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Crustal Structure from Gravity and Magnetic Anomalies in the Southern Part of the Cauvery Basin, India

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Abstract: The gravity and magnetic data along the profile across the southern part of the Cauvery basin have been collected and the data is interpreted for crustal structure depths.The first profile is taken from Karikudito Embalecovering a distance of 50 km. The gravity lows and highs have clearly indicated various sub-basins and ridges. The density logs from ONGC, Chennai, show that the density contrast decreases with depth in the sedimentary basin, and hence, the gravity profiles are interpreted using variable density contrast with depth. From the Bouguer gravity anomaly, the residual anomaly is constructed by graphical method correlating with well data and subsurface geology. The residual anomaly profiles are interpreted using polygon and prismatic models. The maximum depths to the granitic gneiss basement are obtained as 3.00 km. The regional anomaly is interpreted as Moho rise towards coast. The aeromagnetic anomaly profiles are also interpreted for charnockite basement below the granitic gneiss group of rocks using prismatic model.

Key words : Cauvery Basin, Gravity, Variable density contrast, Granitic gneiss basement, Magnetic, Charnockite Basement

1. INTRODUCTION

The Cauvery basin is located between 9^{o}N-12^{0}N latitudes and $78^{o}30^{1}$E - $80^{o}30^{1}$E longitudes on the east coast of India and covers 25,000 sq. km on land and 35,000 sq. km offshore. It consists of six sub-basins and five ridge patterns. The basement is comprised of the Archean igneous and metamorphic complex predominantly granitic gneisses and to a lesser extent khondalites.Sastri et al (1973, 1977 and 1981) and Venkatarengan (1987) provided the earliest details on stratigraphy and tectonics of the sedimentary basins on the east coast of peninsular India. The Cauvery basin has come into existence as a result of fragmentation of the eastern Gondwanaland which began in the Late Jurassic (Rangaraju et.al, 1993). Lal et al (2009) have provided a plate tectonic model of the evolution of East coast of India and the NE-SW trending horst and grabens of Cauvery basin are considered to be placed juxtaposing fractured coastal part of Antarctica, located west of Napier Mountains The Cauvery basin is a target of intense exploration for hydrocarbons by the Oil and Natural Gas Corporation (ONGC) and has been extensively studied since early 1960. This is one of the promising petroliferous basins of India. Many deep bore-wells have been drilled in this basin in connection with oil and natural gas exploration. These wells revealed a wealth of information about the stratigraphy and density of the formations with depth. The Cauvery basin is for the most part covered by Holocene deposits. Sediments of late Jurassic to Pleistocene age crop out in three main areas near the western margin of the basin and gently dip towards the east. The oldest sediments in this basin are Sivaganga beds of late Jurassic age. The maximum sediment thickness of the basin is about 6000m (Prabhakar and Zutshi, 1993).O.N.G.C.

conducted gravity and magnetic surveys in the Cauvery basin in 1960s (Kumar, 1993) and presented the Bouguer gravity anomaly map. Avasthi et al (1977) have published gravity and magnetic anomaly maps of Cauvery basin. Verma (1991) have analyzed few gravity profiles in the Cauvery basin. Subrahmanyam et al (1995) has presented offshore magnetic anomalies of Cauvery basin. Ram Babu and Prasanti Lakshmi (2004) have interpreted aeromagnetic data for the regional structure and tectonics of the Cauvery basin. The geological and geophysical work clearly delineated the presence of a number of ridges and sub-basins trending in NE-SW directions (Prabhakar and Zutshi, 1993 and Hardas, 1991): They are: i. Pondicherry sub-basin ii. Tranquebar sub-basin iii.Tanjavur sub-basin IV.Nagapattinam sub-basin v. Palk Bay sub-basin and vi. Mannar sub basin and i. Madanam Ridge ii. Kumbakonam Ridge iii.Karaikal Ridge iv. Mannargudi Ridge v. Mandapam Ridge. The gravity and magnetic surveys are carried out in the entire Cauvery basin along nine profiles, at closely spaced interval, and placing the profiles at approximately 30 km interval and perpendicular to various tectonic features. In this paper gravity and magnetic anomaly profile is PP' presented along the tectonic map of Prabhakar and Zutshi (1993).The gravity anomalies are interpreted with variable density contrast for granitic gneiss basement and the aeromagnetic profiles are interpreted for the chornockite basement below the granitic gneiss group of rocks

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2. MATERIALS AND METHODS. GRAVITY AND MAGNETIC SURVEYS

The gravity, magnetic and DGPS(Differential Global Position System) observations are made along three profiles across the various tectonic features (Prabhakar and Zutshi, 1993) in the central part of the Cauvery basin as shown in Fig.1.Gravity measurements have been made at approximately 1.5 to 2km station interval. Gravity readings are taken with Lacoste-Romberg gravimeter and Position locations and elevations are determined by DGPS(Trimble).The HIG (Haiwaii Institute of Geophysics) gravity base station located in the Ist class waiting hall of Vridhachalam railway station is taken as the base station. The latitude and longitude of this base are $11^{0}32^{1}06.45885^{11}$N and $79^{0}18^{1}59.19866^{11}$E respectively. The gravity value at this base station is 978227.89 mgals. With reference to the above station, auxiliary bases are established for the day to day surveys. The Bouguer anomaly for these profiles is obtained after proper corrections viz (i) drift (ii) free air (iii) Bouguer and (iv) normal. The Bouguer density is taken a value of 2.0gm/cc after carrying out density measurements of the surface rocks. The gravity observations are made along available roads falling nearly on straight lines .The maximum deviations from the straight lines at some places are around 5 km. Total field magnetic anomalies are also observed at the same stations using Proton Precession Magnetometer but the data is later found to be erroneous. In order to get magnetic picture, aeromagnetic anomaly maps in topo sheets 58M, 58N, 58J, 58K, 58O, 58L, 58H covering the total Cauvery basin on land from GSI are procured and anomaly data is taken along these three profiles. The total field magnetic anomalies are observed at an elevation of 1.5 km above msl. IGRF corrections are made for this data using standard computer programs and the reduced data is used for interpreting magnetic basement.

Gravity profile along PP'

The profile (PP') runs from Karikudi(Latitude 10°01.06.84367"N and Longitude 78°33'13.8292"E) to Embale, (Latitude 9°01'08.47826"Nand Longitude 78°59'12.71739"E) covering a distance of 50 km and 23 stations are established along this profile (Fig.1).The data is collected on 20/3/2007. This profile passes across the Tanjavur sub-basin, Mannargudi ridge (Fig.1). The profile is sampled at 5 km station interval .The minimum and maximum Bouguer gravity anomalies

over the basins and ridges are -45,-35,1.8 and 2,-17,0.7,.The profile is passing through one ONGC well which was drilled upto a depth, of; 1500.00 meters and did not reach granitic gneiss basement and is plotted as dotted lines in Fig.1,(Jayakondam-1).The basement depths based on sub-surface geology (Prabhakar and Zutshi, 1993), shown in Fig.1, are plotted as dotted curve. Based on this data and by trial and error method of modeling, a smooth regional curve is drawn such that the interpretation of resulting residual anomalies with quadratic density function gives rise to the depths conforming to the depths given by wells and sub-surface geology. The regional is -25mgals at the origin and continuously increases reaching a maximum of 22mgals at 50 km distance from the land border of the basin. The regional is subtracted from the Bouguer anomaly and the residual is plotted as shown in Fig 1. The residual anomaly is interpreted with quadratic density function using polygon model (BhaskaraRao and Radhakrishna Murthy1986) and also with prismatic model (BhaskaraRao 1986).The depths are obtained by iterative method using Bott's method and the results at 10^{th} iteration are plotted as polygon and prismatic models as shown in Fig.1. The errors between the residual and calculated anomalies in both the methods are below $\pm$0.1 mgals. The maximum and minimum depths over the basins and ridges are the interpreted depths are nearly coinciding with the depths given by Prabhkar and Zutshi (1993). The regional is interpreted for Moho depths. For this, the normal Moho value outside the basin is taken as 42km from Kaila et al (1990) and the regional anomaly is obtained by removing a constant value of -25mgals from the regional and a density contrast of +0.6 gm/cc is assumed between the upper mantle and crust. The depths to Moho are deduced from the regional anomaly by Bott's method and the Moho rise is plotted at the bottom of Fig.1 and the Moho is identified at 34.0 km depth near the coast to 42 km on land border of the basin in NW.

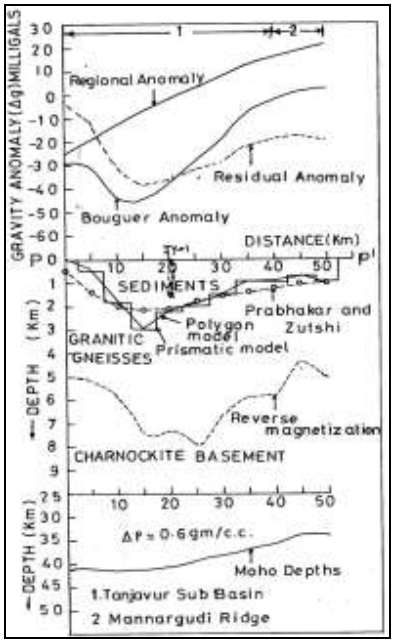

Figure 1. Interpretation of gravity anomaly profile along PP'

Magnetic profile along PP'

The magnetic data for the profile PP' is taken from two topo sheets (58J and 58K).To construct the profile, the observed stations are placed on topo sheets of the magnetic anomaly map and a mean straight line is drawn. The points of intersection of the magnetic contours with the straight line are noted and these values are plotted against the distance .This aeromagnetic data was collected in the year 1983 and diurnal corrections were made before contouring the data. IGRF corrections made to this data using 1985 coefficients as and the magnetic anomaly profile is constructed. The length of the magnetic anomaly profile is 50 km and is sampled at 5 km interval. The magnetic anomalies vary from 36ηT to 164ηT. The anomalies are interpreted for magnetic basement structure below granitic gneisses using prism model. The profile is interpreted by taking the mean depth of the basement at 5.0 km and constraining the depths to upper and lower limits of the basement as 2.0 km and 8.0 km respectively. The FORTRAN computer program TMAG2DIN to interpret the profiles is taken

from Radhakrishna Murthy (1998). The program is based on the Marquadt algorithm and this seeks the minimum of the objective function defined by the sum of the squares of the differences between the observed and calculated anomalies. A linear order regional, viz; Ax+B, is assumed along this profile and the coefficients A and B are estimated by the computer. The profile is interpreted for different magnetizations angles (Φ)+18,-18 and intensity of magnetizations (J) 450.The average value for the total field (F)39780 , inclination (i)4.0 and declination (d)0.0 along this profile and the measured angle between the strike and magnetic north (α)22. Based on this data, the magnetization angle Φ is calculated to be 11.00°. But by trial and error, the best fit of the anomalies for Φ and J. The values of the objective function, lamda (ג), regional at the origin (A), regional gradient (B) and the no.of iterations executed for normal as well as reverse magnetization. Here the objective function for normal magnetization is 3.46 and that of reverse magnetization is 18.51. The residual anomaly after removing the regional from the observed anomaly is plotted in the figure 2. The differences between the residual and the calculated anomalies are negligible as shown in the figure 2. The interpretations of the depths for normal and reverse magnetizations for charnockite basement. The depths for these two interpretations are not much different. As the average susceptibility of the granitic gneisses is of the order of $10*10^{-6}$cgs units and that of charnockite is $2000*10^{-6}$cgs units, granitic gneiss basement cannot explain the observed magnetic anomalies. The modeling results place the charnockite basement 0 to 8 km below the granitic gneiss basement along this profile. The existence of charnockite basement below granitic gneisses was also noted by Narayaswamy (1975).

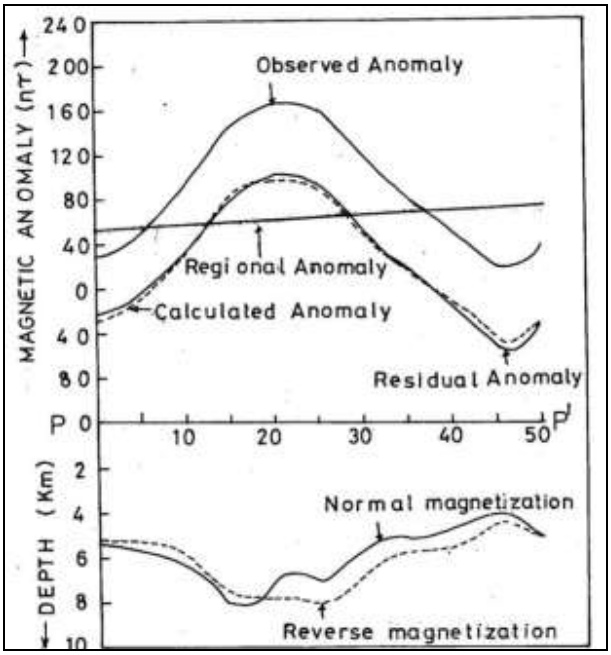

Figure 2. Interpretation of total field magnetic anomaly profile along PP'

3. RESULTS AND DISCUSSION.

The gravity and magnetic surveys have been carried out along profile laid perpendicular to various tectonic features, approximately at 30 km interval, in the southern part of the Cauvery basin. The subsurface geology and information available from the boreholes along these profiles are used to estimate the regional in the case of gravity anomalies. The residual gravity anomalies are interpreted for the thickness of the sediments in the basins and on ridges using variable density contrast. The density data obtained from various boreholes drilled in connection with oil and natural gas exploration is used to estimate variable density contrast, which is approximated by a quadratic function. The gravity anomalies are interpreted with polygon model (BhaskaraRao and Radhakrishna Murthy 1986) and also with prismatic model (BhaskaraRao, 1986), and the depths are plotted and these are nearly the same for both the methods: The basement for the sedimentary fill is the

granitic gneiss group of rocks. The maximum depths obtained in the Tanjavur sub-basin is 3.0 km along PP' profile. The regional anomaly is interpreted for Moho depths and it is rising towards coast along these profiles. The Moho depth outside the basin is taken as 42 km and the Moho depths near the coast are obtained as 34.0 km for the PP'. The gravity studies clearly brought out the structure of the sedimentary basin along the profile and supplement the geological studies. The aeromagnetic anomalies along these three profiles are also interpreted as a basement structure below the sediments. The magnetic basements do not coincide with the gravity basements. The depths obtained for chornackite basement for normal and reverse magnetizations are nearly the same. The best fit for the observed magnetic anomalies is obtained for chornackite basement structure0 to 8 km below the granitic gneiss basement. The values of magnetizations angle and intensity of magnetization show that the anomalies are caused by remanent magnetization. There is no correlation between the basements obtained by gravity and magnetic methods. A close fit with the observed magnetic anomalies is obtained for reverse magnetization. However, the charnockite basement structure for normal and reverse magnetizations are not much different. The interpretation of magnetic anomalies clearly brought out the existence of charnockite basement below the granitic gneiss basement. The observed magnetic anomalies can be best explained with the intensity of magnetizations 450 gammas for PP'. The modeling results for various profiles place the chornackite basement at 0 to 8km below the granitic basement.

4. CONCLUSIONS.

The profile PP' runs from Karikudi to Embale covering a distance of 50 km. This profile passes across the Tanjavur sub-basin and Mannargudi ridge.The residual anomaly is interpreted with quadratic density function using polygon and prismatic models. The depths obtained by gravity methods on the Tanjavur sub basin and Mannargudi ridge are 1.8 km, and 0.7 km respectively. The interpreted depths are nearly coinciding with the depths given by Prabhakar and Zutshi (1993) and drilled depths. The regional gravity anomalies are interpreted for Moho depths. The Moho is identified at 34.0 km depth near the coast to 42 km on land border of the basin in NW. The magnetic anomaly profile is interpreted with different intensity of magnetizations (J) and dips (Φ) for charnockite basement. There is no correlation between the basements obtained by the gravity and magnetic methods. The observed magnetic anomalies can be best explained with the intensity of magnetization of 450 gammas and dips of ±18.0 degrees. The objective functions for normal and reverse magnetizations are 3.46 and 18.51 respectively.

5. ACKNOWLEDGEMENTS

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Design and Fabrication of Duplexer for GSM900 Band Applications

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Abstract: This paper presents the design technique and simulation of Duplexer for GSM 900 band applications using microstrip technology.Two band pass filters with unequal impedance are designed. One filter with the 890-915MHz band and other filter with the 935-960MHz. Then these two filters are combined together in parallel to act as a duplexer with the uplink frequency band as 890-915MHz and downlink frequency band as 935-960MHz.The simulation is done using ADS software. Next, tuning and optimization are applied to achieve the low insertion loss.The proposed duplexer is a proof of concept for realizing duplexer functions using microstrip technology. In general, duplexers are built using high quality factor cavity filters. However, to prove the concept, duplexer is fabricated using FR-4 material which is readily available in India.
Keywords: Advanced Design System (ADS), Bandpass Filter (BPF), Fractional Bandwidth (FBW)

1. INTRODUCTION

The duplexer is a device that isolates the receiver from the transmitter while permitting them to share a common antenna. The duplexer is often the key component that allows two way radios to operate in a full duplex manner. An ideal duplexer provides perfect isolation with no insertion loss to and from the antenna. A conventional duplexer is a three-port device and normally consists of two band pass filters and impedance transforming circuit to allow both filtered to connect to a common antenna port. [4,6]

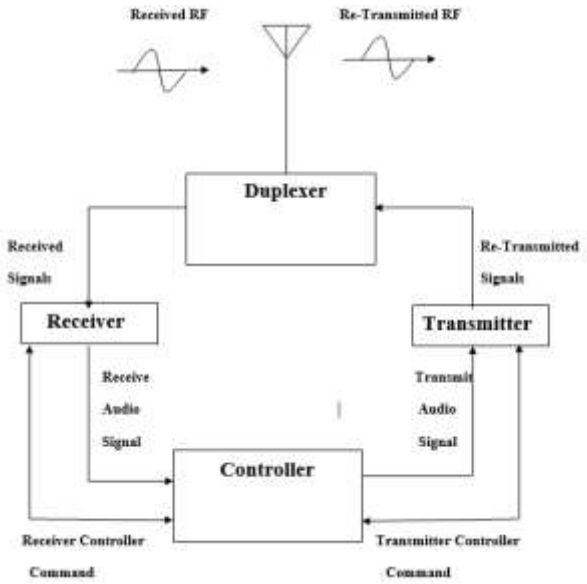

Figure 1:Block diagram illustrating the working of duplexer.

The working of duplexer is as shown in the figure 1. During transmission, signals from controller are transmitted to antenna through transmitter band pass filter which rejects the signals having frequency range other than 890-915MHz.
During reception the signals received by antenna are passed to controller through receiver band pass filter which rejects signals having frequency range other than 935-960MHz.

1.1Band pass filter:

Filters are indispensable devices in many systems and applications including wireless broadband, mobile, satellite communications, radar, navigation, sensing and other systems. With the development of these systems, mostly induced by great commercial interests, limited electromagnetic spectrum has to be shared among more and more systems. Thus, there is an increasing demand for RF, microwave and millimeter wave filters with more stringent requirements.These filters are employed in various systems to select or confine signals with specified spectral limits. Electronic filters are circuits that have signal processing functions. i.e. they transform an input signal to obtain an output signal with the required characteristics. In the frequency domain filters are used to reject unwanted signal frequencies and to pass signals of desired frequencies.

A bandpass filter only passes the frequencies within a certain desired band and attenuates others signals whose frequencies are either below a lower cut-off frequency or above an upper cut-off frequency. The range of frequencies that a bandpass filter allows to pass through is referred as passband. A typical bandpass filter can be obtained by combining a low-pass filter and a high-pass filter or applying conventional low pass to bandpass transformation.A band pass filter is an electronic circuit which allows the signals with the desired frequency band and supresses the signals out of that band.

1.2 Microstrip

Microstrip is an electrical transmission line which can be fabricated using printed circuit board technology and is used to convey microwave frequency signals[1][7]. It consists of conducting strip separated from a ground plane by a dielectric layer known as substrate as shown in figure 2.
Microstrip line is used to carry electromagnetic waves or microwave frequency signals. Microstrip lines will have low to high radiation, will support 20 to 120 ohm impedance, supports Q factor of 250.

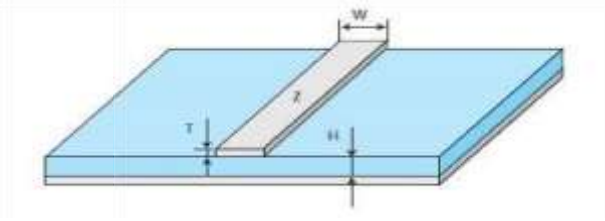

Figure 2: Microstrip structure

Microwave components such as Antennas, Couplers, Filters, Power dividers etc. can be formed from microstrip, the entire device existing as the pattern of metallization on the substrate.
Microstrip is much less expensive than traditional waveguide technology, as well as being far lighter and more compact.

1.3.ADS Software

Advanced Design system (ADS) is an automation software produced by Agilent EEsof EDA, a unit of Agilent technologies. It provides an integral design environment to designers of RF electronic products such as mobile phones, pagers, wireless networks, satellite communication etc.
Agilent ADS supports every step of the design process like layout, simulation, frequency-domain and time-domain circuit simulation and electromagnetic field simulation allowing engineers to full characterize and optimize RF design without changing the tools.

2. DESIGN FLOW

Two chebyshev bandpass filters are designed with the frequency bands 890-915MHz and 935-960MHz. The pass band ripple is taken as 0.5dB.Insertion loss and return loss are required to be maximum of 2dB and minimum of 10dB respectively.
The job in designing any type of filter is to calculate its order. So the order of the filters are calculated by using the below equation

$$N \geq \frac{La + Lr + 6}{20\ \log_{10}\left(S + \sqrt{(S^2+1)}\right)} = 6 \quad \ldots\ldots\ldots\ldots\ldots\ldots 1$$

Where, N is the order of the filter
La= Attenuation in stop band
Lr=Ripple in pass band=0.5
S =Selectivity factor of the filter

$$= \frac{Stop\ band\ frequecy}{Pass\ band\ frequency} \geq 1$$

The chebyshev filter coefficients are obtained from the table 1.

Table.1:Chebyshev filter coefficients with 0.5 dB ripple.

N	g1	g2	g3	g4	g5	g6	g7	g8	g9	g10	g11
1	0.6986	1.0000									
2	1.4029	0.7071	1.9841								
3	1.5963	1.0967	1.5963	1.0000							
4	1.6703	1.1926	2.3661	0.8419	1.9841						
5	1.7058	1.2296	2.5408	1.2296	1.7058	1.0000					
6	1.7254	1.2479	2.6064	1.3137	2.4758	0.8696	1.9841				
7	1.7372	1.2583	2.6381	1.3444	2.6381	1.2583	1.7372	1.0000			
8	1.7451	1.2647	2.6564	1.3590	2.6964	1.3389	2.5093	0.8796	1.9841		
9	1.7504	1.2690	2.6678	1.3673	2.7939	1.3673	2.6678	1.2690	1.7504	1.0000	
10	1.7543	1.2721	2.6754	1.3725	2.7392	1.3806	2.7231	1.3485	2.5239	0.8842	1.9841

From the table chebyshev filter coefficients for low pass filter with order N=6 are,
g0=1,g1=1.7254,g2=1.2479,g3=2.6064,g4=1.3137,g5=2.4758,
g6=0.8696,g7=1.9841.

If order of the filter is N, then the microstrip coupled line filter will have N+1 coupled lines. So that here the number of microstrip coupled lines in both the filters will be 7.
To design the microstrip coupled line band pass filters,the admittance, odd and even mode excitation line impedances of each coupled lines are to be calculated. These parameters are calculated by using the below equations.

$$J_{01} = \frac{1}{Z_O} \times \sqrt{\left(\frac{\pi}{2} \times \frac{FBW}{g_0 g_1}\right)} \quad \ldots\ldots\ldots\ldots 2$$

$$J_{i,i+1} = \frac{1}{Z_O} \times \frac{\pi}{2} \times FBW \sqrt{\left(\frac{1}{g_i g_{i+1}}\right)} \quad \ldots\ldots\ldots 3$$

$$J_{n,n+1} = \frac{1}{Z_O} \times \sqrt{\left(\frac{\pi}{2} \times \frac{FBW}{g_n g_{n+1}}\right)} \quad \ldots\ldots\ldots\ldots 4$$

Where,J – Admittance
$Z_O = 50$ Ohm;

$$FBW = \frac{\omega_2 - \omega_1}{\omega_0}$$

The admittance of each microstrip coupled lines of both the filters are calculated by using the equations 2-4.
The above calculated admittance values are used to obtain the odd and even mode line impedances using below equations:

$$Z_{oe} = Z_O\,(1 + Z_O J + (Z_O J)^2) \quad \ldots\ldots\ldots\ldots 5$$

$$Z_{oo} = Z_O\,(1 - Z_O J + (Z_O J)^2) \quad \ldots\ldots\ldots\ldots 6$$

The odd and even mode line impedance values will be substituted in Linecalc tool of ADS.At this point we need to decide the type of substrate to be used in fabrication of designed filters.So here we have taken the FR-4 substrate. The specifications of FR-4 substrate are tabulated in the table 2.

Table 2: FR-4 substrate specifications

Thickness	35um
Height	1.6mm
Dielectric constant,εr	4.6

The admittance,odd and even mode line impedances for 890-915MHz uplink band pass filter are tabulated in the table 3.

Table 3: Admittance, Zoe Zoo values for uplink filter

MCLIN	Admittance(Ohms)	Zoe(ohms)	Zoo(ohms)
MCLIN 1	0.173732555	60.1957	42.8225
MCLIN 2	0.035490933	51.8375	48.2884
MCLIN 3	0.028876315	60.1957	42.8225
MCLIN 4	0.028143854	51.4467	48.6324
MCLIN 5	0.028876618	51.4855	48.5978
MCLIN 6	0.035492342	51.8376	48.2883
MCLIN 7	0.173733896	60.1958	42.8224

The admittance, odd and even mode line impedances for 935-960MHz downlink band pass filter are tabulated in the table 4.

Table 4: Admittance, Zoe Zoo values for down link filter

MCLIN	Admittance(Ohms)	Zoe(ohms)	Zoo(ohms)
MCLIN 1	0.173732555	59.9210	42.9542
MCLIN 2	0.033809354	51.7476	48.3666
MCLIN 3	0.027508141	51.4132	48.6624
MCLIN 4	0.026810383	51.3764	48.6954
MCLIN 5	0.027508428	51.4132	48.6624
MCLIN 6	0.03810696	51.9779	48.1672
MCLIN 7	0.169568152	59.9160	42.9592

The Width (W),length (L) and Spacing(S) of microstrip conductor calculated by using Linecalc tool are tabulated in the table 5 and 6.

Table 5: Width, Spacing andLength of uplink filter

MCLIN	Width (mm)	Spacing(mm)	Length(mm)
MCLIN 1	2.7354	0.7	45.1944
MCLIN 2	2.1371	2.5206	43.3990
MCLIN 3	1.9955	4.3427	44.7556
MCLIN 4	4.0815	5.4698	44.7577
MCLIN 5	2.3382	6.9602	44.7556
MCLIN 6	2.8274	4.4069	45.2838
MCLIN 7	1.7816	0.3	45.6463

Table 6: Width, Spacing and Length of downlink filter

MCLIN	Width (mm)	Spacing(mm)	Length(mm)
MCLIN 1	2.4757	1.029	43.0272
MCLIN 2	2.9619	5.2224	42.618
MCLIN 3	2.9749	6.4583	42.6326
MCLIN 4	3.0955	6.1750	42.6346
MCLIN 5	2.6228	6.3106	42.6326
MCLIN 6	2.9051	4.5305	42.6100
MCLIN 7	1.3462	0.7309	43.4570

3. IMPLEMENTATION IN ADS

As a final step, the coupled line band pass filters are designed in the ADS simulation software environment. It accepts filter parameters and produces physical dimensions of the filter layout and a simulation of the filter response.[2]

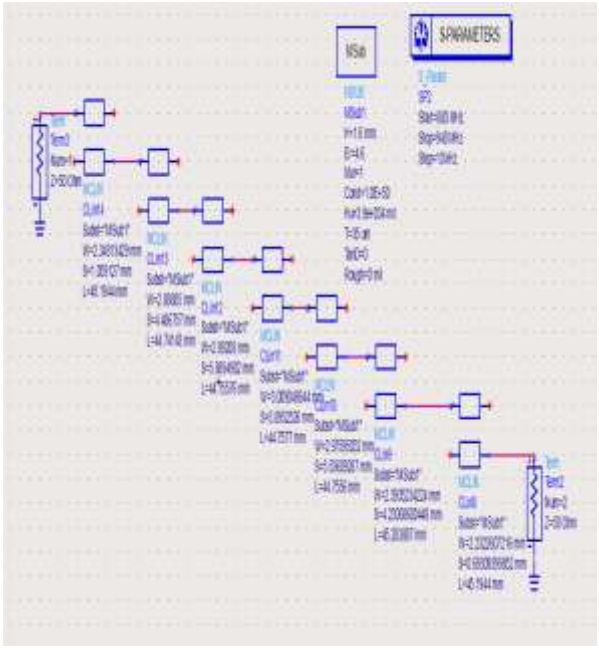

Figure 3: Schematic of uplink band pass filter

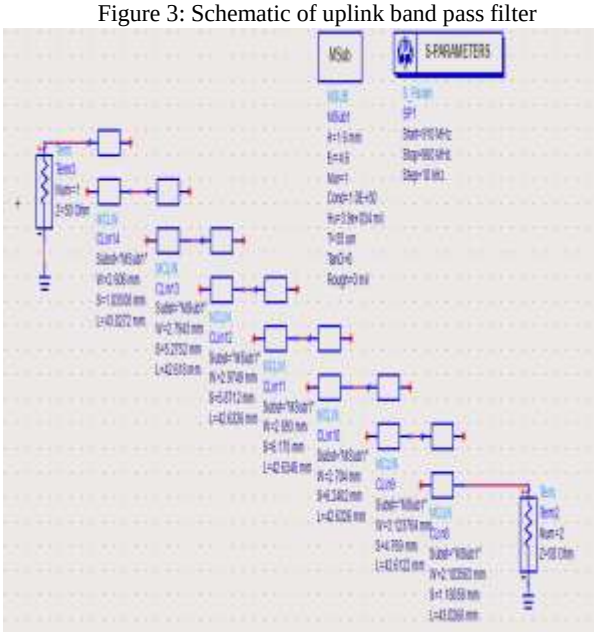

Figure 4: Schematic of downlink band pass filter

The figures 3 and 4 shows the ADS schematics of uplink (890-915MHz) and downlink (935-960MHz) respectively. Both the filters are designed with the unequal impedance condition such that the impedance at the input and output of each filter are 50 ohms and 100 ohms respectively.

To design a duplexer, these two band pass filters are combined in parallel. There are different approaches to combine the BPF's to

make a duplexer. One among that is, by using the power divider. When a power divider is used, there will be a 3 dB loss occurs. So that, here we have used a novel approach of 2 unequal impedance filters combined in parallel without a power divider. As a result, net impedance of parallel combined filters will be 50 ohms at all the 3 ports.So that this acts as a DUPLEXER as shown in figure 5.

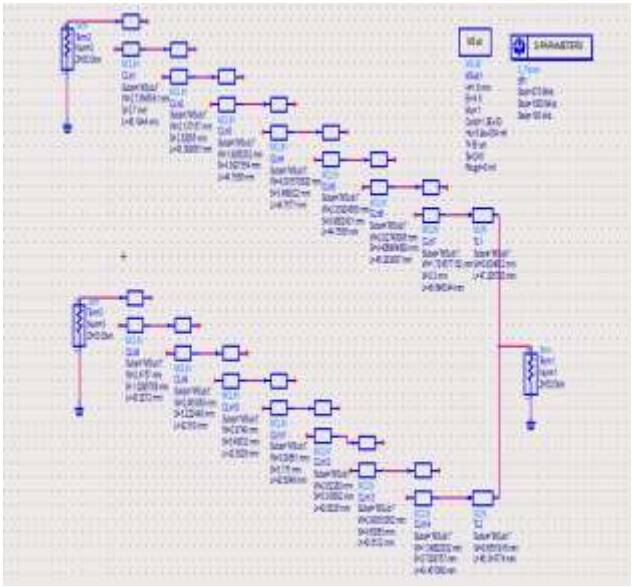

Figure 5: Schematic of Duplexer

3.1 Simulation

Uplink (890-915MHz) response:

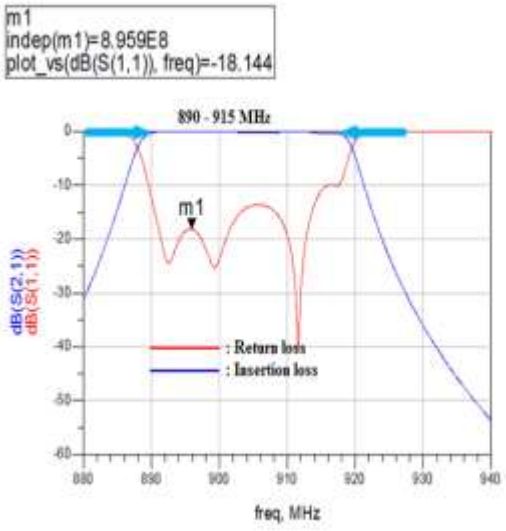

Figure 6: Response of uplink band pass filter

The figure 6 shows the response of uplink band pass filter. The filter passes the signal with the band 890-915MHz, has the ripple less than -1dB and return loss < -10dB.

Downlink (935-960MHz) response:

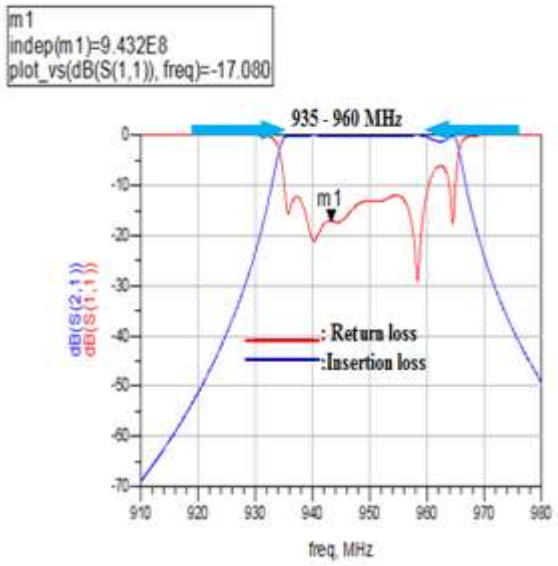

Figure 7: Response of downlink band pass filter

The figure 7 shows the response of downlink band pass filter. The filter passes the signal with the band 935-960MHz, has the ripple less than -1dB and return loss < -10dB.

Duplexer response:

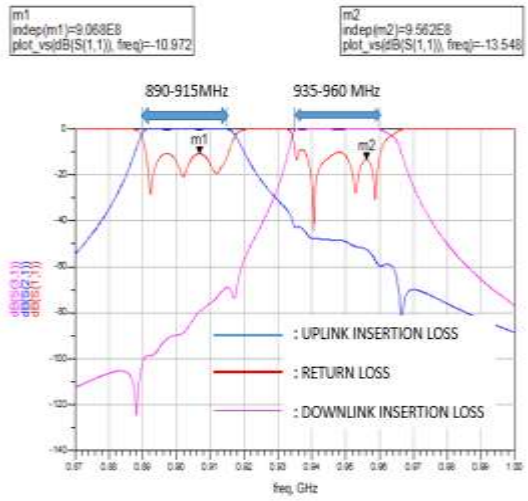

Figure 8: Response of Duplexer

The figure 8 shows the response of duplexer in which the transmitter has the band 890-915MHz and receiver has the band 935-960MHz. High isolation between transmitter and receiver is achieved .The return loss and ripple is obtained as less than -10 dB and -0.5 dB respectively.

The Layout of combined microstrip coupled line band pass filter of un-equal impedance (DUPLEXER) for 890-915 MHz and 935-960 MHz band is shown in the figure 9.

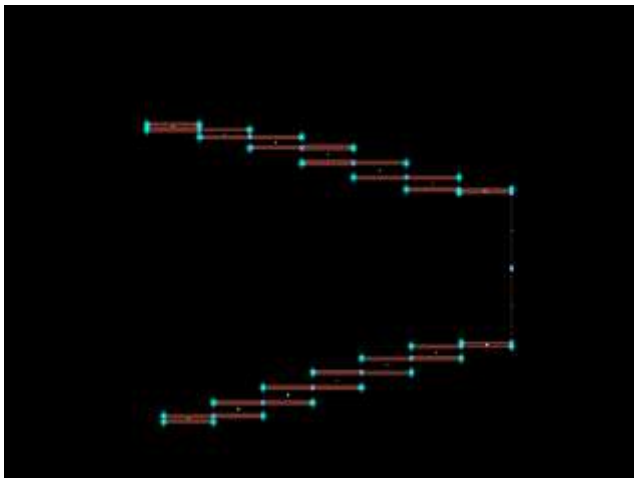

Figure 9: Layout of DUPLEXER

3.2 Fabrication and Tested Results

The designed duplexer is fabricated by using the flame retardant -4 (FR_4) substrate which is readily available in india. Generally, the FR-4 material has 0.3 dB loss per 10 mm.So that the large length designs fabricated using FR-4 materials results in high insertion loss.
The image of the fabricated duplexer is shown below.

Figure 10: Fabricated Duplexer

Tested values of the duplexer are tabulated in the table7and 8.

Table 7: Uplink tested results

Parameter	Lower Frequency (890MHz)	Upper Frequency (915MHz)	Centre frequency (902.6MHz)
S21	-32.26dB	-31.16dB	-23.955dB
S11	-5.34dB	-9.663dB	-12.073dB

Table 8: Downlink tested results

Parameter	Lower Frequency (935MHz)	Upper Frequency (960MHz)	Centre frequency (947.4MHz)
S21	-41.781dB	--30.6dB	--31.621dB
S11	-4..677dB	-8.616dB	-8.354dB

4 CONCLUSION

The designed duplexer is a proof of concept for realizing duplexer function using microstrip technology. In general, duplexers are built using high quality factor (Q) cavity filters. However, to prove the concept, Duplexer is fabricated using FR-4 material which is readily available in INDIA.
The 'Q' achievable in microstrip technique is 100 times less than the cavities. Further FR-4 material is highly lossive for long transmission length like parallel coupled filter, where length is more than 300 mm. Such large lengths result in high insertion loss of the order of 24 to 30dB. Since tangent factor of FR-4 is 100 times less than RT duroid material.

6. FUTURE SCOPE

For the duplexer realization, the isolation required is around 60dB. However recently less than 60 dB is also being used. In this paper, an attempt is made to build the duplexer using microstrip technology at low frequencies in GSM band.
In future the activities carried out in the proposed paper may be taken as basis and improve upon the design by using different materials for realizing high isolation between transmitter and receiver.

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Facile Synthesis and Characterization of Pyrolusite, β-MnO_2, Nano Crystal with Magnetic Studies

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Abstract: MnO_2 nanoparticles have been synthesized by a simple combustion method using $MnSO_4.4H_2O$. The crystalline phase, morphology, optical property and magnetic property of the as prepared nanoparticle were characterized using XRD, FT-IR, FT-Raman, SEM, UV-Vis, PL and VSM respectively. Structural studies by XRD indicate that the synthesized material as tetragonal rutile crystal structure. FT-IR and FT-Raman analysis revealed the stretching vibrations of metal ions in tetrahedral co-ordination confirming the crystal structure. The PL and UV analysis having an emission band at 390 nm, showed a prominent blue peak at 453 nm as well as a green emission lines at 553 nm with band gap energy of 3.2eV. Magnetic measurements indicate that the Néel temperature of the β-MnO_2 structures is 92.5K for H_c = 100 Oe which showed antiferromagnetic behaviour.
Keywords: Nanostructures; Chemical synthesis; X-ray diffraction; Magnetic properties.

1. INTRODUCTION

Nanostructured manganese dioxides and their derivative compounds have special attention owing to their potential application in photonics, catalysis, magnetic fluids and magnetic resonance imaging [1] Manganese dioxide (β-MnO_2, Pyrolusite) is a magnetic transition metal consisting of Mn^{4+} cation and O_2^{2-} anion. The different crystallographic forms are responsible for their electrochemical and magnetic properties [2]. The stable isomorph of MnO_2 is the mineral pyrolusite, β-MnO_2. It is a tetragonal rutile type ($P4_2/mnm$ (136) space group), in which the basic motif is an infinite chain of MnO_6^{8-} octahedra sharing two edges. However, the bridging Mn-O distances within a chain are shorter than the apical Mn-O distance within the basal planes. The structure consists of strings of MnO_6 octahedra and empty channels corresponding to a width of (1×1) octahedron [3]. However there are only few reports on the synthesis of Mn based nanoparticles and relating its magnetic characteristics with particle size [4].

Various approaches have been used to fabricate manganese dioxide, such as self-reacting microemulsion [5], precipitation [6], room-temperature solid reaction [7], sonochemical [8], hydrothermal methods [9] and combustion synthesis [10]. The combustion synthesis method is a powerful approach for synthesizing various forms of manganese oxides and affords advantageous features including the use of mild synthesis conditions such as pH and temperature, and a wide range of precursors that can be used. Henceforth, the controlled synthesis of manganese dioxide nanostructures with favourable surface morphology, phase structure, crystallinity, and high reproducibility remains a considerable challenge [11].

This paper reports the controlled synthesis of MnO_2 nanostructures via combustion without using any physical template and addition of any surfactant. The structural, morphological, vibrational, optical characteristics and field dependent magnetization study of the synthesized material is also presented.

2. EXPERIMENTAL ANALYSIS

2.1 Synthesis of nanopowders

A modified auto igniting solution combustion technique, was used for the synthesis of MnO_2 nanoparticles. Aqueous solution containing ions of Mn was prepared by dissolving stoichiometric amount of high purity $MnSO_4.4H_2O$ in double distilled water in a beaker. Citric acid was added to the solution containing Mn ions. Amount of citric acid was calculated based on total valence of the oxidising and the reducing agents for maximum release of energy during combustion. Oxidant/Fuel ratio of the system was adjusted till the ratio was at unity. The solution containing the precursor mixture was heated using a hot plate in a ventilated fume hood. The solution boils on heating and undergoes dehydration accompanied by foam. The foam then ignites by itself on persistant heating giving voluminous and fluffy blackish grey product on combustion. The combustion product was calcinated at about 750 ^{0}C for 1 hour. The final powder was collected for characterization and characterised as single-phase nanocrystals of MnO_2.

2.2 Characterization.

The as-prepared nanopowders were characterized by XRD (XPERT – PRO) diffractometer using Cu k_α radiation source in the region 20^0–90^0. Fourier transform infrared (FT-IR) spectra were recorded using a Thermo Nicolet, Avatar 370 FT-IR Infrared spectrometer. Fourier transform Raman spectra were recorded using Bruker RFS FT-Raman Spectrometer. SEM picture was recorded using a JEOL/EOJSM – 6390 instrument. The UV-Vis absorption spectra were recorded for the as prepared samples using a Shimadzu UV–Vis 2400 PC spectrophotometer. The PL spectra were recorded using Shimadzu RF 5301PC spectrophotometer in the range 300 – 550nm. VSM measurements were performed using a Quantum Design Vibrating sample magnetometer. The sample was measured between 1KOe – 15KOe at 15K. ZFC and FC measurements

were carried out at 100 Oe and the blocking temperature was determined.

3. RESULTS AND DISCUSSION

Figure 1a shows the XRD pattern of the synthesised material where all the diffraction peaks in the pattern can be indexed to tetragonal β- MnO_2 (JCPDS card No 24-0735) with space group $P4_2/mnm$ (136) in primitive lattice. The diffraction pattern exhibits characteristic peaks having tetragonal phase of β- MnO_2 with lattice constants a = 4.3743 Å and c = 2.8573 Å, which are in good agreement with the reported data (a = 4.3999 Å and c = 2.8739 Å). The broad diffraction peaks maybe due to the nanosize effects on the products. The calculated average crystallite size was 23.05nm. The XRD pattern showed that they are predominantly composed of tetragonal lattice structure.

Figure 1b shows FT-IR spectra of as-prepared β-MnO_2 nanoparticles without any thermal treatment displays three significant absorption bands in the range of 400 – 700 cm^{-1}, where stretching and bending vibrations of $[MnO]_n$ units are showing up and are in good agreement with the published [12]. The vibrational frequency located at 574 cm^{-1} is the characteristic of Mn–O stretching modes in tetrahedral sites. The bands at 486 and 513 cm^{-1} corresponds to the distortion vibration of Mn-O in an octahedra framework [13]. A small band at 3420 cm^{-1} is caused by the stretching vibrations of the OH bond and other weak band at 1631 cm^{-1} due to the bending vibrations of OH molecules. The peak at 1021cm^{-1} is attributed to the OH bending modes to γ-OH. The FT-IR spectrum confirms the crystal structure of the sample and shows the existence of crystallization water in the sample which is necessary for battery activity [14].

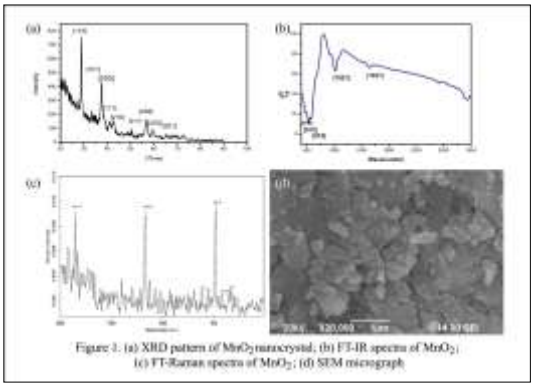

Figure 1. (a) XRD pattern of MnO_2 nanocrystal; (b) FT-IR spectra of MnO_2; (c) FT-Raman spectra of MnO_2; (d) SEM micrograph

The Raman spectrum of β-MnO_2 nanopowder in figure 1c has three bands at 629, 538 and 498 cm^{-1} which agrees well with the previous reports on the β-MnO_2 phase [15]. The Raman band at 629 cm^{-1} is attributed to the B_{2g} mode and involves antisymmetric Mn–O vibrations. The Raman band at 538 cm^{-1} can be assigned to the A_{1g} mode and is indicative of a well-developed rutile-type framework. Here, the E_g mode is assigned to the band at 498 cm^{-1}. The Raman scattering band assignment is consistent with those reported for rutile type compounds [16]. The peaks at 1824 cm^{-1} and 1168 cm^{-1} is ascribed to stretching and bending vibrations of the OH group [17].

SEM micrograph shown in figure 1d reveals the overall appearance of the combustion derived product. The particles are nearly spherical in shape has uniform size and distribution with varying sizes and indicates the agglomeration of nanoparticles [18].

Figure 2a shows the UV- Vis spectra of MnO_2. It is found that most molecules consists of few humps rather than sharp lines which shows that the molecule is absorbing radiation over a band of wavelengths. This is due to an electronic level transition is usually accompanied by a simultaneous change between the numerous vibrational levels. The band gap energy of the as prepared sample is E_g=3.185 eV [19].

PL spectra were measured for the sample in the range of 300-800nm is shown in figure 2b. The sample was excited at 360 nm, two sharp peaks at 380nm and 552nm observed in the emission spectrum. This indicates that MnO_2 nanopowder has a prominent blue emission peak at 380nm as well as a weak green emission at 553nm [20]. The bandgap energy was about 3.45eV.

The figure 2c shows the temperature dependence on magnetization of β-MnO_2 sample in the zero-field cooling (ZFC) and field cooling (FC) procedures. The magnetic moment is enhanced below 100K which can be confirmed by the deviation from the linear behaviour of the M against T curve. MnO_2 has been reported as an antiferromagnetic material with a Neel temperature, T_N of 92K. Both the ZFC and FC loops deviate from antiferromagnetism under magnetic field, showing high remanent magnetism and a strong coercive field. Bulk β-MnO_2 undergoes a transition to AFM state at $T_N \approx 92.5$ K that exhibits both long and short range magnetic order [21]. Figure 2d shows the hysteresis loop of the β-MnO_2 nanoparticle at 15K. The hysteresis loops are not saturated under ±20k Oe due to the contribution of the antiferromagnetic core which is a common phenomenon in nanocrystalline oxide materials. The hysterisis loop shows a maximum

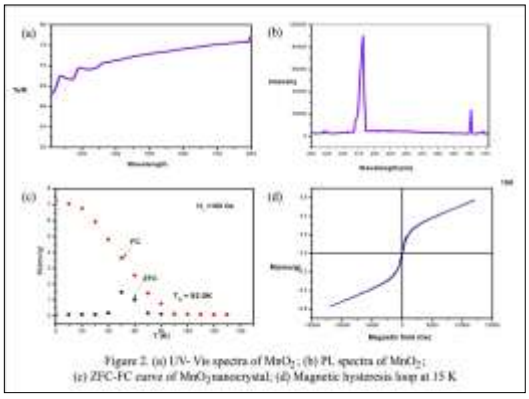

Figure 2. (a) UV- Vis spectra of MnO_2; (b) PL spectra of MnO_2; (c) ZFC-FC curve of MnO_2 nanocrystal; (d) Magnetic hysteresis loop at 15 K

symmetric magnetization, M_{max} at 0.57093 emu/g and remanence value is estimated to be 14.339 emu/g with a remanence ratio of 0.2511.The coercivity H_C of the synthesized nanoparticle was 50.21Oe.

4. CONCLUSION

In this paper, a simple auto igniting combustion method has been successfully used to prepare β-MnO_2 nanoparticles, which are indexed as tetragonal rutile pyrolusite. As synthesized MnO_2 nanoparticle have been identified using XRD analysis which were proven to be single crystal in nature with an average particle size of 23 nm. The structural and functional studies were carried out using FT-IR and FT- Raman techniques. FT-IR

analysis showed a vibrational frequency as the characteristics of Mn-O stretching vibration in the tetrahedral site. The other two characteristic peak corresponds to the distortion vibration of Mn-O in an octahedral framework confirming the rutile β-MnO_2. FT-Raman analysis revealed the characterstic peak with Mn-O vibration of the rutile type compound. The photoluminescence study showed two emission lines in the blue and green region. The UV-Vis analysis showed vibrational level transitions and some electronic states. The band gap obtained from PL and UV-Vis was found to be in the range 3.185eV – 3.45eV. The magnetic measurements revealed a Neel temperature T_N of 92.5K at 100e above which the material behaves as antiferromagnetic. The remanent magnetization and coercivity was found to be 14.339 emu/g and 50.21Oe respectively.

5 ACKNOWLEDGMENTS

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Applications of Nano Technology in textile mills in Madurai, Coimbatore and Mumbai

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Abstract: This paper deals with the applications of nano coated motors in Textile mills present in Indian Smart Cities such as Mumbai, Madurai and Coimbatore. Black soil is present mostly in these cities. They are suitable for the growth of cotton. So, many textile based industries are present in these cities. Many motor manufacturing companies are also present in these cities to design, model and create new innovative machines used for the textile industries. Some special machines are also used for the textile mills. One of the special machines is nano coated induction motor. These types of nano coated motors are called as special machines because they are having nano coated enamel on their windings. Their performance is very good when compared to that of the normal induction motor. The quality of the industries was improved by using the nano coated motors. This paper shows the literature about the applications of nano coated motors in Textile mills in Indian cities.

Keywords: Nano coated motors, Textile mills, Madurai, Coimbatore, and Mumbai

1. INTRODUCTION

The industrial applications of nano electrical drives are numerous. In India, textile mills are numerously present in Mumbai. Hence, Mumbai is also called as Manchester of India. Especially, in Tamil Nadu, textile mills are mostly located in Coimbatore, Erode, Tiruppur and Madurai. So, Coimbatore is called as Manchester of South India. Electrical motors are mostly used for Textile applications for various operations. Hence, motor manufacturing companies are present in Coimbatore. It is also one of the biggest cities in India. It is the third largest city in Tamil Nadu next to Madurai. Madurai, Coimbatore, Erode and Tiruppur cities are announced as Smart cities in India to improve the infrastructure and all the facilities in these cities [1]. To select a particular motor for a given application, knowledge of the following things is very much necessary.

1. The torque speed characteristics of the industrial load are important. This selects the type of motor used to drive the load.

2. The environmental conditions in the industry where the motor is used. This decides the ambient temperature at which the motor operates.

3. Duty cycle of the load and the frequency of starting and braking. The KW rating of the motor is decided by the load cycle. Very frequent starting and braking of the motor alters the KW rating of the motor.

4. Speed control decides the type of motor.

5. Nano Electric motors are employed as drive motors in many applications such as

- Textile mils
- Cranes and hoists
- Steel rolling mills
- Paper mills
- Cement mills
- Machine tool applications
- Sugar mills
- Turbo compressors

- Coal mining
- Centrifugal pumps
- Ball mills

2. PROCESS INVOLVED IN TEXTILE MILLS

The The several process involved in textile mills by the time the finished cloth comes out of a mill from its basic raw material, cotton picked up from the fields are
1. Ginning
2. Blowing
3. Cording
4. Drawing
5. Combing
6. Spinning
7. Looming

The requirements of the motors are different for different process. Drive consideration for textile mills

2.1 Ginning

The process of separating seeds from the picked raw cotton obtained from the field is called as ginning. This might be done in the mills located near the fields or in the industrial location itself [2]. The ginned cotton is transported to the industrial area in the form of bales. Speed range of ginning motors is 250 to 1450 rpm. The load speeds are nearly constant. No speed control is needed. Squirrel cage induction motors are used for this purpose [3]. High efficiency squirrel cage induction motor or nano coated cage motors may be used to improve the quality of ginning.

2.2 Blowing

The ginned cotton in the form of bales is opened up and is cleaned up in a blowing room. Three phase induction motors are used for this purpose. Speed control is not required. Synchronous speed of the motor is 1000 or 1500 rpm. Energy efficient nano coated motors can also be used for this purpose to improve the time of motors used in textile mill.

2.3 Cording

Cleaned cotton is converted into laps by the means of lap machines. 3 phase squirrel cage induction motors are used as lap machines. Cording is the process of converting laps in to slivers.
Requirements of the cording motors

1. The motor used for cording should have a large moment of inertia to accelerate the drum.
2. The motor has to withstand prolonged accelerating periods.
3. The motor should have high starting torque.
4. It should also have low starting current so that the starting losses should be Minimum.
5. The motor must have sufficient thermal capacity to with stand the heat produced by the losses which are occurring under the prolonged acceleration period.

The specifications for cord motors are given in standard IS: 2972, 1964. 3phase totally enclosed far cooled squirrel cage Induction motors with high starting torque are used. The rating of the motor depends upon the type of fabric. For light fabric, 1.1 to 1.5 KW motors are used whereas for heavy fabric, motors with rating of 2.2 to 5.5KW may be used. The operating speed of the motors is in the range of 750 to 1000 rpm. Normally squirrel cage motors having 8/6 poles with the speed range of 750 to 1000 rpm are used. Based on the literature survey carried on the applications of nano fillers used in the electrical motors, nano cage motors (or) nano filler mixed enamel coated 3 phase squirrel cage induction motors with the above mentioned speed range can also be used to improve the performance of the textile mills. Nano coated motors have the following advantage.

1. High efficiency
2. Lower harmonics
3. Higher thermal withstanding capacity
4. Improved power factor
5. Good speed regulation
6. Reduced EMI
7. Improved speed – torque characteristics

Slip ring Induction motors is used with rotor resistance starters to give high starting torque at low starting current. The operation is continuous uninterrupted.

2.4 Drawing

Drawing machines are used to convert the slivers into uniform straight fibre. The motor must be capable of stopping instantaneously, in case of sliver breaking. The drawing machines are self brake motors. The motor is also subjected to inching to place up the broken sliver again. The inching operations are 20 in amount. There is no necessity for a clutch when the brake forms an integral part of the motor. Hence the motor becomes compact.

2.5 Combing

Combing and lap operation take place after the drawing process. The combing process is used to upgrade the fibre. The slivers are converted into laps before combing. Normal squirrel cage motors are used for these operations. Spinning is the next process after combing and lap operations.
Requirements for spurring motors

1. Motor should have smooth acceleration to drive the speed frame.
2. The motor should be capable of working in high ambient temperatures.
3. The motor must be totally enclosed to prevent the cotton fluff getting deposited on the motor surface.
4. The motor must have slow, smooth and uniform acceleration having thermal reserve to avoid yarn breakage.
5. The spinning motor must be capable to do: Drawing, Twisting and Winding operations.
6. Its starting torque must be 150-200% and the peak torque should be 200-250%.
7. The motor must have an acceleration time of 5to10s.
8. The operating speed is 500rpm.
9. The KW rating of the motor is decided by
    a. Ring frame
    b. Number of spindles.
    c. Ring diameter.
    d. Spindle speed.
10. A normal motor is not suited for spinning operations. A two speed pole change motor may be used. These motors are bulky and costly. But, it has several advantages.

• It allows setting of any speed difference by adjusting the pulley diameters and speed ratios.

• The yarn tension can be adjusted independently.

• There is no interruption in production even when one motor fails.

Before the thread is ready for spinning it is thinned down in two or three stages by processing it on a speed frame. The strengthened yarn is wound on bobbins.
For mule spinning a group drive may be employed. The motor should have high starting torque and operating slip. A slip ring motor with rotor resistance control or high torque cage motors may be used. Nano coated motors can also be used.
For operation like winding, warping and sizing, normal motors are used. Low speed motors are used. Reduction in speed using a gearing unit may be done. When the yarn is transferred from the Bobbin, a speed drop of nearly 100rpm is necessary. So, for these operations, high slip motors are used.

2.6 Looming

The weaving of yarn in to cloth is called as looming. It is done in looms. The drives may be either semi group drives or individual drives depending upon the quality of the required cloth. The speed required is 600 to 750 rpm.
Requirements of a loom motor

1. Starting torque must be high.
2. The duty cycle consist of frequent starting stopping. Clutch may be used to avoid frequent starting and stopping of the motor.
3. The operation requires a reciprocating mechanism. A flywheel is used for smoothing and to avoid current and tuque pulsations present during and conversion of rotary motion to linear reciprocating motion.
4. Totally enclosed should be used to avoid burring of the cotton fluff due to motor heating.
5. Loom motors must withstand the effects of humidity.
6. Speed of the motors is in the range of 100 to 750 rpm.

The loom motors are normally 3 phase Induction motors with high starting torque. These motors are totally enclosed and fan cooled. The fan cooling is used to avoid the collection of cotton fluff on the motor surface.
i. The motor deign depends upon the following parameters:

ii. Torque and current pulsations due to reciprocating motion frequent starting and stopping decided the KW rating of the motor.

iii. Fabric decides the size of the motor. For light fabric, motors of rating up to 1.5KW are used while motors of rating 2.2 to 3.7KW are employed for heavy fabric.

7. Brake motor is used to stop the motor in the cage of thread breaks. Special design of textile mill motors are required owing to the location of the motor, running condition and the torque requirements while staring. In textile mills, the motors are located in places where there is a lot of dust. The cotton fluff may be deposited on the motor causing the following on the effects

i. It affects natural cooling of the motor.

ii. It caused the temperature rise of the motor.

iii. It increases the electro static discharge and EMI. To prevent these effects, the following suggestions are made.

- Totally enclosed and fan cooled motors are used.
- Nano coated motors having lower temperature rise and reduced EMI shall be used. It can also improve the quality of the textiles and its performance. It has been proved from various experiments.

3. ALGORITHM FOR THE DESIGN OF NANO MOTORS

1. Manufacture the nano fillers by using ball mill method
2. Augment the particle size by using SEM analysis [4]
3. Mix the nano fillers and the enamel by ultrasonic vibrators
4. Coat and impregnate the windings of different types of motors with the various nano fillers
5. Test the different nano coated motors [5]
6. Compare the results
7. Justify the nano coated motor which is having the superior characteristics when compared to other motors.

4. EXPERIMENTAL WORKS NEEDED FOR THE DESIGN OF NANO MOTORS

1.Ball mill was used to manufacture the nano fillers used in nano coated motors used in Textile industries. Al_2O_3, SiO_2, TiO_2, ZrO_2, ZnO, SiC were used as nano fillers used in nano coated motors [6].
2. SEM was used to augment the particle size of fillers before and after Ball milling process.
3. Ultra sonic vibration process was used to mix the enamel and nano fillers [7]
4. Nano filler mixed enamel was used as the coating and impregnation for the windings of the motor [8].
5. Different types of testing were conducted to determine the performance of the nano coated motor. They were
a. Direct loading [9]
b. Temperature test
c. Harmonics Measurement
d. EMI Measurement [10]
6. The readings should be taken and compared between the different types of nano coated motors used in Textile mills.

5. ADVANTAGES OF NANO COATED MOTORS

The following are the advantages of nano coated motors:

1. Higher efficiency [11]
2. Wide operating temperature range
3. Reduced Harmonics
4. Reduced EMI
5. Increased life time
6. Reduced losses
7. Improved Cooling
8. Reduced noise
9. Lesser amount of powder to produce large output
10. The quality of the industries will be increased by these motors.

6. LIMITATIONS OF NANO COATED MOTORS

The most important drawbacks of nano coated motors are:

1. Powder manufacturing is time consuming
2. Expensive equipments were employed for synthesis and characterization of nano fillers

7. CONCLUSIONS

In the upcoming future, the use of nano coated motor in textile mills can bring the following considerable changes when compared to the conventional motors used in textile mills.

1. Improvement of accuracy and quality of the output
2. Enhancement of the life time of the machines
3. Reduction of the maintenance cost
4. Improvement of thermal withstanding capacity
5. Improved slip, power factor, speed torque characteristics and efficiency. So nano coated motors can be used in the machine tools.
6. Reduction of vibrations and noise.

8. ACKNOWLEDGEMENT

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Applications of Nano Electrical Machines used in Ball mills for Nano and Pyro Technology Based Industries in Sivakasi

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Abstract – Nano fillers play a vital role in increasing the performance of different types of motors. In recent days, nano technology shows a tremendous improvement in the manufacture of high performance electronic devices and circuits, electrical apparatuses and equipment. In this paper, a wide literature survey was done on the filled of nano dielectrics and nano coated motors. Comparison of different nano fillers coated motors was done to show which motor was having superior performance characteristics compared to other motors. Based on the literature survey on the previous research works carried out in the field of applications of nano technology in the coating of nano fillers to the enamel used in the motors. Ball mills are using three phase induction motors for the mechanical operations. Ball mills are used to manufacture the nano powders used for both the nano technology and pyro technology. Industries should be well equipped with safety devices to avoid the fire accidents. Industries should follow the safety norms to avoid the fire accidents. Pyro technology based research centre was located in Sivakasi to understand and motivate the engineers, people to make an interest towards Pyro industries and to train the persons about the safety measures while working with the nano pyro powders used in the nano pyro industries. The powders used here are always in the nano range. But, the people were unaware of this technique. So, this paper will create some knowledge to the people who are working in nano pyro based industries present in Sivakasi. Sivakasi was an industrial city located in South India having more than 15000 nano pyro based industries. So, this paper will educate the engineers, managers and the persons who are all associated with these industries.

Keywords: Motor, nano fillers, SEM, Ball mill, Efficiency, Harmonics, EMI

1. INTRODUCTION

The Nano electrical machine design involves the application of nano science and nano technology to produce

1. Cost effective
2. Durable
3. High Quality and
4. High Efficiency machines

The nano electrical machines are designed as per standard specifications. The requirements like low cost and high quality are conflicting in nature and so a compromise should be done between them [1]. The nano electrical machines are classified into

1. Static and
2. Dynamic Machines

Nano transformer is a static machine whereas nano motors and generator are dynamic machines. Nano transformer converts electrical energy from one level to another level without changing frequency. It is a static electromagnetic device. It consists of two or more windings which link with a common magnetic field. An iron core serves as a path for magnetic flux. The basic constructional elements of a nano transformer are

1. Windings
2. Core
3. Tank
4. Cooling tubes and
5. Insulation

It has two windings. One is called as high voltage winding and another is called as low voltage winding. One of the winding is connected to supply and it is called as primary. Another winding is connected to load and it is called secondary. The different types of transformer are

1. Core type
2. Shell type
3. Berry type

In core type, the windings surrounded the core whereas in shell type, the core surrounds the windings. The core and winding assembly is housed in the tank. Nano filler mixed is used for insulation. Cooling tubes are provided around the tank surface in order to increase the effective cooling surface [2]. Nano rotating machines convert electrical energy to mechanical energy or vice-versa. The conversion takes place through magnetic field. The required magnetic field is produced by an electromagnet which requires a core and winding. The basic principle of operation is governed by faradays law of electromagnetic induction. Every rotating machines has the following quantities

1. Field flux
2. Armature flux
3. Voltage
4. Current
5. Mechanical force

In generator, the armature is rotated by a mechanical force inside a magnetic field or the magnetic field is rotated by keeping armature stationary. By faradays law of electromagnetic induction an emf is induced in the armature. When the generator is loaded, the armature current flows which produces armature magnetic field. Hence, in a generator, by the presence of a magnetic field and mechanical force, armature magnetic field is produced.

The mechanical force developed by the motor is due to the reaction of two magnetic fields. A current carrying conductor has a magnetic field around it. When it is placed in armature magnetic field, it experiences a mechanical force due to the reaction of two magnetic fields. Hence in a motor by the presence of two magnetic fields, a mechanical force is developed.

Any rotating machine requires two magnetic fields. One is stationary and another one is revolving. Hence a rotating machine will have a stationary and rotating electromagnet, each consisting of a core and winding. The stationary electromagnet is called stator and the rotating electromagnet is called is called rotor.

The basic constructional elements of rotating machine are stator and rotor. In DC machines, the stator consists of filed core and windings. The rotor consists of armature core and windings. The rotor consists of filed core and windings. The basic constructional elements of DC machines are

1. Stator
i. Yoke
ii. Field pole
iii. Pole shoe
iv. Field winding
v. Inter pole

2. Rotor
i. Armature core
ii. Armature winding
iii. Commutator

3. Brush and Brush holder

CNT based materials can be used for brushes.

4. Insulation

Enamel (or) varnish is used to coat windings to provide insulation between the windings. Enamelled copper wires are used as conductors. Hence, enamel is used for two purposes

1. Coating of the conductors
2. Coating of the windings

In nano coated motors, the enamel mixed with nano fillers is used for the coating of the windings. The basic constructional elements of squirrel cage induction motors are

Stator
- i. Frame
- ii. Stator core
- iii. Stator winding

Rotor
- i. Rotor core
- ii. Rotor bars
- iii. End windings

2. ALGORITHM FOR THE DESIGN OF NANO MOTORS

1. Manufacture the nano fillers by using ball mill method [3]
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8. Reduced noise
9. Lesser amount of powder to produce large output
10. The quality of the industries will be increased by these motors.

5. LIMITATIONS OF NANO COATED MOTORS

The most important drawbacks of nano coated motors are:

1. Powder manufacturing is time consuming
2. Expensive equipments were employed for synthesis and characterization of nano fillers

6. CONCLUSIONS

This paper shows the wide knowledge required for the design of nano coated motors used in Nano Pyro Industries located in the South Indian city called as Sivakasi. The following tests should be conducted for the design and checking of the nano coated motors:

1. SEM Results
2. Direct loading

Load test was used to find the performance of the motor in terms of efficiency

3. Temperature test
4. Harmonics Measurement
5. EMI Measurement

7. ACKNOWLEDGEMENT

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Enhancing the Security of Vehicles and the Work of the DVLA Using GSM/SMS Technologies

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Abstract: Vehicle theft is seen as occurring almost on daily basis. From the survey carried out for this research, over 90 percent of respondents testified to its existence. This research took a closer look at collaborations of Driver and Vehicle Licensing Authority and the Security Services in combating this crime. It also sought the readiness of vehicle owners, DVLA and Ghana Police Service to embrace technology integration.
A critical look at vehicle security in terms of its theft related problems, the integration of GSM/SMS technology into the Driver and Vehicle Licensing Authority Registration Database, making it easily accessible by the Security Services like the Ghana Police Service for quick and easy verification of driver or vehicle license status as well as the genuineness in relation to the ownership, in the fight against vehicle theft is very vital. Security personnel can send an SMS to the proposed system and instantly get reply containing significant particulars of the Vehicle and the owner.

Keywords: Vehicle Security; Verification; Database; DVLA; GSM; License; SMS Technology; Security service

1. INTRODUCTION

Vehicle theft and crime are fast becoming a canker in Ghana. The very nature of the crime and the relatively large sums of money involved in investing in vehicles makes it worse than petty theft. Car snatchers are constantly finding newer ways of evading car owners and the law. Vehicle crime is not limited to car snatching alone; more common incidents include driving without license, driving a car using the wrong type of, such as using a privately registered vehicle for commercial purposes or driving a heavy duty vehicle where a high level license is required.

From the previous readings and knowledge, the use of technology to fight vehicle theft and crime remains a largely untapped area especially in Ghana. This study looked at ways of using technology to combat car crime and theft. Further make recommendations have also been made on a specific but appropriate technology.

A "Ghana 2011 OSAC Crime and Safety Report" (2011) outlined the overall crime and safety situation in Ghana. In this report, the US Department of State's Bureau of Diplomatic Security has rated Ghana as a high crime threat post. It is indicated that vehicle crime in Ghana is a major concern. Using Nigeria as a case study, Bassey et al (2010) found out that a large percentage of stolen vehicles from Nigeria find their ways into neighboring countries including Ghana and vice versa. All these stolen vehicles with foreign registration numbers find their ways through the borders into Ghana or Nigeria for re-registration at the DVLA. The situation is not different in Ghana; vehicles which are stolen sometimes are carried outside the country for resale or re-registered at the DVLA of Ghana. According to a (Customs and Excise Preventive Service (CEPS) post by The Spectator (2008), when a vehicle is detected stolen at the ports and the owner is identified to be resident in a foreign country, the owner is made to bear the cost of returning the vehicle. However stolen vehicles whose owners could not be traced are confiscated and given to the state after which they disposed off accordingly. The information is however silent on what happens to those who stole the vehicles?

The Motto Transport and Traffic Directorate (MTTD) of the Ghana Police Service (GPS) is a governmental institution whose main objective among others is "to prevent and detect motor crimes and offences" as appeared in (ghanapolice.info, n.d.).

Vehicle theft is a crime which cannot be solely handled by the security agencies especially the Ghana Police Service (GPS), but through collaborative effort with individuals and stakeholders. It is in the light of this that the GPS in 1958 became a member of Interpol. And by 1976 Ghana became the first African country to host the Interpol General Assembly (Interpol.int, n.d.). In addition, the GPS has been actively cooperating with police services within and outside the sub-region in the fight against trans-national crimes such as drug trafficking, human trafficking, terrorism, internet fraud, stolen vehicles, trafficking in small arms and light weapons and money laundering (ghanapolice.info, n.d.). Prioritizing vehicle crime, The Interpol General Secretariat has developed a system called an Automated Search Facility-Stolen Motor Vehicle (ASF-SMV) database to support police in member countries in the fight against international vehicle theft and trafficking. According to Interpol (2013), close to 152 countries use this database and in 2010 more than 34,000 motor vehicles were reported to have been discovered worldwide through the ASF-SMV database. Also, statistics indicate that there has been a steady increase in the use of INTERPOL SMV database by member countries both in terms of number of records contributed and the number of searches carried out (Interpol.int, n.d.).

In the local front, the Ghana Police Service relies solely on the DVLA database for their information on registered licenses. The

DVLA has a number of mandates which include maintaining registers containing particulars of licensed motor vehicles, driving instructors, driving schools and drivers of motor vehicles. Thus, the DVLA is constantly striving to live up to expectation. Currently, the DVLA is making efforts to include a feature on their website for the checking of license status online (dvlaghana.gov.gh, n.d.). Even though very difficult, efforts are being made from time to time by CEPS to bring to book all vehicles which are not duly registered. With all these measures in place, this research revealed, there still exists massive evasion of all kinds of licenses at the DVLA.

Since the first indicator of validation of a registered vehicles is its number plate, a gaping opportunity for car snatchers is created in a situation where a fake number plate go undetected. It is therefore convincing that, there are a large number of vehicles which are using fake number plates. Checking the veracity of a vehicle number is also a very slow system for the law enforcement agencies that have no means of instantly checking vehicle details. Similarly, the veracity of driver licenses is difficult to ascertain since there is no readily available database.

The availability of a centralized database easily accessible to the police even on mobile devices can help to reduce and fight crime in this area. This is the main motivation for this research.

2. OBJECTIVES OF THE RESEARCH

The research proposes a model GSM/SMS (Global System for Mobile communication/Short Message Service) technology that can access the DVLA register to boost the work of security services in their zeal to combat vehicle related crime. The specific objectives;

- Explore the possibility and sustainability of integrating SMS technology with DVLA database
- To make the DVLA register easily accessible by security personnel
- To recommend a suitable technology for implementing the recommendations of the research

3. EXISTING SYSTEM OVERVIEW

Traditionally, preventing car theft is by the use of immobilizer keys, which was first introduced by Honda in the year 1997. It subsequently became mandatory in all new cars sold, the earliest was in Germany in January 1 1998 and the latest was in Canada in the year 2007. Early models of immobilizer keys made use of a static code in the ignition key which can be recognized by an RFID (Radio Frequency Identification) loop around the lock barrel and compared with that of the vehicle's Engine Control Unit (ECU) for a match. When the code cannot be recognized, the ECU will stop fuel from flowing and ignition cannot take place (Tech-Spot, 2007). But according to Copes et al (2006) as cited in Tahir and Tahir (2008), there has been an evident increase in the number of vehicles being stolen due to key theft. Vehicle keys have been taken away from their owners by burglary, robbery or without their consent, thus making the use of immobilizer keys as a security measure less effective, because after getting hold of the key an intruder will be able to drive away the vehicle without any obstruction.

Cahoon (2006) drew the attention to the use of a portable memory device in place of a key. According to a US Patent 7006914 as cited in Tahir and Tahir (2008) a portable memory device can be used in place of a key for the following purpose: "A portable memory device used in substitution of an automobile key and interfaced with an automobile onboard computer and ignition system. The portable memory device contains data that, when read by the onboard computer, enables the ignition system."

It can be noted that the portable memory device introduced by Cahoon (2006) does not completely remove the use of a key, but that it is an alternative to the use of a key. To this end the problems associated with the use of the key do also apply to that of the portable memory as well.

In addition, Song (1993) in his U.S Patent Number 5208756 came out with a system in this same direction. In his system, a small hidden device placed in the vehicle is activated through Dual Tone Multi Frequency (DTMF) signals which are transmitted from any telephone station. When the activation is done, the device then determines the power at which normally transmitted control channels are received from the several base stations of the network. Based upon these determinations, the location of the vehicle in respect of the separate distances from each of the base stations is then determined based on calculations, using triangulation. The information about the location of the vehicle is then transmitted through a voice synthesizer back to the telephone station from which the activation signal is received. The location information is also transmitted digitally to a central station where the position of the vehicle is displayed on a computer screen along with a graphical representation of a map of the region served by the cellular telephone network.

More on the application of cellular network, Sheffer and Thompson (1993) designed a system which makes it possible for an emergency message transmission to a remote monitoring station in the event a theft sensor is activated on the vehicle. The monitoring system then detects the cell site identification codes from adjacent cellular transmitter and provides a message including the vehicle identification, cell site identification and signal RSSI (Received Signal Strength Indication). Then based on this information received, a centralized stationed computer then determines the location of the stolen vehicle.

Taking a critical look at the inventions of Sheffer and Thompson (1993) as well as that of Song (1993), it could be noted that, there is a great reliance on a centralized computer for the determination of the location of the stolen vehicle. This ideally will work perfectly if the stolen vehicle is immobile and at the same time not out of coverage area of the cellular network. Because, at the time the location of the vehicle is being tracked, if the arrest team leaves the centralized computer towards where the stolen vehicle is located, and it moves away from such location, you could imagine how difficult it would be to continuously re-communicating this information from the centralized computer to the team.

Following the same suit, Sheffer (1990, 1991), in his U.S Patent Numbers 5055851 and 4891650 also made use of cellular network. In both systems, the stolen vehicle sends an identification code and RSSI level to the closest cell site. The active cell site which receives the information reports the theft to

the cellular Mobile Telephone Switching Office (MTSO) and the MTSO transmits the information to an alarm station which identifies the vehicle and the cell site as well.

The problem associated with the above-mentioned systems are that in most instances, cell sites located in metropolitan areas made use of low-powered 120º directional antennas to cover a densely populated and developed area which may have a large number of buildings, highways, parking lots, garages and other facilities which make it possible for the thief to hide the vehicle. Thus, although systems may be able to locate the general location of the vehicle with respect to a cell site antenna, the probability of locating the vehicle in the shortest possible time is very small and mostly based on luck.

Furthermore, cell sites located in urban areas cover very large areas with high-powered, Omni-directional antennas, this makes finding the location even more difficult since the antennas are Omni-directional as opposed to being sectioned. In either case, buildings, underground parking lots, mountains and other obstacles may cause the towers to report false RSSI (Received Signal Strength Identification) readings to the MTSO (Mobile Telephone Switching Service).

Another problem that can be seen is the reluctance of the cellular service providers to allow their cellular infrastructure system to be integrated with a foreign application due to security reasons. Since this will be exposing their infrastructure software to externals who might leak information to their competitors.

A need therefore exists for providing a vehicle tracking method and system using the existing cellular network infrastructure which can overcome the problems associated with the prior art. Thus, Savoie and Boulay (1999) designed a system with the necessary incorporations. In this system, a cellular transceiver is installed in vehicles. This transceiver continuously operates but on a standby mode which makes it easily accessible to the cellular security provider, and when tracking of a vehicle is initiated, then the transceiver is turned to active mode. The location of the stolen vehicle is determined by paging the cellular transceiver located in the stolen vehicle. A tracking vehicle making use of radio direction finder then receives the information and obtains an accurate bearing on the location of the stolen vehicle. Alternatively, the tracking vehicle with the radio direction finder can determine the location with respect to one or more cell sites using global positioning system receiver. The tracking vehicle can then quickly move to the identified area.

Taking a critical look at the invention of Savoie and Boulay (1999), there is a great job done by having to dedicate a tracking vehicle which will move to the location of the stolen vehicle. But what then happens when the number of stolen vehicles at one particular time interval exceeds one, it then becomes very difficult to implement.

Again the problem of exact position of the vehicle is not still removed, since the tracking of the vehicle is still based on the availability of signal from the network provider. But when the vehicle is probably driven to an underground tunnel or apartment for dismantling, it thus becomes virtually impossible to locate such a stolen vehicle.

Taking advantage of GSM technology and with the proliferation of cellular phones Drori et al (1992) being so innovative took a right direction to integrate vehicle security with that of cellular phones. In his patent on “system for integrating a cellular telephone with a vehicle security system” they described hardware and software for integrating the controller to the vehicle as well as that of the vehicle security to the controller. This system has a feature that allows the vehicle owner to telephone it when he discovers that it has been stolen, thus stopping the engine of the car. Then at certain intervals the coordinates identifying the vehicle location are repeatedly transmitted over the communication system. Making it conveniently possible, to trace for the location of the missing car, especially, at areas with good landmark or street demarcations.

In the situation of Ghana with no effective street names and addresses, the implementation of such a system will not be very effective. Moreover, a thief could easily disable the cellular telephone from the vehicle which will automatically make the security system dump.

Still taking GSM to a different angle, Ruchita et al (2008) came out innovatively. In their research on GSM based car security system, it was made possible for the security system to be alert, such that, the moment the system senses that the car is being stolen, a SMS is immediately sent to the owner’s mobile through a GSM modem. At the same time an alert in the form of an alarm blows drawing the attention of nearby people. In this security system it is made possible to sense five parameters for security which include; Vibration sensing, Obstacle sensing, Revolution sensing, Micro switches (where door1 and door2 open) and Battery sensing. When the system detects anything in at least one of the five sensing points it generate sound as well as send SMS through a GSM modem to the owner’s phone. Their research made use of a low cost and highly reliable Microcontroller AT89S52 in their system. There is also the incorporation of a buzzer in the system which is responsible for the sound when one of the five parameters is sensed. They came to a conclusion that, this type of system is more advantageous than the simple car security system, since it gives real time information as well as gives alert to nearby people.
While acknowledging the great work of this research, the following observations could be made: The car cannot be safe if the GSM modem is not in working condition or the network for that particular operator is down.

With a lot of shortfalls which seem to have arisen from the preceding inventions, Tahir and Tahir (2008) saw the need for a multifactor authentication mechanism that can easily be embedded into vehicles and which will prevent all sorts of car theft. Their proposed scheme called BioFIM (Biometric Flash Identification Module) was designed and could recognize its owner by the use of features like a combination of fingerprints, portable flash drive and digital certificates. Because of the use of features which are personal to the owner, an overall conclusion was drawn from their research that, this scheme was more resilient against car theft than the existing schemes in terms of security and user convenience.

But on the contrary it could be realized that just as the immobilizer keys, it is only for a matter of time. Criminals will be able to make discoveries into all possibilities of disarming such a security system since in the first place it is embedded into the vehicle itself.

Still on finding solutions to vehicle security, Zhang et al (2005) gave it a little twist. In their research conducted in the area of vehicle location tracking and monitoring based on GPRS (General Package Radio Services) technology in 2005, Zhang et al (2005) analyzed the shortcomings in traditional vehicle communication systems, their paper presented an intelligent vehicle monitoring system and described the design procedure of hardware and software in details. They compared the two data transmission protocols in GPRS network; their paper then gave a consideration to (User Datagram Protocol) UDP/IP as the vehicle communication protocol.

In a similar fashion, Tan (2010) proposed a Vehicle Monitoring System that would be a high technology system including a sophisticated integration of Geographical Information System (GIS), Global Positioning System (GPS) and other modern communications technologies. Tan's Vehicle Monitoring System would monitor vehicles' accurate positioning, with the aid of communication technology and digital maps. The paper introduced the composition, the operating principle, the overall functions and system structure of vehicle monitoring system.

Referring to both Tan and Zhang et al, there is a reliance on GPRS for the transmission of data. There is a challenge in this direction considering the frequency of power cuts, which is the main source of energy for our telecommunication radios.

4. SYSTEM OVERVIEW

The purpose of the system is to provide easy, convenient and on the spot verification of vehicle license and its related information to the security personnel.

In this system a Security Person can send SMS to the SMS gateway server. The server then converts this into an HTTP request and sends to the web application and then receives an HTTP response, and subsequently converts it back to an SMS message and then relays it back to the Security Personnel. The overview can be illustrated in figure 1.

Figure 1. System Overview

4.1 CONCEPTUAL FRAMEWORK OF THE SYSTEM

The system is a web application that is built in accordance with the Web Application Framework (WAF), using the Model-View-Controller architectural pattern. This model allows for division of any software application into three interconnected parts, so as to separate internal information representation from how it is presented in an acceptable way to the user. Thus, the system consists of three main components, which are controlled and hosted by the web application server, the SMS gateway server and the Database server.

The web application is at the core of the application, carrying out all processing that take place in the system. The web application was built using HTML and CSS for the user interface design and PHP and Java script which carried out all the necessary queries including the request and response queries. The application database was built and managed by MYSQL. This database is interfaced with the web application and maintains all the data from the web user. Taking into consideration how robust the system needs to be, the web application was as well interfaced with an OzekiMessageServer_6.4.1.0. Ozeki Message Server is a powerful and flexible SMS Gateway application which enabled sending and receiving of the SMS messages to and from the mobile user. The interfacing of the web application to that of the OzekiMessageServer was done using the OzekiNG-SMS-Gateway_4.3.3 which gave it the full ability to communicate with the GSM Modem or Phone that will be connected to it.

The Web User will be a staff of the DVLA who will have login credentials to the system. He will be responsible for making new registration entries as well as making updates to the database. He will interact with the system using the web interface. Entries made are saved into the Application database and can be viewed as well.

The SMS User represents the personnel from the security services like the Ghana Police. They will be provided with the mobile number of the application's GSM modem/phone. This user can send an SMS to the mobile number of the application using any mobile phone, the registration number, the chassis number or a combination of the two that needs to be instantly verified for its ownership. This text message is received by the SMS gateway server and relayed to the web application. The web application therefore stores this into the tbrequest table in the application database and at the same time searches in the database for related information to the text received. It therefore stores this found information into the tbresponse table in the database as well as retrieves it and returns it to the SMS gateway server. The SMS gateway server then forwards this message back to the SMS user.

The architectural design of the system illustrated in Figure 2 and Figure 3 represents the database entity relationship diagram

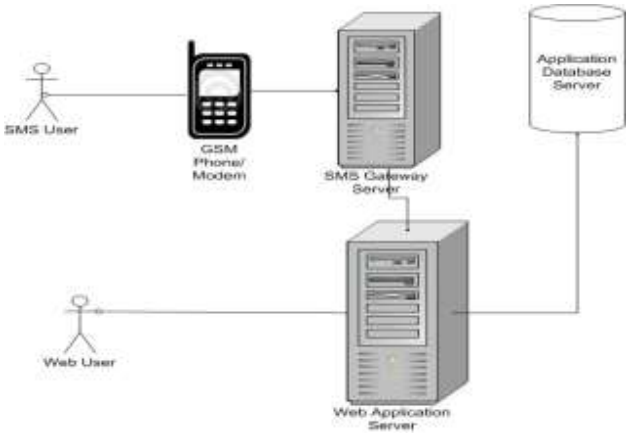

Figure 2. Architecture of the System

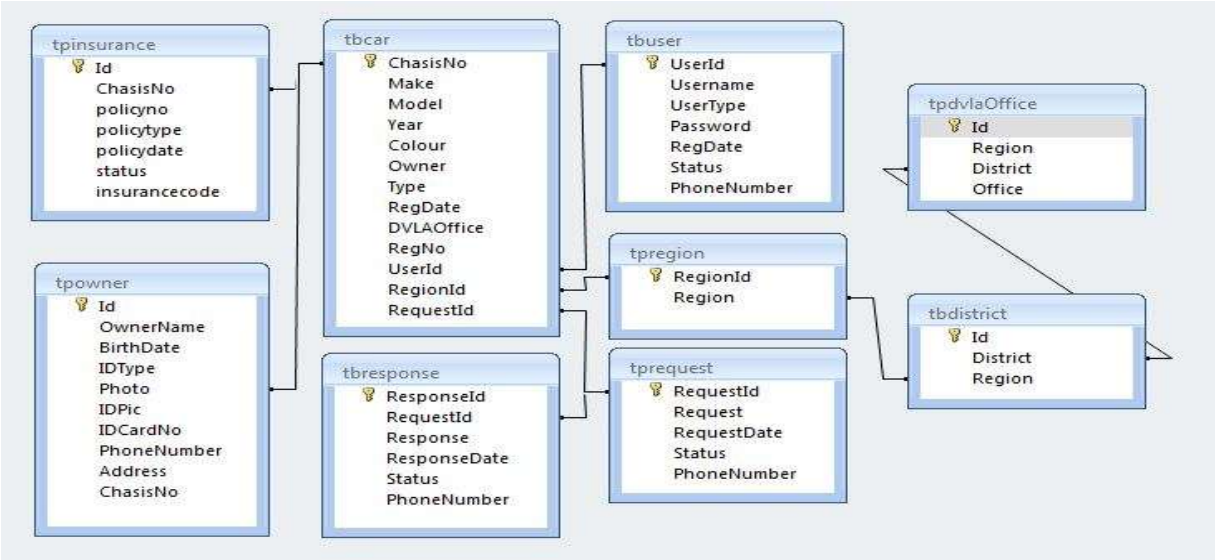

Figure 3. The Entity Relationship Diagram

5. RESULTS AND DISCUSSIONS

The results were obtained after interviews and questionnaires were gathered from a population size of 152 (individuals with the distribution of 7 coming from the DVLA staff which covered all management and representation from all sections. 45 from officials of the MTTD of the Ghana Police Service, both private and commercial vehicle owners being 50, and both private and commercial vehicle drivers taking a population size of 50. The sample distribution was decided by the researcher and largely influenced by the various respective technical people from DVLA, and MTTD of the Ghana police Service and from leaders of commercial drivers association all within the Metropolis of Tamale.

5.1 Vehicle theft

This was a core issue which was critically interrogated, and thus run throughout all the three categories of questionnaires. A large number of respondents attested to the knowledge of the existence of vehicle theft. When the question of "how rampant is the issue of vehicle theft?" was posed, with a total of 139 respondents, only 12 representing 8.6 percent denied the existence of the menace while 127 respondents representing 91.4 percent agreed to the existence of vehicle theft, but had different variation to its frequency as shown in Table 1.

Table 1. Vehicle Theft Occurrence

Occurrence	Frequency	Percent
Daily	40	28.8
Weekly	9	6.5
Occasionally	78	56.1
non-existent	12	8.6
Total	**139**	**100.0**

It was realized that with the modes of vehicle theft, vehicle snatching came on top with a frequency of 47 representing 49.5

percent of a total of 95 respondents. Other modes according to the survey and their frequency of occurrence can as well be seen in the bar chart on Figure 4. This was gathered from both drivers and vehicle owners.

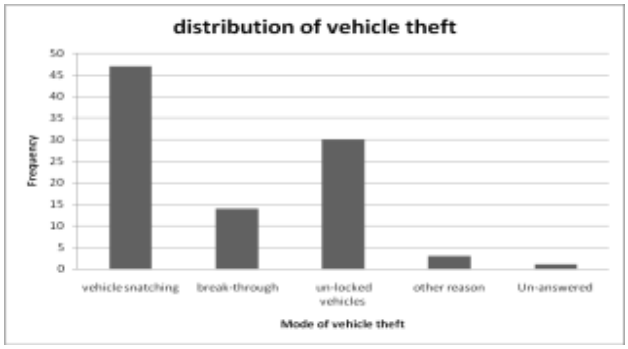

Figure 4. Modes of vehicle theft

5.2 DVLA and GPS Collaboration

It became clear from the survey that the GPS and the DVLA do collaborate, but when asked whether the DVLA had given access to their database to the GPS and other security services. Out of 6 respondents 5 indicated no with the remaining 1 declining to answer as seen in Table 2.

Table 2. Access to DVLA register by Ghana Police Service

Response	Frequency	Percent
No	5	83.3
Unanswered	1	16.7
Total	**6**	**100.0**

But when both the DVLA and the GPS were confronted to find out if there is any law against making the DVLA register accessible to the GPS, an overwhelming majority denied the existence of such a law. With a total of 44 respondents, 56.8 percent said there is no such law. The next highest percentage of about 25 of the respondents was not quite sure of such a law against the access as seen in Figure 5.

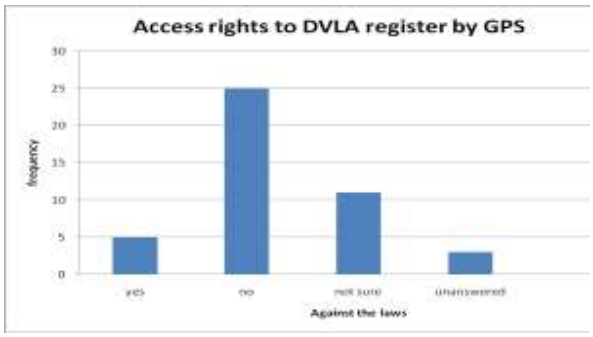

Figure 5. Legal Implications to Gain Access to DVLA Register by GPS

Taking lessons from the above results, one cannot deny the fact that vehicle security does need a great attention. It is therefore very relevant, prudent and timely to have undertaken this research to address the situation of vehicle security. This will give them a good collaboration to help combat vehicle theft

5.3 Technology Integration and Instant Verification

From the research it is noted that 82.1 percent of 95 respondents constituting vehicle owners and drivers agree to be charged a fee for the integration of the technology as in figure

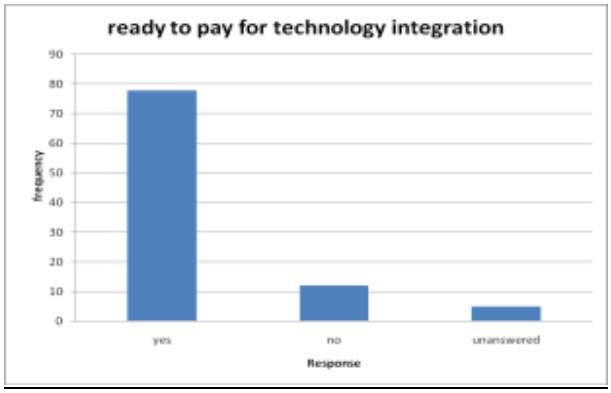

Figure 6. vehicle owners readyness to pay for technology

Still probing further, the researcher sought to know if even vehicle verification will be embraced by all. This was a welcome idea; a total of 125 respondents out of 139 representing 89.9 percent endorsed the idea, this is shown in Table 3. But as to how this should be done, an overwhelming majority indicated it should be by the use of a technology.

Table 3. The Necessity of Instant License Verification

Response	Frequency	Percent
Yes	125	89.9
No	14	10.1
Total	**139**	**100.0**

When they were further confronted with, which technology will be appropriate and convenient? There were interesting responses. Bio-metric verification came on top with a percentage of 68.3 of a total of 139 respondents. This left SMS verification behind with a percentage of 27.3 of the respondents. Insignificantly was the response for the use of phone call or the internet for verification as seen in Figure 7.

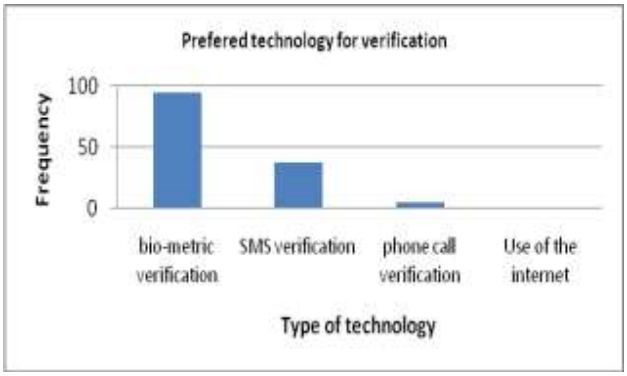

Figure 7. Technology of choice for license verification

Taking a critical look at the responses in Figure 7 and the possible influence on arriving at the bio-metric verification, it is evident that GSM/SMS technology has not been exploited to its maximum. Those respondents probably did not know what SMS referred or have not yet been exposed to the applications of SMS.

5.4 System Implementation and Output

When the system was implemented an SMS message like "hh22222" was sent to the system, this saw a reply as shown in Figure 8. While an SMS message like "Hi" on the other hand had a reply as in Figure 9.

Figure 8. Sample reply with existing details

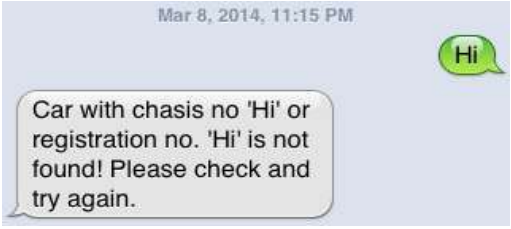

Figure 9. Sample reply for non-existence

6. CONCLUSION AND FUTURE WORK

It became clear from the results that the security of vehicle is of great concern. Thus, instant verification of licenses by the use of a technology was a necessity. The recommended technology for carrying out this verification is the bio-metric with SMS placing second.

There should be in the future a need to design an algorithm which will enable a police man to send the chassis number of a reported stolen vehicle to the database to alert all stakeholders of the said case.

There should be an investigation into the possibilities of integrating bio-metric verification into the current system and a possible implementation of the said technology.

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Detection of PUE Attack by SPARS Model using WSPRT

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Abstract: Cognitive radio is a system which improves the utilization of the spectrum by sensing the white spaces in its vicinity. This sensed information will be utilized by the Secondary User (SU) to transmit the data. But some of the malicious users attacks the system by generating the signal same as that of the primary transmitter. The attack caused by generating the signal same as that of the primary transmitter is called as Primary User Emulation Attack (PUEA). In this paper the Signal Activity Pattern Acquisition and Reconstruction System (SPARS) is used to detect the attack. But this system suffers from low True Positive Rate. To increase the True positive rate or sensitivity a new technique was proposed called as Weighted Sequential Probability Ratio Test (WSPRT). By improving the true positive rate or sensitivity, the detection capability of the system will be improved.

Keywords: Primary User Emulation Attack; Secondary User; Signal Activity Pattern; Signal Activity Pattern Acquisition and Reconstruction System; True Positive Rate; Weighted Sequential Probability Ratio Test; White Space.

1. INTRODUCTION

Cognitive radio is a dynamic spectrum management system which continuously senses the available channels in the wireless spectrum. The sensing process is continuously performed to detect the white spaces. The white spaces are the unused frequency bands of the primary user. The secondary user transmits the information by using the white spaces. But when the primary user comes, the secondary user has to vacate that frequency band. There are several spectral sensing algorithms [1] to detect the white spaces. As the information about the white spaces is continuously updated, the secondary user can jump from one frequency band or white space to another frequency band and continues its transmission.

But some of the secondary users act as selfish or malicious users. The selfish user attacks the unoccupied frequency band. It attacks the unoccupied frequency band for its own transmission. But the malicious user attacks both unoccupied frequency band and the band used by the legitimate secondary user for disturbing the transmission. They disturb the transmission by generating signal same as that of secondary user. The attack caused by generating the signal same as that of primary user is called Primary User Emulation Attack (PUEA) [2].

Primary user emulation attack has severe impact on the cognitive radio network. The impact includes Quality of Service degradation, wastage of bandwidth, connection unreliability and Denial of Service given by [3]. There are several detection schemes to detect Primary User Emulation Attack (PUEA) like Location Based Method, Hearing is believing [4], Dogfight [5], Belief Propagation [6] etc.

In this paper, a new detection technique called Signal Activity Pattern Acquisition and Reconstruction System (SPARS) technique [7] is used to detect the Primary User Emulation Attack. The advantages of the SPARS technique includes

1. SPARS technique doesn't require prior knowledge of Primary Users like location of primary user.
2. It has no limitation on static primary users or primary users with extractable identities.
3. This technique directly targets the objective of the attacker, which the attacker cannot hide.
4. Utilizes a "tolerance interval" technique to test the normality of the reconstruction error.

The SPARS system uses the Bayesian method [8] for data fusion to train SPARS and for Signal Activity Pattern (SAP) reconstruction. The sparse modeling has been widely used in the literature to solve various problems in science and engineering fields [9]-[11]. SPARS system suffers from byzantine failure problem. The Byzantine failure problem can be caused by malfunctioning sensing terminals or Spectrum Sensing Data Falsification (SSDF) attacks. The Spectrum Sensing Data Falsification (SSDF) attack was shown in Figure.1. A malfunctioning sensing terminal is unable to conduct reliable local spectrum sensing and may send incorrect sensing reports to the data collector. In an SSDF attack, a malicious secondary intentionally sends falsified local spectrum sensing reports to the data collector in an attempt to cause the data collector to make incorrect spectrum sensing decisions. Either case could potentially cause interference to legitimate secondary users and result in under-utilization of fallow licensed spectrum. We consider the Byzantine failure problem [12] from the perspective of data fusion techniques. This problem causes the decrease in True Positive Ratio.

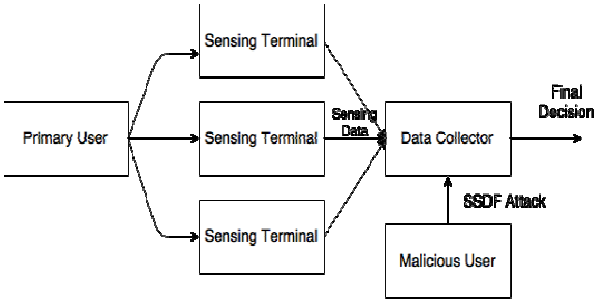

Figure.1 Spectrum Sensing Data Falsification Attack

True positive rate or Sensitivity measures the proportion of positives that are correctly detected as Primary User Emulation Attack. To improve the true positive ratio, a new technique was proposed called as Weighted Sequential Probability Ratio Test (WSPRT) [12] to improve robustness against Byzantine failures.

Rest of the paper organized as follows, Section II explains the WSPRT Technique, Section III explains the System Model, Section IV explains Simulation Results and Section V concludes the paper.

2. WSPRT TECHNIQUE

To improve true positive rate, WSPRT technique is used. WSPRT is composed of two parts.

1. A credit maintenance/ reputation maintenance/ weight allocation module and
2. A sequential hypothesis test module

In the credit/reputation/weight module, a terminal's credit is allocated based on the accuracy of its sensing. If it's local sensing report is consistent with the global decision, its credit receives one point bonus, otherwise one point penalty. The weight is defined as the normalized credit, and is applied as the index of probability ratio in the test.

Let r_i is the each user's reputation, its weight is w_i and H_0, H_1 are Hypothesis then decision variable

$$W_n = \prod_{i=0}^{n} \left(\frac{P[u_i / H_1]}{P[u_i / H_0]}\right)^{w_i} \quad (1)$$

Decision rule is as follows

If $W_n \geq \lambda_1 \rightarrow Accept\ H_1$

If $W_n \leq \lambda_0 \rightarrow Accept\ H_0$

If $\lambda_0 < W_n < \lambda_1 \rightarrow Take\ another\ Observation$

Decision threshold λ_0 and λ_1 is identified by false alarm probability Q_f and Miss Detection probability Q_m .

$$\lambda_0 = Q_m / (1 - Q_f) \quad (2)$$

$$\lambda_1 = (1 - Q_m) / Q_f \quad (3)$$

Assuming, the reputation of a single cognitive radio user is expressed as r_i, each users local decision is u_i and it is compared with the fusion center final decision u then update the reputation according to the rule

$$r_i = r_i + (-1)^{u_i + u} \quad (4)$$

The weight of each user can be adjusted as

$$w_i = f(r_i) = 0, r_i \leq g \quad (5)$$

$$w_i = f(r_i) = r_i + g / \max(r_i) + g, r_i > g \quad (6)$$

Where

$w_i = 0$ judges the user to the malicious user

In order to obtain a hypothesis test using Weighted Sequential Probability Ratio Test (WSPRT), it is essential to obtain the probability density function pdf of the received signal at the secondary user due to transmission by the primary and the malicious users.

3. SYSTEM MODEL

We consider a scenario where all secondary and malicious users are distributed in a circular grid. A primary user is located at some distance from all the users. The Secondary users sense the spectrum to detect the presence of the primary transmission. The secondary users 1 measure the received power on a spectrum band. If the received power is below a specified threshold then the spectrum band is considered to be vacant (white space). If the received power is above the specified threshold then based on the measured power, they decide whether the received signal is from a primary transmitter or by a set of malicious users. We design a WSPRT to obtain a criterion for making the decision mentioned above.

We make the following assumptions to perform the analysis.

1) Take M malicious users in the system.
2) Take the minimum distance between primary transmitter and the users is d_p .
3) Consider the power transmitted by the primary transmitter is P_t and by the malicious user is P_m.
4) Take the circular grid of radius R and assume that the positions of secondary and malicious users are uniformly distributed and statistically independent.
5) Consider the position of the primary transmitter is fixed at a point (r_p, θ_p) and this position is known to all the users in the grid.
6) The Rayleigh fading of RF signal generated by the primary transmitter and malicious secondary users can be ignored..
7) The loss due to shadowing at any secondary user is normally distributed with mean 0 and variance σ_p^2 and σ_m^2 , respectively.
8) The path loss exponent for the propagation from the primary transmitter to any secondary users is 2 and that between any malicious user and any secondary user is 4.
9) For any secondary user fixed at co-ordinates (r, θ) , no malicious users are present within a circle of radius R0 centered at $(r, \theta)^3$.
10) There is no communication or co-operation between the secondary users. The impact of Primary User Emulation Attack (PUEA) on each secondary user is analyzed independently.

Since there is no co-operation between the secondary users, the probability of successful PUEA on any user is same as that on any other user. Hence, without loss of generality, we analyze the probability density function pdf of the received signal at any one secondary user. We transform the co-ordinates of all malicious users such that the secondary user of interest lies at the origin (i.e., at (0, 0)).

Then the primary transmitter is at a co-ordinate (d_p, θ_p)[4].

All malicious nodes are uniformly distributed in the annular region with radii R0 and R by assumption 4. This scenario is shown in Figure.2. In order to obtain a hypothesis test using Weighted Sequential Probability Ratio Test (WSPRT), it is essential to obtain the probability density function pdf of the received signal at the secondary user due to transmission by the primary and the malicious users.

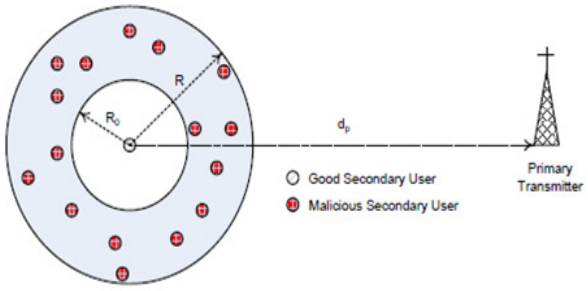

Figure. 2 Cognitive Radio Network in a circular grid with Secondary and Malicious Users

No malicious users can be closer than R_0 to the secondary user because if this restriction is not posted, then the power received due to transmission from any subset of malicious users present within this grid will be much larger than that due to a transmission from a primary transmitter thus resulting in failed PUEA all the time.

4. SIMULATION RESULTS

In this section we present simulation results of the proposed method. In our simulation, we take range = [-5 5 -5 5], M best=4, n=20, Max Generation=100.

The receiver operating characteristic (ROC) curve of SPARS is a plot of the true positive rate, i.e., 1- miss-detection probability versus the false positive rate, i.e., the false alarm probability.

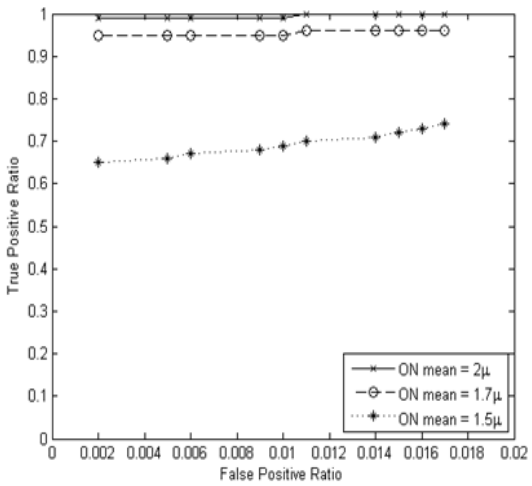

Figure. 3 ROC curves of SPARS for detecting smart attackers

Figure.3 shows the ROC curves of SPARS for detecting smart attackers. A smart attacker can manipulate its ON/OFF periods so that the mean ON/OFF period is more close to the one of PUs. Specifically, a smart attacker randomly generates a small fraction of very short ON periods.

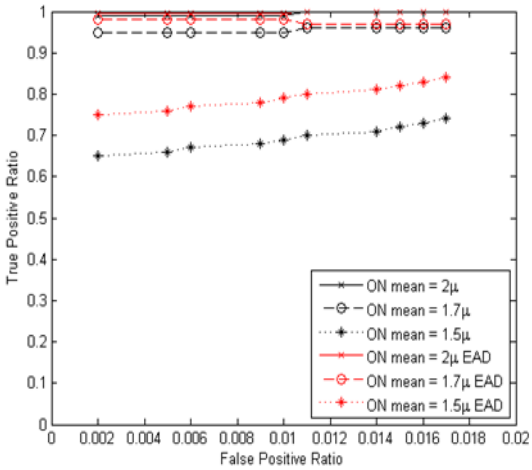

Figure. 4 ROC curves of SPARS for detecting smart attackers using WSPRT

Figure.4 shows the improvement of true positive rate in proposed method compared to the existing method which is achieved by using Weighted Sequential Probability Ratio Test (WSPRT) technique.

5. CONCLUSION

The SPARS model is an efficient detection technique which is used to detect the PUE attack based on the Signal Activity Pattern (SAP). This system suffers from low True Positive Ratio due to the impact of byzantine failure problem. In this paper, we proposed a technique called Weighted Sequential Probability Ratio Test. The performance of the SPARS model can be increased by increasing the sensitivity or True Positive Ratio of the system, which will be achieved by using the WSPRT technique.

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A Mediating Role of Knowledge Management System in the Relationship between Information Technology Infrastructure and E-Government Performance

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Abstract: This paper as a qualitative paper attempts to review extant research in term of e-government performance, knowledge management system, and information technology infrastructure. Nowadays, various countries are trying to improve their performance by using information technology. In this regard, knowledge management can be considered an influential factor which plays a vital role in the relationship between IT infrastructure and e-government performance. In the sequel, this paper proposes a framework which can be applied for future study.

Keywords: Knowledge Management System, Information Technology Infrastructure, E-government, Performance.

1. INTRODUCTION

Through growth and development of technology these days, not only the companies but also governments also attempt to use technology in order to improve their performance. E-government (Electronic Government) includes some digital interactions between citizens and the government known as G2C, business/commerce and government (G2B), employees and government (G2E), between government /agencies and government (G2G) and also government interaction with citizens (C2G). Generally delivery models of e-government could be summed up briefly as the (Turban et al., 2009; Bonson et al., 2012):

- G2C (government to citizens)
- G2B (government to businesses)
- G2E (government to employees)
- G2G (government to governments)
- C2G (citizens to governments)

It is clear that for improving the e-government performance there should be some preparations. One of the critical topics in e-government is IT infrastructure (Welch et al., 2005; Heeks and Bailur, 2007). This infrastructure should be developed in a way that improve and increase the e-government performance. Most of developing countries are attempting to improve this infrastructure in their e-governments. It is clear that according to different dimensions of IT, there is a need to understand its weaknesses (Ramirez et al., 2010; Turban et al., 2008). This will help to improve IT infrastructure and the performance of e-government will be increased.

One of the important topics in e-government is decision making. Usually important decision makings require having enough and categorized information. This information sometimes is explicit in minds of the experts and sometimes is written and documented. Thus, related to using the existed (DSS) decision support system in e-government, there should be knowledge management system. On the other hand, knowledge management system in e-government is not well recognized. This can be considered as the gap of previous studies. The conducted researches by Yang et al. (2012) demonstrated that IT application (both advanced and basic tools) can impact project performance and knowledge management system (KM) at the same time. In addition, Nonaka and Takeuchi (1992, 2007) in their SECI model explained that knowledge sharing as one of the dimensions of KM system can lead to knowledge creation. Hence, the existed knowledge in background of e-government related to improving the performance can be managed. Managing this knowledge will facilitate the decision making because decision makers can concentrate on different aspects more appropriately.

As it was mentioned before, for managing the knowledge there should be IT infrastructure. Hence this study aims to justify the relationship between IT infrastructure, KM system and thereby e-government performance.

2. LITERATURE REVIEW

2.1. E-government

The strategy of e-government is one of the critical factors for modernization of public sector by means of developing and understanding organizational structure, interaction approaches with business and citizens and also minimizing costs and layers of process regarding organizational business. It brings a wide range of information for businesses and citizens via internet. By the way, e-government's role is not just bringing services and information to the citizens that can be offered by commercial companies. The e-government can develop helpful strategic connections among departments with public sector firms and also create a communication between different levels of the government for example local and central city.

This communication and connection will improve the cooperation among them via facilitating the implementation and provision of government transactions, strategies and also policies and in addition better running and using the governmental information, resources and processes (Cabinet Office, 2000; Heeks, 2001). Also the government can transfer the funds electronically into the other agencies of the government and bring information for public staffs by means

of internet or intranet. Cabinet Office (2000) and Tyndale (2002) stated that e-government advanced the communications among various parts inside the government and as a result individuals will not need to repeatedly ask about similar information from various providers of the service.

By means of a web portal which is integrated, the businesses and citizens can do the transactions with agencies in government with no need to visit many different departments/ministries in different physical places. Also, strategy of e-government helps the public sector or firms to directly interact and operate better with the businesses and there will be no importance about their locations. This will have digitizing procurement services for the businesses for improving their service quality, cost effectiveness as well as convenience (Heeks, 2001; McClure, 2000).

Moreover, government officials and leaders are highly know about the e-government potential for promoting the performance of governmental firms and bring some benefits for business partners and the citizens. By the way, e-government adoption is not totally straightforward and could not be accomplished in a short time and instead it needs an architecture integrative framework method to put the government services and information online. This can be a reason that why a lot of governmental firms still are in beginning stages of adopting e-government. The other critical reason regarding this delay is that e-government needs remarkable changes in organizational infrastructure that as a result can increase resistance. So these reasons make the scholar to creat an architecture integrative framework for the adoption of e-government.

2.2. Knowledge Management

In an uncertain economy, the knowledge is the source that can lead the company to CA (Nonaka and Von Krogh, 2009). In this regard, a company should increase the knowledge inside the organization for being successful (Nonaka and Toyama, 2007).

Based on statements of Brian Newman (1995) knowledge management (KM) is the process of gathering, creating, disseminating and utilizing the knowledge. KM has been found and understood since so many years ago. These days, different scholars have knowledge about using it including philosophers, scribes, teachers and priests (Cochrane, Webb & Newman, 1995).

The question here is that if KM has been utilized since many years ago what is the role of KM in case of information these days? The mentioned progresses are existed and they have a deep impact on decision making and action taking of individuals. They both probably are made in different types of knowledge. As Thomas Bertels (1998) noted, managing the renewal system knowledge of organizations is knowledge management or KM.

I. Providing supportive structure for the organization
II. Putting IT-Tools
III. Facilitation employees of the organization

Thomas Bertels is a practical person, highly focused on practical aspects of knowledge in case of having effective enhancements.

Knowledge management has so many different definitions and those published supporting terms by different experts and authors. Maarten Sierhuis is known as a person who defined the KM as following (Alavi and Leidner, 2001).

The capability of managing knowledge is called KM or known as knowledge management. Information management is remarkably common and familiar. It is a term that people need sources for comprehension of the information as well as having the ability to use them within the organizations (Scalea, 2008). In addition, information planning and information analyses concepts are initiated from knowledge management as well. currently the organizations are looking for knowledge sources so they will need many new ideas and methods for organizational management. in order to do different techniques such as knowledge technology and knowledge planning, different methods should be developed for examining the organizational knowledge sources (Wong&Aspinwall, 2005).

Based on statements of Gregory Wenig , the KM has been provided firm many different actions which the organization achieves from their experiences or others and in addition they can fulfill the mission of the company by logical and rational knowledge observation. These actions can be helpful for developing organizational structure, technology and strategies based on cognitive approaches for improving the existed knowledge yield and providing new knowledge. The necessary attempt is that the surging of cognitive system (computer, organization, human or may be the combination of them all) for using, maintaining and achieving knowledge for realizing how to find solution for issues and making the best decisions possible (Firestone, 2001).

2.3. Related Research on Knowledge Management and Performance

By considering the fact that e-government performance is close to project performance there are many different researches that show the important role of KM. Generally, many experts have stated that information technology provides significant benefits for KM. In addition, it was revealed that KM has a critical key role for projects and performance of the organizations. The beneficial management of built facility requires influential KM in order to support it properly (Rooke et al., 2010).

In previous researches, knowledge management was known as relevant to results of critical performance (Egbu, 1999, Liu, 2004, Carrillo, 2006, Adenfelt, 2010). In addition, in 1999, Carayannis examined the role of KM relevant to growing synergistic symbiosis between IT and organizational cognition. The previous researches demonstrated that knowledge management has a mediating role regarding the existed relationship between information technology and performance results (Chen & Liang, 2003). Then, Yang et al. (2012) expanded the previous studies through adding the relationships among IT application, KM and project success for capital faculty.

Moreover, there are several studies (e.g. Gudi and Becerra-Fernandez, 2006) about the existed relationship among project performance, KM, project risk, team adoption and project success (Fig.1).

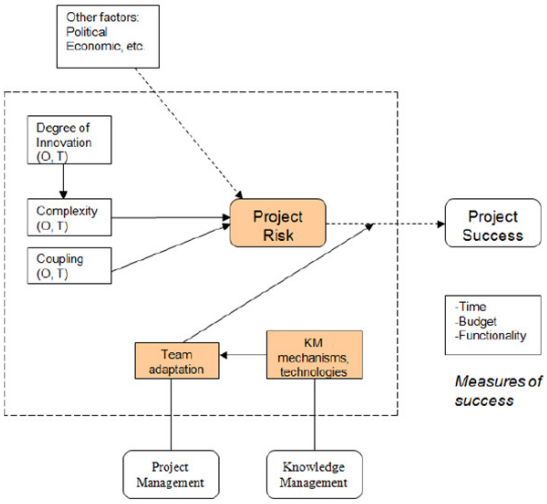

Figure 1: Gudi and Becerra- Fernandez (2006)

Ismail et al. in 2009 presented an integrated model which connects sharing knowledge to project management in order to increase success of a project. In this framework, organizational and individual motivation elements have critical role for improving knowledge sharing and as a result success of the project (Fig.2).

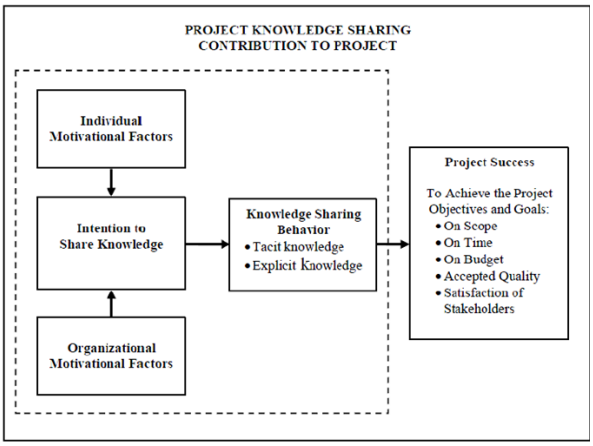

Figure 2: Ismail et al. (2009)

According to Figure 2 above, organizational and individual factors enhance the knowledge sharing intention. In next level intention can increase behavior of knowledge sharing which in turn increases project success.

Yeong and Lim (2011) suggested an integrity framework which connects project management to knowledge management in order to increase project success. In this framework both organizational and individual motivation elements have critical role for improving the knowledge sharing which leads to more project success (Fig.3).

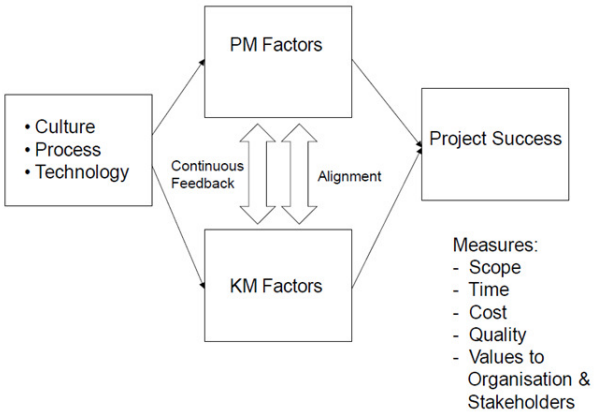

Figure 3: Yeong and Lim (2011)

3. PROPOSED FRAMEWORK AND FUTURE STUDY

As it discussed above, there are enough evidences to show that information technology can affect knowledge management and e-government performance. In this regard, figure 4 shows this relationship based on intervening role of KMS.

Future study at first used qualitative approach for understanding the information technology infrastructures' weakness. This approach will contribute to define proper IT infrastructures. In the next step, future study should attempt to utilize questionnaire for testing the below framework.

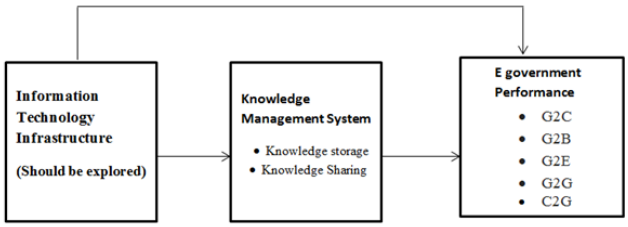

Figure 5: Proposed Framework

Because of the fact that the emphasis of e-government is on G2C, G2B, G2E, G2G, and C2G so it is important to design the most appropriate questionnaire after interviewing with the experts.

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Improving Technological Services and Its Effect on the Police's Performance

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Abstract: The role of police department in any country is critical. It is obvious that improving the technology in police department can be done with safety and contributes to improve its economy. This paper, first tries to recognize the existed weaknesses in used technologies. Then, it will suggest the best approach. The proposed framework of this study points out to two different moderating roles that can be considered as technical contributions. Moreover, the combination of this proposed framework is new for current study. This framework is concentrated on technology improvement, knowledge management system, technology acceptance, police performance, and ministry performance.

Keywords: technology improvement, knowledge management system, technology acceptance, police performance, and ministry performance.

1. INTRODUCTION

The emerging and new technologies have a remarkable key role in every day work of the police and it equips the officers with investigative and enforcement devices that are able to provide them safety, information as well as higher efficiency and effectiveness.

Enforcing and developing comprehensive policies of agency about the use and deployment is a major step for understanding the value promised by technologies and is necessary for making sure the public that their civilized liberties and privacy are all protected and understood.

The advancements in technology provided the possibility for recording and monitoring each of the interactions among public and police by means of body worn and in car video, accessing to expanded network of private and public video systems, as well as enhancement in use of those smart phones which have recording abilities by officers and the citizens. In this case police will be able to track the suspect by means of GPS technologies for tracking and the officers also can be tracked by (AVL) automated vehicle location systems.

The system of (ALPR), automated license plate recognition can be considered as the plates of license for vehicles insight of officers while they are in field and it will alert them very fast when the vehicle was reported as being wanted or stolen. The identity can be established or verified remotely through biometric precisions by means of mobile scanners of fingerprint or software for facial recognition. They can map the crime when they are being reported, the technology of gunshot detection is able to alert the enforcement of law quickly at the time that firearm is being discharged and the cameras have the capability to be programmed for concentrating on location of gunshot and provide live videos for both officers and dispatchers.

According to the mentioned points above, it can be concluded that using new technologies is necessary in order to improve police performance. However, the important point is the fact that if the employees of this organization are interested to use this technology or not? In addition, another question is that how the new technologies can be used in higher organizational levels.

For answering the first question we can refer to the conducted studies by some researchers such as Delone and Mclean (2004). These researches mainly emphasized on factors such as quality, technology acceptance and etc.

In order to answer the second question, we can refer to the value of knowledge management system (KMS). Previous studies (e.g. Yang et al., 2012) demonstrated that KM can affect the project performance. Hence, studying the role of KM system in macro dimensions have been discussed less. On the other hand, using e-government these days facilitated the relationship between government organizations. However, the existed knowledge and experience in police department can be used to positively improve e-government performance.

Because of the fact that every country uses new technologies in its e-government so police departments also need new and modern technologies to be engaged with. It is clear that police department should evaluate and improve itself. On the other hand the employee behavior regarding usage of new technologies is one of the common issues in organizations. The experiences of polices in case of using new technologies and its weakness and strength points should be considered for making macro decisions and this can highlight the role of KM. according to the complexity and ambiguity for improving the performance of Ministry of Internal Affair, this research attempts to study the relationship among technology acceptance of employees, technology improvement, Ministry and KM performance and also department performance.

2. LITERATURE REVIEW

2.1. Theory of Acceptance Model

There are many various research related to different models of consumer acceptance. Among them some are relevant to a specific model or theory and the rest try to make comparison between models and join them in order to get better results.
The model of technology acceptance (TAM) is one of the famous models in case of customer acceptance which was presented by Davis (1989). All of the customers generally may use high tech products and services for not only taking advantage but instead for having the experiment with their usage (Kulviwat, Bruner, Kumar, Nasco, and Clark, 2007). The primary goal of TAM would be providing a definition for different dimensions of adoption which are all general for being employed in many innovative technology activities (Davis, Bagozzi, and Warshaw, 1989).

This model focuses on two main considerations as easy to be used and usefulness. The assumed benefit is the degree to which a potential customer might think by using a specific device or tool which can improve their total performance and also the easy to be used assumption is the fact that to think using a specific technology will not require high work and energy levels.

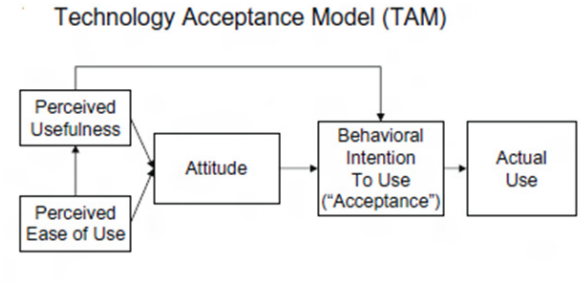

Figure 1: TAM by Davis (1989)

In researches about the field of societal sciences, the existed causality analyses the relationships significantly influences the efficiency of decision making. Previous investigations which studied the (TAM) or technology acceptance model and also (UTAUT) known as use and acceptance technology theory in general employ structural equation modeling (SEM).

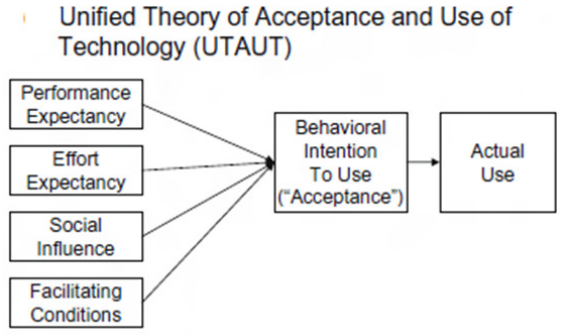

Figure 2: UTAUT

The collected statistical data however, allows the analysts to modify the mentioned model in order to prepare an appropriate model of fitness and basically SEM is misused when the data is fit rarely for structural equation modeling. Conceptual model or theory can be expanded through analytical results based on the developed hypotheses (Wu, Huang, Tzeng and Wei, 2010).

2.2. IS Success Model

The IS or information system concept is a remarkably accepted tool for assessing the IS (Lin, 2006). In case of MIS for managing the IS scholarships, a lot of experts suggested different IS success models (Seddon and Kiew, 1994, Mclean and Delone, 1992, 2003, 1997; Pitt et al., 1995). These models bring many definitions or factors for IS success systems that influence the noted IS success. The models are theoretically generated and empirically examined. Thus, many scholars did investigations about success factors of these models that are being employed for evaluating the IS successes as well as performance. After reviewing above 180 articles in field of IT investment evaluation factors that were published in 1970s and 1980s, then Mclean and DeLone (1992) proposed a model for IS success which had six main variables related to IS success, information quality, system use, system quality, user satisfaction and finally organizational and personal impacts.
This model presented coherent and dependent factors used by the IS experts, it achieved a lot of critiscm. Firstly, employing the information system in provided model by DeLone and McLean can have different interpretations for being analyzed appropriately. In addition using the information system has a problematic and controversial role for IS success model. Then, because of the fact that satisfaction has individual impacts of information system within the organizational context, looking for cause path from user satisfaction to individual impacts is not useful. Finally, this model cannot fully explain the relationship between impacts of user satisfaction and individual / organizational (Edward, 2005). This definition for this construct is as follows:

1. System quality: evaluating the information processing system on its own
2. Information quality: evaluating the IS output
3. Using information: IS consumption and output of receiver
4. Satisfaction of users: reaction of receiver for utilizing the output from IS
5. Personal influence: Influence from information relevant to behavior of recipient
6. Organizational influence: Impact of information for firm's performance

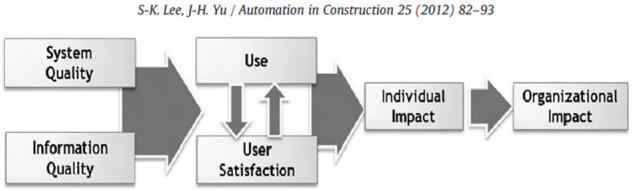

Figure3: IS success mode by Mclean and Delone (1992)

In 1994, Seddon & Kiew reviewed an altered version of developed model by DeLone and McLean (1992) which had three below primary differences:
(a) For being useful the use was modified, (b) one new factor, systems importance also were noted for defining different user assumptions which are related to satisfaction as well as usefulness of the users and at last (c) stimulation causality among user satisfaction and use has been replaced with casual single way for instance being useful always results to upstream for two third from developed model of Mclean (1992). Moreover, Seddon in 1997, introduced an IS success model which demonstrates that society impact is considered as the net IS advantage (Fig.2.7).

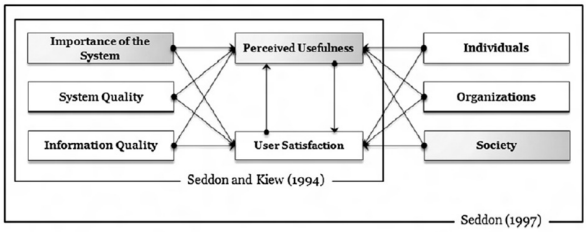

Figure 4: IS success model by Seddon and Kiew (1994)

The IS success model developed by Pitt et al. (1995) revealed the fact that service quality is another quality factor for developed model by Mclean and DeLone (1992). All of the measurement items for evaluating the service quality are

SERVQUAL which is altered and suggested by A. Parasuraman et al. (1998); so the other validity was tested (Fig.5).

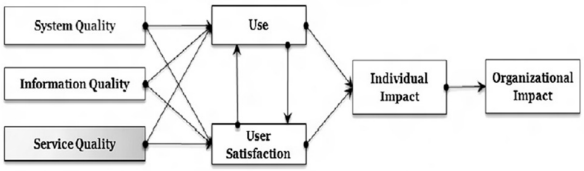

Figure 5: IS success model by Kawan et al. (1995)

2.3. Knowledge Management System

In a not certain economy, a company can reach CA by means of knowledge (Nonaka et al., 2009). In this regard, a company for reaching success increases the internal knowledge of the organization (Nonaka et al., 2009).

Based on statements of Brian Newman (1995) the collection process which results in creation, knowledge utilization as well as dissemination is known as (KM) or knowledge management. Knowledge management has been recognized and realized for many decades ago. These days different scholars know the usage of knowledge for example philosophers, scribes, teachers and also priests (Newman et al., 1995).

Here the question is that if KM has been used for decades so what is the role of KM relevant to information nowadays? The mentioned progresses are existed and they have a remarkable impact on decision making as well as action taking. They both probably are made with different types of knowledge. Based on Thomas Bertels statements, renewal system knowledge management of organizations is called as knowledge management or KM for example (Savage &Bertels, 1999)

I. Developing supportive structure for the firm
II. Putting IT-Tools
III. Facilitation the organization employees

The practical person, Thomas Bertels, highly focused on practical aspects of knowledge for real improvements. The conducted researches by Yang et al. (2012) and Tsai (2001) demonstrated that knowledge management has the capability to impact performance.

3. CONCLUSION AND FUTURE STUDY

The role of police department in any country is critical. It is obvious that improving the technology in police department can be done with safety and contributes to improve its economy. This study, first tries to recognize the existed weaknesses in used technologies. Then, it will suggest the best approach. The proposed framework of this study (See Figure 6) points out to two different moderating roles that can be considered as technical contributions.

According to the mentioned points above, technology acceptance models show that which factors might impact "use". In addition, IS success model based on some factors such as quality attempts to extend the impact of "use" and "user satisfaction" on individual performance and organizational performance.

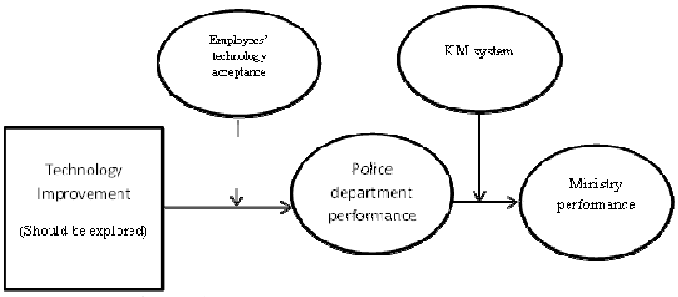

Figure 6: Proposed Framework

On the other hand, KM has been recognized as one of the important factors in previous studies which have the potential to impact performance and also macro decision makings. It should be mentioned that the relationships in this framework all have been supported by previous studies.

Firstly, future study can apply the qualitative approach. This approach helps to explore the weaknesses in the current technology which is being applied. Secondly, several hypotheses should be developed based on the proposed framework. To test the hypotheses, the quantitative approach is efficient.

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Relationship between transformational leadership, Innovation, Learning and Growth, and Internal Process: Government Organizations

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Abstract: The main purpose of this paper is to justify and discuss the relationship among transformational leadership, innovation, learning and growth, internal process within government organizations. Transformational leadership style consists of five components namely vision, intellectual stimulation, inspirational communication, personal recognition, and supportive leadership. Besides, innovation, learning and growth, and internal process are considered as three main perspectives of organization's performance.

Keywords: Transformational leadership, Government organizations, Innovation, Learning and Growth, Internal process.

1. INTRODUCTION

The government organizations in any country can be considered as the most important sources in different countries for citizen satisfaction and economic growth (Kim, 2005; Trottier et al., 2008; Cho and Park, 2012). In this regard there are a lot of policy makings on improving the performance of these organizations.

The government organizations always attempt to improve their performance. The reason is that this country is dependent to these types of organizations for attracting foreign investors, tourists and also increasing the economic activities (Al-Khouri, 2012). The previous studies on the role of human resource management demonstrated that enhancing human resource and investing on it is one of the influential factors on organizational performance. For example Huselid (1995) are among those scholars that emphasized on this aspect. Moreover, RBV or resource based review support this relationship.

One of the important factors which can impact the organizational performance is leadership style. The conducted researches by (Dvir et al., 2002; Pieterse et al., 2010; Wang et al., 2011; Grant, 2012; Moynihan et al., 2012) demonstrated that transformational leadership has the capability to impact different dimensions of performance. This can be supported by many different theories such as social exchange theory (Emerson, 1976) and agency theory (Eisenhardt, 1989).

Because of the fact that government organizations are the main focus of this study, may be eliminating the financial performance brings more reliability for studying the performance. By considering that learning and growth, innovation and internal process can be acceptable dimensions for measuring the performance (through utilizing conducted researches by Kaplan and Norton; 2001), it can be concluded that the existed relationships among these three dimensions were not highly focused in previous studies. On the other hand, transformational leadership has different dimensions including inspirational communication, vision, personal recognition, intellectual stimulation and also supportive leadership that studying the impact of each of them separately can be a gap in previous researches.

One of the methods for improving the performance is using the practices and discussions of human resource management. Related to the influential factors on performance, there are still some ambiguities about dimensions of performance and the relationships between them. However, this study aims to justify and show the relationship between transformational leadership style, innovation, learning and growth, and internal process in government organizations.

2. LITERATURE REVIEW

2.1 EMPRICAL Support for the Transformational Leadership Model

Bycio et al. (1995) used MLQ-1 in order to realize the five factor model that is efficient and effective enough for the gathered data and contains charisma, intellectual stimulation, individualized consideration as well as managed by the exception. However, this study could not provide enough proof in order to support transformational leadership model (Tepper& Percy, 1994; Bycio et al., 1995). Moreover, there are many contradictions in reported proof about the structure of the model. Particularly, they recognized a positive relationship among leadership factors that can support transformational leadership model (Tejeda, Scandura, &Pillai, 2001; Carless, 1998; Avolio et al. 1999).

It can be said that a two factor model which shows an active and passive dimension from leadership has been assumed as being efficient. Based on the latent factor correlation, it was demonstrated that transformational leadership scales are strongly interrelated (rs ranged from .83 to .91). In addition, the contingent reward scale had relationship with transformational scales positively (rs ranged from .79 to .83). This model showed that latent factor's average inter correlation among the scales of transformational leadership was equal to .88, and the latent factor's average inter correlation of transformational scales and contingent rewards were .81.

Avolio et al. (1999) introduced so many models for factor structure related to MLQ-5X. The original model could not provide enough data because of the latent factors inter correlation among the variables of transformational leadership and the high levels of latent correlation among transformational factors and contingent reward. It was noted that subscales of MLQ have high degree of correlation and amount of the variance for the explained scales which have been mentioned with a paradigm of high order.

At last, six factor model was developed through reduced items category and was the most appropriate model for the data when it was compared to a series of existed models

conceptually. However, the latent factors' average inter correlation regarding transformational scales was .94 (rs ranged from .91 to .95), and the average correlation among the transformational scales and contingent reward was .90 (rs ranged from .86 to .93). in addition, Carless (1998) investigated the MLQ-5X and asserted that there is a model which is proper hierarchical regarding data collection that has charisma, individualized consideration as well as intellectual stimulation revealing various aspects of second order structure known as transformational leadership.

According to the above results, the scholars employed a lot of tactics when they studied the transformational leadership. In addition, Carless noted that MLQ-5X cannot test the individual behaviors coming from transformational leadership but instead can assess the single and hierarchical paradigm of the transformational leadership.

According to Schriesheim, Williams and Pillai (1999), they utilized a global measurement for transformational and transactional leadership opposite to studying the individual sub dimensions. The other scholars used a set of items for assessing the transformational leadership for example Tejeda et al., (2001). This approach was remarkably come from empirical results and it was not following a powerful and theoretical rationale for explaining the key factors allocation to the variables. Other experts for instance Fetter, Podsakoff, Moorman and MacKenzie (1990), introduced their own measures of transformational and transactional leadership.

These three mentioned strategies have some benefits and however we can conclude that adopting an approach that is theoretically driven is critical when evaluating the sub dimensions from transformational leadership. So, we should review the theoretical models developed by Bass (1985) as well as understanding 5 sub dimensions relevant to transformational leadership that can show the level's validity in which not relevant concepts will stay not relevant to each other. In addition, the developed theoretical model by Bass can be used in order to get better outcomes.

2.1.1 Vision

According to Bass (1985), the most important transformational leadership aspect is the charisma. According to empirical findings which support this definition, the understood Meta analytical results shown that charisma is remarkably linked to mechanism of effectiveness for instance satisfaction from the leaders (Kroeck, Sivasubramaniam and Lowe, 1996). Scholars had a key role in definition of charisma (Beyer, 1999; Barbuto, 1997). Beyer examined the fact that critical components of charisma were dramatically ignored.

Weber (1968) noted that charisma has five dimensions as ideas bringing radical solutions to problems, gifted person, social crisis, a set of followers interested in exceptional individuals who believe that leader has transcendent powers and also the validity of talents and leaders extraordinary gifts along with many repeated achievements.

In general, charisma as mentioned in transformational model, cannot incorporate all of the noted components such as the effect of surrounding environment of leaders and followers, individual connected qualities to charisma and the existed relationship between charismatic leaders and followers along with leader's transcendent powers which have not been yet explored in previous studies. The vision is known as the critical factor of leadership which is incorporated in a charismatic logical framework.

House (1977) noted that vision is an ideal that demonstrates shared values of the stakeholders. Also McClelland (1975) noted that vision results in adapting organizational values and objectives which can motivate individuals to adapt all of behaviors since the behavior itself is attractive while compared to leader attractiveness or charisma.

In this study, vision can be known as the implicit and mental expression of image that can be idealized regarding future and it is formed by organizational values. It is a general theme when there is charisma. According to Weber (1968), a good vision is a basic element that affects charisma. Based on House (1977), the charisma leaders demonstrate behaviors for example ideology articulation that increases goal clarity, task focus and also value congruence. Current study tries to focus on vision. It can contribute for better recognition of broader idealized concept constructs of the charisma presented by Bass.

2.1.2 Inspirational Communication

Bass (1985) suggested that charismatic leaders utilize emotional talks and inspirational allures to arouse motivation of employees that leads to self-interest give up for having better good. Later, Bass (1999) asserted that inspirational motivation and charisma are shown when leader a desirable future is being envisioned by leader, and effectively articulates how it should be achieved, he provided an example, set high performance standards and demonstrates confidence and determination in all of the planned tasks. This will suggests that inspirational motivation and vision could possibly be combined as one united construct.

Bass (1985) asserted that those leaders who are charismatic use the inspirational allures and emotional talks to raise the employee motivation for self-interest giving up and having well-being. Even though many scholars have talked about the fact that it is good to make a difference between vision and inspirational motivation (McClelland, 1975; Barbuto,1997), in following discussion a class of theoretical rationale will be suggested in order to create a difference between vision components of charisma and constructs of inspirational leadership:

Downton (1973) mentioned inspirations are action or powers of raisin emotions or the intellect. Also Yuki (1981) stated that inspiration is the extent to which the leader stimulates enthusiasm among task subordinates which they have accomplished and outwardly comments for making up the confidence for subordinates for performing the assignments successfully and get the team goals in the most appropriate way possible.

In addition, Bass (1985) limited employing the inspirational leadership term when a leader employs none intellectual and emotional qualities for impacting the process. He mentioned that inspirational leaders place emotional qualities to impact the process by means of emotional methods and communications.

Oral communication is assumed as the recruiting aspect in existed definitions regarding inspirational leadership. It is generally used as the motivational tool to enhance follower's emotions, so, the result of joining inspirational leadership and oral communication, we can focus on inspirational communication. It is the employment of emotions appeals and statements to increase the followers' emotions.

In this study, it is noted that inspirational communication can be assumed as the paradigm which is explained as a verbal expression from related positive messages to organizations and employees; these statements provide motivation and confidence among organizational parties.

2.1.3 Supportive Leadership

These explanations about individualized consideration shifted into discussing about one recognized aspect which is supportive leadership. For instance Avolio and Bass (1995, p.

202) stated that leader demonstrates higher individualized consideration through showing general and positive support for attempts of the followers.

The element that totally differing transformational leadership from other new leadership theories is known as 'individualized consideration'. Bass (1985) noted that individualized consideration occurs while the leader has some developmental orientation which shows they will work for having more development inside the organization. Additionally, he demonstrated individualized consideration to followers and properly reacts to their specific needs.

Additionally, there are so many experts in transformational leadership field who also focused on supportive leadership. According to Padsakoff et al. (1990) individualized support is known as the leader's behavior that shows they consider followers and their unique needs.

This study focuses on supportive leadership and uses extensive researches that were done for this discussion. House (1996, p, 327) noted a supportive leader shows a behavior for satisfaction of preference from subordinates and requirements for example demonstrating their concern about subordinates welfare and creating friendly and supportive work environment psychologically. The supportive leadership is the key factor if having effective leadership (House, 1971). Hence, we define supportive leadership is the expression of concerns about followers and their individual well- being within working environment.

2.1.4 Intellectual Stimulation

The intellectual stimulation is one of the remarkable underdeveloped dimensions of transformational leadership according to Lowe et al. (1996). By the way, this leadership factor has some behavioral patterns that increases the followers interest regarding organizational issues which effectively help to develop their ability to solve the by means of new methods (Bass, 1985).

It was recognized that the effects of intellectual stimulation are clear in enhancing the followers' capability to conceptualize, comprehend and analyze the problems and high quality solutions that they provide for the organization (Bass and Avolio, 1990). This leadership factor was not the subject of extensive researches, by the way, it contains a more comprehend series of behaviors in comparison to the other transformational leadership sub dimensions.

Hence, this study maintained the intellectual stimulation which was adopted by Bass et al (1985). The intellectual stimulation is known as raising awareness and employee's interest about problems and advancing their ability to solve these issues.

2.1.5 Personal Recognition

Based on the theoretical proofs it was realized that there is a remarkable relationship among sub dimensions of transformational leadership and transactional leadership in such a way that the transactional leadership contributes to management through contingent reward and exception. The individual recognition as the contingent reward will give the reward to the followers for getting high performance levels. As Bass (1985) mentioned, a praise expression for the well done works, promotion recommendations and payment increases as well as commendations about best attempt are the examples of contingent reward behaviors.

According to empirical evidence in past studies, the contingent rewards significantly and positively are correlated with transformational leadership and shows a similar relationship method for the sub dimensions that are transformation in general (Tepper & Percy, 1994; Den Hartog, Van Muijen, &Koopman, 1997).

There exist a lot of reasons that have been proposed for defining these relationships. In addition, Goodwin et al. (2001) noted that contingent reward scale as assessed by MLQ-5X will get the behaviors that are linked to negotiations about rewards for improvement in performance. Additionally, those associated behaviors to reward provision according to performance are also evaluated by the contingent reward scale. These experts asserted that leader's negotiation for allocating rewards to best performances demonstrates a specific transactional leadership type.

However, by means of giving rewards to followers with well performance it is possible to demonstrate a transformational progress because followers and leaders within transformational leadership contexts have a lot of personal investments regarding vision and all of them are developed in order to be effective organizational participants in the best way. Thus, followers think that the performance level consistent to vision of the firm, will be recognized and specified and will be given a reward.

Goodwin et al. (2001) supported the two factor solution for contingent reward by using (CFA) or the confirmatory factor analysis. These experts interpreted their own achievements as providing support for the fact that contingent reward has transactional and transformational processes. This is highly consistent with work systems models which have good performance (Vandenberg, Richardson, & Eastman, 1999; Becker & Gerhart, 1996; Arthur, 1994) and can make differentiation among the reward which has role of controlling mechanism and the reward that acts as the system's designed component for increasing the commitment of the employees.

2.2 Relationship between Innovation, Learning and Growth, and Internal Process

A lot of researches (Dvir et al., 2002; Pieterse et al., 2010; Wang et al., 2011; Grant, 2012; Moynihan et al., 2012) have been conducted about the impact of transformational leadership on organizational performance. These researches emphasize on different dimensions of performance. These dimensions are learning, innovation and internal process. In addition, a lot of researches have been conducted about the relationship between innovation and learning but these are as one way relationships. However, this can be considered as the gap of previous studies. Moreover, the impact of innovation and learning on none financial performance did not receive enough focus from the past studies. According to Kaplan and Norton (2001), in (BSC) balanced score card four different dimensions can be considered for performance including customer, internal process, financial and learning and growth. Through eliminating the financial performance and customer perspective (government organization), may be the internal process can be considered as another important perspective of performance.

3. PROPOSED FRAMEWORK AND FUTURE STUDY

Through using the extant studies and also some theories such as social exchange theory and RBV theory this study proposed the below framework (Fig.1).

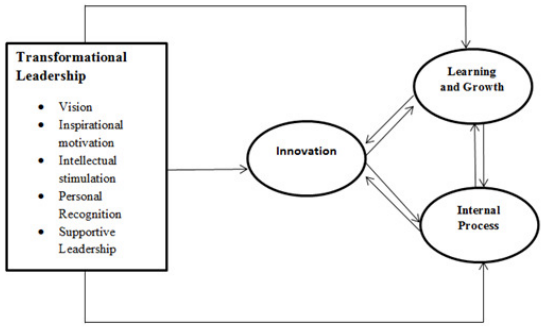

Figure1: Proposed Framework

Through quantitative approach future studies will be capable to examine the relationships between these variables. First, some hypotheses should be developed. Then, the questionnaire should be designed. In order to test the framework, future study needs the middle and top manager experience, so they can be considered as population of study. It should be mentioned that, innovation, learning and growth, and internal process are three dimensions of the performance. However, the interaction between theses dimensions can highlight the importance and priority of each of them. In other words, quantitative approach' results propels future study to develop a new frameworks. In that framework we can see the intervening variables.

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Total Antioxidant Capacity of Labdane and Pimarane Diterpenoids of *Juniperus phoenicea* L

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Abstract: Although *Juniperus phoenicea* L is a widely distributed wild tree in the south of Saudi Arabia, but its phytochemical and physiological evaluation is still poor. The chromatographic separation of the CH_2Cl_2/MeOH, 1:1 extract of *J, phoenicea* L. fruits gave β-sitosterol, stigmasterol, four labdane and two pimarane diterpenoids, including new labdane diterpenoid. Additionally, the volatile compounds of the main petroleum ether extract, as well as the steam-volatile constituents were identified by GC/MS. The separated compounds were identified by spectral tools. The new diterpenoid was identified as 5,9,10-triepicupressic acid.
A previous false identification of sandracopimaric acid, from the fruits of *Juniperus phoenicea* L. grown in Egypt, was detected and declared to be revised.
Total antioxidant capacity of extracts was estimated using total antioxidant capacity kit of Biodiagnostic, based on Koracevic et al., for biological fluids, with slight modification to suit extracts. Ascorbic acid was used as a reference antioxidant compound. Reasonable results were obtained by applying the modified method on petroleum ether extract, methylene chloride extract and ethyl acetate extract of *Juniperus phoenicea* L.

Keywords: *Juniperus phoenicea* L.; labdane diterpenoids; pimarane diterpenoids; 5,9,10-triepi-cupressic acid; total antioxidant capacity.

1. INTRODUCTION

Different extracts of *Juniperus phoenicea* L. were found to be highly physiologically active. Oils of berries and leaves showed very high cytotoxic activities against many cell lines. Additionally, the antimicrobial activity and minimum inhibitory concentration of leaf and berry oils showed high activity against most of the tested strains [1, 2]. The essential oils obtained by supercritical fluid extraction at different pressures were active as antiviral, antiproliferative and antimicrobial [3]. The antioxidant activity by using DPPH and ABTS assays of J. phoenicia was determined [5 ,4].
J. phoenicea leaf extracts show a remarkable effect in enhancing liver and kidney functions and may thus be of therapeutic potential in treatment hepatotoxicity and nephrotoxicity [6].
The aqueous extract of *J. phoenicia* caused a dose dependent protection of rats against castor oil induced diarrhoea and reduced castor oil induced enteropooling. The extract also caused a dose dependent decrease in intestinal transient and showed a significant dose dependent relaxant effect on rat ileal smooth muscle [7].
Many phytochemical investigations of *J. phoenicea* indicated the separation of essential oils [1, 3, 4, 8], labdane and pimarane diterpenoids, with remarkable unsaturation [2, 9], furanone glucosides [10, 11], and phenyl propanoids [9, 12, 13]. Although many chemical research publications were found on *J. phoenicea*, from diverse countries; Tunisia [4, 5, 8], Morocco [9], Egypt [1], Italy [3], and France [10-13], but only one research publication was found on *J. phoenicea* from Saudi Arabia [14], which has reported the isolation of some sesquiterpenes and diterpenes. In this research article, we aimed to phytochemically and physiologically reinvestigate *J. phoenicea*. We could report the isolation of four labdane and two pimarane diterpenoids, including a new labdane diterpenoid, in addition to the identification of the volatile compounds of petroleum ether extract by GC/MS. Additionally,

the total antioxidant capacity of extracts was estimated using total antioxidant capacity kit of Bio-diagnostic, based on Koracevic et al. [15], for biological fluids, with slight modification to suit extracts.

2. EXPERIMENTAL

2.1 General

^{1}H NMR spectra were taken on Bruker 600 MHz at King Fahd Center for Medicinal Research, KAU, Jeddah, Saudi Arabia; GC/MS analysis was performed on A Perkin Elmer Clarus 500 GC-MS (Perkin Elmer, Shelton, CT, USA). The software controller/integrator was TurboMass version 5.4.2.1617. An Elite-1 GC capillary column, Crossbond® 100% dimethyl polysiloxane (30-meter × 0.25 mm ID × 0.25 µm df, Perkin Elmer) was used. The carrier gas was helium (purity 99.9999%) and flow rate was 0.9 mL/min. Source (EI+): source temperature, 270°C. GC line temperature was 210°C. Electron energy was 70 eV, and trap-emission was 100 v. The oven was programmed as follows: initial temperature was 100°C (hold 2 min) to 250°C (rate °15C/min, hold 4.0 min). The injector temperature was 260°C. The MS scan was from 40to 500 m/z (500 scan/sec). The injection volume was 1.0 µL, and the Split ratio was .40:1 Samples were acquired by applying the total ion chromatogram (TIC) scan modes. An average TIC scan of each peak, at definite retention times, was saved using the TurboMass software to characterize the closed peaks obtained from the MS chromatogram of the analyzed samples. The screw-capped (PTFE/silicon) 1-ml autosampler vials (12 mm × 32 mm) used for recovery were purchased from Waters (Milford, MA, USA).

2.2. The plant material

Juniperus phoenicea L. fruits were collected from Nemas City, near Abha, KSA, in August 2012 by the third Author, and identified by Faraj Elghamdi, Assistant Professor of Plant Taxonomy, Botany Department, Faculty of Science, KAU, Saudi Arabia. A voucher specimen was deposited under the number HKAU 1791 in the Herbarium of the Biology Department, Faculty of Science, King Abdulaziz University.

2.3 Processing of the plant material

The dried and grinded fruits, 377 g, were extracted by soaking at room temperature in CH_2Cl_2/MeOH, 1:1, 1800 mL. The CH_2Cl_2/MeOH extract was obtained by filtration and washing the plant material with CH_2Cl_2/MeOH mixture, 240 ml. The collected filtrate was left in fume cupboard with suction for overnight to be concentrated to its¼ volume. Dilution with water, 200 ml, and exhaustive solvent extraction, using a separatory funnel, by petroleum ether (40-60ºC), followed by CH_2Cl_2, then AcOEt and finally n-BuOH gave the crude extracts Jp1, 13.6 g, Jp2, 1.6 g, Jp3, 17.4 g and Jp4, 7.03 g, respectively.

2.4 Separation of compounds

The pet. ether extract, Jp1, 5.6 g of which, was steam distilled. The distillate was extracted with diethyl ether and the ether extract was dried over anhydrous Na_2SO_4 to give the steam volatile fraction, Jp1a, 220 mg, which was analysed by GC/MS. A sample from the pet. ether extract, Jp1 was analysed by GC/MS. The steam nonvolatile material left in the distillation flask was extracted with diethyl ether and the ether extract was dried over anhydrous Na2SO4 to give the steam non-volatile fraction, Jp1b, 2.34 g.

The non-volatile fraction, Jp1b, was separated on silica gel CC, eluted with pet. ether (40-60oC) then pet. ether containing increased amounts of diethyl ether. The fractions 4 and 5 (out of 5), eluted by 2% ether in pet. ether and 1, 2 and 3 (out of 6), eluted by 5% ether in pet. ether, 267 mg, contained a mixture of 1 and 4 (4:1). The fraction 1 (out of 5), eluted by 10% ether in pet. ether, 14 mg, contained a mixture of 1, 5 and 6 (6:3:1). The fraction 4 (out of 11), eluted by 20% ether in pet. ether, 70 mg, contained 3. The fraction 10 (out of 11), eluted by 20% ether in pet. ether, 10 mg, contained β-sitosterol, and stigmasterol, (1:1).
The CH2Cl2 extract, Jp2, contained main component 2, which was purified by TLC (silica gel, diethyl ether/petroleum ether 1:50, Rf 0.72). To get rid of Na2SO4 crystals from AcOEt extract, as well as to fractionate it, it was loaded on 100 g silica gel (0.063-0.200 mm)/alumina, 1:2, in an addition funnel, and eluted by CHCl3/pet. ether, 3:1, then CHCl3 and finally 5% MeOH in CHCl3 to give two fractions Jp31 and Jp32, 110 and 59 mg, respectively. The fraction Jp31 gave by TLC (silica gel, diethyl ether/petroleum ether 1:50) compound 2 (110 mg, Rf 0.5). The fraction Jp32 contained fats (saturated fatty acids). The n-BuOH extract, Jp4, contained sugars and glycolipids.

2.5 The GC/MS analysis

The pet. ether extract, Jp1, gave by GC/MS α-thujene (Rt 3.05 min, 0.5%), α-pinene (Rt 3.14 min, 4.8%), sabenene (Rt 3.49 min, 1.4%), β-pinene (Rt 3.55 min, 1.2%), 3-carene (Rt 3.90 min, 1.9%), bornyl acetate (Rt 6.64 min, 1.0%), 4-terpenyl acetate (Rt 7.13 min, 1.2%), α-terpenyl acetate (Rt 7.22 min, 3.6%), α-cubebene (Rt 7.38 min, 1.0%), β-cedrene (Rt 7.92 min, 1.7%), cedrol (Rt 9.45 min, 3.3%), geranyl geraniol (Rt 12.55min, 4.3%), a mixture of 1, 2, 3 (Rt 13.72 min, 10.4%), a mixture of 4, 5 (Rt 14.48min, 28.4%), and 6 (Rt 14.85 min, 35.5%). The steam-volatile fraction of pet. ether extract, Jp1a, gave by GC/MS trans citral (Rt 5.55 min, 0.9%), terpinen-4-ol (Rt 5.59 min, 0.9%), α-terpineol (Rt 5.65 min, 1.6%), bornyl acetate (Rt 6.64 min, 1.8%), α-terpenyl acetate (Rt 7.13 min, 0.5%), β-cedrene (Rt 7.92 min, 1.4%), cedrol (Rt 9.45 min, 4.5%), α-cadinol (Rt 9.79 min, 1.8%), geranyl linalool (Rt 12.19 min, 4.1%), Z,E,E-geranyl geraniol (Rt 12.30 min, 3.2%), E,E,E-geranyl geraniol (Rt 12.55 min, 18.2%), linoleic acid (Rt 13.21 min, 2.3%), linolenic acid (Rt 13.29

min, 2.3%), stearic acid (Rt 13.70 min, 11.4%) unknown fatty acid (Rt 13.99 min, 6.8%), unknown fatty acid (Rt 14.71 min, 7.7%), unknown fatty acid (Rt 15.61 min, 12.7%), unknown fatty acid (Rt 16.70 min, 14.5%).

2.6 5,9,10-triepi-cupressic acid, 3:

Amorphous material, ^{1}H NMR: δ 5.90, 1H, dd (17.4, 10.8), H-14, 5.21, 1H, dd (17.4, 1.2); 5.06, 1H, dd (10.8, 1.2), H-15, H-15', 1.27, 3H, br s, H-16, 4.83, 1H, br s ; 4.49, 1H, br s, H-17, H-17', 1.23, 3H, s, H-18, 0.59, 3H, s, H-20; ^{13}C NMR: d 39.35, C-1, 20.10, C-2, 38.20, C-3, 44.39, C-4, 56.57, C-5, 26.29, C-6, 38.94, C-7, 148.30, C-8, 56.72, C-9, 40.89, C-10, 18.13, C-11, 41.58, C-12, 73.96, C-13, 145.23, C-14, 111.95, C-15, 29.23, C-16, 106.78, C-17, 28.30, C-18, 183.60, C-19, 12.95, C-20.

2.7 Total Antioxidant Capacity

Total antioxidant capacity of extracts was estimated using total antioxidant capacity kit of Bio-diagnostic [16], based on Koracevic et al. [15], for biological fluids, with slight modification to suit extracts.

2.8 Reagents

Substrate (H_2O_2, R1 from Bio-diagnostic)

Chromogen (3,5-dichloro-2-hydroxybenzene sulphonate, R2 from Bio-diagnostic)

Enzyme-Buffer (superoxide dismutase - Sodium phosphate buffer: 100 mmol/litre, pH 7.4, R3 from Bio-diagnostic)

2.9 Procedure

R1 was diluted with distilled water (1:1000) immediately before use (10 µl R1 was mixed with 10 ml distilled water). Equal volumes of R2 and R3 were mixed immediately before use (working reagent). The sample, 50 mg, was dissolved in methanol, 10 ml (pet. ether extract, CH_2Cl_2 extract, AcOEt extract). Ascorbic acid, as a reference antioxidant compound, 50 mg, was dissolved in methanol, 10 ml.
A blank experiment was conducted by mixing 20 µl distilled water and 0.5 ml diluted R1, standing 10 minutes, adding 0.5 ml of working reagent, standing 5 minutes, dilution with 1 ml distilled water and reading the absorption at 512 nm.
Ascorbic acid solution experiments were conducted by mixing 20, 10, 5 µl, separately, with 0.5 ml diluted R1, standing 10 minutes, adding 0.5 ml of working reagent, standing 5 minutes, dilution with 1 ml distilled water and reading the absorption at 512 nm.
Sample experiments were conducted by mixing 40, 20, 10, µl solution, separately, with 0.5ml diluted R1, standing 10 minutes, adding 0.5 ml of working reagent, standing 5 minutes, dilution with 1 ml distilled water and reading the absorption at 512 nm.

2.10 Calculation

%Inhibition = [(AB –AS)/ AB] x 100
where: AB is the absorbance of the blank sample, and AS is the absorbance of tested extract.

3. RESULTS AND DISCUSSIONS

The chromatographic separation of the extract of J. phoenicea L. fruits gave β-sitosterol, stigmasterol, four labdane 1-4 and two pimarane diterpenoids, 5 and 6, including a new labdane diterpenoid, 3. Additionally, the volatile compounds of the main petroleum ether extract, as well as the steam-volatile constituents were identified by GC/MS.

Compound 1 as E-communic acid was isolated previously from Juniperus taxifolia by Muto et al. [17]. Compound 2 was identified as 13-epi-torulosal, isolated previously from Juniperus rigida by Woo et al. [18]. Compound 4 was identified as 15-norlabda12,(17)8-E-diene 14-carboxaldehyde 19-carboxylic acid, isolated previously from Platycladus orientalis by Kuo and Chen [19]. Compound 6 was identified as isopimara-7-en-18-oic acid, isolated previously from *Pinus armandii* heartwood [20]. Compound 5 as sandracopimaric acid was identified by spectral data and confirmed by comparing ^{1}H NMR data with the corresponding compound isolated previously from Juniperus taxifolia [17] and with the 4-epimer, isolated previously from *Illicium jiadifengpi* [21]. In the 4-epimer, the methyl group (C-18) absorbs at 1.26 ppm instead of 1.21 for the methyl group (C-19). Sandracopimaric acid 5 and 4-episandracopimaric acid differ also in the chemical shift value of the methyl group (C-20), where in the former it absorbs at 0.84 ppm, versus 0.73 in case of the 4-epimer [21]. El-Sawi and Motawe [2] reported a diterpenoid as sandracopimaric acid from the fruits of Juniperus phoenicea L. grown in Egypt. They reported H-14, H-15, H-16 and H-20 at unjustified d values of 6.85, 3.59, 4.20 and 1.59 ppm, respectively. The identification of this compound is doubtful and should be revised. Compound 3 was separated from fraction 4 of the pet. ether nonvolatile fraction, Jp1b, eluted by 20% ether in pet. ether. It gave M+ at m/z 320, in agreement with $C_{20}H_{32}O_3$. The structure of 3 was elucidated by ^{1}H NMR. The 1H NMR spectrum of 3 (Table 1) was almost similar to that of 2, with the aldehydic proton signal no longer present and the methyl signal of C-18 shifted down-field from 0.97 in 2 to 1.23 ppm in 3, in agreement with 19-carboxylic acid. The good co-incidence between the signals of the side chain (H-14, H-15, H-15', H-16) in both compounds (2 and 3) indicated the same constitution of the side-chain at C-9 (Table 1). Comparing the ^{1}H NMR data of 3 with those of 13-epi-cupressic acid [18], 4,13-diepi-cupressic acid [22] and 4-epi-cupressic acid [23] indicated that H-16 in 13-epi-cupressic acid [18] shifted up-field by 0.09 ppm. Thus, the opposite configuration at C-13 is more probable.

Comparing the ^{13}C NMR data of 3 with those of 13-epi-cupressic acid [18] (Table 2) indicated obvious shifts in δ_C values of C-4, C-5, C-6 (- 0.29, - 0.17, +0.11, respectively), as well as those of C-10, C-20 (- 0.49, - 0.75, respectively) and those of C-13, C-16

(- 0.96, + 0.47, respectively). This indicated more probably the opposite configuration at C-5, C-10 and C-13. Comparing the ^{13}C NMR data with those of 4-epi-cupressic acid [23] (Table 2) indicated obvious shifts in δ_C values of C-5, C-6 (- 6.17, + 1.21, respectively), as well as those of C-10, C-20 (- 1.09, + 2.25, respectively) and those of C-3, C-4, C18, C19 (+ 0.60, + 3.51, - 10.70, - 2.30, respectively). This indicated more probably the opposite configuration at C-5, C-10 and C-4.

The NOESY experiment showed clear noe effects between H-20, H-17, H-17', H-16, H-18, H-11, H2α and H7α, as well as between H16, H18, H-14, H-15, H-17, H-7α and H-11. Thus 3 was identified as 5,9,10-triepicupressic acid.

The total antioxidant capacity considers the cumulative effect of all antioxidants present. Total antioxidant capacity of extracts was estimated using total antioxidantcapacity kit of Bio-diagnostic [16], based on Koracevic et al. [15], for biological fluids, with slight modification to suit extracts. Ascorbic acid was used as a reference antioxidant compound. Reasonable results were obtained by applying the modified method on petroleum ether extract, methylene chloride extract and ethyl acetate extract of *J. phoenicea* L.

Table 3 indicated the volumes taken from petroleum ether extract, methylene chloride extract and ethyl acetate extract of *J. phoenicea* L. and the corresponding absorptions at 512 nm. It is clear that as the quantity of extract increased, the (·OH) inhibition% increased and the absorption at 512 nm decreased. Table 4 and figure 2 indicated the (·OH) free radical inhibition % of ascorbic acid at concentrations 100, 50, 25 µg/ml. Table 5 and figure 3 indicated the (·OH) free radical inhibition % of petroleum ether, methylene chloride and ethyl acetate extracts of *J. phoenicea* L. at concentrations 200, 100, 50 µg/ml. A remarkable increase of (·OH) inhibition % happened when the concentration of the extract has been risen from 50 to 100 µg/ml. After that, the duplication of the extract concentration from 100 to 200 µg/ml has a little effect on the (.OH) inhibition %.

If we take into account that the molar mass of ascorbic acid is 176 g/mol, while average molar mass of J. phoenicea diterpenoids is about 310 g/mol; and also that extracts are not pure diterpenoids, we will realize that the J. phoenicea diterpenoids have remarkable total antioxidant capacity. The total antioxidant capacity of *J. phoenicea* diterpenoids could be attributed to the large unsaturation that accommodates the free radicals.

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Table 1: ^1H NMR data (600 MHz, $CDCl_3$, δ value, multiplicity (J value in Hz)) of 5,9,10-triepi-cupressic acid (**3**), compared with those of **2**, 13-epi-cupressic acid [5], 4,13-diepi-cupressic acid [10] and 4-epi-cupressic acid [11].

H-atom number	^1H NMR data of compound **3**	Compound **2**	13-Epi-cupressic acid	4,13-Diepi-cupressic acid	4-Epi-cupressic acid
14	5.90, 1H, dd (17.4, 10.8)	5.90, 1H, dd (17.2, 10.8)	5.88, 1H, dd (17.0, 10.5)	5.81, 1H, dd (17.2, 10.8)	5.92, 1H, dd (17, 10)
15, 15’	5.21, 1H, dd (17.4, 1.2); 5.06, 1H, dd(10.8, 1.2)	5.21, 1H, br d(17.2); 5.06, 1H, br d(10.8)	5.18, 1H, dd (18.0, 2); 5.02, 1H, dd(10.5, 2)	5.13, 1H, d(17.2); 4.98, 1H, d(10.8)	5.20, 1H, br d(17); 5.07, 1H, br d(10)
16	1.27, 3H, br s	1.27, 3H, s	1.18, 3H, s	1.22, 3H, br s	1.26, 3H, s
17, 17’	4.83, 1H, br s ; 4.49, 1H, br s	4.87, 1H, br s; 4.53, 1H, br s	4.82, 1H, s ; 4.51, 1H, s	4.79, 1H, s ; 4.48, 1H, s	4.84, 1H, br s; 4.52, 1H, br s
18	1.23, 3H, s	0.97, 3H, s	1.22, 3H, s	-	-
19	-	9.74, 1H, s	-	1.18, 3H, s	1.13, 3H, s
20	0.59, 3H, s	0.56, 3H, s	0.61, 3H, s	0.54, 3H, s	0.70, 3H, s

Table 2: ^{13}C NMR data (150.9 MHz, $CDCl_3$, δ value, multiplicity) of 5,9,10-triepi-cupressic acid (**3**), compared with those of 13-epi-cupressic acid [5] and 4-epi-cupressic acid [11].

C-atom number	^{13}C NMR data of compound **3**	13-Epi-cupressic acid	4-Epi-cupressic acid
1	39.35	39.3	38.0
2	20.10	20.0	19.3
3	38.20	38.3	38.8
4	44.39	44.1	47.9
5	56.57	56.4	50.4
6	26.29	26.4	27.5
7	38.94	38.7	38.6
8	148.30	148.6	148.9
9	56.72	56.8	58.0
10	40.89	40.5	39.8
11	18.13	18.0	18.5

12	41.58	41.5	42.5
13	73.96	73.0	73.1
14	145.23	145.1	147.3
15	111.95	110.8	111.5
16	29.23	26.7	29.1
17	106.78	105.7	107.6
18	28.30	28.4	181.3
19	183.60	183.5	17.6
20	12.95	12.2	15.2

Table 3: The volumes taken from petroleum ether, methylene chloride and ethyl acetate extracts of *J. phoenicea* L. and the corresponding absorptions at 512 nm.

Sample	**Volume taken in µl**	**Absorption at 512 nm**	**Inhibition %**
Blank		0.292	0
PE extract	40	0.089	69.5
	20	0.095	67.5
	10	0.218	25.3
CH_2Cl_2 extract	40	0.077	73.6
	20	0.099	66.1
	10	0.273	6.5
AcOEt extract	40	0.134	54.3
	20	0.156	46.6
	10	0.217	25.5

Table 4: The (·OH) free radical inhibition % of ascorbic acid at concentrations 100, 50, 25 µg/ml.

conc. µg/ml	**ascorbic acid**
100	97.86
50	96.41
25	95.72

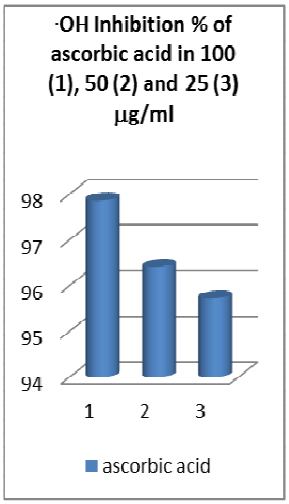
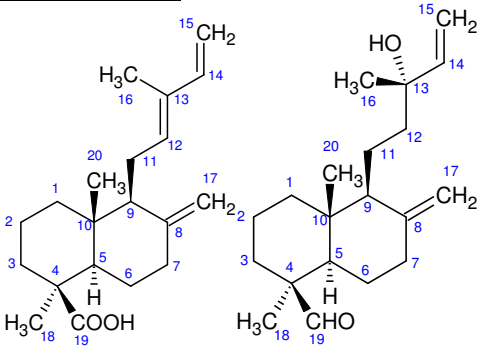


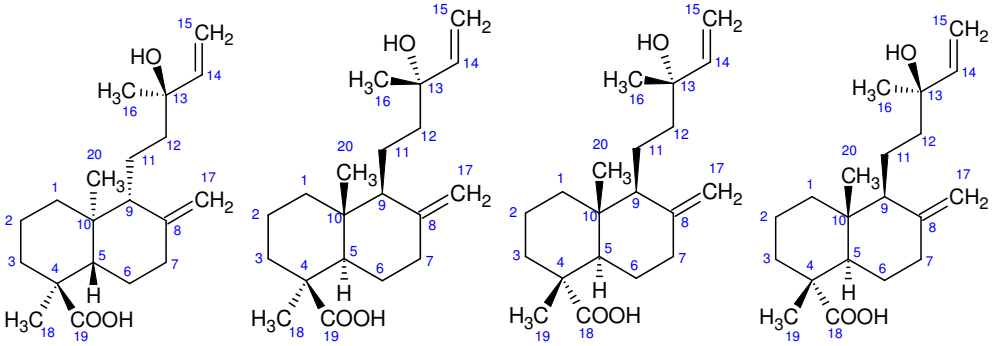
Fig 2: The (·OH) free radical inhibition % of ascorbic acid at concentrations 100, 50, 25 µg/ml.

Table 5: The (·OH) free radical inhibition % of petroleum ether, methylene chloride and ethyl acetate extracts of *J. phoenicea* L. at concentrations 200, 100, 50 µg/ml.

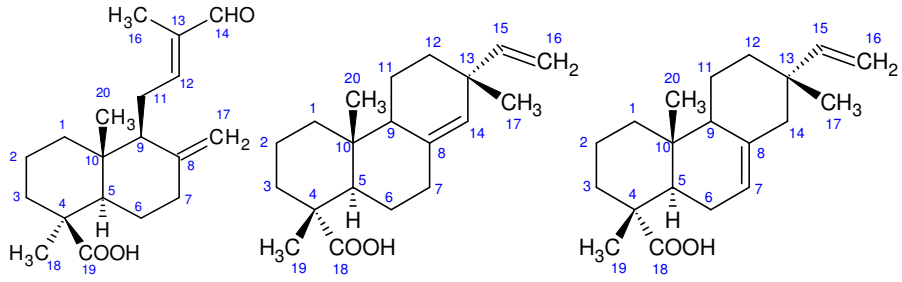
Conc. in µg/ml	**PE extract**	**CH_2Cl_2 extract**	**AcOEt extract**
200	69.5	73.6	54.3
100	67.5	66.1	46.6
50	25.3	6.5	25.5



E-Communic acid (**1**) 13-Epi-torulosal (**2**)



5,9,10-Triepicupressic acid (**3**) 13-Epi-cupressic acid 4,13-Diepi-cupressic acid 4-Epi-cupressic acid



15-Norlabda-8(17),12E-diene 14-carboxaldehyde 19-carboxylic acid (**4**) Sandracopimaric acid (**5**) Isopimara-7-en-18-oic acid (**6**)

Fig. 1: Isolated diterpenoids from *Juniperus phoenicea* L. fruits

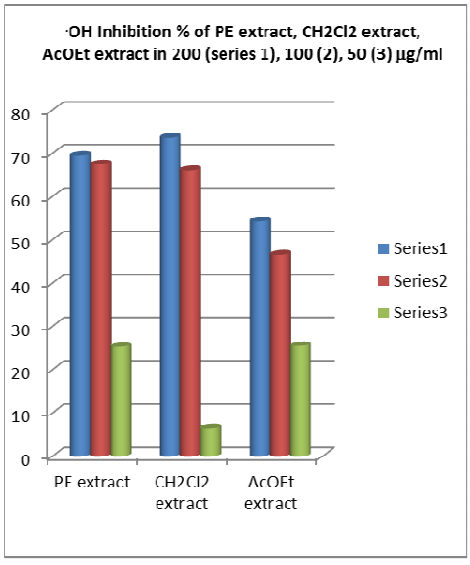


Fig 3: The (.OH) free radical inhibition % of petroleum ether extract, methylene chloride extract and ethyl acetate extract of *J. phoenicea* L. at concentrations 200, 100, 50 µg/ml.

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Photo-Oxygenation of Trans Anethole

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Abstract: Photo-oxygenation of *trans* anethole **(1)**, the main constituent of anise essential oil, using tetraphenylporphyrine (TPP) as a singlet oxygen sensitizer in chloroform gave 4-methoxybenzaldehyde (*p*-anisaldhyde) **(2)**, 2-(4-methoxyphenyl)propan-2-ol **(3)** as well as *erythro* and *threo* 1-(4-methoxyphenyl)propane-1,2-diol **(4a, 4b)**. The structures of the photo-oxygenation products were elucidated by spectral means.

Keywords: Photo-oxygenation, anethole, tetraphenylporphyrine, 4-methoxybenzaldehyde, 2-(4-methoxyphenyl)propan-2-ol**,** 1-(4-methoxyphenyl)propan-1,2-diol.

1. INTRODUCTION

Essential oils play an important role in our life because of their therapeutic activities and various applications in food industries. Essential oils are mixtures of various components like shikimates, mono-and sesquiterpenoids. The unsaturated essential oil compounds are easily oxidized, upon exposure to light, air and enhanced by temperature [1].
Photo-oxygenation reactions were carried out by several workers on some authentic individual monoterpenes, which occur frequently as major constituents of essential oils. We found that photo-oxygenation of essential oils has improved their biological activities [2].
The biological activities of *trans* anethole, as the main constituent of aniseed oil, before and after photo-oxygenation, including free radical scavenging, antimicrobial, deoxy ribonucleic acid (DNA) and protein cleaving, in addition to their hypoglycaemic effect were studied by Dawidar et al.,2008 [2].

Anise oil is obtained from the seeds of *Pimpinella anisum* L. (Umbeliferae). Its major constituent is *trans*-anethole (more than 60%) [1].
Schantz and Juvonen, 1969, reported that *trans*-anethole is autoxidized to its β- glycol, the amount of which increased initially during storage but decreased thereafter on further autoxidation *via* anisaldhyde to polymer. Thus the quality of aniseed oil depends on the presence or absence of the degradative oxidation products [3].
Garnero and Roustan, 1979, reported that *trans*-anethole undergoes a serious photo-rections as photoisomerization, photooxidation and photodimerization. Products as anisaldhyde, anise ketone, and anisic acid, are oxygenation products of *trans* anethole [4]. Lewis and Kojima, 1988, studied the mechanism of the photoisomerization, dimerization and oxygenation of *trans*- and *cis* anethole in terms of the role of monomer and dimer cation radicals [5]. Greer et al., 2000, reported on the effects of the added acid to the reaction of singlet oxygen with *trans* anethole. They suggested a new mechanism that invokes a proton transfer from methanol and benzoic acid to the formed perepoxide and Zwitter intermediates [6].
Mang *et al*., 2007, optimized a biocatalytic single-step alkene cleavage for aryl alkene compounds. They employed *trans* anethole as a model substrate, using hydrogen peroxide as an oxidizing agent. The products were identified as anisaldhyde and acetaldehyde [7]. Elgendy and Khayyat, 2008, performed photochemical oxidation of *trans* anethole using hydrogen peroxide where the corresponding epoxy derivatives together with 4-methoxybenzaldhyde were identified. They found that thermal oxidation of *trans* anethole with 3-chloroperoxybezoic acid at room temperature resulted in formation of dimeric epoxide, 2,5-bis(4-methoxyphenyl)-3,6-dimethyl-1,4-dioxin as the only product. Photo-oxygenation of *trans* anethole in the presence of tetraphenylporphyrine, Rose Bengal, or chlorophyll as sensitizers has led to a mixture of 1-(4-methoxyphenyl)prop-2-en-1-yl hydroperoxide and 4-methoxybenzaldhyde [8].

We reported here the identified photo-oxygenation products of *trans*-anethole using molecular oxygen.

2. EXPERIMENTAL

2.1 Materials:

TPP was obtained from Fluka Company. *trans* anethole was supplied by Sigma Company. Photo-oxygenation apparatus consists of sodium lamp (Phillips G/5812 SON), cylindrical jar (15w x 20l x 30h cm) filled with ethanol, sample tube which was inserted in the jar, and cooling unit with alcoholic thermometer. Dry oxygen was supplied from external cylinder. Distance between sodium lamp and sample tube was 10 cm.

2.2 General procedure for photo-oxygenation:

A solution of *trans* anethole (1 ml) in chloroform (50 ml) and a few mgs of tetraphenylporphyrine (TPP) was irradiated for 24 hrs. using the described apparatus. The solvent was evaporated at 20˚C/0.1 torr to give an oily material. The crude photooxygenation products were separated on silica gel column using petroleum ether (60-80˚C) as eluent to remove the sensitizer. The excess of *trans* anethole was eluted by petroleum ether: ethyl acetate (9:1). The photo products were eluted by petroleum ether: ethyl acetate (3:2), and separated by preparative TLC**.**

4-methoxybenzaldehyde (*p*-anisaldhyde) (2)

Colour: Pale yellow oil, UV, λ_{max} (ethanolic solution), nm: 276, 287; IR, ν, (oil film), cm^{-1}: 3020 (C–H, aromatic, str.), 2949, 2866 (CH_3 aliphatic and C-H aldehydic), 1690 (carbonyl group), 1590 (C=C aromatic), 1530 (C=C aliphatic); EIMS, m/z (rel. int.): 136 [M^+] (45) corresponding to $C_8H_8O_2$, 135 [M^+-H] (100), 107 [M^+-CHO] (30), 92 [M^+-CH_3 & CHO] (30), 77[M^+ - OCH_3 & CHO] (70); ^{1}H-NMR (300 MHz, $CDCl_3$) δppm: 3.89 (3H, s, OCH_3, H-7), 7.01 (2H, d, J = 8.7 Hz, H-2 and H-6), 7.84 (2H, d, J = 8.7 Hz, H-3 and H-5), 9.89 (1H, s, CHO, H-8).

2-(4-methoxyphenyl)propan-2-ol (3)

Colour: Light yellow oil, UV, λ_{max} (ethanolic solution), nm: 249, 315; IR, ν, (oil film), cm^{-1}: 3443 (broad band, OH group), 3052 (C–H, aromatic, str.), 2969, 2934 (CH_3 aliphatic), 1380, 1020, and 938; ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm: 1.25 (6H, s, $2CH_3$), 3.88 (3H, s, OCH_3), 6.70 (1H, s, OH), 6.95 (2H, d, J= 8 Hz, H-3, H-5), 8.04 (2H, d, J =8 Hz, H-2, H-6); EIMS, m/z (rel. int.): 166 [M^+] (0.5), 165 [M^+-1] (14), 149 [M^+-OH] (89), 148 [M^+-H_2O] (13), 135 [M^+-OCH_3] (49), 107 [M^+-C_3H_7O] (10), 76 [M^+-OCH_3 & C_3H_7O] (22), 71 (59), 70 (30), 69 (50), 57 (100).

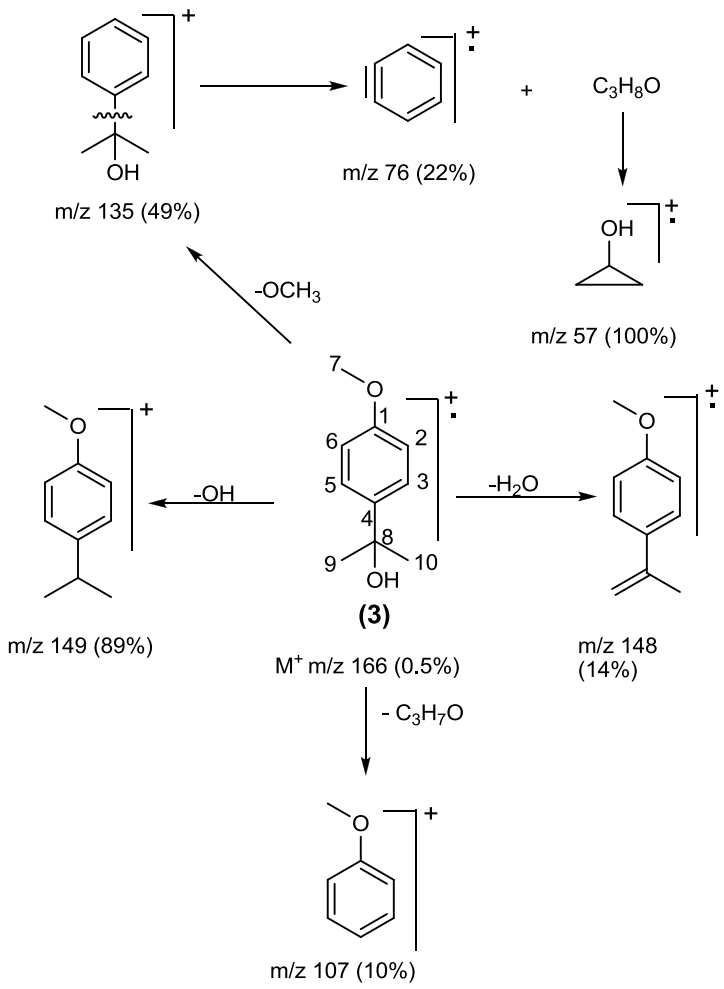
1-(4-methoxyphenyl)propane-1,2-diol (4a, 4b) (2:1 molar ratio)

Colour: Light yellow oil, UV, λ_{max} (ethanolic solution), nm: 269, 282; IR, ν, (oil film),cm^{-1}: 3450-3500 (broad band, OH group), 3062, 3027(C–H, aromatic, str.), 2954, 2925, 2856 (CH_3 aliphatic), 1600 ((C=C aromatic),1450, 1070, and 1027; ^{1}H-NMR (300 MHz, $CDCl_3$) δ ppm (4a): 1.05 (3H, d, J= 6.6 Hz, H-10a), 1.750 (1H, br.s, OH), 2.62 (1H, br.s, OH), 3.82 (3H, s, OCH_3), 3.84 (1H, m, H-9a), 4.33 (1H, d, J = 7.8 Hz, at C-8a), 6.89 (2H, d, J= 8.7 Hz, H-2a, H-6a), 7.29 (2H, d, J= 7.8 Hz, H-3a, H-5a); ^{1}H-NMR (300 MHz, $CDCl_3$) δ ppm (4b) : 1.11 (3H, d, J= 6.6 Hz, H-10b), 1.75 (1H, br.s, OH), 2.62 (1H, br.s, OH), 3.82 (3H, s, OCH_3), 4.00 (1H, m, H-9b), 4.60 (1H, d, J = 7.8 Hz, H-8b), 6.89 (2H, d, J = 8.7 Hz, H-2b, H-6b), 7.29 (2H, d, J = 7.8 Hz, H-3b, H-5b); EIMS m/z (rel.int.): 182 [M^+] (3), 167 [M^+-CH_3] (6), 151[M^+-OCH_3] (4), 148 [M^+-2OH] (28) 164 [M^+-H_2O] (5), 137 [M^+-H_2O & C_2H_4] (82), 136 (10), 135 (22), 133 (5), 109 (28), 107 [M^+-$C_3H_7O_2$] (10), 97 (36), 85 (51), 84 (25), 83 (68), 81 (28), 71 (57), 69 (65), 57 (100), 54 (78).

3. RESULTS AND DISCUSSIONS

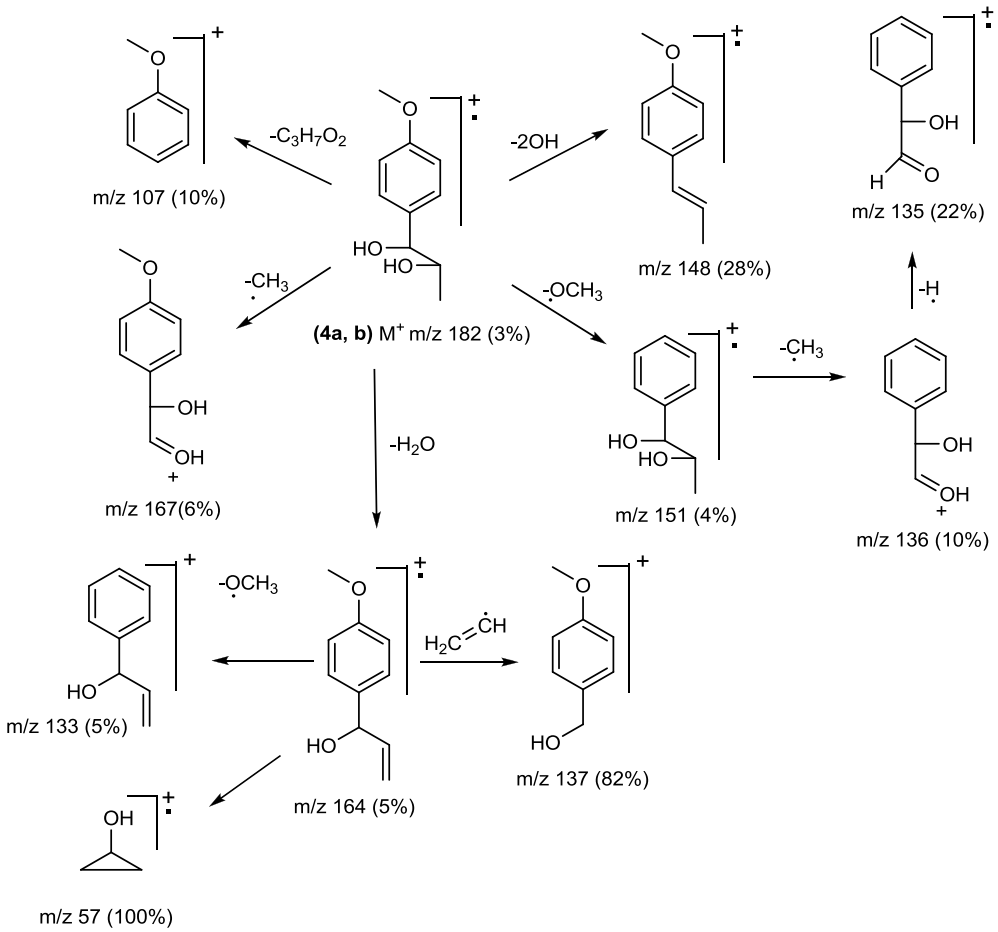
The reaction was carried out in $CHCl_3$, in the presence of tetraphenylporphyrine (TPP) as a singlet oxygen sensitizer at -20˚C for 24 hrs. The resulting mixture was separated to three products identified as 4-methoxybenzaldehyde (*p*-anisaldhyde) **(2)**, 2-(4-methoxyphenyl)propan-2-ol **(3)** and *erythro* and *threo* 1-(4-methoxyphenyl)propane-1,2-diol **(4a, 4b)**.

The IR spectrum of **(2)** showed the carbonyl absorption band at 1690 cm^{-1}. Its ^{1}H-NMR spectrum revealed the presence of a singlet at δ 9.89 ppm, characteristic for the aldehydic proton and signals of *p*–disubstitued benzene (AA'BB' spin system at δ 7.84 ppm with coupling constant 8.7 Hz). Additionally, the spectrum showed the methoxyl protons at δ 3.89 ppm as a singlet. The mass spectrum of (**2**) indicated a M^+ at m/z 136 (45%) corresponding to the molecular formula $C_8H_8O_2$, and a base peak at m/z 135 (100%) due to [M^+-H].
The ^{1}H-NMR spectrum of **(3)** showed a *p*–disubstitued benzene (AA'BB' spin system at δ 8.04 and 6.95 ppm with coupling constant 8 Hz), two methoxyl and hydroxyl protons singlets at δ 3.88 and 6.70 ppm, respectively. This is in addition to a singlet of six protons at δ 1.25 ppm which was assigned to a dimethyl carbinol group. The mass spectrum of (**3**) showed ion peaks due to [M-OH], [M-H_2O], [M-OCH_3], [M-C_3H_7O] at m/z 149, 148, 135, and 107 respectively.



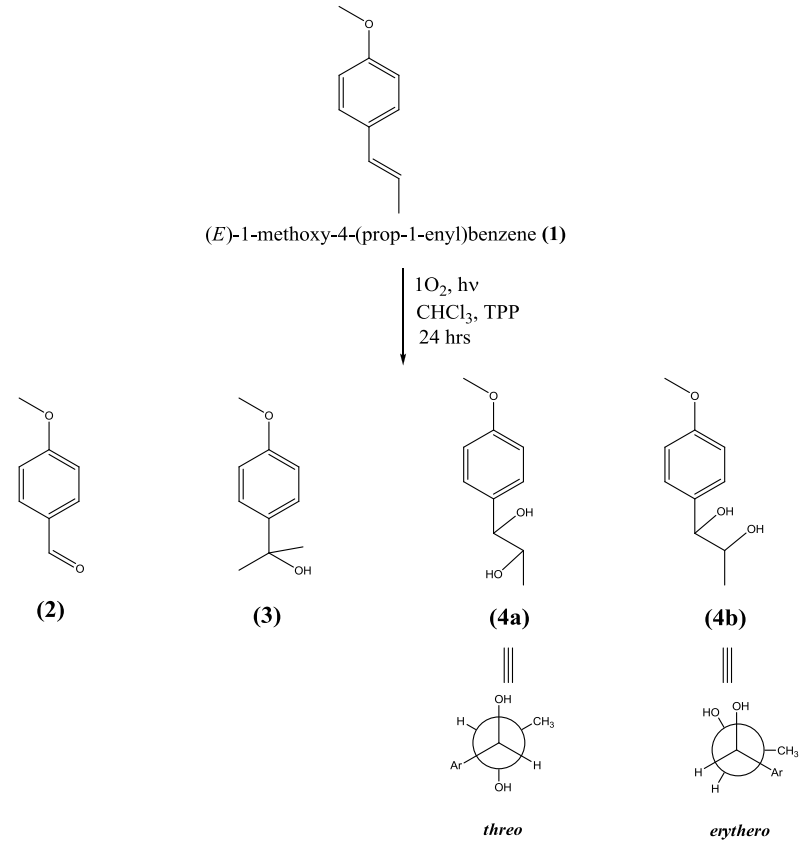
A proposed fragmentation pattern of 3

Products **(4a, b)** as a mixture were identified as *erythro* and *threo* 1-(4-methoxyphenyl)propan-1,2-diol. The IR spectrum revealed the presence of hydroxyl groups, due to the absorption broad band at 3450 -3500 cm^{-1}. ^{1}H-NMR spectrum showed *p*–disubstitued benzene (AA'BB' spin system at δ 7.29 and δ 6.89 ppm with coupling constant 8.7). The spectrum also showed a singlet at δ 3.82 ppm for the methoxyl groups. Protons of methyl groups in positions C-10a and C-10b gave the characteristic doublets at δ 1.05 and 1.11 ppm with coupling constant 6.6 Hz, whereas protons at 8a and 8b showed two doublets at δ 4.33 and 4.60 ppm with coupling constant 7.8 Hz for both. Protons at C-9a and C-9b appeared as multiplets at δ 3.84 and 4.00 ppm, respectively. Protons of hydroxyl groups were viewed at δ 1.75 and 2.62 ppm. The mass spectrum showed a molecular ion peak M^+ at m/z 182 (3%) corresponding to the molecular formula $C_{10}H_{14}O_3$.



A proposed fragmentation pattern of 4a and 4b

A probable formation of *p*-anisaldhyde (**2**) and the glycols 4a, 4b may be through the dioxetane intermediate. Whereas, the photo product **(3)** may be obtained through 1, 2 carbon shift followed by singlet oxygen attack in the protic solvents.



Scheme 1: Photo-oxygenation of *trans* anethole (1)

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A Review on Basic Concepts and Important Standards of Power Quality in Power System

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Abstract: This paper deals with the basic of Power quality in power system. In addition basic definition and important concepts was discussed in simple way. This paper also covers the important power quality standards. In addition IEEE, IEC, SEMI and UIE Power quality standards are listed. This paper would be helpful for the UG and PG students to study about the basics of Power quality in electrical engineering.

Keywords: Transients, Harmonics, Overvoltage, Voltage flickers, PQ standards

1. INTRODUCTION

Power quality determines the fitness of electric power to consumer devices. Synchronization of the voltage frequency and phase allows electrical systems to function in their intended manner without significant loss of performance or life [1]. The term was used to describe electric power that drives an electrical load and the load's ability to function properly. Without the proper power, an electrical device (or load) may malfunction, fail prematurely or not operate at all [2]. There are many ways in which electric power can be of poor quality and many more causes of such poor quality power.

The quality of electrical power depends upon the following factor

- Continuity of service
- Variation in voltage magnitude
- Transient voltages and currents
- Harmonic content in the waveforms

2. BASIC DEFINITION IN POWER QUALITY

2.1 Power Quality

The term electric power quality broadly refers to maintaining a near sinusoidal power distribution bus voltage at rated magnitude and frequency. Other definition of power quality refers to the delivery of high grade of electric service maintaining a sinusoidal load, bus voltage and current at stipulated magnitude and frequency.

2.2 Custom power devices:

The technology of the application of power electronics to power distribution system for the benefit of a customer group of customers is called custom power [12]. The device used for this purpose is called custom power devices.

Example of custom power devices are DSTATCOM, DVR and UPQC.

2.3 Brownout

Brownout by definition is low voltage for an extended period of time (greater than half a cycle) in which the magnitude of the voltage is reduced [3].

2.4 DC offset

The presence of a dc voltage or current in an ac power system is termed DC offset. This can occur as the result of a geomagnetic disturbance or asymmetry of electronic power converters.

2.5 Inter harmonics

Voltage or currents having frequency components that not integer multiples of the frequency at which the supply system is designed to operate (example: 50 or 60 Hz0) are called inter harmonics [4]. They can appear as discrete frequencies or as a wideband spectrum. Inter harmonics can be found in networks of all voltage classes.

2.6 Voltage flickers

Voltage flickers is rapidly occurring voltage sags caused by sudden and large increases in load current. Voltage flicker is most commonly caused by rapidly varying loads that require a

large amount of reactive power such as arc furnaces, electric welders, rock crushers, sawmills, wood chippers, metal shredders and amusement rides [11]. It can cause visible flickers in lights and cause other processes to shut down or malfunction.

2.7 Harmonics

Harmonics is a sinusoidal component of a periodic wave or quantity having a frequency that is an integral multiple of the fundamental power frequency. The equation representing a harmonic frequency is given by:

$$fh=f1*h$$

Where f1 is the fundamental frequency and h is the harmonic order.

2.8 Voltage and Current distortion

Voltage distortion is any deviation from the nominal sine waveform of the line voltage. Current distortion is any deviation from the nominal sine waveform of the AC line current [5].

2.9 Oscillatory transients over voltages

Switching operations within the distribution network are a major cause of oscillatory transients over voltages. Such operations include

• Switching of utility capacitors banks

• Switching of circuit breakers to clear network fault

• Switching of distribution feeders to rearrange the networks for maintenance or construction.

2.10 Waveform distortion

It is the deviation from an ideal sine wave of power frequency principally characterized by the spectral content of the deviation. Harmonics is one of the causes of many types of waveform distortion.

2.11 Sag

Voltage sag is an event in which the RMS voltage decreases between 0.1 and 0.9 per unit at the power frequency. It lasts for durations of 0.5 cycles to 1min.

2.12 Swell

Swell is an event in which the RMS voltage increases between 1.1 and 1.8 per unit at the power frequency. It lasts for durations of 0.5 cycles to 1min.

2.13 Impulsive transients

An impulsive transient is a sudden, non-power frequency change in the steady state condition of the voltage and/or current waveforms that is essentially in one direction, either positive or negative, with respect to those waveforms. The most common cause of this type of transient is lightning.

3. BASIC CONCEPTS IN POWER QUALITY

3.1 Most common power quality problem

Voltage sags are considered the most common power quality problem. These can be caused by the utility or by customer loads. These sags will be from 3 to 30 cycles and can be single or three phase [6]. Depending on the design of the distribution systems, a ground fault on 1 phase can cause a simultaneous swell on another phase.

3.2 Specifications for good power quality of power

The variation of electrical quality should be within guaranteed tolerance limit. The wave should be a pure sine wave within allowable limits for distortion.

Voltage should be balanced in all 3 phases.

Supply should be reliable.

The earthing system should serve its purpose properly.

3.3 Power quality important

Power quality is an increasingly important issue for all businesses. Problems with powering and grounding can cause data and processing errors that affect production, damaged product and service quality [10].

3.4 Causes of sags

Voltage sags are usually associated with system faults but can also be caused by the switching of heavy loads. Voltage sags are caused by motor starting, for example, an induction motor will draw six to ten times its full load current. This lagging current causes a voltage drop across the impedance of the system.

3.5 Components of waveform distortion

• DC offset
• Notches
• Flickers
• Harmonics
• Noises
• Inter harmonics

3.6 Classifications of power quality events in short duration events

• Sag
• Swell
• Interruption

3.7 Types of power quality solutions available on the market today

There are hundreds of manufacturers making thousands of different power quality solutions today. The categories of these solutions are

• Utility based solutions for the substations level.
• User based solution for whole facility protection.
• User load level solutions for specific loads.

3.8 Power quality problems can be detected by following method

• A Piece of equipment misoperates at the same time of day.
• Circuit breakers trip without being overloaded.
• Equipment fails during a thunderstorm.
• Automated systems stop for no apparent reason.

3.9 Various power quality issues

• Poor load power factor

• Harmonics contents in loads
• Notching in load voltages
• Unbalanced loads
• Supply voltage distortion
• Voltage sags/swell
• Voltage flicker

3.10 Effects of brownout

• Temporary low line voltage.
• Shutdowns.
• Loss of microprocessor memory.
• Loss of control.
• Overheating of motors- insulation breakdown.
• Protective device tripping.
• Speed variation
• Reduced motor torque, which can lead to stalling [7].

3.11 Adverse effects of low power factor

• Increased line losses I^2R
• Wasted generation capacity (KVA)
• Wasted distribution/transformer/capacity (KVA)
• Wasted system capacity (KVA)
• Reduced system efficiency (KW)
• Increased maximum demand (KVA) and related charges.
• Possible power factor charges.

3.12 Different types of sag mitigation devices

Dynamic Voltage Restorer (DVR)
Active series compensators (Transformer less series injection)
Solid State (static) Transfer switches (SSTS)

3.13 Important role of a DVR

The basic idea of a DVR is to inject a controlled voltage generated by a forced commuted converter in series to the bus voltage by means of an injecting transformer [8].

3.14 Harmonics effects on devices and loads

• Insulation stress (voltage effect)

• Thermal stress (current effect)

• Load ruptures (abnormal operation)

3.15 Various causes of over voltages

• Atmospheric discharges, i.e, lightning.
• Switching operations in the public grid and low-voltage mains.
• Electrostatic Discharges.
• Ferro resonance

4. IMPORTANT STANDARDS OF POWER QUALITY

The most universally accepted standards for power quality are IEC and IEEE standard. Both standards adopt some of the other organization standards [9]. For example IEEE adopts some of ANSI standards as IEEE standards for some specific issues. The following Table 1 shows the important power quality standards

Table 1 Important power quality standards

S. No.	Abbreviation	The standard name
1	IEEE	Institute of Electrical and Electronics Engineer
2	IEC	International Electro technical Communication
3	CENELEC	European committee for Electro technical Standardization
4	ANSI	American National Standards Institute
5	NER	National Electricity Regulator
6	SEMI	Semiconductor Equipment and Material International
7	UIE	International Union for Electricity Applications

4.1 IEC Standards

The following table 2 shows the Some IEC standards for power quality events

Table 2 Some IEC standards for power quality events

IEC 61000 2-5:1995[2], IEC 61000 2-1:1990[3], IEEE 1159:1995[4]	Characterization of power quality events
IEC 61000 2-1:1990[3], IEEE 1159:1995[4], IEC816:1984[6]	Transients
IEC 61000 2-1:1990[3], IEEE 1159[4],	Voltage sag/swell
IEC 61000 2-1:1990 [3], IEEE 1159:1995[4]	Interruptions
IEC 61000 2-1: 1990[3]: IEEE 519:1992[7], IEC61000 4-7: 1991[8]	Harmonics
IEC 61000 4-15: 1997[9]	Voltage flicker

4.2 IEEE Power Quality Standards

• IEEE Std 141-1993, IEEE Recommended Practice for Electric power Distribution for Industrial Plants (IEEE Red Book) (ANSI).

• IEEE Std 142-1999, Recommended practice for Grounding of Industrial and Commercial power Systems (IEEE Green Book) (ANSI).

• IEEE Std 241-1990, IEEE Recommended Practice for Electric Power Systems in Commercial Buildings (IEEE Gray book) (ANSI).

• IEEE Std 242-1986, IEEE Recommended Practice for Protraction and Coordination of Industrial and Power Systems (IEEE Buff Book)(ANSI).

• IEEE Std 399-1990, IEEE Recommended Practice for Industrial and Commercial Power Systems Analysis (IEEE Brown Book) (ANSI).

• IEEE Std 446-1987, IEEE Recommended Practice for Emergency and Standby power Systems for Industrial and Commercial Application (IEEE Orange Book) (ANSI).

• IEEE Std 487-1992, IEEE Recommended Practice for the Protection of Wire Line Communications Facilities Electric Power Stations.

• IEEE Std 493-1990, IEEE Recommended Practice for the Design of Reliable Industrial and commercial power Systems (IEEE Gold Book) (ANSI).

• IEEE Std 518-1982, IEEE Guide for the Installation of Electrical Equipment to Minimize Noise Inputs to Controllers from External Sources (Reaff 1990) (ANSI).

• IEEE Std 519-1992, IEEE Recommended Practice and Requirement for Harmonics Control in Electric Power Systems (ANSI).

• IEEE P519A, Guide for Applying Harmonics Limits on Power Systems.

• IEEE Std 602-1986, IEEE Recommended Practice for Electric Systems in Health Care (ANSI).

• IEEE Std 739-1995, IEEE Std 739-1995 IEEE Recommended Practice for Energy Management In Industrial And Commercial Facilities (The Bronze Book) Systems (ANSI).

• IEEE Std 929-2000, IEEE Recommended Practice for Utility Interface Photovoltaic (PV) Systems (ANSI).

• IEEE Std 1001-1988, IEEE Guide for Interfacing Dispersed Storage and Generation Facilities with Electric Utility Systems (ANSI).

• IEEE Std 1035-1989, IEEE Recommended Practice: Test Procedure for Utility Interconnected Static Converters (ANSI).

• IEEE Std 1050-1989, IEEE Guide for Instrumentation and Control Equipment Grounding in Generating Station (ANSI).

• IEEE Std 1100-1992, IEEE Recommended Practice for Powering and Grounding Sensitive Electronic Equipment (Emerald Book) (ANSI).

• IEEE Std 1159-1995, IEEE Recommended Practice for Monitoring Electrical Power Quality.

• IEEE Std 1159.1-2003, IEEE Guide for Recorder and Data Acquisition Requirements for characterization of Power Quality Events.

• IEEE Std 1159.2-2003, IEEE Power Quality Event Characterization Status Under Preparation.

• IEEE Std 1159.3-2003, IEEE Recommended Practice for the transfer of Power quality data.

• IEEE Std 1250-1995, IEEE Guide for Service to Equipment Sensitive to Momentary Voltage Disturbance (ANSI).

• IEEE P1346-1998, Recommended Practice or Evaluating Electric Power Systems Compatibility with Electronic Process Equipment.

• IEEE P1433, Power Quality Definition Status:

• IEEE P1453, Voltage Flicker Status:

• IEEE Std C57.110-1986, IEEE Recommended Practice for Establishing Transformer Capability when Supplying Non sinusoidal Load Currents (ANSI).

• IEEE Std C62.41-1991, IEEE Recommended Practice on Surge Voltage in Low Voltage AC Power Circuits (ANSI).

• IEEE Distribution, Power and Regulating Transformers Standards Collection, 1995 Edition (C57) (ANSI).

• IEEE Surge Protection Standards Collection, 1995 Edition (C62) (ANSI).

4. 3 IEC Power Quality Standards

IEC 61000 Series, Electromagnetic Compatibility (EMC) defines for the following:

Part 1: Definition and Methodology 61000-1-X: Dealing with fundamental definition, etc.

Part 2: Environment 61000-2-X, deals with the characteristics of the environment will be supplied, and its compatibility levels.

Part 3: Limits 61000-3-X, define the permissible emission that can be generated by the equipment connected.

Part 4: Tests and measurements 61000-4-X, Testing and measurement techniques provide detailed guidelines for measurement equipment.

Part 5: Installation and mitigation 61000-5-X, provide guidelines for cabling of electrical and electronics systems, etc. They also describe protection concepts from high-altitude nuclear explosions.

Part 6: Generic immunity and emission 61000-6-X, defining immunity and emission levels required for equipment in general categories or for specific types of equipment.

4.4 SEMI Power Quality Standards

• SEMI F47-0200, Specifications for Semiconductor Processing Equipment Voltage Sag Immunity.

• SEMI F42-0600, Test Method for Semiconductor Processing Equipment Voltage Sag Immunity.

4.5 UIE Power Quality Standards

• UIE-DWG, Guide to Quality of Electrical Supply for Industrial Installation, Part 1: General Introduction to Electromagnetic Compatibility (EMC).

• UIE-DWG, Guide to Quality of Electrical Supply for Industrial Installations, Part 2: Voltage Dips and Short Interruption.

• UIE-DWG, Guide to quality of Electrical Supply for Industrial Installations, Part 3: Voltage Distortion

• UIE-DWG, Guide to Quality of Electrical Supply for Industrial Installation Part 4: Voltage Unbalance.

• UIE-DWG, Guide to Quality of Electrical Supply for Industrial Installation Part 5: Flicker.

5. CONCLUSION

This paper shows the basic concepts of power quality in power system. A special attention was also given to the important of power quality standards. It was the part of Power Quality subject. This paper would give a special knowledge for the UG students to study some fundamentals of power quality.

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Photo-Oxygenated Derivatives from Eugenol

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Abstract: Photo-oxygenation reaction was performed on eugenol (**1**) (2- methoxy-4-(2'-propenyl) phenol) in chloroform as a solvent and tetraphenyl porphrine (TPP) as singlet oxygen sensitizer. Irradiation of the reaction mixture was carried out by sodium lamp at -20 °C for six hrs., during which dry oxygen was allowed to pass through the reaction mixture. Two hydroperoxides (**3**) and (**4**) were formed. Eugenol methyl ether (**2**) was also photo-oxygenated under the same conditions of eugenol, where only the side chain was photo-oxygenated at position C-1' to give product (**5**). In addition to the epoxide derivative of eugenol methyl ester (**8**) was prepared and its reaction with aminoantipyrine was carried out to give product (**9**). Product (**8**) could be considered as a DNA- alkylating agent.

Keywords: Eugenol, Photo-oxygenation, Eugenol hydroperoxide, Eugenol methyl ether, Antipyrine, DNA-alkylating agent.

1. INTRODUCTION

Eugenol, [2-methoxy-4-(2'-propenyl) phenol], a pale yellow liquid is the major constituents of clove essential oil (80-87 %) obtained from the buds of *Eugenia caryophyllata* (family Myrtaceae) [1]. Eugenol was subjected to extensive biological, medicinal and chemical studies. For example it was reported as antimicrobial [2], antioxidant [3], anticancer [4] and anti-inflammatory agent [5]. Eugenol was also used as a dental medicament due to its analgesic effect [6]. Moreover, it inhibits glulathione-δ-transferase (GST) and cause protection against background damage of liver [7].

Eugenol was converted into 2-methoxy-4-(prop-2-en-1-yl) phenyl hydroperoxide by oxidation with H_2O_2 under irradiation [1]. Thermal oxidation of eugenol with $3\text{-}ClC_6H_4CO_3H$ at room temperature produced 2-methoxy-4-(oxiran-2-ylmethyl) phenol, while sensitized photochemical oxygenation (using Rose Bengal or chlorophyll) gave 4-hydroperoxy-2-methoxy-4-(prop-2-en-1-yl)cyclohexa-2,5-dien-1-one [1].

The major photochemical product from eugenol found to be 4-cyclopropy-2-methoxyphenol in addition to 2-(3-methoxy-4 hydroxybenzene)-1-methylethyl iso-propyl ether were obtained [8]. On the other hand, when eugenol was exposed to sunlight in iso-propanol for 10 days under atmospheric oxygen, numerous compounds were produced including those produced by irradiation with a mercury lamp [8].

Eugenol was irradiated in a methanol solution for various periods. The main photochemical product was 4-cyclopropyl-2-methoxyphenol (12-28%). In addition to the cyclopropyl derivative, three methanol solvent addition products, 2-methoxy-4-propylphenol (4-7%), 2-methoxy-4-(2-methoxypropyl)phenol (3-7%), and 2-methoxy-4-(1-methoxypropyl) phenol, were formed. The solvent addition products were not obtained when MeCN was used as a solvent. The eugenol-related compounds, methyleugenol also produced cyclopropyl derivatives. 1-cyclopropyl-3,4-dimethoxyeugenol upon photochemical irradiation. The photochemical reaction mechanisms of eugenol are postulated to be di-π-methane rearrangement, disproportionation reaction, and addition reaction. The cyclopropyl derivatives possessed an interesting floral, spicy odor [9].

Due to the versatile medicinal and pharmaceutical applications of eugenol, we wish to report here our obtained results of eugenol photo-oxygenation reaction in addition to its methyl ether.

2. EXPERIMENTAL

2.1 General

Ultraviolet spectra were recorded on a Unicam UV 2100 ultraviolet spectrophotometer. Infrared Spectra were performed on a Unicam Sp 2000 infrared spectrophotometer. ^{1}H-NMR Spectra were obtained in $CDCl_3$ on Brucker 250 MHz apparatus. The photolysis apparatus used are a sodium lamp (phillips G/5812 SON) and a tungsten-halogen lamp (Lohuis R75). Thin layer chromatography (TLC): polygram SIL G/UV 254 nm, Macherey-Nagel. Column chromatography: silca gel 60 (0.063-0.200 mm), Merck. For the removal of the solvent a rotatory evaporator (at 20 °C /15 torr) was used.

2.2 Isolation of eugenol

The volatile clove oil was extracted from clove (*Eugenia caryophyllusi*) by steam distillation. Eugenol was isolated by treatment of the extracted oil with an aqueous sodium hydroxide solution (3-5%). The non-phenolic constituents were extracted with chloroform. The aqueous alkaline solution was acidified with dilute hydrochloric acid to give eugenol (1) (80-87 %), which was extracted by chloroform.

2.3 Methylation of eugenol

A solution of eugenol (**1**) (2 gm) in acetone (8 ml) and in the presence of sodium hydroxide (20 ml, 56%) was stirred on an ice bath. During the stirring, dimethyl sulphate (2 ml) was added dropwise to the reaction mixture which was stirred for 6 hours, then poured on ice cold water. Methyl eugenol ether (**2**) was extracted with chloroform (3x20 ml), washed with water (3x20 ml) and dried over anhydrous sodium sulphate. The solvent ($CHCl_3$) was evaporated under reduced pressure to give methyl eugenol ether (2) as a pale yellow oil (1.604 gm, 80% yield).

2.4 Photo-oxygenation of eugenol (1)

A solution of **1**(1 gm) and 2 mg tetraphenyl porphrine (TPP) in $CHCl_3$ (20 ml) was irradiated externally by means of a sodium lamp (Phillips G/5812 SON) at -20 °C for 6 hours. During the irradiation a continuous steam of dry oxygen gas was allowed to pass through the reaction mixture at a slow rate to avoid the solvent evaporation (TLC, peroxide test by KI, 10%). The solvent was removed at 20°C/ 0.1 Torr to give gummy material. The crude products were purified by column chromatography on silica gel by elution with a solvent mixture of petroleum ether 60-80°C and ethyl acetate (4:1) to give eugenol hydroperoxide derivative (**3**) (150 mg, 15% yield) and eugenol dihydroperoxide derivative (**4**) (80 mg 8% yield), both were obtained as pale yellow oils.

2.5 Photo-oxygenation of methyl eugenol ether (2)

A solution of **2** (1 gm) was photooxygenated as in the case of **1**. The crude product was purified by column chromatography as above to give the methyl eugenol hydroperoxide derivative (**5**) as the sole oily product.

2.6 Photo-irradiation of eugenol dihydroperoxide derivatives (4)

A solution of **(4)** (0.5 gm) in benzene (20 ml) was irradiated externally by means of tungsten- halogen lamp at room temperature for 10 hours. Ferric chloride test of the reaction mixture showed phenol was formed. The solvent was removed under reduced pressure to give a gummy material, which was purified by column chromatography, on silica gel adsorbent. Elution of the column with the solvent mixture of petroleum ether 60-80 °C and ethyl acetate (4:1) yielded eugenol dihydroxide derivative (**6**) as a viscous oil.

2.7 Photo-irradiation of methyl eugenol hydroperoxide derivative (5)

A solution of **5** (0.5 gm) in benzene (20 ml) was irradiated as in the case of **4**. Ferric chloride test of the reaction mixture showed phenol formation. The purification of the crude photo- product (**6**) was carried out as in the case of **6** where it gave methyl eugenol hydroxide derivative (**7**) as viscous oil.

2.8 Epoxidation of methyl eugenol ether (2)

A solution of **2** (0.8 g, 5 mmol) in $CHCl_3$ (25 ml) was added portionwise to *m*-chloroperbenzoic acid (CPBA) (l0 mmol, 80%) at 0 °C. The reaction mixture was stirred at room temperature (TLC, peroxide test by KI, 10%). It was washed with a saturated aqueous solution of $NaHCO_3$ (3x10 ml), then with distilled water (3xl 0 ml). The organic layer was separated, dried over anhydrous Na_2SO_4 and evaporated under reduced pressure at room temperature. The crude residue product was purified by column chromatography on silica gel adsorbent. Elution of the column with the solvent mixture petroleum ether 60-80 °C and ether (9:2) gave eugenol epoxide (**8**) as viscous oil.

2.9 Treatment of epoxide derivative (8) with antipyrine

A mixture of epoxide (**8**) and antipyrine (0.168 g 1.2 mmol) was fused at 120 °C for 20 min. The crude product was recrystallized from ethanol to give the adduct (**9**) as gummy brown material (0.0293 g, 60 % yield).

Spectral data of compound (1):

UV (Ethanol), λ max: 232, 289 and 342 nm
IR (Thin Film), ν: 3543, 3019, 2938, 2847, 1609, 1513 and 1145 cm^{-1}
^{1}H-NMR ($CDCl_3$), δ ppm: 6.92 (d, 1H, J=10 Hz, H-9), 6.92 (m, 2H, H-5,8), 6.0 (m, 1H, H-2), 5.80 (s, 1H, OH), 5.20 (m, 1H, H-la), 5.10 (s, 1H, H-1b), 3.90 (s, 3H, OCH_3 and 3.40 (m, 2H, H-3).

Spectral data of compound (2):

UV (Ethanol), λ max: 233, 280 and 349 nm
IR ($CHCl_3$), ν: 3076, 3017, 2937, 2836, 1620, 1592, 1514, and 1146 cm^{-1}
^{1}H-NMR ($CDCl_3$), δ ppm: 6.70 (d, 1H, J=10 Hz, H-9), 6.65 (m, 2H, H-5,8), 5.9 (m, 1H, H-2), 5.05 (m, 1H, H-1a), 5.00 (s, 1H, H-1b), 3.78 (s, 3H, OCH_3), 3.76 (s, 3H, OCH_3) and 3.30 (m, 2H, H-3).

Spectral data of compound (3):

UV (Ethanol), λ max: 236, 278 and 414 nm
IR ($CHCl_3$), ν: 3540, 3469, 3074, 3014, 2939, 2847, 1640, and 1608 cm^{-1}
^{1}H-NMR ($CDCl_3$), δ ppm: 7.30 (s, 1H, OOH), 6.63 (d, 1H, H-9), 6.15 (d, 1H, H-8), 5.60 (m, 1H, H-2), 5.50 (s, 1H, H-5), 5.14 (s, 1H, H-1a), 5.07 (m, 1H, H-1b), 3.80 (s, 3H, -OCH_3) and 2.60 (m, 2H, H-3).

Spectral data of compound (4):

UV (Ethanol), λ max: 236, 278, 348, and 414 nm
IR ($CHCl_3$), ν: 3540, 3433, 3014, 2939, 2847, 1640, 1608 and 1512 cm^{-1}
^{1}H-NMR ($CDCl_3$), δ ppm: 8.6 (s, 1H, OOH), 7.70 (m, 1H, H-2), 7.5 (d, 1H, H-3), 6.80 (d, 1H, H-9), 6.40 (d, 1H, H-8), 6.70 (s, 1H, -OOH), 5.00 (s, 1H, H-5), 4.20 (d, 2H, H-l) and 3 .85 (s, 3H, -OCH_3).

Spectral data of compound (5):

UV (Ethanol), λ max: 272, 291, 314, 336, 414, 480, 512, 546, 590 and 654 nm
IR ($CHCl_3$), ν: 3540, 3027, 2938, 1600, 1514 cm^{-1}
^{1}H-NMR ($CDCl_3$), δ ppm: 7.71 (m, 1H, H-2), 7.53 (d, 1H, H-3), 6.85 (d, 1H, H-9), 6.70 (m, 2H, H-5, 8), 6.35 (s, 1H, -OOH), 4.30 (m, 2H, H-1), 3.87 (s, 3H, -OCH_3) and 3.86 (s, 3H, -OCH_3).

Spectral data of compound (6):

UV (Ethanol), λ max: 274, 299, 311 and 415 nm
IR ($CHCl_3$), ν: 3500, 3100, 2980, 1720, 1600 and 1500 cm^{-1}
^{1}H-NMR ($CDCl_3$), δ ppm: 7.70 (m, 1H, H-2), 7.50 (d, 1H, H-3), 6.85 (d, 1H, H-9), 6.40 (d, 1H, H-8), 5.90 (s, 1H, OH), 5.00 (s, 1H, H-5), 4.30 (s, 1H, OH), 4.1 (d, 2H, H-1) and 3.8 (s, 3H, -OCH_3).

Spectral data of compound (7):

UV (Ethanol), λ max: 271, 314, 330, 348 and 409 nm
IR ($CHCl_3$), ν: 3500, 3150, 2960, 1600 and 1500 cm^{-1}
^{1}H-NMR ($CDCl_3$), δ ppm: 7.70 (m, 1H, H-2), 7.50 (d, 1H, H-3), 6.80 (d, l H, H-9), 6.70 (m, 2H, H- 8, 5), 3.90 (m, 2H, H-l), 3.85 (s, 3H, -OCH_3), 3.83 (s, 3H, -OCH_3) and 3.55 (s, 1H, OH).

Spectral data of compound (8):

UV (Ethanol), λ max: 234, 274, 284, and 376 nm
IR ($CHCl_3$), ν: 3017, 2939, 2915, 2838, 1593 and 1514 cm^{-1}
^{1}H-NMR ($CDCl_3$): δ ppm = 6.8 (m, 3H, H-5, 8, 9.), 3.88 (s, 3H, -OCH_3), 3.86 (s, 3H, -OCH_3), 3.13 (m, 1H, H-2), 2.80 (d, 2H, H-3), 2.76 (dd, 1H, H-1 a) and 2.53 (dd, 1H, H-1 b).

Spectral data of compound (9):

UV (Ethanol), λ max: 271, 300, 314 and 367 nm
IR ($CHCl_3$), ν: 3408, 3060, 2983, 2873, 1642, 2592 and 1495 cm^{-1}.
^{1}H-NMR ($CDCl_3$), δ ppm: 7.4 (m, 3H), 7.2 (m, 2H, arom.), 6.75 (m, 3H, H-5,8,9), 3.80 (s, 3H, CH_3), 3.77 (s, 3H, -OCH_3), 3.1 (m, 1H, H-2), 2.76 (s, 3H, CH_3), 2.87 (s, 1H, OH), 2.73 (d, 2H, H-3), 2.65 (d, 2H, H-l), 2.1 (s, 1H, NH) and 2.06 (s, 3H, N-CH_3).

3. RESULTS AND DISCUSSIONS

Schunk and his group in 1988 reported that irradiation of eugenol by low pressure mercury lamp using isopropanol as a solvent produced two photolytic products that were identified as cyclopropyl-2-methylphenol and 2-(3-methoxy-4-hyderoxybenzene)-1-methylethyl isopropyl ether [8]. In our work, eugenol was isolated from clove buds (*c.f.* experimental part) and subjected for photo-oxygenation reaction in chloroform and in presence of (TPP) as a singlet oxygen sensitizer. It was irradiated externally by a sodium lamp at -20 °C for six hrs. Eugenol hydroperoxide (**3**) and eugenol dihydroperoxide (**4**) were formed in the reaction mixture. These products were further purified using CC and their structures were proved using IR and ^{1}H- NMR spectroscopy.

IR spectrum of eugenol monohydropreoxide (**3**) revealed the presence of absorption bands at 3540, 1640 and 1608 crn^{-1} corresponding to hydroperoxide (-OOH), carbonyl (CO) and (C=C) groups respectively. The ^{1}H-NMR spectrum indicated the presence of doublet signals at δ 6.63 and 6.15 ppm for cyclic AB system at C-8 and C-9. A singlet signal at 7.3 ppm was assigned for the hydroperoxide group (-OOH).

The IR spectrum of eugenol dihydropreoxide (**4**) was identical with that of eugenol monohydropreoxide (**3**). In the ^{1}H-NMR spectrum two signals as singlet at 8.6 and 6.7 ppm were assigned for two hydroperoxide groups. It is interesting to consider the bifunctionality of eugenol towards the reaction with singlet oxygen. From the previous photo-oxygenation reaction, we have seen that the singlet oxygen may either react at the phenolic site to produce the dienone hydroperoxide [10] or at the allylic site to afforded the corresponding allylic hydroperoxides through the ene reaction [11]. The observed mode of selectivity is however, exclusive formation of (**3**). Subsequent photo-oxygenation of (**3**) led to the formation of bis-hydroperoxyde (**4**), in which now the ene reactivity manifests itself (**Scheme 1**). Such mode of selectivity between phenolic site reactions *versus* allylic ene site reaction appears unprecedented. A possible rational for this mode of selectivity might be due to the higher nucleophilicity of the phenloic versus the allylic site in eugenol. It was believed

that the singlet oxygen in the lowest unoccupied molecular orbital (LUMO) was combined with the diene group in the benzene ring in the highest occupied molecular orbital (HOMO) as [4+2] cycloaddition through suprafacial - antraficial approach. Whereas, the ene mechanism happened through the formation of peroxirane transition state.

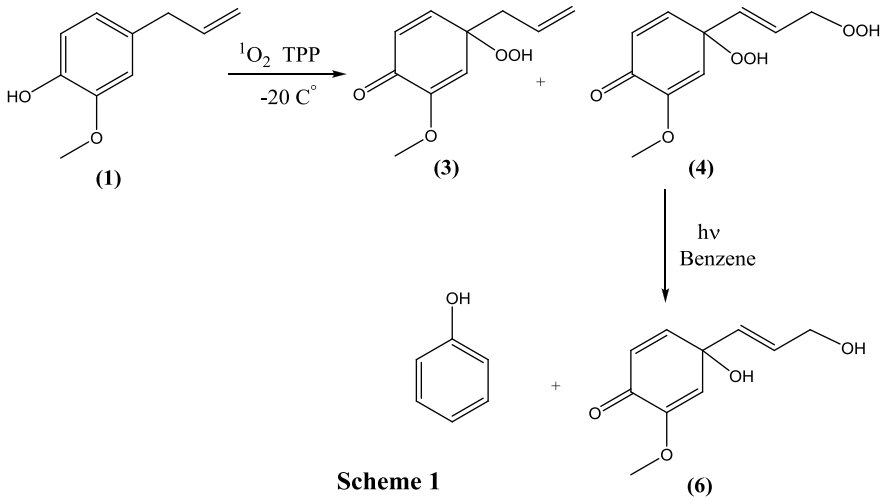
On the other hand, the phenolic site of eugenol was blocked by replacing the phenolic OH group by methoxy group (methyl eugenol ether (**2**). The eugenol methyl ether was subjected to photo-oxygenation reaction with the same conditions for eugenol. The expected methyl eugenol ether hydroperoxide (**5**) was obtained as a sole product (**Scheme 2**). The IR spectrum showed absorption band at 3540 cm^{-1} corresponding to hydroperoxide group (-OOH), which was in agreement with the ^{1}H-NMR singlet at δ 6.36 ppm.

The hydroxyl radical (·OH) sources that almost have been applied as DNA cleavage reagents are synthetic ones. Adam and his co-workers were the first to use the natural hydroperoxide derivatives (imperatorine hydroperoxid) for damage DNA photochemically [10]. To explore the search for natural hydroxyl radical sources for DNA-cleavage, the eugenol hydroperoxide derivative (**4**) was photolysized in benzene as a radical trap in the absence of singlet oxygen sensitizer. This afforded eugenol dihydroxide derivative (**6**) in addition to phenol. The ^{1}H-NMR of the photolytic product (**6**) revealed the presence of two singlets peaks at δ 5.90 and 4.30 ppm for two hydroxyl groups. Similarly, photolysis of methyl eugenol hydroperoxide derivative (**5**) was carried out under the same conditions used for compound (**4**), where it afforded the corresponding hydroxyl derivative (**7**) and phenol. The ^{1}H-NMR spectrum of product (**7**) indicated a signal at 3.55 ppm as singlet for one proton assigned for the hydroxylic function group.

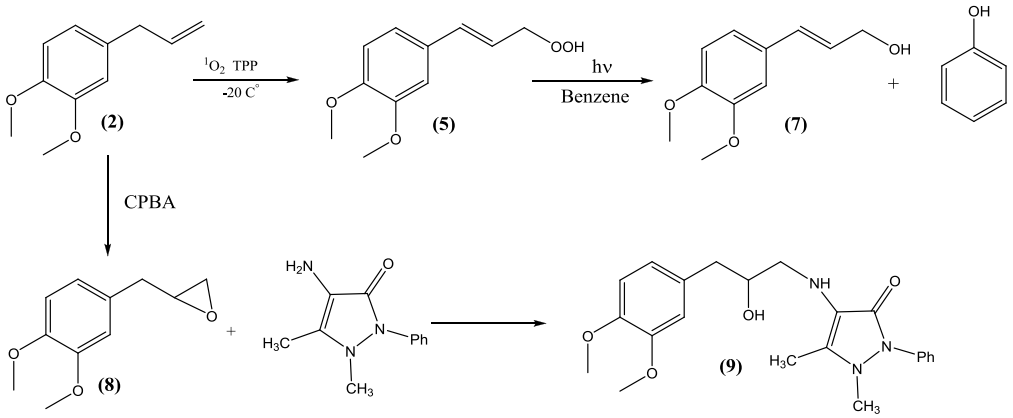
In this work, it has been proven that the new eugenol hydroperoxide (**3**), dihydroperoxide (**4**) and eugenol methyl ether hydroperoxide derivatives (**5**) affording the corresponding hydroxyl products (**6, 7**) upon the photolysis under the conditions stated. Therefore, the photolytic products (**6**), and (**7**) are expected to be hydroxyl radical generators in skin when these are treated with DNA under the known irradiation conditions.

The efficiency of the epoxides as DNA- alkylating agents is well known [11]. Thus, methyl eugenol epoxide (**8**) which was prepared from compound (**2**) using *m*-chlorobenzoic acid (CPBA) was proven from its ^{1}H- NMR spectrum (*c.f* experimental part). It is believed that an epoxide such as compound (**8**) features a new type of alkylating agent for DNA. The aminoantipyrine derivative (**9**) was prepared by fusion of compound (**8**) with aminoantipyrine. The IR spectrum of (**9**) showed the presence of an α, β-unsaturated carbonyl group at 1642 cm^{-1}. Its ^{1}H-NMR showed signals at 3.80 ppm and 3.77 ppm as singlets which were assigned for the two methoxy groups, in addition to signals for the olefinic methyl and CH_3-N appeared at 2.76 and 2.06 ppm respectively.

From the present work, it has been shown that a DNA- alkylating agent was prepared from the natural product eugenol and made available for application and investigation of its genotoxic potentiality.



Scheme 1



Scheme 2

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Structural Health Monitoring and Strengthening Of Bridges

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Abstract: This paper presents one bridge which were either rehabilitated or strengthened by using FRP composites. The resulting structure was then tested for the effect after using FRP composites for Rehabilitation and strengthening. In this paper, Structural Health Monitoring basics are covered and need for SHM in future in or India scenario. Use of FRP composites in Rehabilitation and Strengthening of structures is becoming increasingly popular and is opening new possibilities in construction and rehabilitation of structures.

Keywords : Rehabilitation, Structural Health Monitoring, Bridge Strengthening, Repair

1. INTRODUCTION

In the recent years, rapid deterioration of exiting bridge structures has become a serious technical and economical problem in many countries, including highly developed ones. Therefore, bridge rehabilitation is one of the most important tasks in civil engineering. Bridge rehabilitation process should be preceded by assessment and evaluation of the structure to determine its actual technical condition and to select the proper rehabilitation techniques and materials. The reasons leading to deterioration of the existing bridge are more or less same in every country.

a) Increase in traffic flows and weight of vehicles, especially their axle loads, compared to the period when the bridges have been designed and constructed.
b) Harmful influence of environmental pollution, especially atmospheric ones, on the performance of structural materials,
c) Low quality structural material as well as bridge equipment elements, such as expansion joint, waterproofing etc.

2. SCOPE OF WORK

The focus of this present work is to study the effectiveness of the bridge rehabilitation with respect to different aspect such as strain measurement, vibration measurement, deflection measurement, temperature measurement etc. The project contains one case study which are as follows.

Rehabilitation and Testing of Karal Rail Over Bridge at JNPT, Navi Mumbai

3. AIMS AND OBJECTIVES

The aims and objectives of "Rehabilitation and structural health monitoring of bridge superstructure" dissertation are as follows:

1) To study strengthening techniques of bridge rehabilitation.

2) To study the effectiveness of the FRP material and external pre-stressing in the field of bridge rehabilitation.

3) To study the different type of damages in concrete structure.

4) To study the behavior of the bridge before and after strengthening.

5) To develop a 24 x 7 bridge monitoring system for deflection, vibration and strain measurements for vehicular loading.

4. CASE STUDY

Port at Nhava-Sheva, Navi Mumbai is managed by Jawaharlal Nehru Port Trust (JNPT). This port is one of the busiest port and handles about 70% of container traffic of whole INDIA has constructed Rail over bridge at Karal for efficient traffic flow. The construction of this bridge was completed and opened for traffic since 1991. This bridge consists of 36 spans of varying lengths with 37 expansion joints. The total length of bridge is 700 m.

Upon critical inspection and the comparison of the design load versus the strength of the girders of the Karal ROB, it was observed that

1. The girders provided in the bridge are not adequate to resist the design vehicle load as per revised IRC recommendation,
2. occurrence of the structural cracks in the girders (i.e. vertical crack in the centre and diagonal cracks at the end) which prove the structural inadequacy of the girders and
3. Presence of visible sag in the superstructure, it confirms that the superstructure may not be quite adequate to resist the increased vehicular traffic load on the Karal ROB in recent years.

5. SCHEME FOR STRENGTHENING THE BRIDGE

1. The girders and slab of the bridge have been strengthened by placing the additional steel truss system along the two main girders in each lane (i.e. along the girder 2, 3, 6 and 7 are to be placed in each span of and 1, 4, 5 and 8 remain as it is). The truss system is supported by bridge deck/slab and cross girders using the M32 high strength bolts. This truss system is designed to take about 50% of the load carrying capacity of the existing girders. [8, 10,12,13,14-20]

Connection of truss over main beam

Pre-stressing Mechanism in Truss

2. The bearings provided in the bridge between girders and piers were damaged and were insufficient to take the increased load. Elastomeric bearings have thickness around 75mm and it become 25mm because of heavy traffic load. It is suggested to replace all the existing neoprene/elastomeric bearings with the new elastomeric bearings as shown in Figure 6.4.

Replacement of damaged Bearings with new

3. It is also recommended to replace the expansion joints of the bridge with the Wabocrete Strip Seal Expansion Joint System.

4. It is recommended to strengthen the RCC girder beams with FRP Carbon laminates.

5. In order to further improve the structural strength of the bridge, it is recommended that the fiber reinforced plastic composites wrapping around the girder.

6. To check the strength of FRP wrapping and steel truss different types of measurements have been taken before and after the strengthening.

Groove for carbon Fibre composites laminates

Carbon fibre wrapping

6. TEST SCHEME AND INSTRUMENTATION

The various measurements to ascertain strengthening effect has been presented below.

1. Measurement of strain, deflection and vibration of three spans of the Rail Over Bridge of JNPT at the identified locations under the static and rolling load before rehabilitation/retrofitting.
2. Measurement of strain, deflection and vibration of the three spans of the Rail Over Bridge of JNPT at the same identified locations under the same static and rolling load after retrofitting.

Besides this, to estimate condition of concrete in existing structure, Rebound hammer tests and Ultrasonic Pulse Velocity (UPV) tests were also proposed before strengthening.

7. NDT ON SUPERSTRUCTURE

1) Testing of Bridge girder using UPV (Ultrasonic Pulse velocity) test to obtain quality of concrete. All the girders will be tested at minimum 3 locations on each under direct transmission. (Figure 6.6 (a))
2) Testing of Bridge girder using Rebound hammer to estimate the characteristic strength of the girder. All the girders have been tested at minimum 12 locations (6 locations on each face of the girder.(Figure 6.6 (b))
.

Table 1
Rebound Hammer Test Results of RCC Girder Beams
(DIGI Schmidt 2000 Rebound Hammer)

Sr. no	Location	Avg. fck in MPa
Bay 1		
1	Girder Beam 1	59.5
2	Girder Beam 2	55.3
3	Girder Beam 3	53.1
4	Girder Beam 4	58.2
5	Girder Beam 5	60.5
6	Girder Beam 6	53.4

[13,10,12]

Table 2
Result of Ultrasonic Pulse Velocity Measurements of RCC Girder Beams

Sr. No.	Location	Pulse Velocity in Km/Sec	Concrete Quality
1	Girder Beam 1	3.57	Good
2	Girder Beam 2	4.11	Good
3	Girder Beam 3	4.22	Good
4	Girder Beam 4	4.36	Good
5	Girder Beam 5	4.17	Good

[13,10,12]

Table 3

Average Central Deflection (mm)

	Span-1	Span 2
Before strengthening	5.38 mm	5.18 mm
After strengthening	3.93 mm	3.65 mm
Reduction in defection	1.46 mm	1.53 mm
% reduction in deflection	-27.10%	-29.50%

[2, 13, 10]

Table 4

Average Flexural Strain (με)

	Span 1	Span 2
Before strengthening	450 με	407 με
After strengthening	198 με	188 με
Reduction in Flexural Strain	262 με	219 με
% Reduction in Flexural Strain	-58.20%	-53.80%

[2,5,13,10]

Table 5

Crack Width of Diagonal Cracks near Support (Change in change width over a gauge length of 200mm in με)

	Span 1	Span 2
Before strengthening	80 με	90 με
After strengthening	42 με	28 με
Reduction in Shear Strain	38 με	52 με
% Reduction in Shear Strain	47.5 (%)	57.8 (%)

[2, 5, 13, 10]

Table 6

Average Acceleration (mm/s^2)

	Span 1	Span 2
Before strengthening	21.38 mm/s^2	35.91 mm/s^2
After strengthening	11.43 mm/s^2	15.93 mm/s^2
Reduction in Acceleration	9.95 mm/s^2	19.98 mm/s^2
% Reduction in Acceleration	46.5 (%)	55.6 (%)

[2,3,7,5,13,10}

8. CONCLUSIONS

1. Central defections obtained under standard loads indicate significant improvement in the flexural stiffness of the RCC girder beams after rehabilitation and effectiveness of the pre-stressed steel truss straitening system. Reduction in deflection of all the two spans indicates that the flexural strengthening system (FRP laminate and Pre-stressed steel truss system) is effective in sharing the vehicular loads. An average of 26% reduction in the deflection of bridge superstructure under standard loads has been observed.

2. Flexural strains measured under standard loads indicate significant improvement in the flexural stiffness of the RCC girder beams after rehabilitation and effectiveness of the pre-stressed steel truss straitening system. Reduction in flexural strain of all the three spans indicates that the flexural strengthening system (FRP laminate and Pre-stressed steel truss system) is effective in sharing the vehicular loads. An average of 53% reduction in the flexural strain in RCC girder beams under standard loads has been observed.

3. Change in the width of the diagonal shear cracks on the RCC girder beams near the support have been measured before and after strengthening with the help of omega type strain gage based transducer. An average of 56.8% reduction in the shear strain in RCC girder beams under standard loads has been observed. Reduction in the shear strain after rehabilitation indicates significant enhancement in the shear stiffness as a result of FRP wrap and Steel truss system.

4. Reduction in the vibration of the superstructure was envisaged due to rehabilitation of RCC girder beams and strengthening with steel truss system. An average reduction of 8.5% in fundamental frequency of vibration is achieved. In addition to this, the amplitude of acceleration has been reduced by 50%. The increase in fundamental frequency of vibration and reduction in amplitude of acceleration indicate that the significant improvement in the overall stiffness of the structure.

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New Technique for Measuring and Controlling the Permeability of Polymeric Membranes

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Abstract: Membranes have wide uses in industry and medicine applications. Polymer membranes are important materials because of their high chemical resistance, but they are of weak mechanical resistance against high pressures. Therefore, it was essential to modify a permeability measuring technique free from high pressure application. The current work represented a modification for the permeability measuring technique of membranes, where ionic salt was added with known concentration to water as common solvent and the electrolyte current was measured behind the membrane. The electrolysis current was correlated to the flow rate of water across a polyvinyl alcohol (PVA) membrane. Some other problems were raised such that polarization on electrodes and changes in electrolyte contents during the long time of the slow process. Pulsed potential on electrodes resolved these problems and other associated problems like rush in current and the double layer capacitance effect. An empirical equation was suggested to evaluate the permeability of polymer membranes by this modified method. Easy and accurate measurement of permeability helped authors to change the permeability of PVA membranes by adding copper nano particles in membrane to reduce its permeability, and adding silicone dioxide micro particles to the PVA membranes to increase its permeability. Authors suggested a mechanism for these permeability changes. Scanning electron microscope images for the filled PVA membranes supported the suggested mechanism.

1. INTRODUCTION

Membrane operation or membrane processes may be regarded as a unit operation in chemical engineering. They are widely used in industrial applications in different fields like chemicals, food, gas, water and wastewater treatment, pharmaceuticals and more. Membrane systems are based on the use of synthetic membranes that permit the concentration and separation of solutions without thermal damage. Particles are separated on the basis of their molecular size and shape using pressure and specially designed synthetic and semi-permeable membranes [1].

Membrane processes provide efficiency and operational simplicity, high selectivity and permeability for the transport of certain components. It is possible to achieve high compatibility as between different membrane operations as between membrane operations and traditional industrial

applications in integrated systems. In order to analyze their economic impact, it is necessary for membrane processes to be characterized by low operational energy, good stability under operative conditions, environment compatibility, easy scale-up, great flexibility, and good control of effectiveness with the possibility of reaching advanced levels of automation and remote control [1]. The most important property of membranes is their ability to control the rate of permeation of different species [2]. The permeability is a measure of the ability of a porous medium to transmit fluids measured in the units of length square or darcies (1 D = $0.98692\times10^{-12}m^2$) [3].

Two models used to describe the mechanism of permeation. One of them is the solution-diffusion model, in which permeates dissolve in the membrane material and then diffuse through the membrane down a concentration gradient. Permeates are separated because of the differences in the solubility of the materials in the membrane and the differences in the rates at which the materials diffuse through the membrane [2]. If a concentration gradient of permeate molecules is formed in the medium, simple statistics show that a net transport of matter will occur from the high concentration to the low concentration region. For example, when two adjacent volume elements with slightly different permeate concentrations are separated by an interface, then simply because of the difference in the number of molecules in each volume element, more molecules will move from the concentrated side to the less concentrated side of the interface than will move in the other direction. This concept was first recognized by Fick theoretically and experimentally [2]. In 1856, Darcy investigated the flow of water through sand filters for water purification [4].

By empirical observation Darcy noticed that fluid flow was directly proportional to the hydraulic gradient [4], resulting in the following equation

$$q = KA\frac{h_2 - h_1}{l}$$

where q represents the volumetric flow rate of water downward through the cylindrical sand pack of cross-sectional area A and height l, h_1 and h_2 are the hydraulic head above the standard datum of the water in the manometer located at the input and output ports respectively, and K is a constant of proportionality found to be characteristic of the rock media. Most of the techniques for measuring permeability are based on Darcys equation where pressure $(h_2 - h_1)$ is essential parameter. Many polymeric membranes are deformed under pressure, and hence their surface areas are changed releasing markedly error. Therefore it is essential to develop the measuring technique in order to measure the coefficient of permeability for thin polymeric membranes with satisfactorily degree of accuracy.

The current work aims to design, setup and use a modified measuring system for permeability of a thin polymer membrane and then use this system as a very helpful technique for measuring the change in permeability of polymeric membranes.

2. THEORETICAL PRINCIPLE

To achieve the goals described in the previous section we start by designing the system which we going to use in our study. The main idea is to detect and demonstrate the process of permeability and diffusion through simple electrochemical reaction. To do this we going to design a system consist from two chambers, in the first one of them an electrolyte solution is contained and the second one a free of ion solution is contained. The membrane under investigation is held in between of them. In this situation the system is kept under equilibrium and the static pressure on both sides of the membrane is the same where $H_1 = H_2$. The system is illustrated in figure (1).

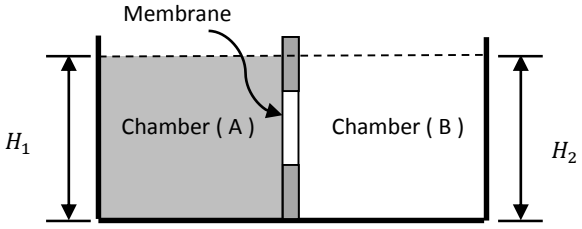

Figure (1): Schematic structure of the main unit

At the beginning of this process there will be no flow expected through the membrane due to the time consumed in the swilling and wicking processes inside the membrane [5]. The time duration consumed in these processes is related to the physical properties of the membrane under investigation. After a while and according to the ficks law of diffusion, the electrolyte starts to flow from chamber (A) which is high in concentration to chamber (B) which have the lower concentration and this will be steady-state flow. As the electrolyte in the chamber (B) starts to reach saturation, the process of diffusion starts to slow down. The expected behavior of the above process is described in figure (2).

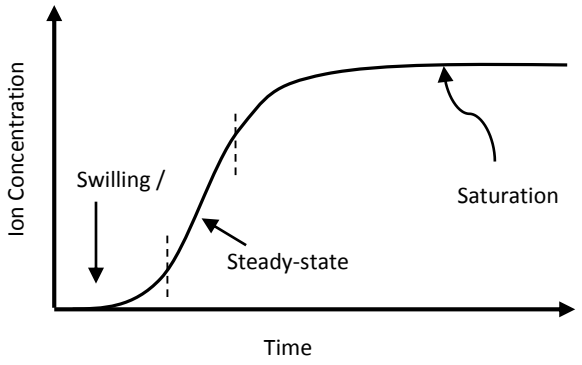

Figure (2): General behavior of the concentration change in chamber B

3. EXPERIMENTAL

The main idea on which the suggested technique was designed depends on the electrolysis phenomenon. On this base it was possible to measure both of molar and ionic permeability's of a polymer membrane by any ionic bonds compound.

Setup of the suggested measuring system:

As shown in figure (3A) the experimental setup is consisting from an external container which will be referred as the electrolyte container and an internal container which will be referred as the distilled water container. The Distilled water container is placed inside the electrolyte container. The circuit board which will be referred as the electrode PCB is attached to the distilled water container and connected to the DAQ device which is connected to the PC.

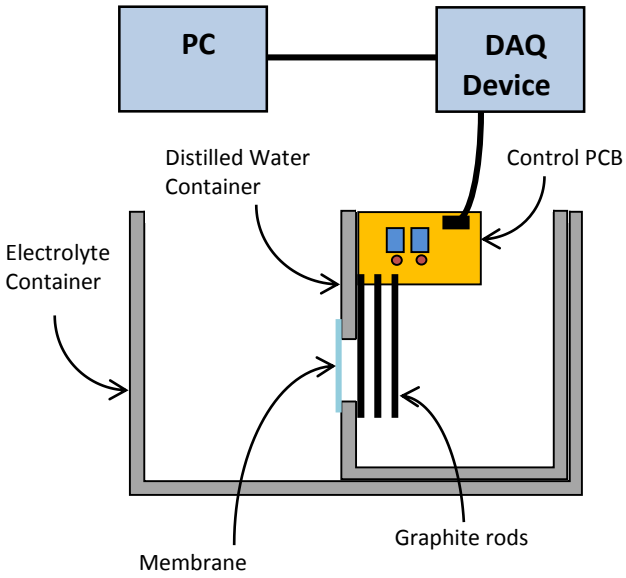

Figure (3A): Schematic diagram for the real used system

The electrolyte container is made of grade A transparent acrylic sheets of 10 mm thickness and internal dimensions of (25 cm W x 18 cm D x 19.5 cm H) the resistivity of the acrylic is about 10^{15} ohm/cm for 6mm thickness sheets and dielectric strength of 30 Mv/m. Acrylic sheets are resistant to most chemicals, can be cleaned easily and corrosion resistant. So it's very suitable for use in our system. The container is approved to be leak free. The distilled water container is constructed from the same materials used for the electrolyte container with internal dimensions of (16 cm W x 12.5 cm D x 20 cm H). The front side of the container is equipped with circular hole of diameter 4.5 cm, a rubber ring is circulating the hole at distance 5 mm from the hole contour. Four small holes of diameter 4 mm are drilled around the hole for membrane holder fixation. Four stainless steel screws and bolts are installed and fixed in position using waterproof epoxy to prevent leakage of the electrolyte through

the screws opening. Figure (3B) shows the membrane fixation mechanism.

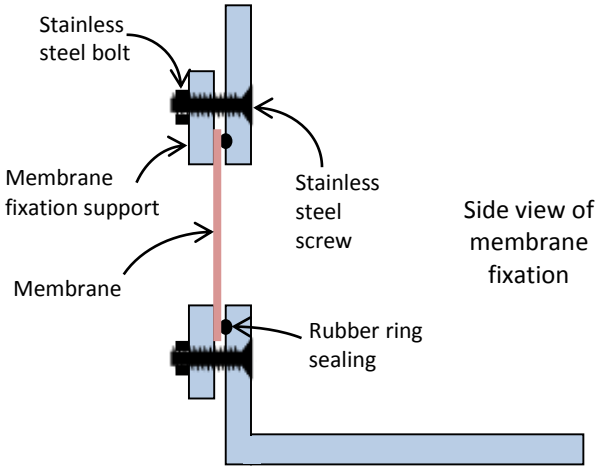

Figure (3B): Fixation of the membrane

The circuit board is assembled on a PCB with an additional depolarization relay. The depolarization relay function is to depolarize the graphite electrodes by applying a charge for certain period of time in the way that the applied polarities on the electrodes are reversed from the applied one during current measurement. Note that this time period must be equal or less than the period used during current measurement. The purpose of adding this relay on the circuit is to minimize the effect of electrodes polarization in the case of long term measurements that extends for several days. Figure (3C) shows the circuit.

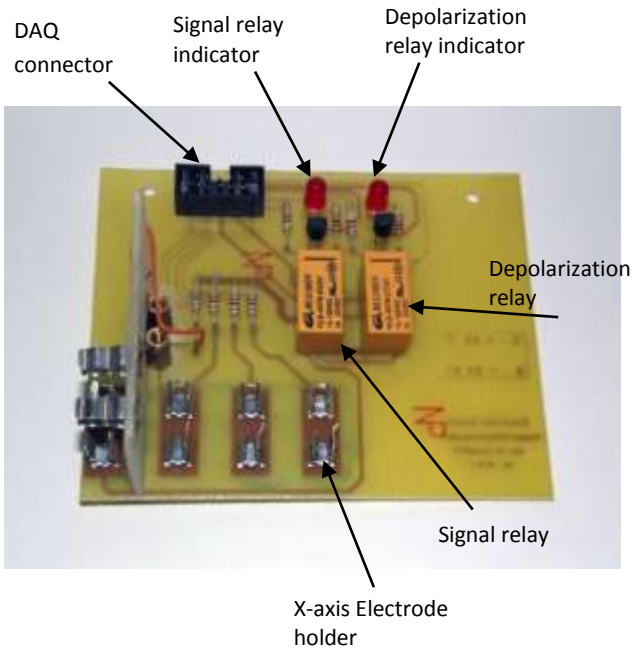

Figure (3C): Electrodes holder and electronic control circuit

System design requirements:

- ***Electrode choices:***

  Electrode choice is very important decision in system design. The electrodes should satisfy the following specifications:

a) Very low resistance so it can detect very low currents as low as 10μA
b) It should be inert electrode which means that the electrode material should not react with any of the reacting species.
c) The electron transfer step is the only reaction step. Which means that other parallel or consecutive steps are absent

According to the above requirements, graphite seems to be the perfect electrode for our mission. Graphite typical resistivity range of $2.5 - 5x10^{-6}\Omega$.m at 20°C and conductivity range of $2 - 3x10^{5}\ S/m$ at 20°C [6]. Graphite is perfect electrical conductor, even with the commercial grades which have higher resistivity and lower conductivity, the above values of resistivity still in the range of μΩ.m which is very accepted in our system and sill verify our design requirements.

- ***Measuring the current through Voltage divider resistor:***

Current measurements are troublesome, because the current appears within a loop and the loop must be opened to insert the measuring instrument. Moreover, this instrument contains a characteristic resistance or impedance that most often changes the circuit parameters and must be compensated to obtain accurate measurements.
This problem can be eliminated by using voltage divider method. Voltage drops are relatively easy to measure with most instruments because the difference in voltage appears between any two points in a circuit. The circuit does not need to be disturbed or changed [7].
The known reference resistor should have a value that is close to the unknown value. A low current as 1.0 μA or less can be measured accurately.

- ***Electrolyte and solvent choice :***

The first requirement of an electrolyte is that it should give rise to a highly

Conducting solution. Potential electrolytes (organic acids and most

bases) dissociate into ions by ionogenic, or ion-forming, chemical reactions with solvent molecules, in contrast to true electrolytes, which often give rise to ionic solutions by physical interactions between ions present in the ionic crystal and solvent molecules. Sodium chloride which is a true electrolyte dissolves by the solvation of Na^+ and Cl^- ions in the salt crystals.

Observed problems during sysem operation:

The fact that system uses the hydrodynamic pressure as a working princible results in long time measurement reaching several days. Due to this long time measurement two problemes affecting the accuracy of the recoreded data are observed. The first problem is the polarization of the graphite electrodes and the second problem is the change in the electrolyte content by consuming the ions during the electrolysis. These problem have been resolved by using the pulsed potential technique as will be discussed later on.

Membrane preparation:

5 gm of PVA (Poly Vinyl Alcohol) from LOBA CHEMIE dissolved in 100 ml of distilled water, the solution placed on magnetic stirrer for 12 hours at 75 °C, the beaker is covered with aluminum foil to minimize the evaporation.

The solution was casted onto glass petri dishes of diameter 70 mm. The casted volume is 10 ml in each petri dish. The solution let to dry for several days at room temperature (about 25 °C) until complete dryness. Then the films were peeled off from the dishes. The peeled films are identical in dimensions with thickness of 0.15 mm.

Electrolyte preparation:

An electrolyte solution of volume 3 liters at the target concentration is prepared by dissolving sodium chloride from BIO BASIC CANADA INC. (MW 58.44, Purity >99.5%, sulfate <0.001%) into distilled water. The solution is left for 1-2 hours for complete dissolution.

4. RESULT AND DISCUSSION

Electrolysis of Aqueous NaCl :

Figure 4 below shows an idealized drawing of a cell in which an aqueous solution of sodium chloride is electrolyzed.

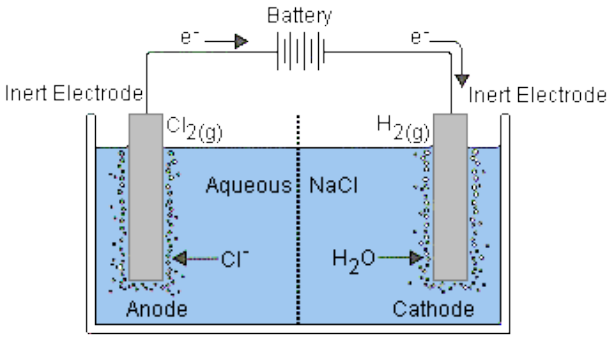

Figure (4): Ideal cell for aqueous NaCl solution.

The Na^+ ions migrate toward the negative electrode and the Cl^- ions migrate toward the positive electrode. But, now there are two substances that can be reduced at the cathode: Na^+ ions and water molecules.

At the Cathode (-):

$$Na^+ + e^- \rightarrow Na \qquad E_{red} = -2.71\,V$$

$$2H_2O + 2\,e^- \rightarrow H_2 + 2\,OH^- \qquad E_{red} = -0.83V$$

Because it is much easier to reduce water than Na^+ ions, the only product formed at the cathode is hydrogen gas.

The cathode reaction will be:

$$2H_2O + 2\,e^- \rightarrow H_2 + 2\,OH^-(aq)$$

There are also two substances that can be oxidized at the anode: Cl^- ions and water molecules.

At the Anode (+):

$$2Cl^- \rightarrow Cl_2 + 2e^- \qquad E_{ox} = -1.36\,V$$

$$2H_2O \rightarrow O_2 + 4H^+ + 4\,e^- \qquad E_{ox} = -1.23\,V$$

The standard-state potentials for these half-reactions are so close to each other that we might expect to see a mixture of Cl_2 and O_2

gas collect at the anode. In practice, the only product of this reaction is Cl_2.

The anode reaction will be:

$$2Cl^- \rightarrow Cl_2 + 2e^- \qquad E_{ox} = -1.36\,V$$

At first glance, it would seem easier to oxidize water (E_{ox}= -1.23 volts) than Cl^- ions (E_{ox} = -1.36 volts). The solution concentration of NaCl controls the potential required to oxidize the Cl^- ion. The deciding factors are:

1- A phenomenon which is known as **overvoltage**: it is the extra voltage that must be applied to a reaction to aid it to occur at the rate, at which it would occur in an ideal system. The measured overpotential required for oxygen oxidation on the graphite electrodes is 0.95 V (table 1). Hence chlorine gas is formed over hydrogen gas.

2- The NaCl concentration: At the cathode the same reduction reaction occurs in both dilute and concentrated solutions.

For the concentrated electrolyte chlorine gas and sodium hydroxide are formed at the anode.

Table (1): Over-potential for different electrodes

Material of the electrode	Hydrogen	Oxygen	Chlorine
Platinum (platinized)	−0.07 V	+0.77 V	+0.08 V
Palladium	−0.07 V	+0.93 V	
Gold	−0.09 V	+1.02 V	
Iron	−0.15 V	+0.75 V	
Platinum (shiny)	−0.16 V	+0.95 V	+0.10 V
Silver	−0.22 V	+0.91 V	
Nickel	−0.28 V	+0.56 V	
Graphite	−0.62 V	+0.95 V	+0.12 V
Lead	−0.71 V	+0.81 V	
Zinc	−0.77 V		
Mercury	−0.85 V		

External resistor value and electrode potential dependence:

The electrolyte resistance can be considered as a fixed value ohmic resistor for fixed value of electrolyte concentration [8]. The main power supply voltage will be shared between the electrodes and the voltage divider resistor as indicated by the following diagram (Figure 5).

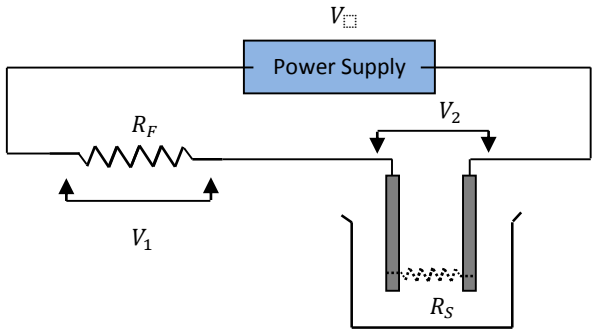

Figure (5): The position of the external resistor in the circuit

From the above circuit we can see that

$$V = V_1 + V_2 \qquad (1)$$

Where;

V is the power supply applied voltage

V_1 is the voltage across the fixed resistor R_F

V_2 is the voltage across the two electrodes immersed in the electrolyte.

The selected maximum value for the power supply is +5V.

A setup to simulate the process has been installed using a beaker filled with electrolyte solution of NaCl of concentration 2 wt%. Using two graphite electrodes the current allowed to flow through the electrolyte. Six different values of the fixed voltage divider resistors are used as follow:

10KΩ, 4.7KΩ, 2.6KΩ, 1 kΩ, 510 Ω, 51 Ω

The voltage from the power source is set to increase from zero to +5V in steps of 0.1 V per minute with the aid of software timed program. The obtained voltage behavior for 10k, 1k, and 51 ohm resistors are shown in figures 6, 7, 8 respectively while the current behavior for all the resistors is show in figure (9).

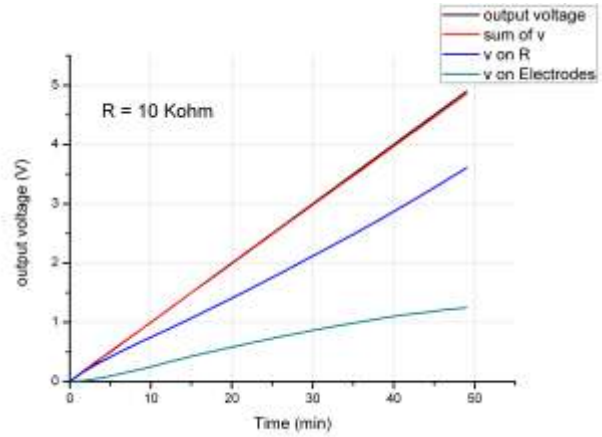

Figure (6): Voltages for external resistance of 10 kΩ

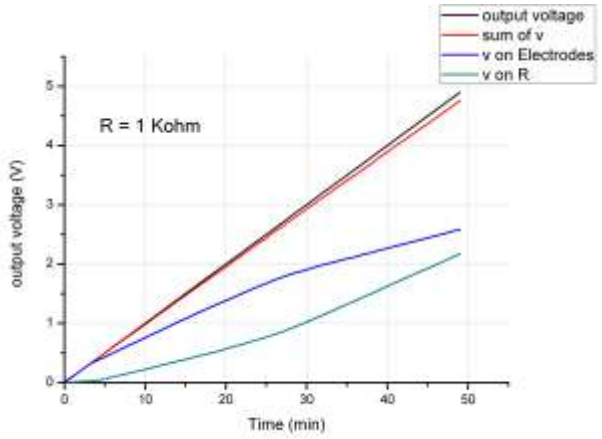

Figure (7): Voltages for external resistance of 1 kΩ

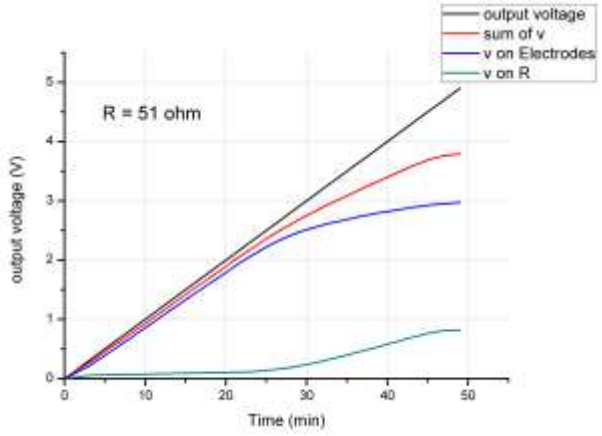

Figure (8): Voltages for external resistance of 51 Ω

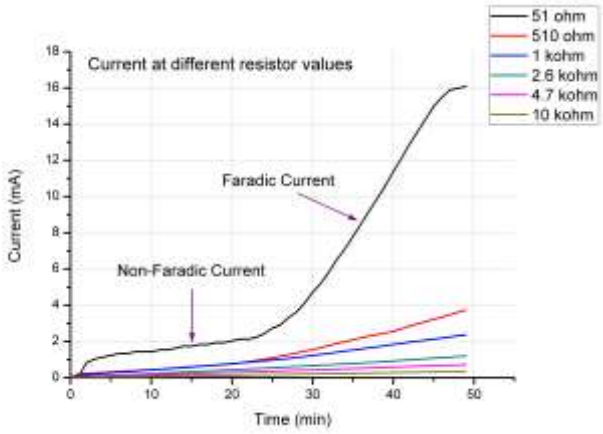

Figure (9): I(t) for different external resistors

The use of power source with value of +5V is appropriate specially when using low voltage divider resistor values. The resistor of value 51 Ω is typical to be used, showing appropriate values of current to be measured and perfect linearity with voltage in the conducting faradic region.

Note that when using a power source of +5V the region corresponding to voltage values from 0 to 2.5V (from 0 to 25 minute in figure (9)) will be neglected since minimal number of ions will be enough to produce a faradic current. The non-faradic current region in figure (9) effect will be minimal since a limited no of ions will transfer the current from non-faradic to the faradic region.

Polarization of Electrodes:

In figure (8) (where the greater voltage deviation occurred) we can relate the value of deviation by the amount of current as seen in figure (9) where the recorded sum values starts to decrease as the current start to increase. Since the fixed resistor can't show such behavior we can assume that the phenomenon is related to the electrodes [9]. The reduced value of voltage on the electrode is caused by voltage drop inside the electrodes causing the measured value to be lower than expected, this phenomena is called "polarization" of electrodes and is varied by: Current value, applied voltage, electrode material and duration of current flow. The magnitude of polarization is more effective by the increasing of any one of the previous four factors.

The effect of long time current flow:

In this experiment we going to simulate the best value obtained for power supply voltage which is 5V for long period of time.
The external voltage divider resistor used is the 5.5Ω. At this value as seen in figure (10) the power supply voltage is kept at the +5v value during the whole 42 hours of the test, and the corresponding current value reaches more than 180mA. The voltage on the electrodes exceeds 4V which is ideal for the electrolysis process. The voltage on the fixed resistor is about 1V and the polarization value is minimal.

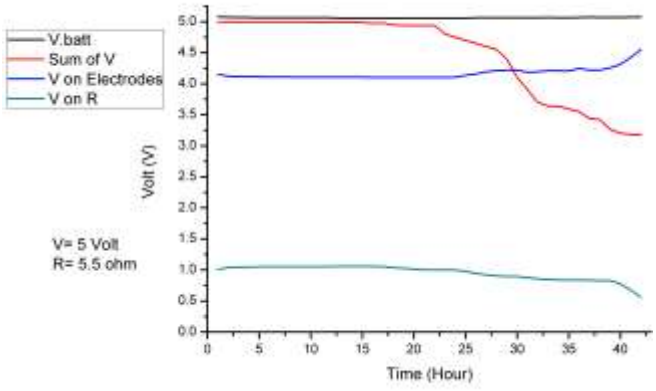

Figure (10): The polarization effect in the electrodes.

As seen in figure (10) in the first 20 hours of the test all the values of power source, polarization, voltage on electrodes and voltage on the fixed resistor are showing linear behavior. But after that time the measured values starts to deviate. While the power supply voltage value is kept stable and fixed, all other values are completely changed. A major voltage drop in the polarization curve is observed.
The current is started to decrease gradually (as seen in figure 11) and this decrease in the current is combined with increase in the solution resistance.
The unexpected deviation from the regular behavior is due to the change in the electrolyte content due to the decrease in the electrolyte ion content and hence increased solution resistance.
In conclusion the DC current value recorded in the electrolysis process can be related to the electrolyte concentration only for fast permeation process.
In low permeability membranes and at low concentration the obtained current values will be inaccurate.

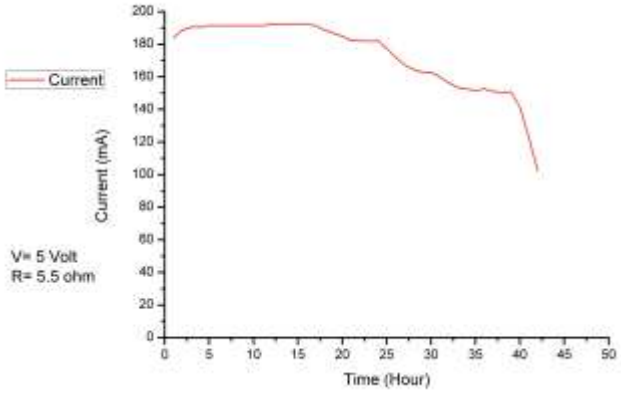

Figure (11): The electrolyte current shows the increase in solution resistance

Pulsed potential technique:

The suggested modified method is focusing on reducing the time that the current allowed to pass through the electrolyte by substituting the continuous potential application on the electrodes by a pulsed potential for a short period of time, thus reducing the effect of electrode polarization and conserving the electrolyte content (Figure 12).

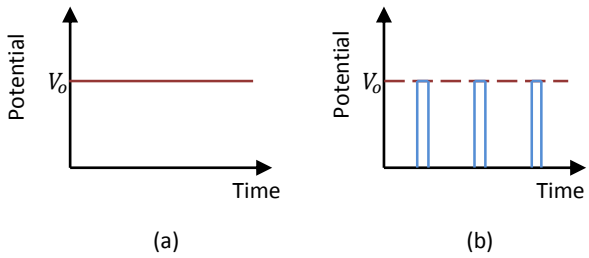

Figure (12) :(a) continuous application of potential V_o , (b) pulsed potential application with the same V_o amplitude.

To achieve our goal the cell design must be modified. The following circuit was used to control the cell potential according to the new enhancements (Figure 13).

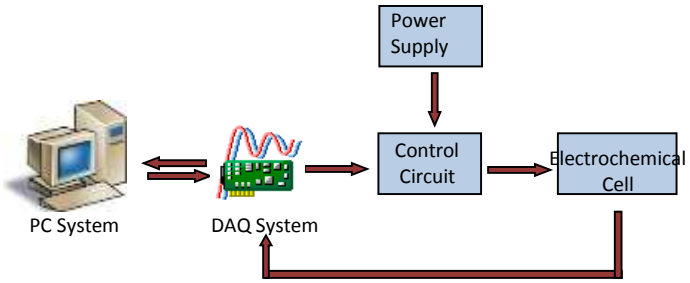

Figure (13): modified measuring system.

The control circuit is demonstrated in figure (14).

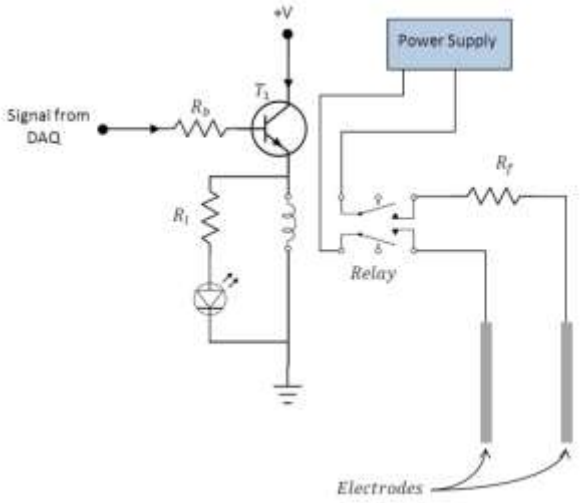

Figure (14): The suggested control circuit.

In the above circuit, the signal coming from the DAQ device is fed to the transistor T_1 through the biasing resistor $R_b$to trigger the relay.

The DAQ device controls the time periods T_{on} and $T_{off}$to form the shape of the applied potential pulse.

However this new technique is combined with two new problems associated with the applied pulse technique, which is formation of the rush in current effect and the double layer capacitance effect. Figure (15a) shows the applied pulsed signal, the resultant signal due to the effect of the double layer capacitance is shown in figure (15b). Figure (16) shows the effect of rush in current and the minimum required pulse width.

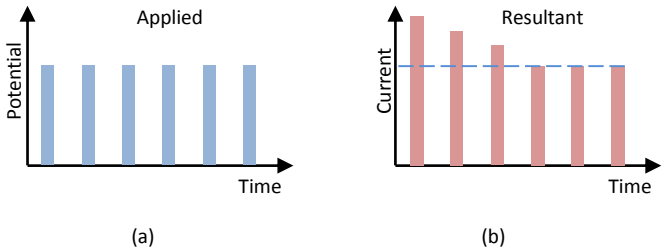

Figure (15): Applied pulses (a) and output current affected by the double layer capacitance (b)

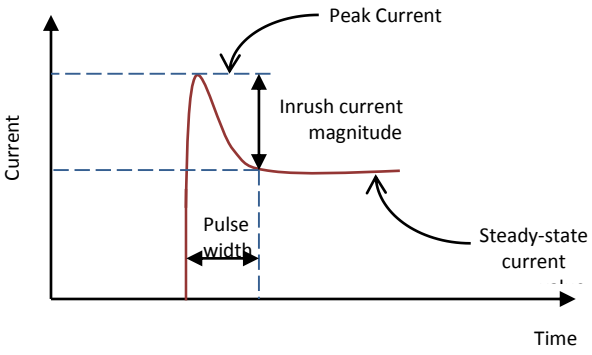

Figure (16): The effect of rush in current on the output current

It's found by experimental trials and measurements that pulse separation above 10 second shows no double layer capacitance effect. Also the pulse width of 3 second was enough to eliminate the effect of the rush in current. Figure (17) show the relation between the applied pulse width and the percentage deviation from the corresponding DC value.

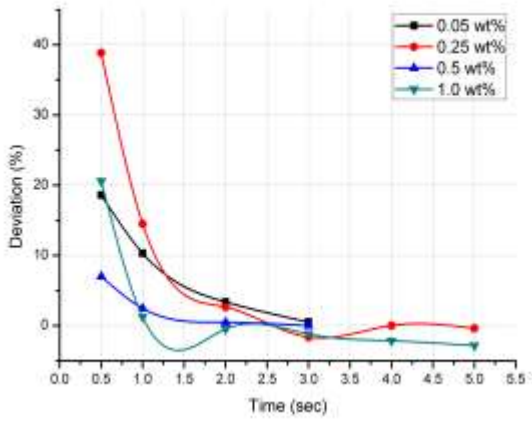

Figure (17): Percentage deviation from DC Value

Permeability investigation using different concentrations:

This test was repeated several times using identical PVA films with the same dimensions, the only changed factor is the electrolyte concentration. In each test the flow rate is calculated under the steady state condition of flow. The rate is obtained as increase in current by time and is recorded in mA/H (milli-ampere per hour) values. Table (2) concludes the obtained flow rates for every concentration used.

Table (2): The flow rate at different concentrations

Concentration (wt%)	Flow rate (mA/h)
0.033	0.035
0.066	0.054
0.133	0.0999
0.266	0.229
0.533	0.61
1.066	1.09
2.133	2.013
3.2	2.49
4.266	2.944

Note that the flow rate is changing according to the change of concentration due to the change in the hydrodynamic fluid pressure, but since the membrane dimensions and material are identical in every test the proportional constant governing the relation between the flow rate and the concentration is the membrane permeability. The data in table (1) is represented graphically in figure (18) using logarithmic scale for concentration.

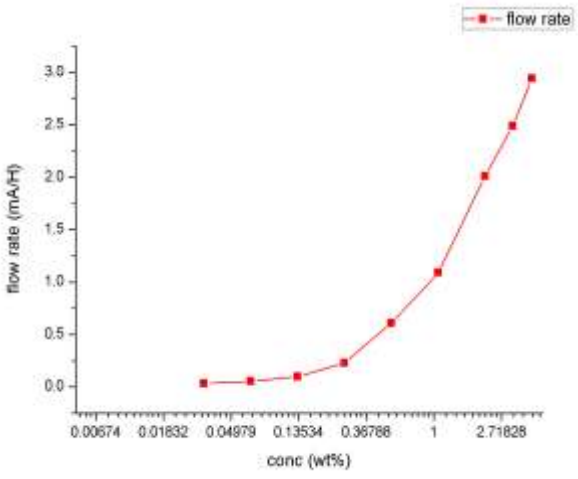

Figure (18): Flow rate as function of concentration.

Empirical System Equation:

The parameters involved in the permeability process can be divided into three main groups:

- Parameters related to the nature of the measurement technique which are the viscosity and concentration of the electrolyte.
- Parameters related to the permeability process itself which is the flow rate through the membrane.
- Parameters related to the sample under investigation which are the sample thickness and area.

Viscosity:

The viscosity of the solution must be involved in our equation as many other permeability equations, however most equations and according to their measurement mechanism use the dynamic viscosity (μ) rather than the kinematic viscosity (ν). The reason of this is based on the fact that, these systems measure the permeability by the aid of fluid flow through the sample under investigation. Unlike these systems our measurement technique uses the hydrodynamic fluid pressure, for this reason we going to use the kinematic viscosity instead of the dynamic viscosity.

The value $1.0244\ x10^{-6} m^2/s$ is taken as the average value for this parameter in our equation for the calculation of permeability over the used range of concentrations.

Flow rate:

The flow rate in our system is calculated by mA/H which is a non-standard unit. So we must convert our flow rate to another standard unit used for measuring the flow rate.

The relation between the system parameters can be expressed by the following three relations [10]:

$$1\ C = 6.24\ x\ 10^{18}\ e$$

$$1\ mole = 96{,}485.4\ C$$

$$1A = 1C/s$$

(where C= Coulomb, e= electron charge, A = Ampere, s = second)

This leads to the following relation:

$$1mA/H = \ 2.877x\ 10^{-12}\ mol/s$$

The previous figure (17) is redrawn after conversion to the IS units.

It's found that the best fit equation for the graph is :

$$k = \frac{Q}{(1 - e^{-\nu Cd/Ab)})}$$

Where,

k is the membrane permeability in m^2

Q is the flow rate in mol/sec

ν is the kinematic viscosity in m^2/s

C is the concentration in mol/m^3

d is the membrane thickness in m

A is the membrane area in m^2

b is a numerical constant of value $5.522372\ x\ 10^{-5}$

Now the modified pulsed technique for measuring permeability of thin polymer films is ready to be used for permeability measurements.

Applications of the system:

The control of the permeability of polymer films is important task in this work. A composite of PVA and nano copper (70 nm) was prepared as a film using the previously described casting method. The films are filled with the copper nano particles with 5, 10, and 20 wt% ratios. Figure (19) shows the obtained flow rate curves and table (3) represents the recorded permeability values for the three films using the system imperial equation.

Table (3): Permeability of copper filled PVA films

Filled copper ratio (wt%)	Permeability k (m^2)
0	$9.082x10^{-12}$
5	$8.86x10^{-12}$
10	$7.974x10^{-12}$
20	$6.955x10^{-12}$

We can see that as the copper particles increase the permeability decrease compared to the pure PVA films (zero ratio in table 3). These results agree with the expected one where as the particles increase in the film more blocking in the flow direction occurs.

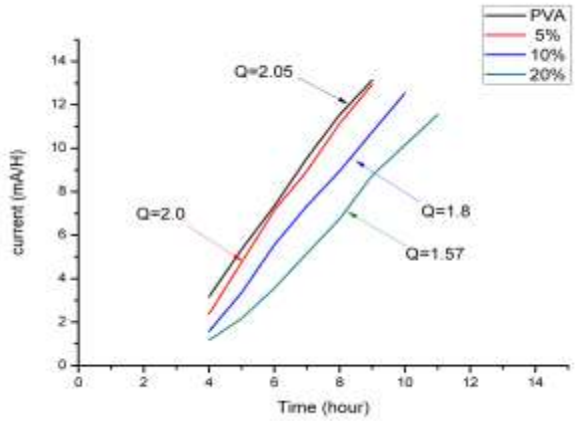

Figure (19): Flow rate for PVA membranes with different copper filling concentrations.

Another set of PVA films using the same preparation method but this time the films are filled with mico particles (100-120 µm) of silicone oxide with 5, 10, and 20 wt% ratios.

The recorded permeability values for the three films using our system imperial equation are represented in table (4), while the flow rate curves are shown in figure (20).

Table (4): Permeability of silicon dioxide filled PVA films

Filled silicone oxide ratio (wt%)	Permeability k (m^2)
0	$9.082x10^{-12}$
5	$1.2x10^{-11}$
10	$9.259x10^{-12}$
20	$7.265x10^{-12}$

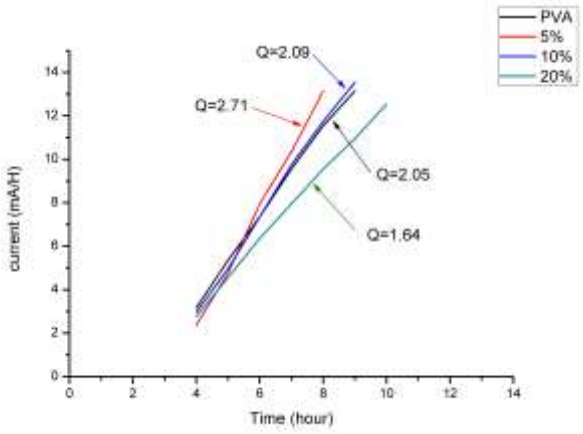

Figure (20): Flow rate for PVA membranes with different silicon dioxide filling concentrations.

From figure 19 it is clear that the flow rate for the 5 wt% filled films is greater than the pure PVA one, which is on the contrary of the expected result.

A theoretical explanation of what can cause this unexpected result assume that the filled particles in the micro scale added new voids between the polymer and the particle surface allowing the flow to be easier through this voids. However another factor is causing the flow rate to be decreased which is the blocking effect of the particle itself.

Thus the permeability depends on two factors work in opposite ways. The first factor, which is the voids allowing more flow rate and hence increased permeability. The second factor which is the blocking effect due to the particle volume leading to reduced flow rate and hence decreased permeability. The obtained flow rate is the net of the above two factors.

Scanning Electron Microscope image supports the discussed theoretical principle above is shown in figure (21).

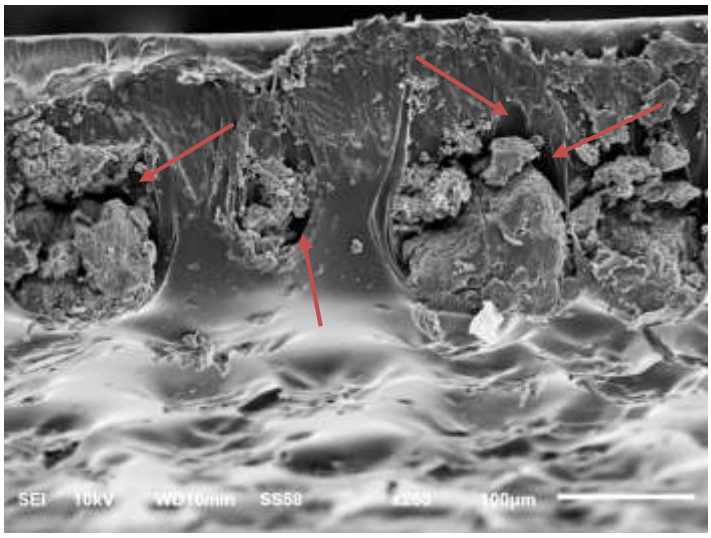

Figure (21): Red arrows aim to the voids around the silicone oxide micro particles

5. CONCLUSION

Permeability of membranes has great importance where membranes are of wide industrial and medical applications. Several techniques are designed to measure the permeability of membranes. Through these methods, fluids are forced to flow across the membrane by applying high pressure. By measuring the pressure difference, membrane surface area, thickness and flow rate of fluid the permeability is calculated.

Recently polymer membranes became one of the basic members of preamble materials. The main disadvantage that restricts the applicability of polymer membranes is there weak mechanical resistance against high pressures. The current work represented great modifications for the permeability measuring techniques. This modification is concluded in addition of ionic salt to water and evaluating the flow rate through the polymer membrane by direct measurement of electrolysis current behind the membrane. Several problems are raised during the establishment of this idea, technical solutions were applied. Finally, applying pulsed potential difference on the used graphite electrodes was an ideal answer for many side problems. By this answer it was possible to write a form for imperial equation correlates the flow rate across membrane, and hence the permeability, with the electrolyte current. This qualified measuring technique could be used to measure permeability of PVA membranes. It could, with aid of the modified technique, to change the permeability of PVA membranes by adding copper nano particles for decreasing permeability and adding silicone Dioxide micro particles to the PVA for increasing permeability of the membranes. Images by SEM supported the mechanism of controlling permeability that assumed by the authors.

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Degradation of Low Density Polyethylene Due To Successive Exposure to Acid Rain and UV Radiation

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Abstract: Utilization of polymer products for outdoor applications is continuously increasing. So the stability of polymers against environmental degradation became top of interests for many researchers. The effect of environmental elements on the polymers stability has been studied, but individually. A solution against an environmental element may conflict with a solution against other element. Therefore current study aimed to clarify a sort of these conflicts, by successive exposure of low density polyethylene (LDPE) films to acid rains and ultra violet (UV) radiation for different times. The used LDPE films are selected from the commercial grads which are used for plants greenhouses, in order to use samples fully protected against environmental elements. It is found that acid rains etch PE films, causing removal for some of the UV stabilizer additives, and hence UV radiation could attack PE films seriously causing remarked oxidative degradation. This study includes wide comparisons between effects of acid rain only, UV irradiation only, acid rain followed by UV irradiation and UV irradiation followed by acid rain exposure. Variations in the chemical composition, morphological structures, thermal and mechanical properties are detected by the IR- spectroscopy, X-ray diffraction, differential thermal analysis (DTA) and tensile tests. A new view for the differentiation between degradations caused by acid rains and UV radiation is discussed. Lot of experimental data are given in many coloured graphs and tables..

1. GENERAL VIEW AND OBJECTIVE

When sulphur dioxide and nitrogen oxides are emitted into the atmosphere, they come into contact with water where they are chemically converted to acidic compounds of sulphates and nitrates. These strong acids are deposited onto the earth's surface as rain, snow and fog and through dry deposition; the name "acid rain" is commonly used for describing this painful mechanism. Sulphur is released when fossil fuels are burned, mainly for electricity production and industrial processes. Oxides of nitrogen are released during burning of all fossil fuels too, including gasoline and diesel fuel, where the nitrogen in the fuel and atmosphere reacts with oxygen. Acid rain contaminates drinking water, damages buildings, by corroding cement, accelerates plastics degradation, and causes metals to rust.

Of the solar wavelengths, the UV-B component is particularly efficient in bringing about photo-damage in synthetic and naturally occurring materials. This is particularly true of plastics, rubber and wood used in the building and agricultural industries. Solar radiation spectrum ranges over 290-300 nm and it consists of just less than 10% of UV radiation but it has sufficient energies to dissociate C-C or C-H bonds in polymer. The free radicals produced in this way may then react freely with the atmospheric oxygen and contribute to further degradation of the polymer, which is called photo-oxidation.

The outdoor service life of common plastic materials is limited by their withstanding solar ultraviolet radiation and other environmental conditions like the acid rain. Many researching efforts have been carried out for evaluating the serious effects of solar UV and acid rains individually, although both environmental elements are acting either simultaneously or successively. As a result, several protection solutions are proposed against each individual element regardless the efficiency of this protection solution in presence of the other element. In the current work, a polymer sample is exposed to acid rain and UV radiation in sequenced manner and the net effects were recorded and analysed. This work aims to present more information to increase the efficiency of polymers protection against all environmental conditions on time. This work tries to show how the UV radiation may restrict the polymer protection against the acid rains attack, and vice versa.

2. INTRODUCTION

Plastics have been employed in agriculture because of their unique properties in comparison with glass, like un-breakability, low price, transparency, flexibility and light weight. Plastics (low density polyethylene, LDPE or polypropylene PP) are now widely used for the construction of plants green houses. In this case plastic films are exposed to the most aggressive environmental conditions. The greenhouse plastic films are attacked by the solar UV radiation along the day time. Many days or weeks around the year, acidic rains attack these films too. Thus the two environmental elements acid rain and UV radiation are attacking the greenhouses plastic films either simultaneously or successively. The successive exposure to these environmental elements is the most dominant case.

The degradation processes of the various types of polymer have specific mechanisms and depend on both the main macromolecular chain nature, structure and on the chemical nature of the branched groups. It is well known, for the oxidation of polyolefin's or rubber (natural and some synthetic types), that hydro-peroxides and the peroxy radicals are intermediates in a long kinetic chain mechanism. In the case of the halogenated polymers the de-hydro-halogenations is the first reaction step followed by the thermal oxidation, while for the polyamides or cellulose the oxidation occurs by hydro-peroxides within a short chain mechanism [1-7].

Two main groups of factors are causing the most polymers degradations, which are:

1 - Chemical factors: oxygen, chemicals, ozone, polymerization catalysts, etc.

2 - Physical factors: light, ionizing radiation, heat, mechanical processing, etc.

The degradation process starts by releasing a free radical either by energetic photon or by breaking a chemical bond thermally or chemically. The is the so called initiating the process which is repeated several times as long as the initiator is active, as shown in figure 1.

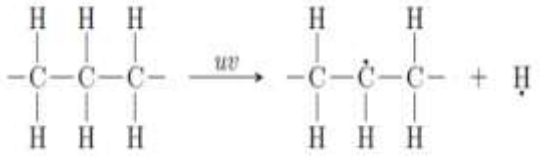

Figure (1): The hydrogen is separated from the polymer chain leaving hydrogen radical (H.) and polymer chain radical (C.).

It is also possible for the C - C bonds to be broken, figure 2:

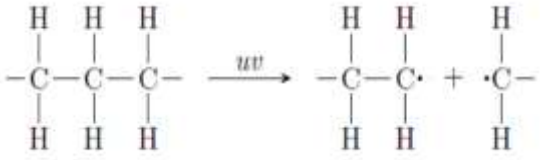

Figure (2): Breaking the C-C bond.

but due to the energy required it is less likely to occur [8]. If the photo-irradiation takes place and oxygen is available then photo-oxidation reactions are able to continue as shown down:

The highly reactive polymer radical (C*) is able to react with oxygen resulting in the formation of a peroxy polymer radical (COO*). Two of the hydrogen radicals (H*) are able to react together resulting in the release of hydrogen gas (H2). The rate of formation of these peroxy radicals is controlled by the propagation of oxygen into the polymer. The newly formed peroxy radical (COO*) is able to extract hydrogen from the polymer chain to form hydro-peroxide and another polymer radical (C*), as shown down:

These hydro-peroxides are unstable and so will decompose to form further radicals from the continued UV radiation [9]. Another product commonly associated with oxidation is the production of carbonyl groups (C=O), the formation of which can result in a range of new molecules. The formation of carbonyl groups is also thought to play a key role in the chain scission of the polymer back bone [10]. The formation of a simple ketone group which is measurable by IR spectroscopy with absorption at 1722 cm-1 is common. Another common carbonyl group seen in photo-oxidised LDPE is aldehyde, measurable by IR spectroscopy with an increased absorption at 1730 cm-1 .The formation is thought to typically result in the scission of the polymer chain.

Polyethylene (PE) resins in their natural state are inherently unstable and degrade when exposed to oxygen (air oxygen). The degradation is similar to the rusting (or oxidation) of untreated iron in that the polymers change colour to yellow-brown and begin to flake away until the material becomes useless. When PE degrades, chain scission takes place. The physical properties of the polymer deteriorate and its average molecular weight (chain length) decreases, melt flow rate increases and a powdery surface eventually forms. Polymer degradation is a natural phenomenon that cannot be totally stopped. Instead, resin producers seek to stabilize the colour and physical properties of their polymers for a reasonable life span, which varies depending on the end user requirements. Auto-oxidation continues unless countermeasures are taken to halt the process. One way to terminate auto-oxidation is by adding various antioxidants to the resin. Antioxidants (A/O) are a class of chemicals with varying chemical compositions and methods of terminating auto-oxidation. The antioxidant chemicals are additives for specific operation; other additives are widely used for other polymer properties modifications. Additives such as heat stabilizers, light stabilizers, slip agents, plasticizers, and antioxidants represent some of the most common classes of compounds used to tailor polymer properties for specific applications. So, commercial final polymer products should contain some types of additives, these chemical additives may be reacting with some or all environmental elements. For example; acid rains may react with the antioxidant at the surface (etches the surface), and hence the surface will be opened to the UV radiation attack, and so on. Therefore, studying the effect of UV radiation on polymer samples after wetting them in acid rain simulating solution is very important step for evaluation the efficiency of the used antioxidant. With the same logic, in order to examine the chemical resistance of a polymer against acid rain, the polymer sample should be exposed to UV radiation before the examination.

3. EXPERIMENTAL MEASURES:

The polymer used in the current study is commercial polyethylene films that are manufactured in Egypt for plants greenhouses usage. Plasticizer, antioxidant, UV stabilizer, anti-static charging and slip agents are added to the used PE films with unknown ratios. Film thickness is 0.08 mm

1- Sample treatments:

The commercial PE film was cut into small pieces each of area equivalent to that of the A4 paper sheet. These pieces are divided into four groups plus one piece that is taken as blank sample (denoted later as fresh film) which is not treated at all. Each group is subjected to a specific treatment as following:

- First group: consists of 6 pieces, all pieces are immersed in big basin filled with acid rain simulating solution. After one week one piece is picked out the solution and washed with the tap water and then left to dry in oven at about 40oC for 2 hours. After two weeks the second piece is drawn from the basin and dried too, and so on for the rest of group samples. Samples of this group are denoted as (AR 1-6). Exposure time in acid rain is considered in units of week.

- Second group: consists of 6 pieces, one piece is irradiated by intensive UV radiation for one day and then drawn out of radiation stream. The next piece is irradiated for two days, and so on for the rest of this group samples. Samples of this group are denoted as (UV 1-6). Exposure time in UV radiation is considered in units of day.

- Third group: consists of 6 pieces, one piece is immersed in the acid rain solution for one week and dried, then it is irradiated by same UV for one day. Second piece is immersed in the acid rain solution for two weeks and then irradiated by the UV radiation for two days, and so on for the reset pieces of this group. Samples of this group are denoted as (AR & UV 1-6).

- Forth group: consists of 6 pieces, one is irradiated by the same UV for one day and then immersed in the acid rain solution for one week and dried. Second piece is irradiated by the UV radiation for two days, and then immersed in the acid rain solution for two weeks then dried, and so on for other pieces of the group. Samples of this group are denoted as (UV&AR 1-6).

2 – The acid rain simulator

(Schulz, et al, 2000) showed that, the pHs of a real acid rain even at the aggressive environments lied in the range of 3.5-4.5. Acid rain etches the acrylic polymer and strongly damages the surface coating [11]. Another authors said that acid rain is formed when the pH of rain water is below 5.6. As the literature does not provide any exact specification for the chemical content of the acid rain, it is usually assumed to be the mixture of sulphuric acid and nitric acid of pH 4.3 – 4.5 [12]. Therefore a mixture of sulphuric and nitric acids of pH 3.6 was prepared and used in this work as acid rain simulator to represent the aggressive acid rain that is normally characterizing industrial zones and around classical power stations. The pH values were measured by a digital pH-meter model 350 from Jenway Co, with glass probe.

3 – UV source

The used UV radiation source containing three germicidal UV lamps from General Electric Co., model G15T8, 436 mm length, 25.5 mm diameter, 15 W radiation powers and 254 nm characteristic wavelength for 10,000 average useful life. The distance between the light source lamps and samples is (15 cm). Each sample is exposed to this radiation for different periods ranged from 1 to 6 days, continuously.

4 – Infrared spectrophotometer

Infrared spectroscopy is a versatile experimental technique and it is relatively easy to obtain spectra from samples in solution or in the liquid, solid or gaseous states. The first dispersive infrared instruments employed prisms made of non-absorbing materials for IR-wavelengths such as sodium chloride. The popularity of prism instruments fell away in the 1960s when the improved technology of grating construction enabled cheap, good quality gratings to be manufactured [13]. In the present work, an instrument model NICOLET- IS10 from Thermo Scientific Co., USA is used. Polymer samples from each sample group were examined after exposure to the selected treatment for detecting the molecular changes, if any.

5 – X – Ray diffraction measurements

X - ray diffraction is a powerful tool for the identification of the crystallization state of solids. The crystallization state includes degree of crystallization, crystal size, crystals type, rate of crystallization and crystal distribution as special case. The X-ray diffraction charts may provide well information about the macro-molecular orientations. The mean orientation factors (k) may be calculated as the ratio between intensity of crystalline maxima for samples treated and untreated analogues [14]. The x-ray tube that used in the present work was adjusted at the following measurement conditions: Cu target, voltage of 40 kV at 30 mA. (Shimadzu6000, Japan).

6 – Thermal analysis

Differential Scanning Calorimetric (DSC) technique is widely used to investigate the properties of polymers upon heating on certain range at specific rate. Melting and crystallization are examples of phase transitions of the first order. This means a transition where the heat capacity as a function of time and temperature exhibits a discontinuity, which has the shape of a peak. The area under the peak in the thermo-gram is directly proportional to the energy that is emitted or absorbed during changes of state in the sample. The highest point in the peak reflects the temperature or time when

the largest part of a sample is melting or crystallizing or when a polymerization or curing reaction occurs at its highest rate. Differential thermal analysis (DTA) is also used when the melting point is the task. DTA is excellent technique for the determination of melting temperature of crystalline polymers, where the sharpness of melting peak can represent the degree of crystallinity. Therefore this technique is in-efficient in the case of amorphous (glassy) polymers.

In the present work, the Shimadzu50 (Japan), instrument was used in atmosphere of nitrogen and gas flow of 20 ml/min for sample of weight 10 mg in aluminium pan.

7 - Mechanical Stress – Strain Characterization

There are three factors determine whether a polymer is glassy, rubbery or fibre-forming under a given set of conditions. These are the chain flexibility, the chain inter-attraction and the regularity of the polymer. The relationship has been expressed diagrammatically by Swallow [15]. Failure of polymers in certain applications to carry design loads or occasional accidental overloads may be due to excessive plastic deformation resulting from the inadequate strength properties of the polymer. For the quantification of such failures, the mechanical property of primary interest is the yield strength and the corresponding strain. The ultimate strength, along with the associated strain, also provides useful information [16].

The machine used to measure the recent mechanical properties is Zwick Tensometer Z010, Germany, with calibrated load cell at temperature of 23+ 0.2oC and R.H. of 45 + 5 %.

4. RESULTS AND DISCUSSION

When a material (say polymer) is attacked by acid, the first expectation is occurrence of a chemical reaction. The easier technique to investigate any chemical changes in a material is the IR-spectroscopic analysis. Therefore, PE samples that are subjected to the acid rain (AR) were tested; figure 3 shows the transmittance percent of the AR- group samples.

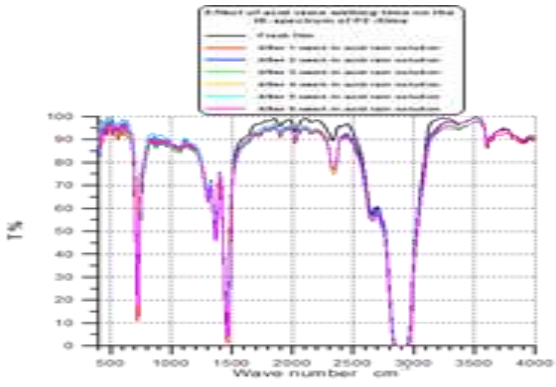

Figure (3): IR – Transmission spectrum of PE samples subjected to acid rainsolution for different periods ranged from 1 to 6 weeks.

Through the first look it is clear that no serious chemical changes have been occurred, which is expected due to the high chemical resistance of PE. A careful evaluation of the spectrum one deduces the etching effect of the acid rain where the PE sample surface became smoother and may be thinner. This is clear from the increasing in contrast of transmitted interference fringes due multi-reflections between the parallel surfaces of the sample as shown in figure 4. The greatest etching effect takes place during the first week, which means that the functional additives used in this commercial PE are acid reactive.

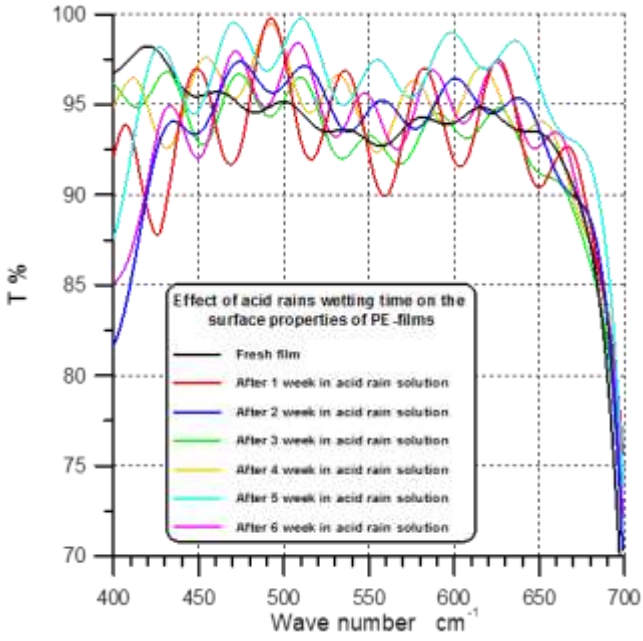

Figure (4): The etching effect of acid rain on the surface optical propertiesof commercial PE samples.

Also, due to the known oxidative degradation of polymers by UV – irradiation, it is expected to observe some oxygen bonds in the structure of PE. The IR-spectrum of UV irradiated PE shows that bond at 1720 cm-1, as shown in figure 5.

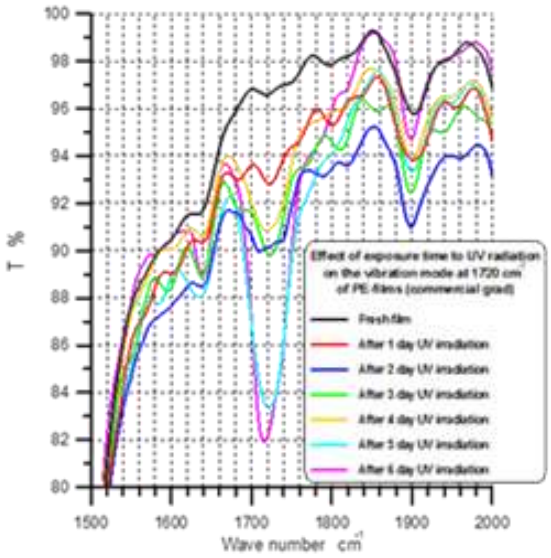

Figure (5): The appearance of C=O bond in the UV-irradiated PE structureafter 3 days of continuous irradiation.

From figure 5 it is clear that the added UV stabilizer is of medium efficiency since it could withstand the intense UV radiation along three days, but after 5 days the efficiency of this stabilizer failed. Figure 6 shows that the added UV stabilizer in the used commercial PE samples was among the chemicals that are removed during the etching effect of the acid rain. The red curve on figure 6 represents the strong existence of the oxide bond (23% on the transmittance scale) by the UV irradiation after the acid rain etching, while the blue curve represents the weak oxidation bond (8% on the transmittance scale) by UV radiation before the etching by acid rain.

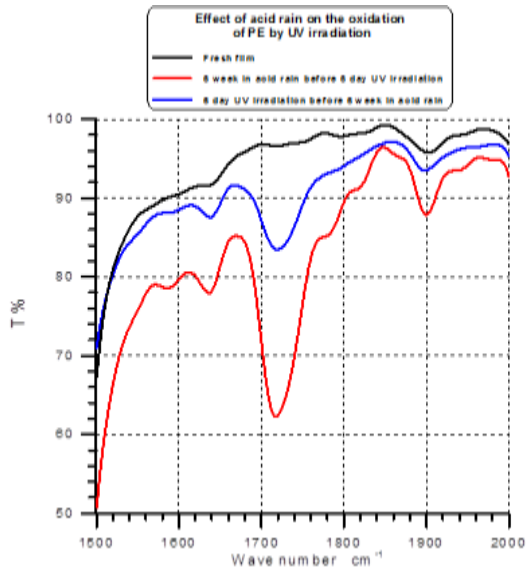

Figure (6): The effect of acid rain etching on the oxidation of PEby UV radiation.

The behaviour shown in figure 6 illustrates that acid rains have reacted and removed the UV stabilizer, then the polymer molecular system became unprotected against UV radiation, and hence when UV radiation attacks the polymer after the acid rains it could to degrade the polymer seriously.

That previous discussion shows the great advantage of studying the effect of successive exposure to environmental elements over the individual studies of each element.

Sequenced effects of environmental elements on polymer materials are not enclosed in the polymer degradation by chemical reactions but these effects are extended to the morphological structure of the polymer molecular system too.

X-ray diffraction technique is among the best methods of evaluating morphology of solid objects. Figure 7 represents the effect of acid rain and UV radiation on the used commercial PE films, individually. The graph shows that exposing PE films to acid rain for 6 weeks induced crystalline enhancement equivalent to that induced by UV irradiation for 6 days. There is no new crystalline structures are observed.

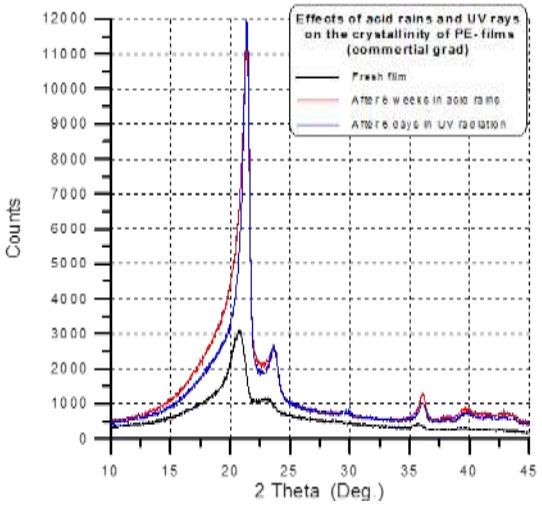

Figure (7): The maximum changes in crystalline state of PE due to acid rain and UV radiation individually.

Figure 8 shows the etching effect of the acid rains on the morphology of PE films; where after etching, the UV could to penetrate the sample with higher intensity and causes more crystalline enhancement.

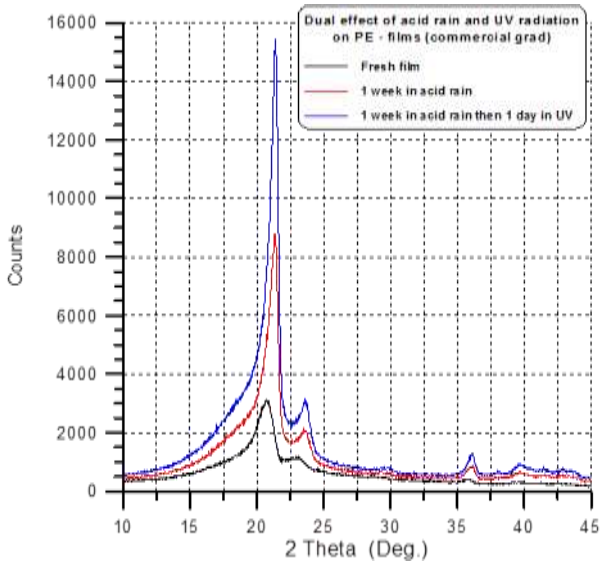

Figure (8): The effect of the etching by the acid rain on the crystalline state of PE films.

From figure 8, it is noted that one week for the sample in acid rain caused limited enhancement in the crystalline state of the polymer sample, but if this sample is subjected to UV radiation after acid rain, the crystalline state of sample material possesses a great enhancement. Figure 9 shows the same effects as discussed above but for reversed sequence.

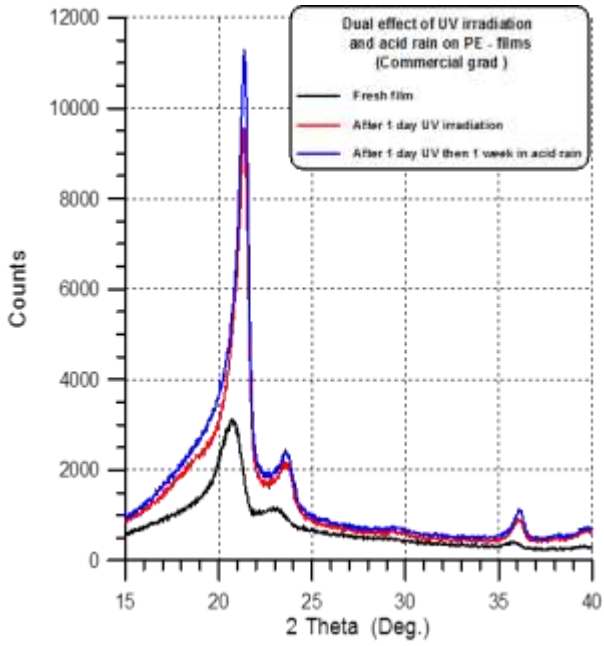

Figure (9): Successive effect of UV radiation and acid rain on the crystalline state of PE films.

It is clear from figure 9 that when acid rain attack follows the UV attack, its effect on the crystalline state of PE sample is very limited. Comparing graphs in figures 8 and 9 with graphs in figure 7, one deduces that the most of morphological variations by acid rain and UV radiation are tack place within the first day of UV and the first week of acid rain exposure times.

It is well known that any variations in the morphological state of a material should show reflections on the thermal properties as well as the mechanical properties of that material. For a single material, there are several thermal properties. The DTA thermo-gram provides information about two different parameters simultaneously, namely; melting point (at the sharp tip of the melting peak) and the relative amount of the present crystalline phase (as the length of the melting peak).

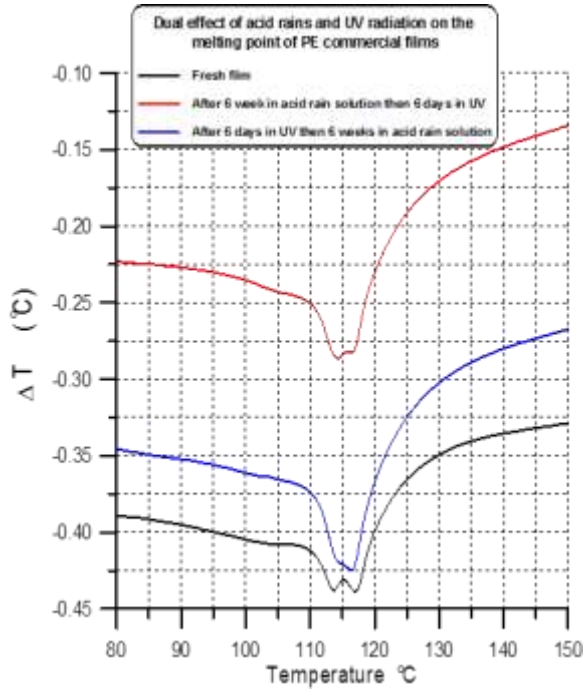

Figure (10): DTA thermo-gram of PE film sample exposed to acid rain and UV radiation in different sequences.

Figure 10 shows that the melting point of PE is 115oC and neither the acid rain nor the UV irradiation has changed this value. This result is confirmed from figures 7 to 9, where the crystals type not changed and no new crystalline phase has been formed due to the external effects. It is noted from figure 10 also that the melting peak of the samples, which exposed to acid rain and UV radiation, are somewhat longer due to the increase of the crystalline amount in the sample by the UV radiation and acid rain. The selected exposure time for both acid rain and UV radiation show limited observable changes in the length of melting peaks (as shown in figure 11), which in contrast with the observable peak changes in the X-ray diffraction patterns.

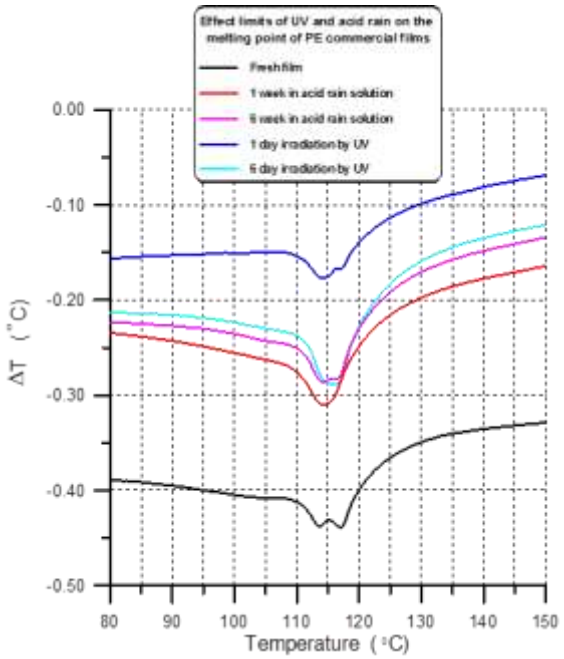

Figure (11): Limited changes in the length of melting peaks through the range of exposure time to acid rain and UV radiation.

Mechanical properties of the PE samples show variations due to the exposure to acid rain and UV radiation, too. Tables (1-3) concluded the observed changes during the tensile test of all samples.

Table (1): The percentage elongation at the yield point

Time interval	UV	AR	AR then UV	UV then AR
0	12	12	12	12
1	9.2	12	7.3	10.9
2	10.7	9.2	5.7	9.0
3	5.7	8.9	7.0	6.6
4	5.7	8.75	3.3	4.6
5	6.6	8.8	3.3	3.9
6	3.6	9.4	3.9	3.3

NOTES: 1- AR = exposure to acid rain, 2- UV = exposure to ultra violet radiation
3- time intervals are in units of weeks for AR and in days for UV

Table (2): The percentage elongation at the breaking

Time interval	UV	AR	AR then UV	UV then AR
0	960	960	960	960
1	980	960	870	825
2	780	840	380	625
3	630	880	290	520
4	590	780	75	220
5	135	780	75	123
6	75	890	74	80

NOTES: 1- AR = exposure to acid rain, 2- UV = exposure to ultra violet radiation
3- time intervals are in units of weeks for AR and in days for UV

Table (3): The elastic modulus in MPa

Of course, all of the observed variations in the mechanical parameters of PE films should be related to formation of the strong C=O as well as the dramatic increase for the amount of crystalline phase by exposure to acid rain followed by UV irradiation. The increase in the crystalline phase makes the material more brittle and hence less ductility, which is clear from the continuous decrease in all tensile parameters. The effect of etching by acid rain appears in the fast and great downfall of the percentage elongation at breaking of the samples (AR then UV) in table (2). This set of tables shows that acid rain alone did not affect the mechanical properties of PE seriously, which supports the high chemical resistance of the PE. These tables show also that the used UV-stabilizer in the commercial PE samples under tests is of medium efficiency, where sample`s mechanical properties resisted UV radiation for maximum 3 days and then downfall.

As mentioned above, the observed variations in the mechanical parameters are symptoms of two factors, which are the formation of C=O bonds (or oxidation) and the increase of crystalline phase. The question arises here is, how one can identify the share or responsibility of each factor in the observed variations? The answer may be found in the rate of changes. As seen in figure 5, the oxidation of PE increases gradually as time increases, this behaviour is coincident with that shown in table 2 for the UV coulomb. Thus one may consider that the variation of percentage elongation at break belongs to the oxidation progress in PE. On the other side, figure 8 shows that most of the crystalline phase enhancements are occurred during the beginning of the action periods, which is coincident with data changes in table 1 for (AR then UV) coulomb, where data changed suddenly after the first time step. Thus one may consider that the variation of percentage elongation at the yield point belongs to the change in size of the crystalline phase.

Generally, in the current case, the rate of oxidative degradation (by UV radiation) is proportional to the rate of changing the

percentage elongation at breaking and the rate of crystalline phase enhancement is proportional to the rate of changing the percentage elongation at the yield point through the tensile test.

5. CONCLUSION

Utilization of polymer products for outdoor applications is continuously increasing. So the stability of polymers against environmental degradation became top of interests for many researchers. The acid rains, UV radiation and heat are the most degrading environmental elements. The effect of these elements on the polymers stability has been studied, but individually. The authors of the current work clam that solutions derived from these individual studies are of limited efficiency, because of their conflicts. The current study clarifies a type of these conflicts. The traditional solution for the UV degradation of polymers is to add certain organic chemical additive to increase the polymer resistance for the UV degradation. Acid rains may react with these chemical additives and restricts their activity against UV radiation, and hence the polymer article becomes unprotected against UV. This work shows that successive exposure to acid rain and UV radiation can minimize the efficiency of some chemical additives. It is better to study effects of all environmental elements in sequenced manner and all collected data should be analysed at once. By this suggested researching regime, a unique high efficient solution can be established. It is found that acid rains have etching effect on the polymer surfaces. Acid rains alone caused no serious degradation, which is due to the high chemical resistance of the used PE polymer. Other polymers, say glassy polymers, may not resist the acid rains attack. Major effects of acid rains are occurred within the first week, longer exposure time to acid rain causes minor effects. In contrast, degradation effects by UV radiation are extended as long as the radiation attacks the polymer until full degradation of the polymer. So, it is recommended, after this study, to prevent accumulation of acid rains on the polymer films for long time.

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