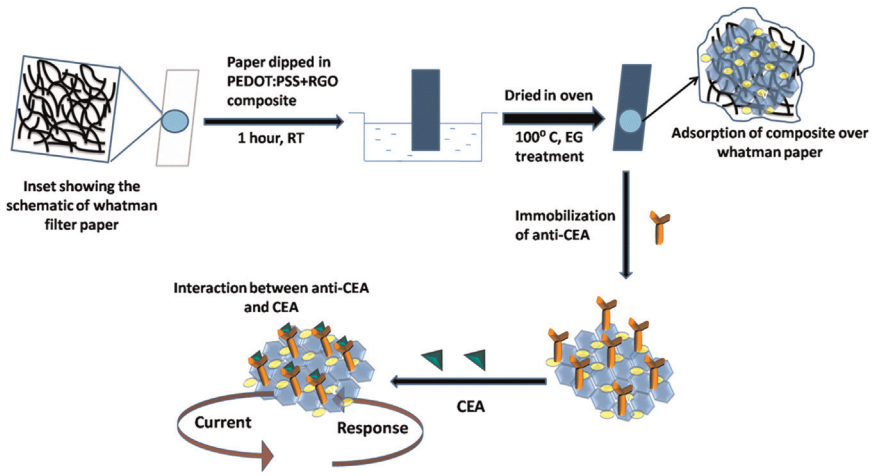

Fig. 1. Schematic of proposed electroactive paper sensor.

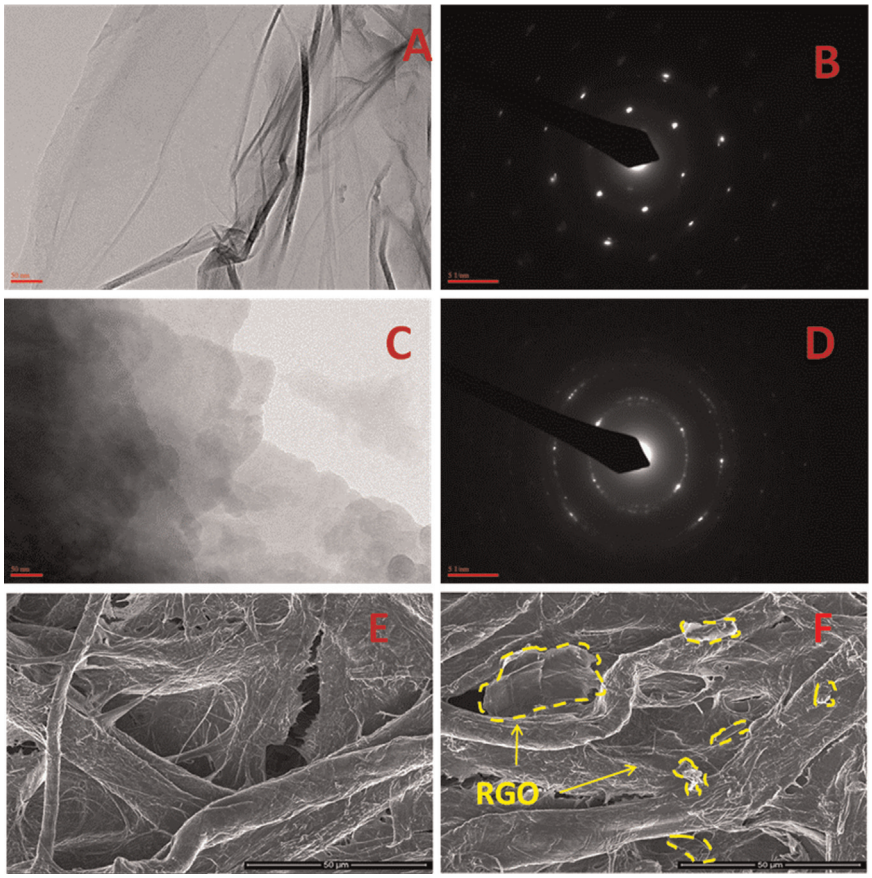

Fig. 2. (A) TEM image of synthesized reduced graphene oxide (RGO) where darker region corresponds to multilayer and lighter region corresponds to a few layer graphene. (B) SAED of RGO, which confirms the hexagonal atomic structure and crystalline nature of the sheets. (C) TEM image of PEDOT:PSS/RGO. (D) SAED pattern of PEDOT:PSS/RGO composite. (E) SEM of PEDOT:PSS adsorbed onto Whatman paper. (F) SEM of PEDOT:PSS/RGO Whatman coated paper.

of the [0001] diffraction of the RGO (Cui et al., 2011). The RGO sheets appear to be uniformly covered with PEDOT:PSS (Fig. 2C). The PSS molecules perhaps assist RGO dispersion via edge-to-face aromatic interactions between the RGO surface and the aromatic rings of the polymer which inhibit the hydrophobic graphene nanoplates from agglomeration, leading to a stable RGO dispersion in the polar solvent (Hyun et al., 2013). The diffused ring like structure observed (Fig. 2D) in the SAED pattern of PEDOT:PSS/RGO composite is because of the amorphous nature of PEDOT:PSS covering the RGO sheets. The SEM of PEDOT:PSS (Fig. 2E) coated paper indicates uniform adsorption of PEDOT:PSS over cellulose fibers of the paper. Because of the high porosity and tiny interfiber air spaces in Whatman paper, the PEDOT:PSS adsorbs into the paper through capillary action and after drying it produces uniform and stable film of PEDOT:PSS on the paper. Fig. 2F shows SEM of PEDOT:PSS/RGO coated paper. PEDOT:PSS/RGO is found to be uniformly adsorbed onto the cellulose fiber wherein some of RGO sheets are entangled in the fibrous network of Whatman paper. To further validate the formation of RGO, and its presence in PEDOT:PSS matrix, electron microscopic studies (SEM, elemental mapping and EDX) of RGO, PEDOT:PSS and PEDOT:PSS/RGO have been carried out (Supporting information Fig. S1).

3.2. Conductivity studies

The PEDOT:PSS coated paper shows conductivity of 1.16×10^{-4} S cm^{-1} (see Supporting information for conductivity calculation). However, on addition of 3% ethylene glycol (EG) in PEDOT:PSS solution, the value of conductivity increases to 1.43×10^{-3} S cm^{-1}. This is due to decreased columbic interactions between PEDOT and PSS molecules that perhaps contribute to reorientation of the polymer chains resulting in improved charge carrier mobility (Ouyang et al., 2005). Further, all studies have been done with PEDOT:PSS doped with 3% EG (Wei et al., 2013). The PEDOT:PSS doped with 3% EG coated Whatman paper has been termed as conducting paper.

The enhancement in the conductivity of PEDOT:PSS film (coated on glass substrate) has been recently reported when the film is dipped in methanol and H_2SO_4 (Alemu et al., 2012; Xia et al., 2012). This is due to ejection of the PSS ions from the PEDOT:PSS film dipped in the solvent, inducing the conformational rearrangement of PEDOT chains leading to higher conductivity. In the present case, effect of solvents such as methanol, H_2SO_4 and ethylene glycol (EG) on electrical conductivity of the conducting paper has been investigated (Supporting information Table S1). We have observed that on flexible substrate (Whatman paper 1), EG treatment shows the highest value of conductivity (3.57×10^{-2} S cm^{-1}) in comparison to methanol (6.8×10^{-3} S cm^{-1}), and H_2SO_4 (8.1×10^{-3} S cm^{-1}). This is in accordance with a similar report wherein the effect of flexibility of material and polyelectrolyte adhesion to substrate was studied (Podsiadlo et al., 2007). The increased flexibility of the EG treated conducting paper due to ejection of PSS results in the strong non-covalent cooperative interactions between PEDOT and cellulose molecules leading to higher conductivities. We have incorporated RGO in the PEDOT:PSS matrix for electrochemical studies since RGO exhibits excellent electrochemical properties (Pumera, 2011). PEDOT:PSS/RGO based conducting paper dipped in EG (electroactive paper) shows almost similar conductivity value (3.12×10^{-2} S cm^{-1}). The as-prepared electroactive paper shows greater degree of flexibility

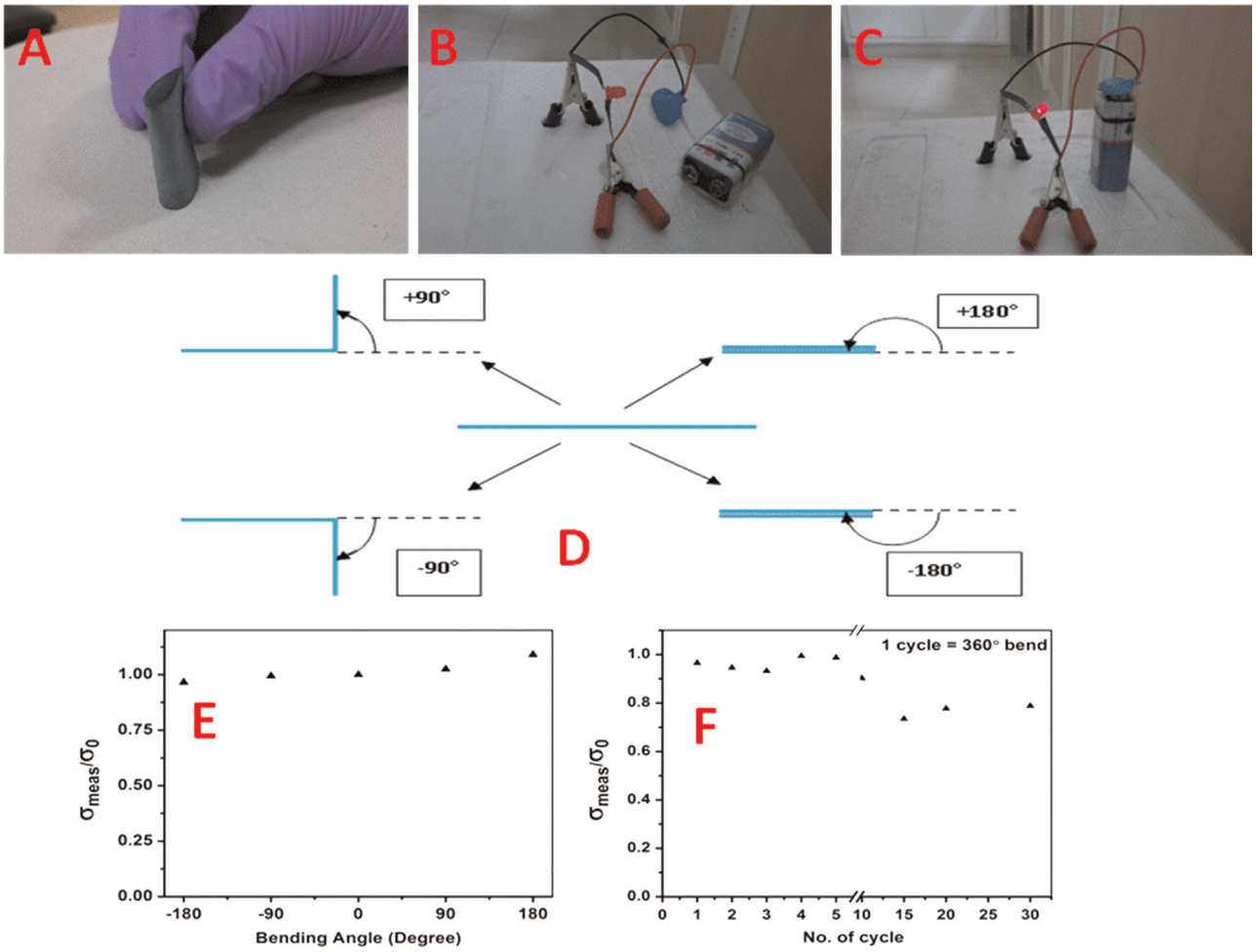

Fig. 3. Optical image of electroactive paper (A) foldable nature of electroactive paper (B, C) demonstration of LED emission when current flow through electoactive paper. Flexibility studies of PEDOT:PSS/RGO based electroactive electrode (D) Schematic diagram of electrode folding at different deformation angle. (E) The ratio of measured conductivity (σ_{meas}) to initial conductivity (σ_o) of electroactive paper with respect to folding angle. (F) The ratio of measured conductivity (σ_{meas}) to initial conductivity (σ_o) of electroactive paper versus folding cycle (1 cycle=360°).

and efficient conductivity as demonstrated in Fig. 3.

The effect of folding (−180° to 180°), repeated folding and unfolding on conductivity of the electroactive paper has been investigated. Fig. 3D describes results of flexibility studies conducted on the electroactive electrode; wherein the positive and negative angles clearly reveal electrode folding in upward and downward direction, respectively. Relative conductivity [(ratio of measured conductivity (σ_{meas}) to initial conductivity (σ_o)] of electroactive electrode is measured as a function of folding angle. Fig. 3E displays variation of the relative conductivity of electroactive electrode indicating deviation of up to 4% under different folding angles. This reveals that electrodes are flexible and there is negligible change in the conductivity. The variation of relative conductivity of electrode with repeated cycle of folding and unfolding (manually) is shown in Fig. 3F. It may be noted that the conducting paper folded after 30 cycles (1 cycle=360° rotation) shows decrease of about 20% in relative conductivity due to tearing of the cellulose threads. A video pertaining to the lighting of an LED lamp when current is passed through the multiple times folded electroactive paper is shown in Movie S1 in the Supporting information.

Fig. 4A presents Schematic of the observed mechanism, showing enhanced conductivity of the EG treated conducting paper. The conducting paper comprises of PEDOT:PSS polymer chains wherein PEDOT molecules present in the core of the insulating PSS are highly conductive in nature. On being treated with ethylene glycol, the core–shell structure of the conducting paper becomes partially linear due to ejection of the PSS molecules. This exclusion of PSS from the surface is perhaps responsible for conformational changes in the polymer film that in turn results in increased conductivity. This has been further confirmed by Fourier transform infrared (FT-IR) spectroscopy and X-ray photoelectron spectroscopy (XPS) studies.

3.3. FT-IR and XPS analysis

FT-IR spectra of PEDOT:PSS/Whatman paper (curve i), conducting paper (curve ii) and conducting paper treated with EG (curve iii) are shown in Fig. 4B. FT-IR spectrum of PEDOT:PSS coated on Whatman paper (spectra i) exhibits characteristic absorption bands at near 670 cm^{-1} and 1060 cm^{-1}, corresponding to C–S and C–O stretching vibration of the thiophene ring in PEDOT (Ely et al., 2014). The bands at 1010 cm^{-1}, 1045 cm^{-1} and 1160 cm^{-1} represent $-SO_3^-$ symmetric and asymmetric stretching vibrations, respectively due to PSS (Alemu et al., 2012). The bands seen at 1392 cm^{-1} and 1537 cm^{-1} are due to C–C and C=C, respectively. In the FT-IR spectrum of conducting paper (curve ii), the intense absorption band at 1060 cm^{-1} is due to addition of EG that causes conformational changes in the polymer structure. The absorption band at 1104 cm^{-1} and 1160 cm^{-1} represents $-SO_3^-$ asymmetric stretching vibration whereas disappearance of $-SO_3^-$ symmetric stretching suggests molecular rearrangement in the PEDOT:PSS leading to increased electrical conductivity. These

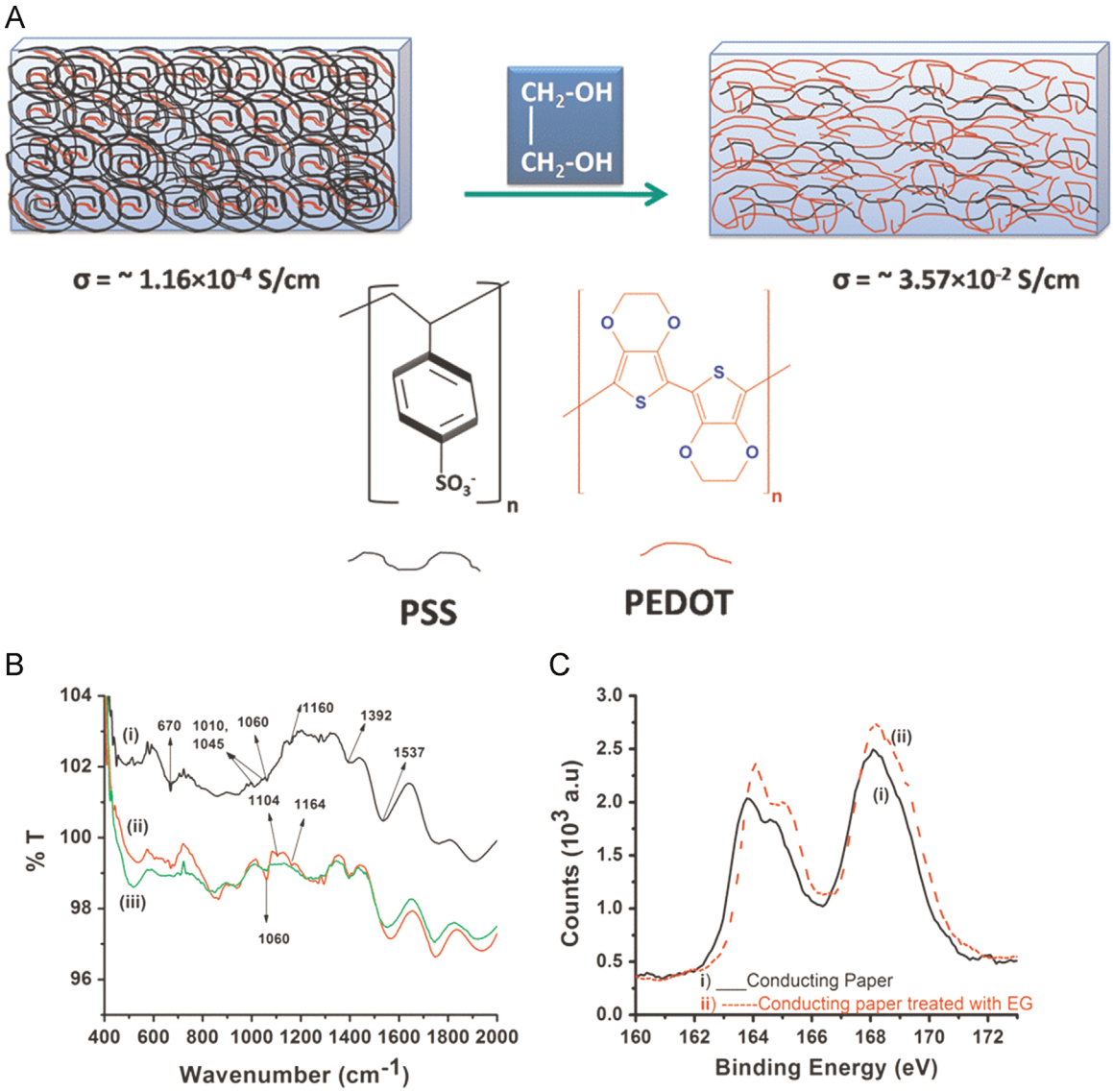

Fig. 4. (A) The schematic illustration of the mechanism of conductivity enhancement on conducting paper surface by EG treatment. (B) The FT-IR spectra of (i) PEDOT:PSS/Whatman paper (ii) conducting paper and (iii) conducting paper treated with EG. (C) X-ray photoelectron spectra (XPS) of (i) conducting paper and (ii) conducting paper treated with ethylene glycol.

results are in agreement with those observed for the conductivity measurements wherein increase in conductivity from $\sim 1.16 \times 10^{-4}$ S cm^{-1} to $\sim 1.43 \times 10^{-3}$ S cm^{-1} occurs when EG is added into PEDOT:PSS. In the FT-IR of the EG treated conducting paper (curve iii), the characteristic bands seen at 1104 cm^{-1} and 1160 cm^{-1} pertaining to the $-SO^{3-}$ stretch of PSS are absent. This indicates removal of PSS from the conducting paper after EG treatment. This removal of PSS after EG treatment is perhaps responsible for the higher conductivity of the conducting paper due to increased exposure of PEDOT. FT-IR spectra of electroactive paper (Fig. S2(i) in Supporting information) indicate an additional broad absorption band at 1106 cm^{-1} that is attributed to C–OH stretching of graphene oxide. Further, the other observed IR bands are the same as seen in curve iii.

Fig. 4C shows XPS of i) conducting paper and ii) EG treated conducting paper. The S(2p) binding energy peak seen at 168 eV corresponds to sulfur due to the presence of PSS, and the doublet peak seen at 163.8 eV and 164.5 eV corresponds to the presence of sulfur in PEDOT (Crispin et al., 2006). The S2p XPS intensity ratio of PEDOT/PSS increases from 0.721 to 0.760 after the conducting paper is treated with EG. This change indicates the removal of some PSS chains from the film. That may perhaps cause conformational change in PEDOT:PSS due to the transition from coiled to linear form leading to increased exposure of PEDOT chains (Fig. 3A) (Alemu et al., 2012). The change in C/S molar ratio evaluated from the scan spectra decreases from 9.63 to 8.17 after the conducting paper is treated with EG. This result is consistent with the removal of some PSS from the film. XPS of electroactive paper is shown in Fig. S2(ii) (see Supporting information). The S2p XPS intensity ratio of PEDOT/PSS present in electroactive paper increases to 0.82. However, the conductivity of electroactive paper is almost equivalent to that of the conducting paper after EG treatment. This may perhaps be attributed to the presence of discontinuous and non-uniform RGO sheet resulting in increased distance between PEDOT chains within the fiber network. Further, the C/S molar ratio increases to 10.1 due to the presence of carbon content of RGO.

3.4. Electrochemical studies

To investigate the charge transfer phenomenon at the conducting paper/solution interface, the electrochemical impedance

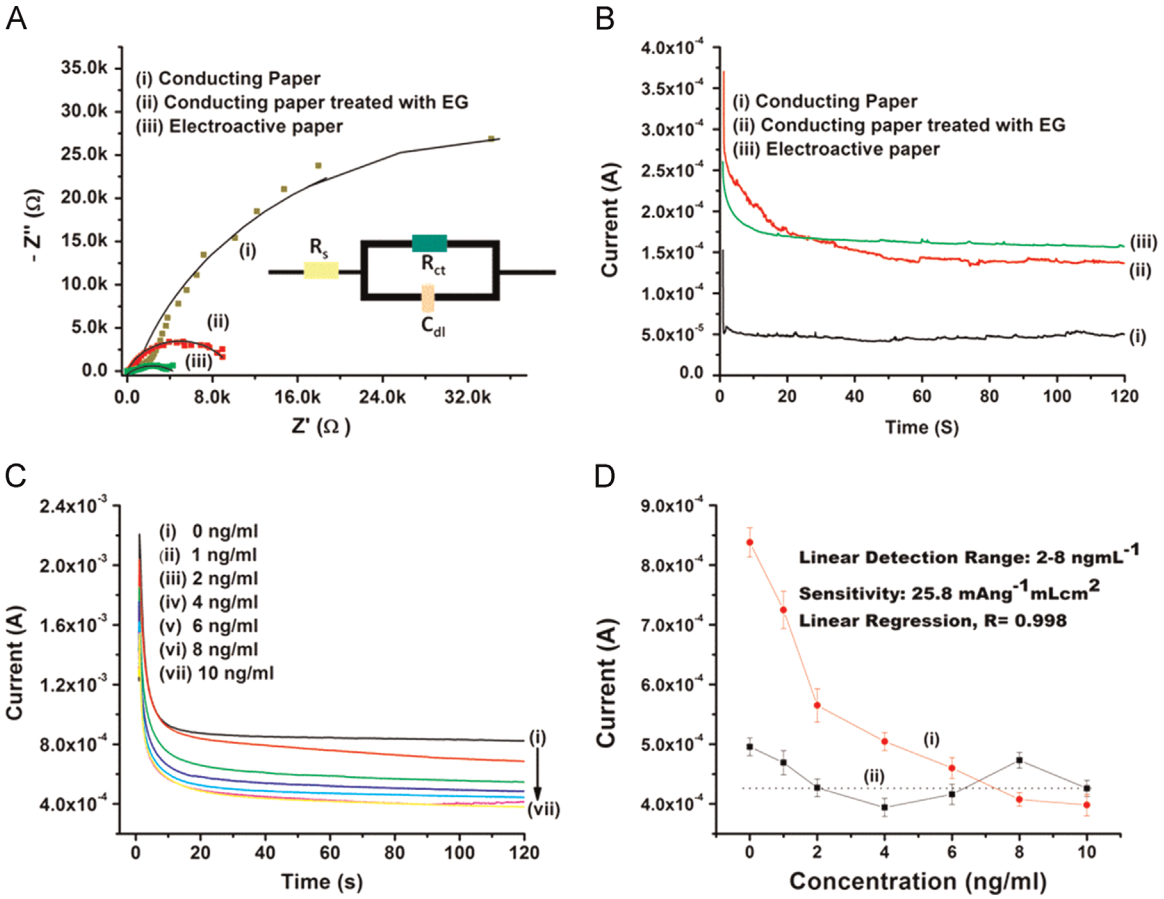

Fig. 5. Electrochemical studies conducted on paper electrode. (A) Electrochemical impedance spectra. (B) Chronoamperometry plot obtained for (i) conducting paper (ii) conducting paper treated with EG and (iii) electroactive paper. (C) Electrochemical response studies of anti-CEA immobilized electroactive paper at different concentration of CEA. (D) Calibration plot between the magnitudes of current recorded and CEA concentration (curve i); control experiment in absence of antibody (curve ii). Conducting paper: EG doped PEDOT: PSS solution coated onto whatman paper; Electroactive paper: EG and RGO doped PEDOT:PSS solution coated onto Whatman paper further treated with EG.

spectroscopy (EIS) studies have been conducted at biasing potential of 0.01 V in the frequency range, 100 kHz to 1 Hz. The Randles circuit is an equivalent electrical circuit that is commonly used to measure the electrochemical impedance comprising of an active electrolyte resistance R_S in series with R_{ct} (charge transfer resistance) in parallel combination of the double-layer capacitance C_{dl} or constant phase element (CPE) of a Faradaic reaction. The diameter of the semicircle in the Nyquist plot gives magnitude of the charge transfer resistance (R_{ct}) at the electrode surface (Daniels and Pourmand, 2007). Fig. 5A shows EIS of the (i) conducting paper, (ii) conducting paper treated with EG, and (iii) electroactive paper. Fig. 5A has been obtained using software (Nova) provided with the Autolab Potentiostat/Galvanostat. The curve fitting has been done assuming Randles circuit [$R_s(R_{ct}\ C_{dl})$] of the electrochemical cell. The various parameters related to the circuit element have been summarized in Table S2 alongwith % error [see Supplementary information sheet]. R_{ct} obtained for conducting paper is 48 kΩ which is maximum (curve i). However, the significant decrease in R_{ct} value up to 7 kΩ (curve ii) is observed in EG treated conducting paper. This is assigned to the conformational changes of the PEDOT:PSS chains from coiled to linear form leading to the higher conductivity due to enhanced electron transfer between solution/electrode interface. It is observed that the R_{ct} value further decreases to 2.8 kΩ (curve iii) in case of the electroactive paper. This may be attributed to excellent electrochemical properties and larger 2D surface area of RGO incorporated in the PEDOT:PSS matrix that increases the permeability of $[Fe(CN)_6]^{3-/4-}$ to the surface of paper electrode. The heterogeneous electron transfer rate constant (K_{ct}) of EG treated conducting paper and electroactive paper has been calculated using Eq. (1) (Bardea et al., 2000)

$$K_{ct} = \frac{RT}{n^2F^2AR_{ct}[S]} \quad (1)$$

where R is the gas constant, T is absolute temperature, F is the Faraday constant, A is the electrode area (cm^2), $[S]$ is the concentration of redox probe (mol/cm^3) and n is the number of transferred electrons per molecule of the redox probe. The heterogeneous electron transfer rate constant (K_{ct}) value of the electroactive paper has been estimated as 1.9×10^{-5} cm s^{-1} which is 2.5 times better as compared to conducting paper treated with EG (7.6×10^{-6} cm s^{-1}). This indicates that the RGO present in electroactive paper electrode exhibits faster electron transfer kinetics as compared to the EG treated conducting paper. Thus the incorporation of RGO improves the electrochemical activity of the electroactive paper as compared to that of EG treated conducting paper.

Fig. 5B shows results of the chronoamperometric studies (current versus time) carried out on conducting paper and EG treated conducting paper at 2 V every 0.1 s. The higher value of the current observed for EG treated conducting paper electrode than that of conducting paper indicates increased electron transfer between solution and electrode due to conformational rearrangement in PEDOT polymeric chains. Further increase in the value of the electrochemical current in case of the electroactive paper electrode is attributed to the enhancement in permeability of the

redox couple {$[Fe(CN)_6]^{3-/4-}$} resulting due to RGO doping. It may be noted that electroactive paper electrode exhibits improved electrochemical performance and signal stability than that of the EG treated conducting paper. Keeping this in view, electroactive paper has been used to detect cancer biomarker, CEA. The monoclonal carcinoembryonic antibodies (anti-CEA) (procured from SigmaAldrich) are physically absorbed onto the PEDOT:PSS/RGO based electroactive paper (Fig. 1). The anti-CEA immobilized paper bioelectrode is washed with phosphate buffer (PBS. 50 mM, 0.9% NaCl; pH 7.4) to remove any unbound antibodies. Different concentrations of the carcinoembryonic antigen (CEA) (1–10 ng mL^{-1}) are prepared via further dilution of stock solution (25 μg mL^{-1}). The response studies of anti-CEA/electroactive paper obtained as a function of CEA concentration (1–10 ng mL^{-1}) have been carried out in phosphate buffer saline (PBS, 50 mM, pH 7.4) containing 5 mM $[Fe(CN)_6]^{3-/4-}$. 10 μL of diluted antigen solution is added into electrochemical cell for each antigen concentration. After adding each CEA concentration the current–time curve is recorded after every 300 s to ensure completion of the immunoreaction. The variation of the response current recorded as a function of CEA (1–10 ng mL^{-1}) is shown in Fig. 5C. The decrease in amperometric current occurs up to a maximum of 10 ng mL^{-1}. This can be attributed to the formation of antigen–antibody complex causing significant rearrangement over the electrode surface that diminishes charge transfer via $[Fe(CN)_6]^{3-/4-}$ leading to reduction in amperometric current (Shim et al., 2008; Wang et al., 2009). Fig. 5D indicates the calibration plot obtained between response current and CEA concentration (curve i). Interestingly, we obtained similar results between electrochemical current and CEA concentration via single shot incubation (different electrode was taken for each concentration) which is shown in Fig. S3. Furthermore, a control experiment was performed to check cross reactivity of the electroactive paper with CEA antigen in the absence of antibodies (curve ii). However, no significant change in current response was observed for the electroactive paper in the absence of antibodies as a function of CEA concentration. A linear relationship is observed in the range 2–8 ng mL^{-1} with a sensitivity of 25.8 μA $ng^{-1}mL\ cm^{-2}$ and follows Eq. (2)

$$I(A) = -25.8\ \mu A\ mL\ ng^{-1} \times [\text{CEA concentration}] + 613.5\ \mu A; \quad R^2 = 0.998 \tag{2}$$

We have compared the sensing performance of the electroactive paper with the conducting paper treated with EG. For this, the electrochemical response studies have been carried out on the anti-CEA immobilized conducting paper treated with EG, in the presence of different concentrations of antigen (1–10 ng mL^{-1}) (see Supporting information Fig. S4). It is found that the electroactive paper is almost 6 times more sensitive than the conducting paper treated with EG for CEA detection.

3.5. Stability, selectivity and reproducibility studies

Fig. 6A shows variation of response current of the immunoelectrode (anti-CEA immobilized electroactive paper) taken at a regular interval of 2 days. It has been found that current value

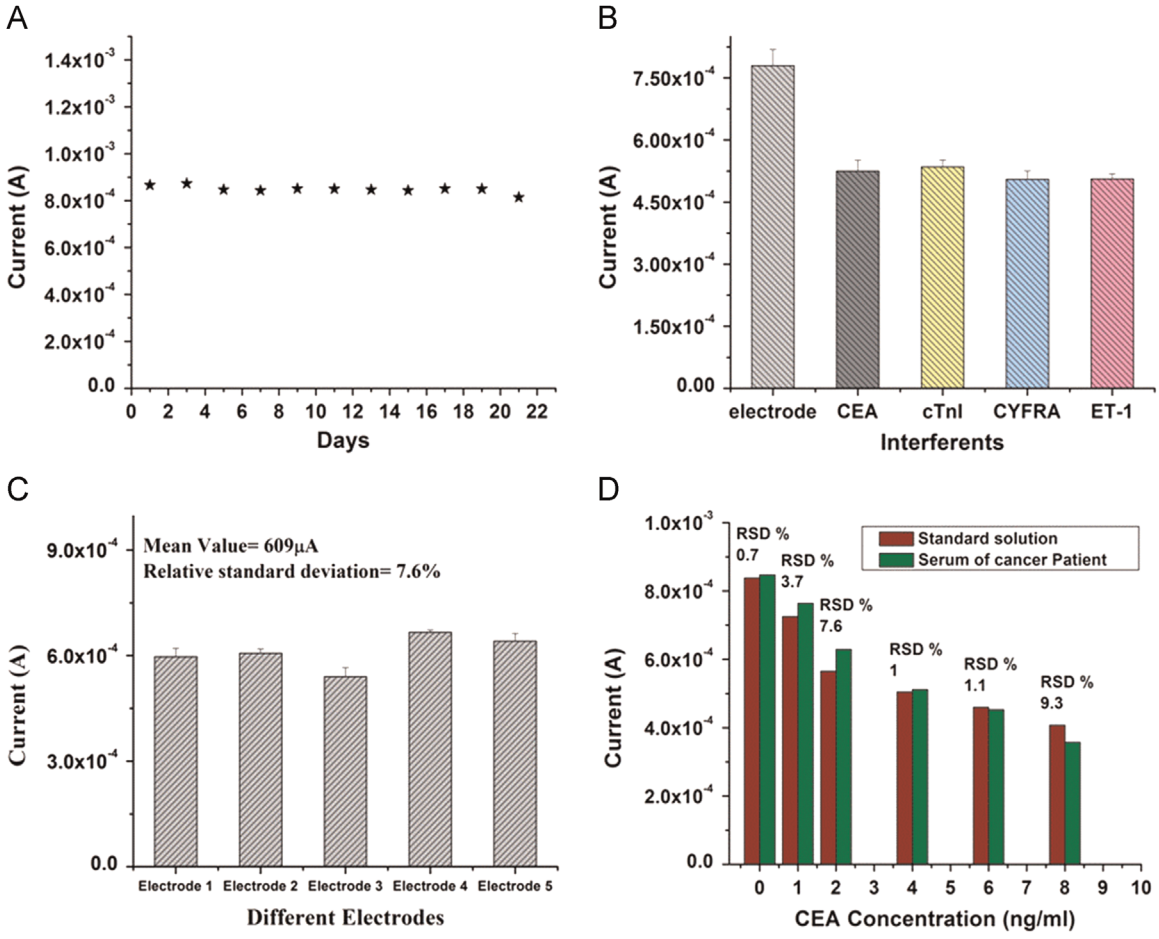

Fig. 6. (A) Electrochemical current response of anti-CEA immobilized electroactive paper electrode (immunoelectrode) measured as a function of time (day). (B) Electrochemical current response of immunoelectrode in the presence of other analytes. (C) Electrochemical current response of different immunoelectrode fabricated via the same set of procedure in the presence of CEA (2 ng mL^{-1}) and (D) CEA concentration values obtained by immunoassay and the electroactive paper method.

decreases to ~7% after 21 days. This indicates that the paper sensor exhibits good stability up to 21 days. The selectivity study of this paper sensor has been investigated in the presence of cardiac troponin I (cTnI), cytokeratin-19 fragment (CYFRA-21-1), and endotheline-1 protein (ET-1) (2 ng mL^{-1}). Fig. 6B shows decrease in current response on addition of CEA (2 ng mL^{-1}) after which we do not observe any significant current change on addition of another antigen indicating high selectivity of the biosensor. The reproducibility of the five different immunoelectrodes fabricated under similar conditions has been investigated in the presence of 2 ng mL^{-1} CEA concentration (Fig. 6C). It is found that this paper electrode shows good reproducibility for five different electrodes with constant surface area as is evident by low value of relative standard deviation (RSD) of 7.6% (mean value = 609 μA). Further each measurement (Fig. 6C) has been repeated 4 times for each electrode and error bars are included accordingly. The low RSD obtained for each electrode (less than 5%) indicates appreciable repeatability of the biosensor.

3.6. Real sample analysis

The results obtained for serum sample of cancer patients using this electroactive paper sensor have been validated using ELISA. The blood samples collected from patient and processed at the Rajiv Gandhi Cancer Institute & Research Centre (RGCI & RC) in Rohini, Delhi, India. Concentration of CEA in the serums of cancer patients was measured at RGCI&RC using the VITROS CEA reagent Pack and the VITROS CEA Calibrators on the VITROS ECi/ECiQ Immunodiagnostic Systems, VITROS 3600 Immunodiagnostic System and VITROS 5600 Integrated System using Intellicheck® Technology. It can be seen that a reasonable correlation occurs between the CEA concentration value obtained by immunoassay and the electroactive paper based electrochemical method (Fig. 6D). As shown in Fig. 6D, the electroactive paper affords good recoveries and acceptable relative standard deviation.

The sensing characteristics of the electroactive paper based electronic paper sensor have been summarized in Table S3 along with those reported in the literature. It may be noted that this low cost flexible electroactive paper sensor can be easily decomposed by simple incineration (see Movie S2). Keeping in view the production of the medical diagnostics kits, this is an added advantage of this new environment friendly disposable electroactive paper sensor.

4. Conclusions

We have demonstrated a flexible and highly conducting paper sensor, based on composite of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) and reduced graphene oxide (RGO). It is found that conductivity of the PEDOT:PSS conducting paper increases by ~300 times when it is treated with ethylene glycol. The incorporation of RGO in PEDOT:PSS conducting paper film indicates excellent electrochemical activity and faster charge transfer kinetics. In order to further improve the performance of conducting paper, suitable selection of solvent and dopant should be investigated. This low cost, flexible and environment friendly conducting paper has been used for cancer biomarker detection. The fabricated PEDOT:PSS/RGO based electroactive paper shows sensitivity of 25.8 μA ng^{-1} mL cm^{-2} in the detection range of 2–8 ng mL^{-1}. The results obtained for serum samples of cancer patients using this paper based sensor have been validated using ELISA. This simple, low cost, flexible and disposable electroactive paper based platform has immense potential for point of care biosensors, flexible electronics and energy storage devices etc.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.bios.2015.05.040.

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RELEVENCE OF WWW IN THE PROFESSIONAL DEVELOPMENT OF LIBRARY AND INFORMATION SCIENTISTS

R.K.SHUKLA*

0. Abstract

describes the URLs useful for LIS Professionals in IT scenario, The resources of professional information from where news, views, and ideas, can be shared are detailed to help LIS Professionals to make them capable to manage the knowledge activities and to facilitate better information services to their end users.

Introduction

Internet has revolutionized the world of information . It is the internet which has made the access to knowledge possible globally . Through internet, anybody can access current information from anywhere in minutes at minimal cost. The world wide web has become an ideal tool for making information available worldwide. Internet and the Networking among the institutions and organizations of Library and Information Science has given an excellent opportunity of resource sharing . Resource sharing and the networking are the powerful tools for increasing productivity and availability of the current information to the library professionals. The job of the library networks are to create mechanisms to facilitate the sharing of resources available in the participating libraries of a network. No library can acquire all the current information nor store all the old information with them.Thus resource sharing helps the libraries and the professionals to keep them update with the latest developments in the field of knowledge.

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Resources available on WWW

Since the inception of WWW, efforts are being made to organize the available information in helpful sequence. Here also an attempt has been made to organize the information available in the WWW relevant to Library and information scientists . Those listed here have been classified under different heads to enable the LIS to develop them shelves professionally by directly referring to to the information available on these sites or by consulting the fellow scientists through list forums listed here.

Softwares: OpenSource

Digital Repository softwares:

Eprints http://www.eprints.org/

Eprints, open Archives Initiative (OAI)-compliant software for eprint archiving, released by Southampton University.EPrints.org maintains an open-source software package (GNU Eprints) that makes it easy for anyone to set up and run an institutional "E-print archive". The term 'E-print' covers both preprints, and also post-prints, electronic copies of articles that have already been accepted and published in an existing journal.

FEDORA (Flexible Extensible Digital Object and Repository Architecture) http://www.fedora.info/

Fedora is an open source digital repository service that gives organizations the tools for managing the existing and emerging content management requirements. At its core is a powerful digital object model that supports multiple representations or views of each digital object

LOCKSS http://lockss.stanford.edu

LOCKSS is open source, peer-to-peer software that functions as a persistent access preservation system. Information is delivered via the web, and stored using a sophisticated but easy to use caching system. LOCKSS model capitalizes on the traditional roles of libraries and publishers. LOCKSS creates low-cost, persistent digital "caches" of authoritative versions of http-delivered content. The LOCKSS software enables institutions to locally collect, store, preserve, and archive authorized content thus safeguarding their community's access to that content. The LOCKSS model enforces the publisher's access control systems and, for many publishers, does no harm to their business models.

Dspace http://www.dspace.org/
DSpace is a groundbreaking digital library system to capture, store, index, preserve, and redistribute the intellectual output of a university's research faculty in digital formats. Developed jointly by MIT Libraries and Hewlett-Packard (HP), DSpace is now freely available to research institutions world-wide as an open source system that can be customized and extended.

Greenstone: www.greenstone.org

Greenstone is a suite of software for building and distributing digital library collections. It provides a new way of organizing information and publishing it on the Internet or on CD-ROM. Greenstone is produced by the **New Zealand Digital Library Project** at the **University of Waikato**, and developed and distributed in cooperation with **UNESCO** and the **Human Info NGO**. It is **open-source, multilingual** software, issued under the terms of the GNU General Public License. Read the Greenstone Fact Sheet for more information.

The aim of the Greenstone software is to empower users, particularly in universities, libraries, and other public service institutions, to build their own digital libraries. Digital libraries are radically reforming how information is disseminated and acquired in UNESCO's partner communities and institutions in the fields of education, science and culture around the world, and particularly in developing countries. We hope that this software will encourage the effective deployment of digital libraries to share information and place it in the public domain.

Automation softwares

Koha :www.koha.org

Koha is a full-featured open-source ILS. Developed initially in New Zealand by Katipo Communications Ltd and first deployed in January of 2000 for Horowhenua Library Trust, it is currently maintained by a team of software providers and library technology staff from around the globe.

Weblis : www.unesco.org

Genisis : www.unesco.org

Winisis: www.unesco.org

Sotware for publishing open accessjournals

Open Journal System (OJS) http://pkp.sfu.ca/ojs
Software for publishing open access conference proceedings

Open Journal Systems

Open Journal Systems (OJS) is a journal management and publishing system that has been developed by the Public Knowledge Project through its federally funded efforts to expand and improve access to research.

OJS Features

1. OJS is installed locally and locally controlled. Editors configure requirements, sections, review process, etc.Online submission and management of all content.
2. Subscription module with delayed open access options.
3. Comprehensive indexing of content part of global system.
4. Reading Tools for content, based on field and editors' choice.
5. Email notification and commenting ability for readers.
6. Complete context-sensitive online Help support.

Software for repository search

Open Archives Harvester

The PKP Open Archives Harvester is a free metadata indexing system developed by the Public Knowledge Project through its federally funded efforts to expand and improve access to research.

The PKP OAI Harvester allows you to create a searchable index of the metadata from Open Archives Initiative (OAI)-compliant archives, such as sites using Open Journal Systems (OJS) or Open Conference Systems (OCS).

Harvester version 2.0 includes the following features:

- Ability to harvest OAI metadata in a variety of schemas (including unqualified DC, the PKP (Open Journal Systems/Open Conference Systems) Dublin Core extension, MODS, and MARCXML). Additional schema are supported via plugins.
- Flexible search interface that allows simple searching and advanced searching using crosswalked fields from all harvested archives. Advanced searching of archives that share the same schema will be possible using fields as defined in the schema. When creating crosswalks for searching, admins can define elements are text, date, or HTML multiple select interface widgets.
- Ability to perform granular harvesting using setSpec and timestamps.
- Ability to perform post-harvest and pre-indexing filtering/normalization on metadata.
- User Interface with CSS and template-based HTML for easy customization.
- Searching is highly scalable (creates an inverted index for searching).

Software for conference management

Open Conference Systems

Open Conference Systems (OCS) is a free Web publishing tool that will create a complete Web presence for your scholarly conference. OCS will allow you to:

- create a conference Web site
- compose and send a call for papers
- electronically accept paper and abstract submissions
- allow paper submitters to edit their work
- post conference proceedings and papers in a searchable format
- post, if you wish, the original data sets
- register participants
- integrate post-conference online discussions

OCS version 2 is currently in development and is scheduled for release in early 2007. New features will include:

- manage conferences that occur more than once (e.g. yearly)
- an expanded review system
- e-mail template system
- localization & translation tools
- credit card payment for registrations
- OAI and Google Scholar-compatible indexing
- automated "thanks-for-submitting" messages
- warning messages for impending deadlines
- accept login/password for participants
- optionally allow early access to papers
- plug-ins (e.g. authentication, TinyMCE)

.

3.2 Digital Archives

- **HighWirePress** http://highwire.stanford.edu/

A division of the Stanford University Libraries, HighWire Press hosts the largest repository of high impact, peer-reviewed content, with 999 journals and 3,799,927 full text articles from over 130 scholarly publishers. HighWire-hosted publishers have collectively made 1,477,698 articles free. With our partner publishers we produce 71 of the 200 most-frequently-cited journals.

- **Open Repository** http://www.openrepository.com/
  Open Repository is a service from BioMed Central to build, launch, host and maintain institutional repositories for organisations. Built upon the latest DSpace repository software the service has been designed to be flexible and cost-effective. BioMed Central's economy of scale makes it possible for organisations that could not otherwise afford to, or lack the infrastructure or technical capacity in-house to run their own repositories.
- **Librarians' Digital Library www.drtc.isibang.ac.in**

- **Lis-eprints http//:eprints.rclis.org**

E-LIS is an open access archive for scientific or technical documents, published or unpublished, on Librarianship, Information Science and Technology, and related areas. E-LIS relies on the voluntary work of individuals from a wide range of backgrounds and is non-commercial. It is not a funded project of an organization. It is community-owned and community-driven. We serve LIS researchers by facilitating their self-archiving, ensuring the long-term preservation of their documents and by providing word-wide easy access to their papers.

- **Cite base:http//:citebase.org**

- **Doar: http//:www.opendoar.org***Open*DOAR is an authoritative directory of academic open access repositories. Each *Open*DOAR repository has been visited by project staff to check the information that is recorded here. This in-depth approach does not rely on automated analysis and gives a quality-controlled list of repositories.As well as a simple list of repositories and a search facility, *Open*DOAR provides tools and support to both repository administrators and service providers in sharing best practice and providing tools to improve the quality of the repository infrastructure.

- **Roar: http://archives.eprints.org**

It is a registry of open access archives

Various activities of Library and Information Centres

a) Acquisitions

http://www.library.vanderbilt.edu **ACQWEB,**

http://www.library.vanderbilt.edu/ **ACQNET,**

http://www.librifoundation.org/ **Libri Foundation,** It is a nationwide non-profit organization which donates new, quality, hardcover children's books to small, rural public libraries in the United States.

b)Cataloging/ Online Catalogs

http://www2.lib.udel.edu/**ALA Godort Cataloging Committee (PURLs)**
http://catalogue.bnf.fr/ **BNF catalogue,**
http://www.mnsfld.edu/ **Book and Library Catalogs (OPACs)**
http://www.tlcdelivers.com **Cataloging - MARC Records,**
http://www.slc.bc.ca/**Cataloging Online Cheat Sheets,**

http://copac.ac.uk **Consortium of University Research Libraries (CURL) (UK) Catalog,**
http://www.du.edu/**GPO Marc Internet Resources,**
http://www.iii.com/ **III INNOPAC,**
http://www.fas.harvard.edu/ **Korean Library Gateway,**
http://www.lib.ku.edu/ **KU Libraries Online Catalog**
http://www.itcompany.com/ **Label Maker,**
http://lcweb.loc.gov/ **Library Catalogs via Z39.50**

lib-web-cats, http://staffweb.library.vanderbilt.edu/
MarcEdit, http://www.onid.orst.edu
MARC Management & OPAC System,
http://www.itcompany.com
MESH (Medical Subject Headings), http://www.nlm.nih.gov/
National Library Catalogues Worldwide,
http://www.library.uq.edu.au/
OCLC Cataloging Course and More, http://www.oclc.org/
Open Source from OCLC, http://www.sitesearch.oclc.org/
Public Access Catalogs, http://www.tlcdelivers.com/
Readerware, http://www.readerware.com/
Sheet Music Cataloging Guidelines, http://www.lib.duke.edu/
Spelling Checker for Database Maintenance,
http://www.itcompany.com/
Spelling Checker for OCLC® Cataloging,
http://www.itcompany.com
Technical Services Law Libarian, http://www.aallnet.org
The Rare Materials Catalog http://www.library.yale.edu/
UNCAT: The Catalog of UNCATaloged Titles,
http://www.sapphirepress.com/UNCAT/
Understanding MARC Bibliographic, http://lcweb.loc.gov/
WebCats, http://www.libdex.com/
ZSearch, http://www.itcompany.com/

C) Classification

Center for Dewey Studies, http://www.siu.edu
Dewey Classifications, http://www.4j.lane.edu/
Dewey Decimal Classification, http://www.mtsu.edu,
http://www.bcr.org/, http://www.tnrdlib.bc.ca/ ,
http://www.july15.com/
Do the Dewey! http://www.thrall.org/
Classification LC et Dewey, http://www.umoncton.ca/
Cutter Tables, http://www.cuttertables.com/
LC Classification Outline, 6th Edition: Contents,
http://www.tlcdelivers.com/

LC Classification Schedules and Manuals from CDS, http://lcweb.loc.gov/
LC Cutter Tables, http://stauffer.queensu.ca/
Library Firsts, http://www.hwwilson.com/
Library of Congress Classification Outline, http://lcweb.loc.gov/
The Alexandrian Library, http://www.greece.org/

d) Collection Development

ACQWEB'S Directory of Collection Development Policies on the Web, http://acqweb.library.vanderbilt.edu/
Evaluating Web Sites for Collection Development, http://www.kclibrary.org/

e) Interlibrary Loan

Inter Library Loan, http://www.tlcdelivers.com/
Kansas Interlibrary Loan Directory (KILD) http://skyways.lib.ks.us/

F)Reference Services

AllRefer.com, http://www.allrefer.com/
All Refer Reference, http://reference.allrefer.com/
Applying information competency to digital reference, http://www.ifla.org/
A Report of library-related Ask services, http://www.vrd.org/
Assessing quality in digital reference services, http://quartz.syr.edu/
A Typology for Ready Reference Web Sites in Libraries, http://www.firstmonday.dk/
Biographical Dictionary, http://www.s9.com/
Cyber librarians' Rest Stop, http://www.thelearningsite.net/
Dictionaries Plus, http://ejw.i8.com/
Digital Reference, http://www.loc.gov/
Digital Reference Services: http://www.lis.uiuc.edu/
Encyclopedia & Reference Resource, http://www.1upinfo.com/
Facets of quality for digital reference services, http://www.vrd.org/
Gale, Free Library Marketing Materials, http://www.gale.com/
Glossary of Library Terms, http://www.library.ualberta.ca/

How Do I Find It? – The Data Reference Interview, http://dpls.dacc.wisc.edu/
Library Collaboration, http://www.lis.uiuc.edu/
ODLIS: Online Dictionary of Library and Information Science, http://www.wcsu.edu/
Promoting information problem solving in digital reference responses, http://www.vrd.org/
Reference Interview, http://www.library.vcu.edu/
Reference Interview, http://www.lis.uiuc.edu/
Reference service via desktop videoconferencing, http://www.slis.ualberta.ca/
Setting up an Ask-an-Expert service, http://www.madsci.org/
Symbols.com: Encyclopedia of Western Signs and Ideograms, http://www.SYMBOLS.com/
The Chicago Historical Society List of Fees, http://www.chicagohistory.org/
The Reference Interview, http://web.utk.edu/, http://infotrain.magill.unisa.edu.
The Virtual Reference Desk (US Dept of Education) http://www.vrd.org/
The Virtual Reference Interview: Equivalencies, http://www.ifla.org/
Virtual Acquisition Shelf & News Desk, http://resourceshelf.blogspot.com/
Virtual Reference Shelf: Library of Congress, 2002, http://www.loc.gov/
Wiktionary, http://en.wiktionary.org/wiki/wiktionary
Wikipedia, http://en.wikipedia.org

Open Source Projects (For Reserve & ILL) http://library.olivet.edu/

g) Serials

Dollars & $ense: the Price of Information, http://www.library.fau.edu/
Electronic Journals in Librarianship and Information Science, http://www.inf.aber.ac.uk/
LIS Periodicals on the Internet, http://www.fortunecity.com/
Library-Oriented Lists & Electronic Serials, http://www.wrlc.org/
LIS-Acq, http://www.jiscmail.ac.uk/
LIS-Serials, http://www.jiscmail.ac.uk/
Newsletter on Serials Pricing Issues, http://www.lib.unc.edu/
Rising Journal Prices, http://www.brown.edu/
Serials Report Prices, http://www.ala.org/

Serials Solution, http://www.serialssolution.com/
SERIALST Archives Search, gopher://moose.uvm.edu/
SERIALST Scope & Purpose, http://www.uvm.edu/
The UCSD Libraries Collections Budget,
http://orpheus.ucsd.edu/collbud/
Tools for Serials Catalogers, http://www.library.vanderbilt.edu/

Disaster Planning And Recovery

American Library Association Disaster Resources,
http://www.ala.org/
Contingency Planning and Management,
http://www.contingencyplanning.com

Disaster Recovery Journal, http://www.drj.com/
Disasters of 2002, http://www.fema.gov/
FAQ on General Preservation, Disaster Preparedness and Response Manual http://www2.lib.ku.edu
Earthquake Information, http://www.lib.washington.edu/
Emergency Management, http://www.nedcc.org/
Florence 30 years after the Flood http://www.mega.it/ or http://www.catpress.com/ Provides pictures, photos, and stories of the conservation efforts during the Flood and afterward.
Guidelines for Managing Mold Contamination,
http://preserve.harvard.edu/
Invasion of the Giant Mold Spore,
http://palimpsest.stanford.edu/
Invasion of the Giant Spore, http://www.ccaha.org/
Kansas Disaster Recovery Assistance Network, (Kansas State Historical Society) http://www.kshs.org/ Provides a Disaster Plan Model for Libraries to copy and modify.
Earthquake Preparedness Handbook, http://www.lafd.org/
Medical Library Association "Community of Caring"'
http://www.mlanet.org/
Mold Resources, http://www.epa.gov/
Mold, Salvage Operations for Water Damaged Archival Collections, http://palimpsest.stanford.edu/
MOULDS, http://www.botany.utoronto.ca/
New York State Program for the Conservation and Preservation of Library Research Materials Disaster
North Dakota State Library Flood Images,
http://www.lib.ndsu.nodak.edu/
Nyberg, Sandra "Invasion of the Giant Spore" SOLINET Preservation leaflet November 1987 http://www.solinet.net/

Remediation of Fungi in Indoor Environments, http://www.ci.nyc.ny.us/
Photo ID Library, http://www.inspect-ny.com/
Planning Resource Packet,http://www.nysl.nysed.gov/
Prague Libraries Flooded, http://www.mlp.cz/
Preservation Planning Software, http://sunsite.berkeley.edu/
Preservation Strategies for Small and Public Libraries, http://www.philobiblon.com/
Proceedings of the 2000 Federal Depository Library Conference, http://www.access.gpo.gov/
San Diego/Imperial County Libraries Disaster Response Network (SILDRN) http://www.ucsd.edu/
Tips on Mold, http://www.lib.virginia.edu/
Tools for Mitigating Earthquake Hazards in Your Home, http://www.abag.ca.gov/
Undergraduate Library 1997 Mold Outbreak, http://gort.ucsd.edu/
What You Should Know About Mold, http://www.dustfree.com/

Library Assessments

ACRL/ALA Task Force on Academic Library Outcomes Assessment Outside the Box, http://www.rwc.uc.edu/
Assessment Plan for the Brenau Trustee Library, http://intranet.brenau.edu/
Assessment Report, http://www.ala.org/
Guidelines for Libraries, Guidelines for Distance Learning Library Services http://www.ala.org/

Preservation

AMIGOS Imaging & Preservation Services, http://www.amigos.org/
Archival Internet Resources, http://www.tulane.edu/
Bookbinding & Conservation of books, http://palimpsest.stanford.edu/
Bookbinding Tutorial, http://www.cs.uiowa.edu/
Care &Handling of Library Materials, http://www2.lib.ukans.edu/
Conservation Online, Cleaning Books and Shelves http://www.nedcc.org/
Digital Preservation, http://www.libraryjournal.com/
Preservation, http://www.e-praxess.net/ , http://libweb.hawaii.edu/

Preservation Leaflets, http://www.solinet.net/
Preservation Office website, http://libweb2.Princeton.EDU/
Preservation Resources, http://sunsite.berkeley.edu/
Preservation Resources (OCLC) http://www.oclc.org/
Preservation Tips On Mold, http://www.lib.virginia.edu/
Preserving Access to Digital Information, http://www.nla.gov.au/
Preserving Library Materials, http://orpheus.ucsd.edu/
Princeton Preservation Office Website, http://libweb2.Princeton.EDU/
Regional Alliance for Preservation, http://www.rap-arcc.org/
Simple Book Repair Manual, http://www.dartmouth.edu/
Thompson Conservation Lab, http://www.teleport.com/

Miscellaneous resources on relevant topics

Open Access – General

Useful Resources

- JISC's Briefing Paper on Open Access
- Open Access Archiving: the fast track to building research capacity in developing countries
- The Scholarly Electronic Publishing Bibliography (SEPB) by By Charles W. Bailey, Jr., Version 64: 10/17/2006
- Transforming access to research literature for developing countries
- Open Access Publications
- The acquisition of open access research articles Arthur Sale

- Open Access Overview (definition, introduction): www.earlham.edu/~peters/fos/overview.htm
- Open Access Webliography: www.escholarlypub.com/cwb/oaw.htm
- SPARC Open Access Newsletter: http://www.arl.org/sparc/soa/
- The Access Principle: The Case for Open Access to Research and Scholarship:

http://mitpress.mit.edu/catalog/item/default.asp?tid=10611&ttype=2

- Open Access: Key strategic, technical and economic aspects: http://www.eprints.org/community/blog/index.php?/archives/93-Open-Access-Key-Strategic,-Technical-and-Economic-Aspects.html
- Framing the Issue - Open Access: http://www.arl.org/scomm/open_access/framing.html
- Nature web focus: Access to the literature: www.nature.com/nature/focus/accessdebate
- Open access on Wikipedia: www.en.wikipedia.org/wiki/Open_access
- Budapest Open Access Initiative: www.soros.org/openaccess
- Berlin Declaration: www.zim.mpg.de/openaccess-berlin/berlindeclaration.html
- Bethesda Statement on Open Access Publishing: www.earlham.edu/~peters/fos/bethesda.htm
- Wellcome Trust Position statement in support of open access publishing: www.wellcome.ac.uk/doc_WTD002766.html
- IFLA Statement on Open Access to Scholarly Literature and Research: www.ifla.org/V/cdoc/open-access04.html
- Open Access Resources: http://www.google.com/Top/Reference/Open_Access_Resources/
- The effect of open access and downloads ('hits') on citation impact: http://opcit.eprints.org/oacitation-biblio.html
- Open Access and the Public Domain in Digital Data and Information for Science: http://www.nap.edu/catalog/11030.html#toc
- Papers by Alma Swan http://www.keyperspectives.co.uk/openaccess/index.html
- Salvador Declaration on Open Access: The Developing World Perspective

Open Access – Archiving

- Open Archives Initiative: www.openarchives.org
- E-prints: www.eprints.org
- DSpace: www.dspace.org

- A Guide to Institutional Repository Software: http://www.soros.org/openaccess/software/
- Directory of Open Access Repositories: www.opendoar.org
- Registry of Open Access Repositories (ROAR) archives.eprints.org
- SHERPA: Securing a Hybrid Environment for Research Preservation and Access: http://www.sherpa.ac.uk/index.html
- Self-Archiving FAQ: www.eprints.org/self-faq
- SHERPA/RoMEO - Publisher copyright policies & self-archiving: www.sherpa.ac.uk/romeo.php
- Institutional Self-Archiving Policy Commitment: http://www.eprints.org/openaccess/policysignup/sign.php
- Registry of Open Access Repository Material Archiving Policies: http://www.eprints.org/openaccess/policysignup/
- Open Access Archiving: www.scidev.net/ms/openaccess/
- ALPSP - Open Archives and Institutional Repositories: http://www.alpsp.org/htp_openarc.htm

Open Access – Publishing

- Directory of open access journals: www.doaj.org
- Public Library of Science: Open Access: www.plos.org/oa/index.html
- PMC Open Access Journals: http://www.pubmedcentral.nih.gov/about/openftlist.html
- SciELO - Scientific electronic library online: www.scielo.org
- Bioline International: www.bioline.org.br
- AJOL - African Journals Online: www.ajol.info
- medIND: Indian Fulltext Bio-Medical Journals Indexed in IndMED: www.medind.nic.in
- BioMed Central: www.biomedcentral.com
- Medknow Publications: www.medknow.com
- Hindawi Publishing: www.hindawi.com
- Open-J-Gate: www.openj-gate.com

Open Access – Discussion fora and blogs

- Open Access News: www.earlham.edu/~peters/fos/fosblog.html
- SPARC-OAForum@arl.org Archive: https://arl.org/Lists/SPARC-OAForum/List.html

- BOAI Forum: www.threader.ecs.soton.ac.uk/lists/boaiforum
- Open Access Archivangelism: www.openaccess.eprints.org
- AMERICAN-SCIENTIST-OPEN-ACCESS-FORUM: www.amsci-forum.amsci.org/archives/American-Scientist-Open-Access-Forum.html
- Open and shut?: http://poynder.blogspot.com/
- OA Librarian: http://oalibrarian.blogspot.com/
- The Imaginary Journal of Poetic Economics Open access textbooks: http://poeticeconomics.blogspot.com/
- DigitalKoans: http://www.escholarlypub.com/digitalkoans/
- The Parachute: http://theparachute.blogspot.com/

Open Access and the developing world

- Open Access to Science in the Developing World by Peter Suber and Subbiah Arunachalam: http://www.earlham.edu/~peters/writing/wsis2.htm
- International Seminar on Open Access for Developing Countries organized by BIREME/PAHO/WHO: http://www.icml9.org/meetings/openaccess/
- Salvador Declaration on Open Access: the developing world perspective: www.eifl.net/docs/Dcl-Salvador-OpenAccess-en.pdf
- Open Archiving Opportunities for Developing Countries by Leslie Chan and Barbara Kirsop: http://www.ariadne.ac.uk/issue30/oai-chan/
- India's march towards open access by Subbiah Arunachalam: http://www.scidev.net/Opinions/index.cfm?fuseaction=readOpinions&itemid=243&language=1
- The Electronic Journal of Information Systems in Developing Countries: http://www.ejisdc.org/ojs2/index.php/ejisdc
- Strategies for Preservation of and Open Access to Scientific Data in China: http://www.nap.edu/catalog/11710.html

Information Literacy

http://www.educause.edu **Information Literacy**
http://glef.org**Information Literacy**
http://www.lib.jmu.edu**Go For The GOLD,**

http://skyways.lib.ks.us/ **Kansas State Literacy Program,**
http://www.library.wwu.edu**Library Resources for Writing,**
http://literacyvolunteers.org**Literacy Volunteers of America,**
http://tilt.lib.utsystem.edu/ **Research Instruction Online (RIO)**
Texas Information Literacy Tutorial (TILT)
http://www.itrc.ucf.edu **Information Literacy Skills,**
http://www.slis.uwm.edu**Web-based and Traditional Instruction**

3.4 LIS Jobs

http://www.ala.org **American Library Association,**
http://www.whittier.edu **Archivist,**
http://www.becomealibrarian.com/**Become a Librarian?**
http://www.lisjobs.com/**Info Career Trends,**
www.Infolibrarian.com **Jobs**,
http://skyways.lib.ks.us/**KPLACE,**
http://www.ifla.org**LIBJOBS,**
http://www.dailybruin.ucla.edu**Library Degree**
http://www.libjobs.com/**Library Jobs,**
http://skyways.lib.ks.us/ **Librarianship,**
http://ils.unc.edu/**Students**

LIS Education Including Distance Learning

http://www.ala.org **American Library Association,**
http://ocls.cmich.edu**Central Michigan University Library,**
http://www.ala.org **Distance Learning Guidelines - ACRL**,
http://www.cc.columbia.edu **Electronic Reserves**
http://www.rrc.usf.edu/ **Florida Distance Learning Reference**
http://internet.ggu.edu**Golden Gate University Library,**
http://www.ignou.ac.in **Indira Gandhi National Open University,**
http://wings.buffalo.edu**Librarian & Faculty for Distance Education,**
http://www.emporia.edu **Library Guides & Instruction Materials,**
http://www.csupomona.edu**Library Information Guides**
http://library.jccc.net **Library Research Guides,**
http://www.washburn.edu **Library Research Guides,**
http://www.arl.org **Role of Libraries in Distance Education**,
http://www.library.wwu.edu **Subject Guides & Bibliographies,**
http://tilt.lib.utsystem.edu **Texas Information Literacy Tutorial (TILT)**
http://www.studygs.net**Study Guides and Strategies,**
http://www.uky.edu**University of Kentucky**,

National/International Organization and Institutions

a) Libraries

Academic Libraries, http://librarians.about.com/
Academic Library Peer Comparison Tool, http://nces.ed.gov/
British Library, http://www.bl.uk/
Cool Library of the Week, http://www.colosys.net/
Current Reviews for Academic Libraries, http://www.ala.org/
eLib Programme, http://www.ukoln.ac.uk/
Gabriel - Gateway to Europe's National Libraries, http://portico.bl.uk/ or http://www.bl.uk/
Institute National de l'Audiovisuel, http://www.ina.fr/
Kansas Library Directory, http://skyways2.lib.ks.us/
Koninklijke Bibliotheek (Netherlands National Library) http://www.kb.nl/
Libdex, http://www.libdex.com/
Libraries, Ancient Greek and Roman (Internet Encyclopedia of Philosophy) http://www.utm.edu/
Libraries for the Future, http://www.fno.org/
Libraries for the Future, http://www.lff.org/
Libraries on the World Wide Web, http://123world.com/
Library of Congress, http://lcweb.loc.gov/ or http://www.loc.gov/
Library Servers Via WWW, http://sunsite.berkeley.edu/
Medical/Health Sciences Libraries, http://www.arcade.uiowa.edu/
Nordic Libraries: Information Servers, http://www.ub2.lu.se/
Presidential Libraries, http://www.nara.gov/
School Libraries on the Web, http://www.sldirectory.com/
Social Responsibilities Round Table (ALA), http://www.libr.org/
The Canadian Library Index, http://www.lights.com/
The UK Academic Map, http://www.scit.wlv.ac.uk/
Transforming Traditional Libraries, http://www.lib.usf.edu/
UK Higher Education and Research Libraries, http://www.ex.ac.uk/

University of Rochester Libraries,
http://www.lib.rochester.edu/

b) Library Schools

Directory of Accredited Master's Programs,
http://www.ala.org/
LIS Schools on the Internet, http://www.db.dk/ ,
http://www.itcs.com/
Library Schools in the US and Canada,
http://slisweb.sjsu.edu/
Rare Books School, http://www.rarebookschool.org/
World List of Departments and Schools of Information Studies, http://informationr.net/

d) Public Libraries

Boulder Public Library, CO http://www.boulder.lib.co.us/
D-Lib Forum, http://www.earl.org.uk/
Guide to Internet Resources, http://www.winsor.edu/
Libri Foundation, http://www.librifoundation.org/ It is a nationwide non-profit organization which donates new, quality, hardcover children's books to small, rural public libraries in the United States.
UK Public Libraries on the Web,
http://dspace.dial.pipex.com/
United States Public Libraries, http://galaxy.einet.net/

e) School And Media Librarians

Developing Educational Standards: Library Media,
http://edstandards.org/
Information Competence: A Forum Series for High Schools, http://library.csusm.edu/
Peter Milbury's Network of School Librarian Web Page,
http://www.school-libraries.net/
State Quantitative School Library Media Standards,
http://edstandards.org/

3.9 Online Reading Materials

a)Online Books

Book Spot, http://www.bookspot.com/
Books2Read.com Bookstore, http://www.books2read.com/
Books On-Line: Archives, http://digital.library.upenn.edu/
BookWire (Bowker) http://www.bookwire.com/
Brave new e-books, http://www.salon.com/
Can E-Books Improve Libraries, http://skyways.lib.ks.us
eBooknet.com,http://www.ebooknet.com/
ebooksonthe.net, http://www.ebooksonthe.net/
Electronic Texts, http://etext.lib.virginia.edu/
Electronic Theses and Dissertations in the Humanities, http://etext.lib.virginia.edu/
Full text Resources, http://ejw.i8.com/
Great Books Index, http://books.mirror.org/
Great Books Online, http://www.columbia.edu/
Internet Book Information Center, http://metalab.unc.edu/ or http://www.internetbookinfo.com/
Net Library, http://www.netlibrary.com/
The eBook Directory, http://www.ebookdirectory.com/
The On-Line Books Page, http://digital.library.upenn.edu/
Utne Reader online, http://www.utne.com/

b) Reading Lists

AllReaders.com, http://www.allreaders.com/
BookBrowser: The Guide for Avid Readers, http://bookbrowser.com/
What's New for Book-Lovers, http://sunsite.unc.edu/
Who Reads What, http://www.gpl.lib.me.us/

3.11 Library Automation and Vendors

Ameritech Library Services, http://www.amlibs.com/
Baker and Taylor, http://www.btol.com/
B H Blackwell Ltd, http://www.blackwell.com/
Brodart Company, http://www.brodart.com/
CARL Corporation, http://www.carl.org/
Computer Error Alerts for Library OPACS, http://warriorlibrarian.com/
Current Awareness Application of New Technologies in Libraries, http://lib.ua.ac.be/
Data Research Associates (DRA) http://www.dra.com/
EBSCO, http://www.ebsco.com/
EZPROXY, http://www.usefulutilities.com/
Follett Software, http://www.fsc.follett.com/

Innovative Interfaces, Inc. http://www.iii.com/
Liblicense, http://www.library.yale.edu/
Library Associates, http://www.libraryassociates.com/
Library Corporation, http://www.tlcdelivers.com/
Library Systems, http://www.librarysystems.com/
Library Tools and Enhancements,
http://www.tlcdelivers.com/
Marcive, http://www.marcive.com/:
Online Computer Library Center, OCLC,
http://www.oclc.org/
Open Source Systems for Libraries,
http://www.oss4lib.org/
PACS-L, http://info.lib.uh.edu/
Public Access Computer Solutions,
http://www.cybraryn.com/
Research Libraries Group, Inc. (RLG) http://www.rlg.org/
Sagebrush Technologies, http://www.sagebrushcorp.com/
SilverPlatter, http://www.sagebrushcorp.com/
SIRSI, http://www.sirsi.com/ /
University Products, Inc.
http://www.universityproducts.com/
VTLS, http://www.vtls.com/
Winnebago Software Company, http://www.winnebago.com/
WinSuite, http://www.itcompany.com/

3.12 Professional Forums

Archives of MLA-L@LISTSERV.INDIANA.EDU,
http://listserv.indiana.edu/
ARL-EJOURNAL Forum, http://www.cni.org/
DLRG, drtc.isibang.ac.in/mailman/listinfo/dlrg
PACS-L, http://info.lib.uh.edu/
Publishers' and Authors' Message Board,
http://www.InsideTheWeb.com/messageboard/mbs.cgi/
SERIALST Scope & Purpose, http://www.uvm.edu/
Typographical Errors Discussion List,
http://www.egroups.com/
Web4Lib, http://sunsite.berkeley.edu/
Open Source Systems for Libraries, http://www.oss4lib.org/

3.13 Standards & Copyright

Open Archives Initiative http://www.openarchives.org/
Chilling Effects Clearinghouse,
http://www.chillingeffects.org/ **Library and Classroom Use of**

Copyrighted Videotapes and Computer Software, http://www.ifla.org/
Library Digitization Projects and Copyright, http://www.llrx.com/

Library of Congress Copyright Office, http://www.loc.gov/
National Information Standards Home Page, http://www.niso.org/
National Library Standards Activities, http://www.nla.gov.au/
Standards (Library of Congress) http://lcweb.loc.gov/
Standards and Guidelines, http://www.ala.org/
Technical standards for electronic bibliographic data/metadata, http://www.mun.ca/
WATCH File - Writers, Authors and Their Copyright Holders, http://tyler.hrc.utexas.edu/
See *Web Based Resources*' page for Copyright at http://ejw.i8.com/

Electronic Resources/aggregators

Academic Index, http://www.academicindex.net/
Academic Info, http://www.academicinfo.net/
Academic Resources.Net online research and reference, http://www.academicresources.net/
Access to Internet and Subject Resources, http://www2.lib.udel.edu/
Andrew's Online Reference Page, http://web.tampabay.rr.com/
The Argus Clearinghouse, http://www.clearinghouse.net/
Beyond Bookmarks, http://www.public.iastate.edu/
Britannica, http://www.britannica.com/
BUBL LINK / 5:15 Catalogue of Selected Internet Resources, http://bubl.ac.uk/
The Center for all Collegiate Information, http://www.collegiate.net/
College and Research Libraries News Internet Resources, http://www.ala.org/
The Cyberlibrarians' Rest Stop, http://www.angelfire.com/
Easy Searcher, http://www.easysearcher.com/
Ejournal SiteGuide: a MetaSource, http://www.library.ubc.ca/
The Gallup Organization, http://www.gallup.com/
Infolibrarian.com, http://www.infolibrarian.com
INFOMINE: Scholarly Internet Resource Collections, http://infomine.ucr.edu/

InfoNation, http://www.un.org/
Information Please, http://www.infoplease.com/ or http://www.infoplease.com/
InfoSurf: Resources by Subject, http://www.library.ucsb.edu/
Internet Detective, http://www.sosig.ac.uk/
Internet Library for Librarians, http://www.itcompany.com/
Let's Find Out, http://www.letsfindout.com/
Librarian Net, http://www.librarian.net/
Librarians' Index to the Internet, http://www.lii.org/, http://sunsite.berkeley.edu/
Librarians' Resource Center, http://www.sla.org/
Librarians' Site du Jour Archive, http://www.JennysCybrary.com/
Library, http://www.library.com/
Library and Related Resources, http://www.ex.ac.uk/
Library Computing Web, http://libcom.cjb.net/
Library Land, http://sunsite.berkeley.edu/
Library Media & PR, http://www.ssdesign.com/
Library of Iberian Resources Online, http://libro.uca.edu/
Library Screen Savers, http://www.libraryhq.com/screensavers.htm
Library Spot, http://www.libraryspot.com/
Library Stuff - July Archives, http://www.librarystuff.net/
Library Websites, http://metronet.lib.mn.us/
LibWeb, http://sunsite.berkeley.edu/
Links Central, http://donmcelyea.com/
LISNews.com, http://www.lisnews.com/
Michigan Electronic Library, http://mel.org/
New York Public Library Internet Resources, http://www.nypl.org/
NewsDirectory.com: a Guide to English-language Media, http://www.ecola.com/
NWREL's Library in the Sky, http://www.nwrel.org/
Official Documents, http://www.official-documents.co.uk/
Ohio RefLinks Project, http://www.reflinks.org/
PINAKES: A Subject Launchpad, http://www.hw.ac.uk/
Roper Center, http://www.ropercenter.uconn.edu/
Book HomePage, University Libraries Virginia Polytechnic Institute and StateUniversity, http://spec.lib.vt.edu/
Really Ready Reference, http://skyways.lib.ks.us/
Ready, 'Net Go! Archival Internet Resources, http://www.tulane.edu/
RefDesk.com, http://www.refdesk.com/
Reference, http://www.webdesk.com/

Reference Links, http://www.reflinks.org/ A volunteer organization of mostly librarians that do a good job of finding, evaluating and classifying web sites by Dewey number.
Repositories of Primary Sources, http://www.uidaho.edu/
Research-It!: Your One Stop Reference Desk, http://www.itools.com/
Smithsonian Institution Libraries Newsletter, http://www.sil.si.edu/
SMC Library Web Links, http://www.ucsm.ac.uk/
Teaching llbrary, http://www.lib.berkeley.edu/
TEK Net Communications - Link to It, http://www.teknetwork.com/
Time Inc. Picture Collection, http://www.thepicturecollection.com/
UNESBIB, http://unesdoc.unesco.org/
United Nations Documentation: research guide, http://www.un.org/
Universal Library Project (CMU) awesome!! http://www.ul.cs.cmu.edu/
University of Florida Faculty Center, http://www.unf.edu/
University Research Directory, http://www.unixl.com/
U.S. Depository Ready Reference Sources, http://www.columbia.edu/
Virtual Reference Desk, http://thorplus.lib.purdue.edu/
Virtual Reference Desk, http://www.vrd.org/
Web Characterization Project, http://wcp.oclc.org/
WWW Virtual Library, http://www.vlib.org/

3.15 Library organisations/associations/networks

a) National

c) Organizations/Associations

Delhi library Association (DLA) , http://www.dlaindia.org

Bombay Science Librarian's Association , http://www.bosla.org.in
Calcutta Library Network (CALIBNET) , http://www.calibnet.org
Central Reference Library, Kolkata, http://www.crl.org
Defence Scientific Information and Documenation Centre (DESIDOC), http://www.drdo.org

Developing Library Network (DELNET), http://www.delnet.nic.in
Documentation Research and Training Centre (DRTC), Bangalore http://www.drtc.isibang.ac.in
Health Education Library for People, http://www.healthlibrary.com
Indian Association of Special Libraries and Information Centers (IASLIC) , http://www.iaslic.org
Information and Library Network (INFLIBNET), Ahmedabad http://www.inflibnet.ac.in
Kesavan Institute of Information and Knowledge Management, http://www.kiikm.org
Mysore Library Network (MYLIBNET), Mysore, http://www.mylibnet.org
National Center for Science Information (NCSI),Bangalore, http://www.ncsi.iisc.ernet.in
National Information System for Science and Technology (NISSAT), New Delhi, http://www.dsir.nic.in
National Institute of Science Communication and Information Resources, New Delhi [Formerly INSDOC] , http://www.niscair.res.in
National Library of India http://www.nlindia.org
National Medical Library, http://www.nml.nic.in
National Social Science Documentation Centere (NASSDOC), New Delhi . http://www.icssr.org
Pune Library Network, http://www.202.41.70.20:6588/punenet/index.asp
Raja Rammohun Roy Library Foundation , http://www.rrrrlf.nic.in SAARC Documentation Centre , http://www.sdc.gov.in
Small Enterprises National Documentation Center [SENDOC] http://nisiet.com/sendoc.asp
Society for Advancement of Library and Information Science [SALIS] http://www.autolib-india.net/salis.html
Society for Information Science [SIS] , http://www.sis-india.netfirms.com
Special Libraries Association, http://www.sla.org
Virtual Information Center , http://www.vic-ikp.info
Uttar Pradesh Library Association (UPLA): http://www.uplaindia.org/
Society for Information Science: http://www.sis-india.netfirms.com

b) International

American Library Association, http://www.ala.org/
Antiquarian Booksellers' Association of America (ABAA) http://www.abaa.org/
Art Library Society, http://anulib.anu.edu.au/
Association for LIS Education, http://www.alise.org/
Bibliographical Society, http://www.bibsoc.org.uk/
CEAL - The Council on East Asian Libraries, http://www.sois.uwm.edu/
Center for Research Libraries, http://wwwcrl.uchicago.edu/ nternational

American Society for Information Science (ASIS) http://www.asis.org

Friends of Libraries USA, http://www.folusa.org/
Indian Association of Special Libraries and Information Centers: http://www.iaslic.org
Institute on 21st Century Librarianship, http://institute21.stanford.edu/
International Association of School Libraries, http://www.iasl-slo.org/
Internet School Library Media Center, http://falcon.jmu.edu/
Library History Roundtable, http://www.spertus.edu/
Library of Congress, http://lcweb.loc.gov/
LIS-related Associations, http://www.lis.uiuc.edu/
List of Library Associations, http://www.execpc.com/
Mountain-Plains Library Association, http://www.usd.edu/
New Breed Librarians, http://www.newbreedlibrarian.org/ Online Computer Library Center, http://www.oclc.org/
Public Library Association, http://www.pla.org/
Rare Maps and Manuscripts of IFLA, http://www.ifla.org/
Research Libraries Group, http://www.rlg.org/
Resources of Scholarly Societies - Library & Information Science, http://www.scholarly-societies.org/
Society of Georgia Archivists, http://www.soga.org/
Special Library Association, http://www.sla.org/
The International Federation of Library Associations, http://www.ifla.org
The Library Association, http://www.la-hq.org.uk/
The Library Web Manager's Reference Center, http://sunsite.berkeley.edu/

The Society of American Archivists, http://www.archivists.org/
Virtual Booksellers Association, http://www.virtual.bookshop.com/
Washington Library Media Association: Information Literacy, http://www.wlma.org/

Library of Congress, http://lcweb.loc.gov/
Asia Library and Information Virtual Association (ALIVA), http://www.aliva.org
Association for Information Management (ASLIB), http://www.aslib.co.uk
Association for Information Management Professionals (ARMA), http://www.arma.org
Australian Library and Information Association, http://www.alia.org.au
Chartered Institute of Library and Information Professionals, UK [CILIP], http://www.cilip.org.uk
Coalition for Networked Information, http://www.cni.org
Council on Library and Information Resources, http://www.clir.org
International Library Information and Analytical Center [ILIAC], http://www.iliac.org
International Federation of Library Associations and Institutions (IFLA), http://www.ifla.org
Library Association, UK, http://www.la-hq.org.uk
National Forum for Information Literacy, http://www.infolit.org
Online Computer Library Center (OCLC), http://www.oclc.com
Patent and Trademark Depository Library Association, http://www.ptdla.org
Scottish Confederation of University and Research Libraries , http://www.scurl.ac.uk
Special Library Association (SLA), http://www.sla.org

Scholory Journals (full Text open access)

Acceso : Revista Puertorriqueña de Bibliotecología y Documentación
ISSN: 15361772
Subject: Library and Information Science
Publisher: Sociedad de Bibliotecarios de Puerto Rico
Language: Spanish
Keywords: information science
Start year: 2003

ACIMED
ISSN: 10249435
EISSN: 15612880
Subject: Library and Information Science --- Medicine (General)
Publisher: Centro Nacional de Información de Ciencias Médicas
Language: Spanish
Keywords: health sciences
Start year: 1993

Anales de Documentación
ISSN: 15752437
EISSN: 16977904
Subject: Library and Information Science
Publisher: Universidad de Murcia, Facultad de Comunicación y Documentación
Language: Spanish, English, French
Keywords: documentation, archival science, librarianship, documental restoration, information literacy
Start year: 1998

Ariadne
ISSN: 13613197

EISSN: 13613200
Subject: Library and Information Science
Publisher: UKOLN. University of Bath
Language: English
Keywords: library and information science
Start year: 1996

Arquivística.net
ISSN: 18084826
Subject: Library and Information Science
Publisher: Arquivística.net
Language: Portuguese, English, Spanish
Keywords: information science
Start year: 2005

Biblios
ISSN: 15624730
Subject: Library and Information Science
Publisher: Biblios
Language: Spanish
Keywords: librarianship, information science
Start year: 1999

Bibliosphere
ISSN: 13118803
Subject: Library and Information Science
Publisher: NBU Library
Language: Bulgarian
Keywords: Bulgarian libraries, librarianship
Start year: 2001

Bibliotime Rivista elettronica per le biblioteche
ISSN: 11283564
Subject: Library and Information Science
Publisher: Università di Bologna
Language: Italian
Keywords: librarianship
Start year: 1998

BiD: textos universitaris de Biblioteconomia i Documentació
ISSN: 15755886
Subject: Library and Information Science
Publisher: Facultat de Biblioteconomia i Documentació of the Universitat de Barcelona, Spain
Language: Catalan, Spanish, English, French
Keywords: library and information science
Start year: 1998

Bilgi Dünyası DOAJ Content
ISSN: 13023217
Subject: Library and Information Science
Publisher: University and Research Librarians Associations (UNAK)
Language: Turkish, English
Keywords: librarianship, knowledge management, information management
Start year: 2002

Biomedical Digital Libraries DOAJ Content
ISSN: 17425581
Subject: Library and Information Science --- Medicine (General)
Publisher: BioMed Central
Language: English
Keywords: digital library content, biomedical settings, academic medical centers, health care institutions
Start year: 2004

Boletín de la Asociación Andaluza de Bibliotecarios
ISSN: 02136333
Subject: Library and Information Science
Publisher: Asociacion Andaluza de Bibliotecarios
Language: Spanish
Keywords: information science
Start year: 1999

The Bonefolder, an e-journal for the bookbinder and book artist DOAJ Content
ISSN: 15556565
Subject: Library and Information Science
Publisher: The Book Arts Web - Peter D. Verheyen
Language: English
Keywords: bookbinding, book arts, decorative techniques, education
Start year: 2004

Bulletin des Bibliothèques de France
ISSN: 00062006
EISSN: 12928399
Subject: Library and Information Science
Publisher: French School of Librarianship and Information Science
Language: French
Keywords: library, information science, publishing, information literacy
Start year: 1990

Bulletin of the American Society for Information Science and Technology
ISSN: 19316550
Subject: Library and Information Science
Publisher: American Society for Information Science and Technology
Language: English
Keywords: library and information science, technology
Start year: 1995

Bulletin of the Medical Library Association
ISSN: 00257338
Subject: Library and Information Science --- Medicine (General)
Publisher: PubMed
Language: English
Keywords: health sciences, librarianship

Start year: 1911
End year: 2001

Chinese Librarianship: an International Electronic Journal
ISSN: d0000912
EISSN: 10894667
Subject: Library and Information Science
Publisher: Internet Chinese Librarians Club
Language: English
Keywords: library and information science
Start year: 1996

Ciência da Informação DOAJ Content
ISSN: 01001965
Subject: Library and Information Science
Publisher: Instituto Brasileiro de Informacao em Ciencia e Tecnologia - IBICT, Brazil
Language: Portuguese, Spanish, English
Keywords: information science
Start year: 1997

Coordinates : Online Journal of the Map and Geography Round Table of the American Library Association. Series A DOAJ Content
ISSN: 15533247
Subject: Geography --- Library and Information Science
Publisher: American Library Association
Language: English
Keywords: maps, cartography, libraries, geography
Start year: 2005

Coordinates : Online Journal of the Map and Geography Round Table of the American Library Association. Series B DOAJ Content
ISSN: 15533255
Subject: Geography --- Library and Information Science

Publisher: American Library Association
Language: English
Keywords: maps, cartography, libraries, geography
Start year: 2005

Cybermetrics: international journal of scientometrics, informetrics, and bibliometrics
ISSN: 11375019
Subject: Library and Information Science
Publisher: Centro de Informacion y Documentacion Cientifica
Language: English
Keywords: library and information science, scientrometrics, bibliometrics, informetrics, Internet
Start year: 1997

cybrarians journal DOAJ Content
ISSN: 16872215
Subject: Library and Information Science
Publisher: cybrarians : The Arabic Portal For Librarianship and Information (Cairo, Egypt)
Language: Arabic
Keywords: librarianship, information science, archives, libraries
Start year: 2004

D-Lib Magazine
ISSN: 10829873
Subject: Library and Information Science
Publisher: Corporation for National Research Initiatives
Language: English
Keywords: library and information science
Start year: 1995

DIGITHUM
ISSN: 15752275
Subject: Social Sciences --- Library and Information Science

Publisher: Fundació per la Universitat Oberta de Catalunya (FUOC)
Language: Catalan, Spanish, English
Keywords: humanities, social science, digital culture, information society, ICT
Start year: 1999

E-JASL: The Electronic Journal of Academic and Special Librarianship
ISSN: 17048532
Subject: Library and Information Science
Publisher: International Consortium for the Advancement of Academic Publication
Language: English
Keywords: library and information science, academic librarianship
Start year: 2002

EBIB
ISSN: 15077187
Subject: Library and Information Science
Publisher: Stowarzyszenie Bibliotekarzy Polskich. Komisja Wydawnictw
Language: Polish, English
Keywords: librarianship, information, library technologies
Start year: 1999

Electronic Journal of Knowledge Management
ISSN: 14794411
Subject: Business and Management --- Library and Information Science
Publisher: Academic Conferences International Limited
Language: English
Keywords: knowledge management
Start year: 2003

Encontros Bibli: revista eletrônica de biblioteconomia

e ciência da informação DOAJ Content
ISSN: 15182924
Subject: Library and Information Science
Publisher: Universidade Federal de Santa Catarina - Ciência da Informação
Language: Portuguese, Spanish
Keywords: library science, information science, information management
Start year: 1996

ETD - Educação Temática Digital
ISSN: 15172539
Subject: Library and Information Science
Publisher: Universidade Estadual de Campinas
Language: Portuguese
Keywords: education, social sciences, technology, media and communication
Start year: 2004

Evidence Based Library and Information Practice DOAJ Content
ISSN: 1715720X
Subject: Library and Information Science
Publisher: University of Alberta Learning Services
Language: English
Keywords: evidence-based librarianship, evidence-based practice
Start year: 2006

High Energy Physics Libraries Webzine
ISSN: 14242729
Subject: Nuclear Physics --- Library and Information Science
Publisher: C E R N - European Laboratory for Particle Physics
Language: English
Keywords: library and information science, high energy physics, physics
Start year: 2000

Human IT: tidskrift för studier av IT ur ett humanvetenskapligt perspektiv DOAJ Content
ISSN: 14021501
EISSN: 1402150x
Subject: Library and Information Science
Publisher: Högskolan i Borås
Language: Swedish, English
Keywords: Internet, computers, information science
Start year: 1997

Infodiversidad DOAJ Content
ISSN: 1514514X
Subject: Library and Information Science
Publisher: Sociedad de Investigaciones Bibliotecológicas
Language: Spanish, Portuguese
Keywords: libraries, library science, information science
Start year: 2004

Information Research: an international electronic journal DOAJ Content
ISSN: 13681613
Subject: Library and Information Science
Publisher: Professor Tom Wilson
Language: English
Keywords: library and information science
Start year: 1995

Information Technology and Disabilities
ISSN: 10735127
Subject: Education --- Library and Information Science
Publisher: E A S I: Equal Access to Software and Information
Language: English
Keywords: information technology, disabilities, education

Start year: 1994

Informing Science The International Journal of an Emerging Transdiscipline DOAJ Content
ISSN: 15479684
EISSN: 15214672
Subject: Library and Information Science --- Media and communication
Publisher: Informing Science Institute
Language: English
Keywords: library and information science, journalism, informing science
Start year: 1997

Interdisciplinary Journal of Information, Knowledge, and Management
ISSN: 15551229
EISSN: 15551237
Subject: Computer Science --- Library and Information Science
Publisher: Informing Science Institute
Language: English
Keywords: information technology, information management, knowledge management, organizational learning
Start year: 2006

Interdisciplinary Journal of Knowledge and Learning Objects
ISSN: 15522210
EISSN: 15522237
Subject: Library and Information Science
Publisher: Informing Science Institute
Language: English
Keywords: knowledge, learning objects
Start year: 2005

International Journal of Doctoral Studies
ISSN: 15568881

EISSN: 15568873
Subject: Library and Information Science --- Computer Science
Publisher: Informing Science Institute
Language: English
Keywords: informing science, information systems, information technology, information science, information security, IT education
Start year: 2006

International Review of Information Ethics
ISSN: 16141687
Subject: Philosophy --- Library and Information Science
Publisher: International Center for Information Ethics
Language: English, German, Spanish, Portuguese, French
Keywords: cyberethics, computer ethics, library and information science
Start year: 2004

Issues in Informing Science and Information Technology
ISSN: 15475840
EISSN: 15475867
Subject: Computer Science --- Library and Information Science
Publisher: Informing Science Institute
Language: English
Keywords: informing science, information technology, trandisciplinary
Start year: 2004

Issues in Science and Technology Librarianship: a quarterly publication of the Science and Technology Section, Association of College and Research Libraries
ISSN: 10921206

Subject: Library and Information Science
Publisher: Association of College and Research Libraries, Science and Technology Section
Language: English
Keywords: library and information science
Start year: 1991

Journal of Digital Information
ISSN: 13687506
Subject: Library and Information Science
Publisher: Multimedia Research Group, Department of Electronics and Computer Science, University of Southampton
Language: English
Keywords: library and information science
Start year: 1997

Journal of Educational Media & Library Sciences
DOAJ Content
ISSN: 1013090X
Subject: Computer Science --- Library and Information Science
Publisher: Tamkang University Press
Language: Chinese, English
Keywords: library science, information science, information technology, publishing, book trade
Start year: 2003

Journal of Electronic Publishing
ISSN: 10802711
EISSN: 10802711
Subject: Library and Information Science
Publisher: University of Michigan Press
Language: English
Keywords: library and information science, electronic publishing
Start year: 1995

Journal of eLiteracy

ISSN: 17454360
Subject: Library and Information Science
Publisher: University of Glasgow
Language: English
Keywords: e-literacy
Start year: 2004

Journal of Information, Information Technology, and Organizations
ISSN: 15571319
EISSN: 15571327
Subject: Computer Science --- Library and Information Science
Publisher: Informing Science Institute
Language: English
Keywords: information systems research
Start year: 2006

Journal of Medical Internet Research
ISSN: 14388871
Subject: Library and Information Science --- Medicine (General)
Publisher: Gunther Eysenbach
Language: English
Keywords: medicine, Internet
Start year: 1999

Journal of southern academic and special librarianship
ISSN: 1525321X
Subject: Library and Information Science
Publisher: International Consortium for the Advancement of Academic Publication
Language: English
Keywords: library and information science
Start year: 1999
End year: 2001

Journal of the Association for History and Computing

ISSN: d0000018
Subject: History --- Computer Science --- Library and Information Science
Publisher: American Association for History and Computing
Language: English
Keywords: history, information science
Start year: 1998

Journal of the Medical Library Association
ISSN: 15365050
Subject: Medicine (General) --- Library and Information Science
Publisher: Medical Library Association
Language: English
Keywords: health sciences, librarianship
Start year: 2002

Library Philosophy and Practice
ISSN: 15220222
Subject: Library and Information Science
Publisher: University of Nebraska, Lincoln libraries
Language: English
Keywords: library and information science
Start year: 1998

LIBREAS - Library Ideas DOAJ Content
ISSN: 18607950
Subject: Library and Information Science
Publisher: Institut für Bibliothekswissenschaft Berlin, BibSpider
Language: German
Keywords: library science, librarianship, education
Start year: 2005

Libres: Library and Information Science Research Electronic Journal
ISSN: 10586768
Subject: Library and Information Science

Publisher: Curtin University of Technology, School of Media and Information
Language: English
Keywords: library and information science
Start year: 1996

medizin-bibliothek-information
ISSN: 16169026
Subject: Library and Information Science
Publisher: Arbeitsgemeinschaft für Medizinisches Bibliothekswesen
Language: German
Keywords: library and information science
Start year: 2001

North Carolina Libraries
ISSN: 00292540
Subject: Library and Information Science
Publisher: North Carolina Library Association
Language: English
Keywords: libraries, librarianship, media centers, academic libraries
Start year: 2002

PERSPECTIVAS EM CIÊNCIA DA INFORMAÇÃO
ISSN: 14139936
Subject: Library and Information Science
Publisher: Escola de Ciência da Informação da Universidade Federal de Minas Gerais
Language: Portuguese
Keywords: information science, library science, archives
Start year: 1996

Pez de Plata: Bibliotecas Públicas a la Vanguardia
ISSN: 07180039
Subject: Library and Information Science
Publisher: Colectivo Pez de Plata
Language: Spanish

Keywords: public libraries, internet, digital divide
Start year: 2003

Revista ACB DOAJ Content
ISSN: 14140594
Subject: Library and Information Science
Publisher: Associação Catarinense de Bibliotecários - ACB
Language: Portuguese
Keywords: information science, librarianship, documentation, archives
Start year: 1996

Revista Digital de Biblioteconomia e Ciência da Informação DOAJ Content
ISSN: 1678765X
Subject: Library and Information Science
Publisher: Sistema de Bibliotecas da Universidade Estadual de Campinas
Language: Portuguese, English, Spanish
Keywords: information science, library science, communication science
Start year: 2003

Revue électronique suisse de science de l'information - RESSI
ISSN: 16611802
Subject: Library and Information Science
Publisher: Haute école de gestion Genève
Language: French, German, English, Italian
Keywords: information science, documentation, archives, Switzerland
Start year: 2005

School Library Media Research
ISSN: 15234320
Subject: Library and Information Science
Publisher: American Association of School Librarians

Language: English
Keywords: library and information science, school librarys
Start year: 1998

Simbiosis. Revista electrónica de ciencias de la información
ISSN: 15483436
Subject: Library and Information Science
Publisher: Graduate School of Information Sciences and Technologies EGCTI), University of Puerto Rico
Language: Spanish, English
Keywords: librarianship, information science, information technology
Start year: 2004

SIMILE
ISSN: 14966603
Subject: Library and Information Science
Publisher: University of Toronto
Language: English
Keywords: library and information science, education, communication, information literacy
Start year: 2001

Solaris Information Communication
ISSN: 12654876
Subject: Library and Information Science --- Computer Science
Publisher: Recherches en Sciences de l'Information et de la Documentation, Groupe Interuniversitaire
Language: French
Keywords: library and information sciences, computer applications, data communications
Start year: 1994

Svensk Biblioteksforskning DOAJ Content
ISSN: 02844354
EISSN: 16535235

Subject: Library and Information Science
Publisher: Swedish School of Library and Information Science
Language: Swedish, English, Norwegian, Danish
Keywords: library and information science, cultural politics, information management, knowledge organisation, information seeking
Start year: 2005

Technology Electronic Reviews, TER
ISSN: 15339165
Subject: Library and Information Science
Publisher: The Library and Information Technology Association (ALA)
Language: English
Keywords: information technology
Start year: 1994

Virginia Libraries
ISSN: 10869751
Subject: Library and Information Science
Publisher: Virginia Library Association
Language: English
Keywords: library and information services, librarianship
Start year: 1996

Vjesnik bibliotekara Hrvatske DOAJ Content
ISSN: 05071925
EISSN: 13346938
Subject: Library and Information Science
Publisher: Hrvatsko knjižničarsko društvo
Language: Croatian
Keywords: librarianship, library and information sciences, libraries
Start year: 2003

Webology DOAJ Content
ISSN: 1735188X

Subject: Library and Information Science
Publisher: University of Tehran, Department of Library and Information Science
Language: English
Keywords: information dissemination, communication processes, World Wide Web
Start year: 2004

4. Conclusion

There are many other web-sites available on the net which are use ful not only for profession development but are very use full in day to day management of libraries and inforation centres. As the availiblity of the sites on the web is hightly volatile hence it is suggested to refer only authoritative sites of well known organizations /associations and those having a standing in the field.

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RESEARCH ARTICLE

Removal of chloride from ground water by Bio adsorption

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Abstract

Chloride in concentration above 600 mg/l tends to give water a salty taste. The concentration of chloride content above 200 mg/l is considered objectionable. Presence of high quantity of chloride content in water resources indicate pollution due to human and industrial wastes and also from the earthen rocks in the subsurface. High chloride concentrations in freshwater can harm aquatic organisms by interfering with osmo-regulation, the biological process by which they maintain the proper concentration of salt and other solutes in their bodily fluids. Difficulty with osmo-regulation can hinder survival, growth, and reproduction. In large concentrations it can create problems to water supply line and human health. This paper deals with removal of chloride by using Bio adsorbent in batch study.

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INTRODUCTION

Chlorides are not usually harmful to people; however, the sodium part of table salt has been linked to heart and kidney disease. Sodium chloride may impart a salty taste at 250 mg/L; however, calcium or magnesium chlorides are not usually detected by taste until levels of 600 mg/L are reached. Chlorides can corrode metals and affect the taste of food products. Therefore, water that is used in industry or processed for any use has a recommended maximum chloride level. Chlorides can contaminate fresh water streams and lakes. Fish and aquatic communities cannot survive in high levels of chloride increase. The chloride ion is negatively charge anion (Cl^-). It is formed when the elements chlorine gains an electrons or when a compound such as hydrogen chloride is dissolved in water or other polar solvent. Chloride salts such as NaCl are very soluble in water. It is an essential electrolyte located in all body fluids responsible for maintaining acid/base balance, transmitting nerve impulses and regulating fluid in and out of cells. Chloride is much larger than a chlorine atom, 167 & 99 pm respectively. The ion is colorless & diamagnetic. In aqueous solution it is highly solvated, being bound by the protic end the water molecules.

All natural waters contain chloride & sulphate ions. Their concentrations vary considerably according to the mineral content of the earth in any given area. In small amounts they are not significant. In large concentrations they present problems. Usually chloride concentrations are low. Sulfates can be more troublesome because they generally occur in greater concentrations. Low to moderate concentrations of both chloride and sulfate ions add palatability to water. In fact, they are desirable for this reason. Excessive concentrations of either, of course, can make water unpleasant to drink. Chloride is commonly found in streams & wastewater. Chloride may get into surface water from several sources including:

- Rocks containing chlorides;
- Agricultural runoff;
- Wastewater from small scale industries ; and
- Effluent wastewater from wastewater treatment plants.
- Produced water from gas and oil wells

A normal adult human body contains approximately 81.7 g chloride .On the basis of a total obligatory loss of chloride approximately 530 mg/day, a dietary intake for adults of 9 mg of chloride per kg of body weight has been recommended (equivalent to slightly more than 1g of table salt per person per day). For children up to 18 years of age, a daily dietary intake of 45 mg of chloride should be sufficient. A dose of 1g of sodium chloride per kg of body weight was reported to have been lethal in a 9 week old child. Chloride toxicity has not been observed in humans except in the special case of impaired Sodium chloride metabolism, e.g. in congestive heart failure. Healthy individuals can tolerate the intake of large quantities of chloride provided that there is a concomitant intake of fresh water. Little is known about the effect of prolonged intake of large amounts of chloride in the diet. As in experimental animals, hypertension associated with sodium chloride intake appears to be related to the sodium rather than the chloride ion.

2. *REMOVAL TECHNIQUES OF CHLORIDE*

2.1 NORCURE CONCRETE CHLORIDE REMOVAL SYSTEM:-

Norcure technology is one of the most important techniques which were taken up in order to address the problem of corrosion of the concrete due to the entry of chlorides. The Norcure process is an electrochemical method of removing chloride ions and drawing them out of the concrete. Using this method, concrete could be rejuvenated without the inconvenience and disruption of conventional demotion and repair, resulting in significant savings. The corrosive nature of sodium chloride (salt) is well known. It can bring about rust on automobiles, and wreak havoc on concrete, where corrosive concentrations of chlorides are often found. The chloride ions percolate deep into the concrete structures due the porous nature of concrete, eventually reaching the reinforced steel or rebar. Furthermore, after this, it begins to corrode the structure, and structures such as parking lots, highways and bridges become vulnerable due to its damaging effects. Once chlorides attack a structure, they quickly eat away at the reinforcing steel, causing cracks to appear. If left untreated, these chloride ions can cause concrete spalls, expose steel reinforcement bars and eventually reduce the structural integrity of the structure to dangerous Levels.

2.2 CHLORIDE REMOVAL USING ION EXCHANGE METHOD:-

Ion exchange works on the basic principle of charge based transport of ions. In a lab scale study on pulp and paper mill, several resins were tested for chloride removal. The resins were either free base forms or hydroxide base forms. The study concluded that two hydroxide ion based resins named IRN78 and 4400OH achieved approximately 50% and 70% chloride removal at a dose of 10 g / L and were the potential resins that may be used in the reduction in chlorides in Pulp and paper mill effluent.

2.3 ULTRA HIGH LIME WITH ALUMINIUM (ULHA) PROCESS:-

Lime softening serves as the favorite alternative for removing scale forming materials. However, the process does not remove silica, chloride or sulfates. A process named Ultra High Lime Softening was therefore devised, which successfully removed silica, but not sulfur and chlorides. Advanced methods are available for the removal of chlorides and sulfates, viz. Reverse osmosis, electro dialysis but lime softening is the cheapest alternative available for recycled cooling water. Also, the process like reverse osmosis is not only expensive, but also difficult to maintain. Occurrence of problems like membrane fouling may require frequent cleaning and production of brine in the form of reject creates a problem of effluent disposal. The Ultra High Lime with Aluminum process is an innovative technology which operates in two stages. The high pH and Calcium content in the first stage allows for removal of sulfate by precipitation as Calcium Sulfo-aluminate ($Ca_6\ Al_2\ (SO_4)_3(OH)_{12}$). Also, these conditions of the first stag allow the precipitation of chlorides as Calcium chloral- aluminates ($Ca_4\ A_{l2}\ Cl_2\ (OH)_{12}$). The cost economics of the process depicted that the capital cost is equivalent to the conventional lime process due to the fact that the same equipment is usable. Operating cost of the UHLA system is slightly higher due to the constant requirement to add aluminum. The sludge that is obtained contains almost 39% aluminum by weight.

2.4 CALCINED LAYER DOUBLE HYDROXIDES (CLDH) METHOD:-

On the basis of an effect known as Memory Effect, it was said that CLDH, within a certain temperature range, has the capacity to regain its original form. Therefore, a study was conducted in order to observe the capacity of

CLDH to assimilate chloride ions from aqueous solution. The study concluded that the assimilation of chloride ions by CLDH was consistent with Langmuir and Freundlich models.

2.5 *ELECTROCHEMICAL METHOD FOR THE REMOVAL OF CHLORIDES:-*

Electrochemical Chloride Extraction (ECE) is essentially a simple electrochemical process which consists of the use of basic principle of ion migration towards oppositely Charged poles. The apparatus contained an anode which was inserted in an electrolyte media. The setup was then applied on the concrete surface. The anode and the reinforcing steel were connected to two terminals of a direct current (DC) power supply such that the anode was positively charged. Due to the charge on the anode, the migration of the Chloride ions from the concrete to the anode field occurred, thereby reducing the chloride content in the concrete, particularly on and around the reinforced steel end. At the termination of the process, chloride free, highly alkaline concrete is obtained, which results in strong repassivation of the embedded reinforced steel and halting of the corrosion of the same. A study was conducted in order to observe the free chloride content in a concrete block during electrochemical chloride removal. It showed that, due to the free chloride removal, bound chloride is dissolved in order to reestablish the equilibrium between bound and free chloride The above literature review clearly indicates the need for research on the application of the biological substances for the chloride removal process. These processes may prove effective solutions for cost economic chloride removal. Therefore, the present paper studies the compatibility of the bio-sorption phenomena for chloride reduction.

2.6 ***BIO ADSORPTION***

Adsorption can be defined as a process in which atoms or molecules move from a bulk phase (that is, solid, liquid or gas) onto a solid or liquid surface. An example is purification of liquid/gases by adsorption where impurities are filtered by adsorption process onto the surface of a high-surface-area solid such as activated charcoal. Molecules that have been adsorbed onto solid surfaces are referred to as adsorbate, and the surface to which they are adsorbed as the adsorbent. The adsorption process can occur at interface between any two phases, such as, liquid-liquid, gas-liquid, gas-solid or liquid-solid interfaces. In the case of liquid-solid interfaces, three types of adsorption have been distinguished: (a) physical adsorption: due to Vander Waal's attraction, (b) chemical adsorption: due to formation of chemical bond and (c) exchange adsorption: due to electrical attraction of solute to the adsorbent. Chemical adsorption is characterized by high energies (> 40 kJ/mol) which are similar to those found between atoms within a molecule (for example, covalent bonds), strong localized bonds and is generally favored at higher temperatures. In physical sorption, the adsorbed molecule remains intact, but in chemisorptions the molecule can be broken into fragments on the surface, in which case the process is called dissociative chemisorptions. However adsorbed molecules are considered not to be free to move on the surface or within the interface and are referred to as "activated" adsorption (Weber, 1972) unlike physical adsorption. Most of the adsorption phenomena are coordination of the three forms of adsorption and are generally termed as sorption, which includes absorption too while desorption is the reverse process. The extent of adsorption depends on physical parameters such as temperature, pressure and concentration in the bulk phase, and the surface area of the adsorbent, as well as on chemical parameters such as the elemental nature of the adsorbate and the adsorbent. Low temperatures, high pressures, high surface areas, and highly reactive adsorbate or adsorbents generally favour adsorption. Biomass used as adsorbent after necessary activation by different methods is referred as Bio adsorption.

3. MATERIAL AND METHODS

3.1 USE OF CHLORIDE SAMPLE & GAJARGHAS (Parthenium) AS BIOADSORBENT

Natural Wastewater Sample with Chloride Concentration 1000 ppm was taken and the preliminary experiments were done with this sample. A plant known as grass / Gajarghas / Parthenium sps. / Congress (Belongs to the family asteraceae) was used as a bio-adsorbent. Before using, the Plant, it was dried & powdered (containing leaves and stem). The word 'Parthenium' has been derived from the Latin word 'Parthenice', meaning reputed medicinal merits. It has been speculated by scientists that the unique properties of this weed can be exploited for different purposes like activated carbon making, biomass generation, pesticide use etc.

Fig 1 Parthenium plant

Parthenium is considered to be one of the ten worst weeds in the world. Parthenium is an herbaceous annual or ephemeral member of the family Asteraceae. It can reach heights of up to 2 m in good soil, and attain flowering in less than 4– 6 weeks of germination. Seeds produced per plant can go up to 25000. Dispersion of the seeds occurs through various vectors like water, muddy surfaces, small animals, vehicles, machinery etc. Partheniumhas a variety of vernacular names, like Congress grass, White top, Star Weed, Carrot Weed, Gajar Ghaas (Hindi), Ramphool, feverfew etc. The pollen and seeds of these plants are known to be a major cause of asthma, and bronchitis. The weed shows the presence of toxins known as Sesquiterpene lactones, parthenin, phenolic acids such as caffeic acid, vanillic acid,anisic acid, panisic acid, and parahydroxy benzoic acid which are known to be lethal to humans as well as animals.

3.2 METHOD OF ACTIVATION OF BIO-ADSORBENT:

Sample collection was done on the basis of the health of the plant through visual observations. Young plants having a fresh green shoot and sizable stem thickness were selected. On collection, the specimens were washed with tap water and then distilled water. Further, for biomass collection, the specimens were subjected to drying in an oven at 100 ^{0}C for three days. Drying was followed by careful crushing of the specimen, and then sieving the mixture through a 500 micron sieve. The obtained biomass was used for the study. The biomass was added to the test solutions in the ratio of 0.10 g: 100 ml test solution. The pH of the sample was maintained at 7, and the chloride concentration at 100% of the initial wastewater solution. The mixture was then incubated in a rotary shaker incubator at 150 rpm and 300 ^{0}C for 60 minutes. On the termination of contact time, the solution was filtered using an ordinary filter paper. The sample was titrated for chloride content using the Argentometric titration method specified in the APHA handbook for water and wastewater analysis. The tests were repeated by carrying out variations in pH, by using different chloride concentration levels, and with variable contact times.

3.3BATCH MODE ADSORPTION EXPERIMENTS

Batch mode adsorption experiments were conducted at room temperature (23- 25 ^{o}C) except where mentioned. Predetermined quantities of adsorbent were added in the beaker and to achieve the degree of mixing and adsorption equilibrium, a magnetic stirrer was employed with speed adjusted at 100 rpm. A paddle stirrer was also employed with speed adjusted at 1000 rpm to check the difference in chloride removal due to different mode of physical mixing of bio-adsorbent ranging from pH 3- 11 which were well adjusted by using 0.1 N of HCl and NaOH whereas extreme pH were adjusted using 1 N acid/base solution. Addition of acid/base solution to adjust the pH never exceeded 1% of the total volume of the reactor.. The amount of Chloride adsorbed by adsorbent was calculated based on the difference of ion concentration in aqueous solution before and after adsorption according to the following equation:

$$q_t = \frac{(C_0 - C_t)V}{m}$$

where, q_t is the amount of chloride ions adsorbed per unit weight of adsorbent (mg/g) at time t, C_0 and C_t are the concentrations of chloride ions (mg/L) at initial time and at time t respectively, V is the initial volume of metal ions sample (L) and m is mass of adsorbent (g). When t is equal to the equilibrium contact time, $C_t = C_e$, $q_t = q_e$, then the amount of chloride ions adsorbed at equilibrium, q_e was calculated using equation as above.

3.4 ANALYTICAL TECHNIQUES

All analyses were carried out according to APHA (1998). Measurement of Chloride was carried out by Argentometric method. Drying and activation of bio adsorbent was done using a drying oven and a muffle furnace respectively. During adsorption experiment, degree of mixing was provided by employing magnetic stirrer or Jar test apparatus (Paddle Stirrer). Solution pH was measured by a digital pH meter. All weighing of reagents and adsorbents was carried out in an analytical weighing balance.

Table 2: Experimental design for batch studies with chloride and Bio-adsorbent

Experimental Set	Variable parameters	Control parameters	Purpose
1	pH	Concentration and Dose	Effect on absorption of chloride due to variation in pH
2	Time	Concentration and Dose	Optimization of time for removal of chloride
3	Dose(1,2,3,4,5,6 7g)	Initial Concentration of chloride: 100 to 1000 mg/L	Adsorbent dose test

4. RESULTS AND DISCUSSION

5.1 Effect of reaction pH in Batch study

Solution pH is one of the most important parameter to reveal the mechanism of adsorption. The effect of solution pH effect is firstly studied by conducting control experiment without any adsorbents. it's clear that the solubility of chloride is consistent from pH range of 2- 12. Secondly, various pH range of chloride solution was contacted with Parthenium bio-adsorbent and the result is shown in fig 2.

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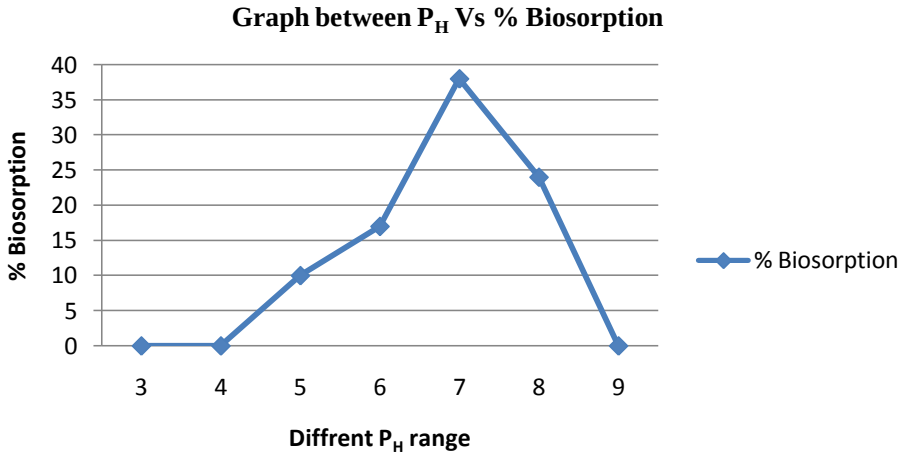

Figure 2: Effect of reaction pH on adsorption of chloride by Parthenium at various reaction pH (Initial Chloride: 100 mg/L; dose: 0.10g/100ml of solution) .

The best level of pH was found as pH 7, where the maximum absorption was observed by Parthenium.

4.2 EFFECT OF ADSORPTION TIME IN BATCH STUDY

The effect of initial chloride concentration on the adsorption was investigated varying initial chloride concentration in the range of 100–1000 mg/L. Batch experiments were performed at solution pH of 7.0 with 1 g/L

bio- adsorbent. Removals of chloride ions (%) with time at a fixed initial chloride concentrations and amounts of chloride adsorbed are shown in Fig 3. and 4 respectively. The equilibrium between chloride and bio-adsorbent was attained within 5 minutes at initial chloride concentration of 100 mg/L and 20 minutes for all higher chloride concentrations. Equilibrium time increased to 90 minutes for almost all chloride concentration to 1000 mg/L and was constant beyond that. The chloride adsorption yield decreased with increase in initial concentration of chloride. At chloride concentration of 100 mg/L, 88% removal was achieved. When initial chloride concentration was increased to 1000 mg/L, chloride removal decreased to 40%. However, chloride uptake increased with increase in initial chloride ion concentration Fig 4. At initial chloride concentrations of 100 mg/L, chloride uptake was 84 mg/g and increased to 400 mg/g at
initial chloride concentration of 1000 mg/L. The reason was probably with increase in concentration, the number of Chloride ions increased and so chances of contact between chloride ions and adsorption sites also increased. This was responsible for higher chloride uptake by unit amount of adsorbent.

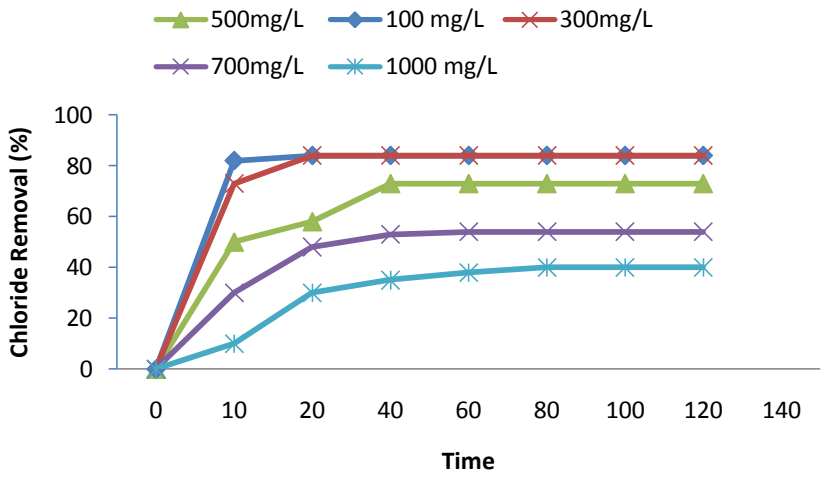

Figure 3: Effect of reaction time on adsorption (%) of chloride by bio-adsorbent at various initial concentration of chloride (Reaction pH: 7; dose: 1 g/L)

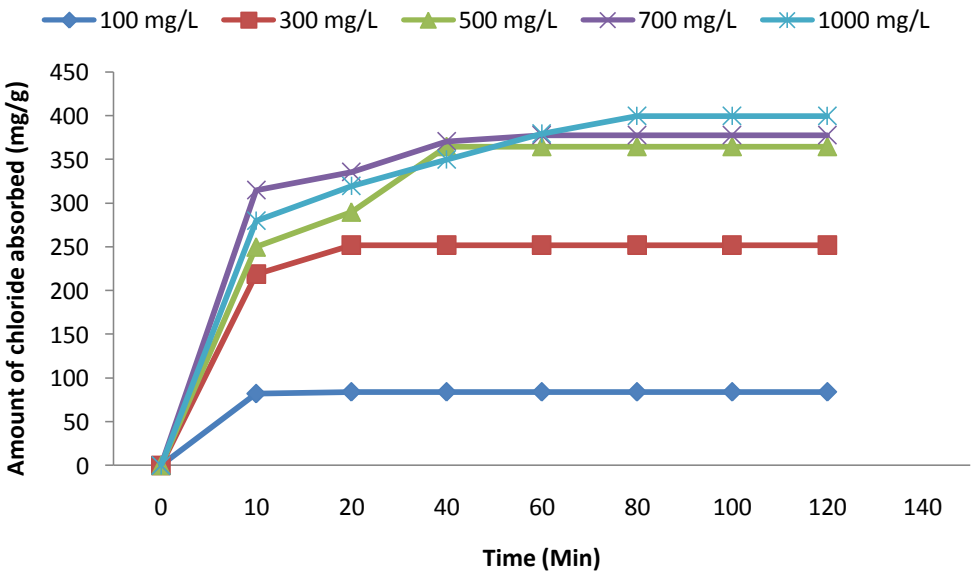

Figure 4: Effect of reaction time on adsorption of chloride (mg/g) by Parthenium bio Adsorbent at various initial concentration of chloride (Reaction pH: 7; dose: 1 g/L)

This process of chloride adsorption was also conducted with a fixed concentration of chloride to. 1000 mg/L as per the actual water sample concentration. The adsorbent dose was kept to 2 g. with a fixed pH of 7. The performance of the absorbent is as shown in the graph below. The contact time was kept to 10 min. to 240 min. with 500 rpm rotating system. This graph shows increased % of bio-adsorption with increased contact time.

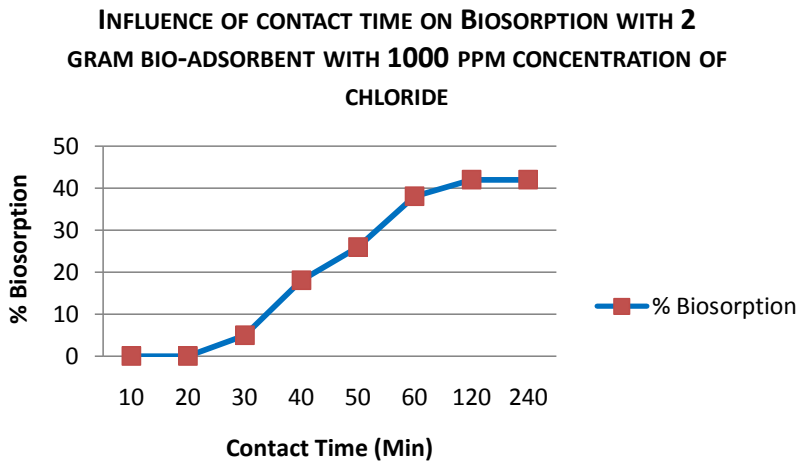

Figure 5: Effect of reaction time on adsorption (%) of chloride by bio-adsorbent at 1000 mg/L initial concentration of chloride (Reaction pH: 7; dose: 2 g/L)

4.3 EFFECT OF ADSORBENT DOSE

Effect of adsorbent dose on chloride uptake was studied by varying the adsorbent dose from 1 g/L to 7 g/L for only one fixed initial chloride concentration of 1000 mg/L. Initial pH was adjusted to 7. Chloride removal (%) and uptake with adsorbent dose for fixed chloride concentrations are shown in Fig.6.. It was observed that chloride removal (%) for fixed concentrations increased from 20% to 60% with increase in the adsorbent dose. The number of Chloride ions of adsorption sites or surface area increases with the weight of the adsorbent and hence results in a higher percent of metal removal at a high dose.

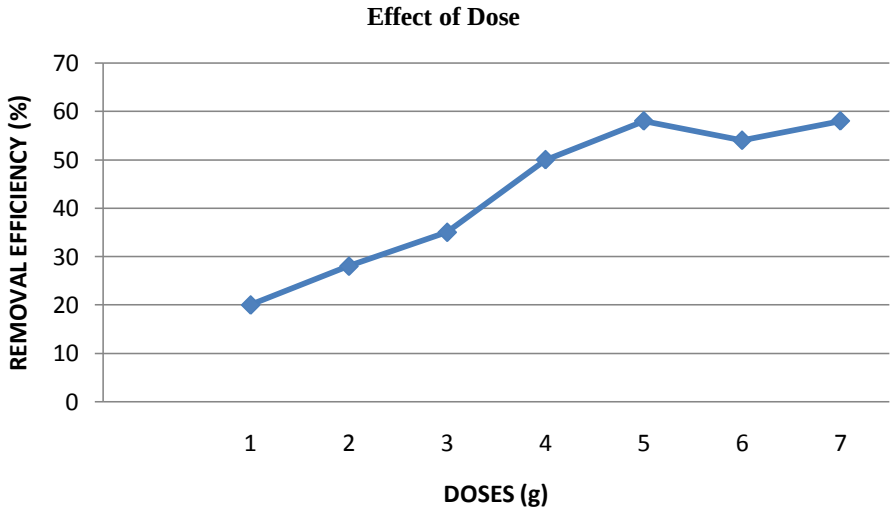

Figure 6: Removal (%) of chloride with varied dose of bio-adsorbent

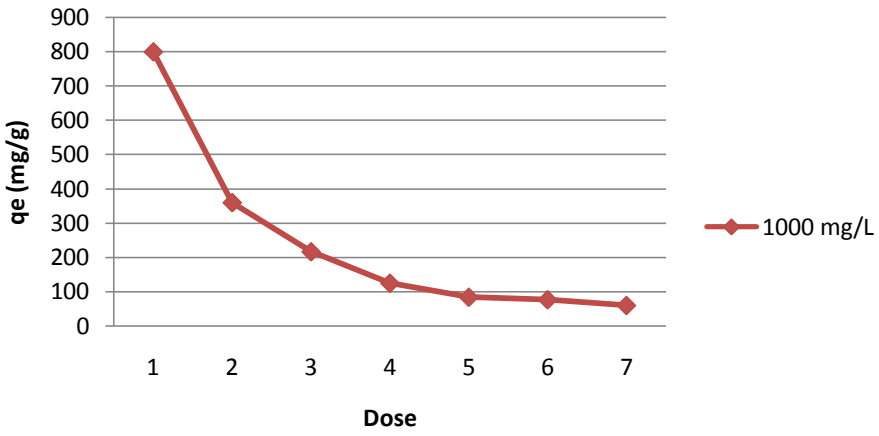

Figure 7: Plot of Removal (q_e) for chloride Vs dose of Parthenium

4.4ADSORPTION ISOTHERM

Adsorption isotherm is a mathematical model or functional expression to depict the distribution of solute between the solid and liquid phase at equilibrium at a constant fixed temperatures. The isotherm model relates the amount of solute adsorbed per weight of adsorbent (q_e), with amount of solute retain in solvent (C_e) at equilibrium. Commonly, the amount q_e increase with increase in C_e value, but not in direct proportion. Several mathematical model or isotherms were developed based on certain assumptions. Langmuir isotherm, Freundlich isotherm, Langmuir-Freundlich isotherm, BET isotherm, Temkin, Redlich–Peterson etc. are some of the well known models out of which Langmuir and Freundlich isotherm are the commonly and mostly applied models in chloride adsorption from aqueous solution.

4.4.1 LANGMUIR ISOTHERM

Langmuir isotherm is based on the following assumptions: (a) each surface site can be singly occupied, (b) there are no lateral interactions between adsorbed species, (c) the enthalpy of adsorption is independent of surface coverage and (d) energy of adsorption is constant thus creating homogeneity of energy on the surface (there is dynamic equilibrium between the adsorption and desorption processes).

$$K_d\theta = K_a C_e(1-\theta)$$

or, $$\theta = \frac{K_a C_e}{K_d + K_a C_e} = \frac{bC_e}{1+bC_e}$$

The adsorption coefficient $b = \frac{K_a}{K_d}$, is related to the enthalpy of adsorption (ΔH) by

$$b = b_0 \exp^{-\Delta H / RT}$$

where b_0 is constant related to entropy, R is the universal gas constant, T is the temperature (^{0}K) (Voice and Weber 1983).

As q_e is proportional to θ, therefore, equation (A) can be written as,

$$q_e = \frac{bQ_m C_e}{1 + bC_e}$$

where q_m is the maximum adsorption for a complete monolayer coverage. Equation (B) can be rearranged in variety of linear forms.

$$\frac{C_e}{q_e} = \frac{1}{Q_m b} + \frac{C_e}{Q_m}$$

$$\frac{1}{q_e} = \frac{1}{Q_m} + \frac{1}{bQ_m C_e}$$

$$q_e = Q_m - \frac{q_e}{bC_e}$$

4.4.*2* *FREUNDLICH ISOTHERM*

Freundlich model or van Bemmelon equation has been developed for adsorption system with emphasis on two factors, namely the lateral interaction between the adsorbed molecules and the energetic surface heterogeneity. The equation has the general form (Freundlich 1906)

$$q_e = K_f C_e^{\frac{1}{n}}$$

but it is well cited in logarithmic form as

$$\log q_e = \log K_f + \frac{1}{n} \log C_e$$

where K_f and n are empirical constant. Here, K_f α RT nb exp(ΔH/RT). Equation (F) suggests that with increase in C_e, adsorption capacity (q_e) would increase without restriction, which is practically impossible. The model may simulate concentrations far outside the range of the defining batch experiment. Extrapolating equation (F) into such concentration regions hence may give results of unknown, but potentially very large error. However in practical situation, adsorption process are sufficiently dilute and one never encounters the region where Freundlich equation breaks down for this region and Freundlich isotherm equation implies that the energy distribution of adsorption site is of exponential (Cooney 1999).

In order to identify the best fit isotherm model, Chi square test was done by the following equation G. (Ho et al, 2005)

$$\chi^2 = \Sigma \frac{(q_e - q_{em})^2}{q_{em}}$$

Where, q_e is the experimental data of the equilibrium chloride uptake (mg/g) and q_{em} is the equilibrium uptake calculated from isotherm models (mg/g).

The linear plots of Langmuir isotherm is shown in Fig. 8 with $1/C_e$ Vs $1/q_e$. Also the linear plot of Freundlich isotherm with In(C_e) Vs In (q_e) is plotted in Fig.9. The correlation coefficients and the coefficients are shown in Table 5. It shows that Langmuir isotherm fitted experimental data better than the Freundlich model as it showed larger R^2 value as compared to the Freundlich model. The Langmuir curves had good linearity (Correlation coefficient > 0.99) for Bio adsorbent doses indicating strong binding of chloride ions to the surface of Parthenium during adsorption. The Langmuir monolayer capacity (a) or maximum adsorption capacity is observed to be 24.39 mg/g. The adsorption equilibrium parameter b, which reflects quantitatively the affinity between the adsorbent and

the adsorbate, is 0.0149 L/g. The essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter (R_L), which is defined by the following relation.

$$R_L = \frac{1}{1 + bC_0}$$

(H)

Where b is the Langmuir constant C_0 is the initial liquid phase chloride ion concentration and for favorable adsorption $0 < R_L < 1$. Separation factor RL indicates the isotherm shape accordingly.

RL >1, Unfavorable

RL=1, Linear

RL lies between 0 and 1, Favorable

RL=0, Irreversible.

Further the plot of comparison of q_e value of experimental and predicted through both Langmuir and Freundlich isotherms is shown in Fig. 10.

Table2 : Coefficients of Langmuir and Freundlich's isotherm

Langmuir				Freundlich			
R^2	a (mg/g)	b (L/mg)	λ^2	R^2	K_f	N	λ^2
0.9901	24.39	0.0149	0.64	0.9364	2.7604	2.9913	1.16

Table 3 : Observation table during batch study

Co (mg/L)	Ce (mg/L)	1/Ce	LogCe	InCe	Qe	1/Qe	logQe	InQe	Ce/Qe g/L	qe(exp)	Qe (Lang)	Qe (Fre)
100	28	0.035714	1.447158	3.332205	7.2	0.138889	0.857332	1.974081	3.888889	7.2	7.1888668	8.409449
200	72	0.013889	1.857332	4.276666	12.8	0.078125	1.10721	2.549445	5.625	12.8	12.633952	11.53158
300	138	0.007246	2.139879	4.927254	16.2	0.061728	1.209515	2.785011	8.518519	16.2	16.418883	14.33323
400	232	0.00431	2.365488	5.446737	16.8	0.059524	1.225309	2.821379	13.80952	16.8	18.924879	17.0516
500	302	0.003311	2.480007	5.710427	19.8	0.050505	1.296665	2.985682	15.25253	19.8	19.961632	18.62297
600	380	0.002632	2.579784	5.940171	22	0.045455	1.342423	3.091042	17.27273	22	20.734372	20.10964
700	490	0.002041	2.690196	6.194405	21	0.047619	1.322219	3.044522	23.33333	21	21.456314	21.8935
800	579	0.001727	2.762679	6.361302	22.1	0.045249	1.344392	3.095578	26.1991	22.1	21.860492	23.14974
900	681	0.001468	2.833147	6.523562	21.9	0.045662	1.340444	3.086487	31.09589	21.9	22.205427	24.44014
1000	750	0.001333	2.875061	6.620073	25	0.04	1.39794	3.218876	30	25	22.389926	25.24153

Table 4: Coefficients of Isotherms

$\chi 2$ of Lengmuir	$\chi 2$ of Freundlich	A	b	Kf	N	R_L
1.72149E-05	0.203162104	24.39	0.014926	2.760467	2.991325	0.401186
0.002154067	0.125694191	24.39	0.014926	2.760467	2.991325	0.250928
0.002957397	0.215112022	24.39	0.014926	2.760467	2.991325	0.182554
0.268756607	0.003768144	24.39	0.014926	2.760467	2.991325	0.143463
0.001319433	0.069969707	24.39	0.014926	2.760467	2.991325	0.118161
0.072809692	0.162430223	24.39	0.014926	2.760467	2.991325	0.100446
0.009915341	0.038016173	24.39	0.014926	2.760467	2.991325	0.08735
0.002595655	0.049861887	24.39	0.014926	2.760467	2.991325	0.077275
0.004259605	0.294626176	24.39	0.014926	2.760467	2.991325	0.069283
0.272499434	0.002333381	24.39	0.014926	2.760467	2.991325	0.06279
0.637284446	1.164974007					

Fig 8-Langmuir Adsorption Isotherms

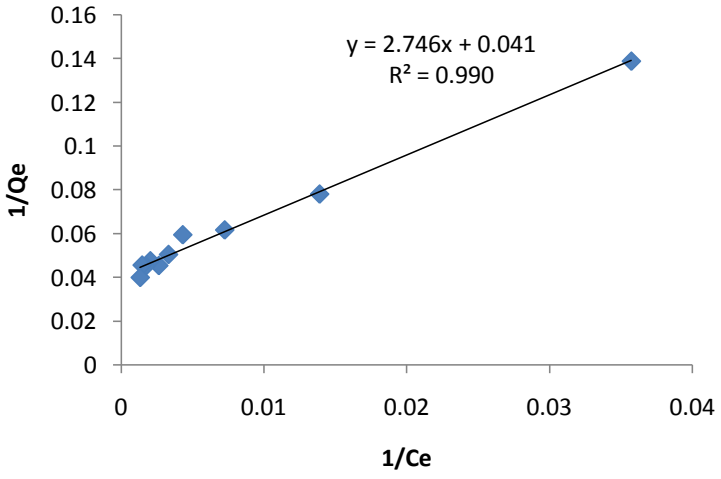

Fig 9-Freundlich adsorption Isotherm

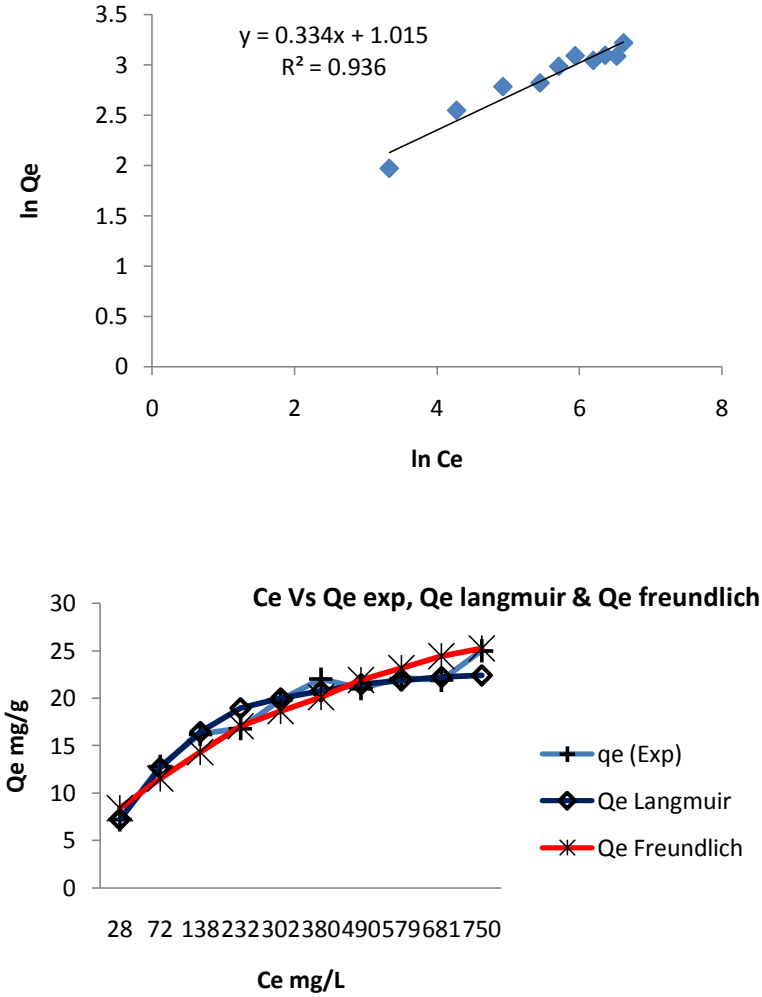

Figure 10: Comparison between experimental q_e and predicted q_e value of Langmuir & Freundlich's isotherm

5.CONCLUSIONS

Following conclusions are drawn from the study.

1. The Parthenium may be used for removal of chloride from the ground water. The Parthenium is showing maximum absorbance at pH 7.
2. During the variation in the adsorbent dose, corresponding increase in the adsorption was noted with increase in the dose in the solution.
3. The batch process results were best suited in to the Langmuir Isotherm instead of Freundlich Isotherm. R^2 of Langmuir is 0.99 and Freundlich is 0.93.
4. Freundlich isotherm 'n' value of 2.99 which is less than 10 and greater than 0 suggest the favourable adsorption of chloride by Parthenium.
5. The performance of Parthenium when subjected to actual water decrease by 15-25% due to the presence of other co-ions.

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