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Anticorrosive Behaviour of Aqueous Extract of *Markhamia lutea* Leaves in Acid Medium

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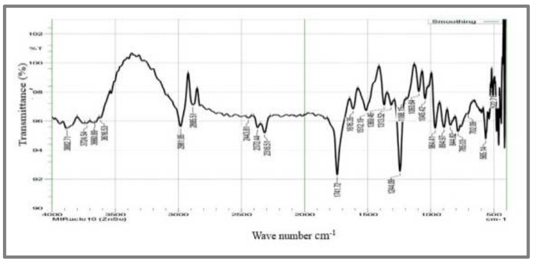
ABSTRACT

The anticorrosive action of Markhamia lutea leaves (MLL) extract on mild steel (MS) specimen in the presence of acid medium was examined by various techniques such as weight loss measurement, immersion time, electrochemical impedance spectroscopy, potentiodynamic polarization, effect of temperature, kinetics and thermodynamic parameters and SEM morphology. The inhibition efficiency was increasing with increase in concentration of the extract. The potentiodynamic polarization technique showed that the inhibitor acts as a mixed type of inhibitor. Electrochemical impedance spectroscopy revealed that the plant extract got adsorbed on the metal surface. The protective film which was formed on the metal surface was proved by SEM morphology.

Graphical Abstract



FTIR spectrum of *Markhamia lutea* leaves extract.

Keywords: Corrosion inhibitor, EIS, SEM, *Markhamia lutea* leaves, Polarization.

INTRODUCTION

Mild steel is the most abundantly used metal for various purposes in industries. Due to its oxidizing nature it undergoes corrosion process. Corrosion is a dangerous as well a serious issue that is being faced by oil and gas industries. Because of this reason frequent replacement of the various parts of the equipments take place every year [1]. In order to overcome this problem, corrosion should be controlled by using the inhibitor. Many organic and inorganic compounds having π-bonds are used as protecting agents against corrosion with high inhibition efficiency [2]. Using chemicals as the inhibitor cause health and environmental problems [3]. The toxic effect of the chemicals led to the use of natural products as anticorrosive agents which are eco-friendly and harmless [4]. Plant products contain phytochemical constituents such as Alkaloids, Carbohydrates, Terpenoids, Phenolic compounds, Glycosides which are the sources of π-electron centers and functional groups such as -C=C-, -OR,-NR_2 [5]. The aim of the study is to identify the inhibition efficiency of MLL extract as green corrosion inhibitor against corrosion of mild steel in 1N HCl using various techniques such as weight loss method, immersion time, SEM morphology, potentiodynamic polarization, electro-chemical impedance spectroscopy. No such reports have been found out in the literature as the use of this plant as the corrosion inhibitor [6].

MATERIALS AND METHODS

Preparation of mild steel specimen: The working electrode used in this study was mild steel which was made into strips of dimension (5x2x0.2) cm. The composition of mild steel is tested. The mild steel strips were provided with a hole of uniform diameter in order to suspend them in the test solution. The same composition of mild steel strips of area 1cm^2 was used for the electrochemical studies. Accurate weight of the metal was taken using four digital electronic balance (shimadzuay220) [1].

Preparation of the plant extract: The leaves of the medicinal plant *Markhamia lutea* were collected, washed, dried in shade for two weeks and ground well into powder. 25g of the powder was mixed with 500 mL of the double distilled water and kept in a water bath for 3h using refluxed condenser and kept overnight. It was then filtered and the filtrate was made upto 500 mL, the stock solution was expressed in terms of mL. The different concentrations of about 5-25 mL were used. Similar kind of preparation has been reported in the recent years [7].

Weight loss method: Mild steel specimens were accurately weighed and immersed in 100 mL of 1N HCl solution without and with the various concentrations of MLL inhibitor. The duration of the immersion time was about 24 h at room temperature. The weights of the immersed specimens were determined. From the mass loss measurements, the corrosion rate and inhibition efficiency were calculated using the following relation (1).

$$CR(mmpy) = \frac{K*W}{D*A*T} \qquad (1)$$

Where, K= 8.76x10^4, D is density in gm/cm^3(7.86), W is weight loss in grams, A is area in cm^2, T is time in hours

$$IE\ (\%) = \frac{W_0 - W_i}{W_0} X\ 100 \qquad (2)$$

Where, W_0 and W_i are the weight loss in absence and presence of the inhibitor [8].

Fourier Transform Infrared (FTIR) Spectrum: FTIR spectra for *Markhamia lutea* leaves was carried out using Fourier transform infrared spectrophotometer. The film was carefully removed and made into pellets by using KBr. FTIR spectra was recorded.

Scanning electron microscopy: The Mild steel specimen was immersed in blank and in the inhibitor solution for 24 h in order to study the surface morphology. The specimens were examined using MIRA3 TESCAN ultra high resolution field emission scanning electron microscope (FE-SEM) equipped with accessories for energy dispersive spectroscopy (EDS) analysis [2].

Effect of temperature: The temperature study revealed the nature of adsorption of the plant extract on the mild steel specimen. It was carried out with variations in the temperature such as 40°C-80°C in water thermostat with and without the inhibitor of different concentrations. The immersion time of each temperature was 2 h time duration [5].

Potentiodynamic polarization method: Potentiodynamic polarization study dealt with the Tafel slope which was used to calculate corrosion current, corrosion potential. In this method the three electrodes such as mild steel acting as working electrode, a platinum foil acting as counter electrode and saturated calomel electrode acting as reference electrode, were used.

The formula used to calculate inhibition efficiency was:

$$IE\ (\%) = \frac{I_{corr} - I^{*}_{corr}}{I_{corr}}\ X\ 100 \qquad (3)$$

Where, I_{corr} and I^{*}_{corr} are corrosion current in the absence and presence of inhibitor.

Electrochemical impedance method: The impedance spectra were taken using the instrument with the three electrode system which was used to study the potentiodynamic polarization [9]. The ($z^{/}$) which was a real part and ($Z^{//}$) which was an imaginary part were measured at different frequency ranges. A plot was drawn between the real part and imaginary part. From the graph the charge transfer resistance (R_{ct}) was calculated. From (R_{ct}) value the inhibition efficiency in the absence and presence of the different inhibitor concentrations were calculated using the formula

$$IE\ (\%) = \frac{R_{ct} - R^{0}_{ct}}{R_{ct}}\ X\ 100 \qquad (4)$$

Where, R_{ct} and R^{0}_{ct} are the charge transfer resistance in the presence and absence of the plant extract [10].

Phytochemical analysis: Using the freshly prepared aqueous extract of *Markhamia lutea* leaves the phytochemical screening was carried out to analyze the secondary metabolites such as Alkaloids, Carbohydrates, Flavanoids, Terpenoids and Phenolic compounds etc.

RESULTS AND DISCUSSION

Weight loss method: The weight loss method was carried out using mild steel strips which were dipped in different concentrations of MLL extracts ranging from 5 to 25mL in 1N HCl solution. The results were listed in table1. It showed that the inhibition efficiency increased and corrosion rate decreased with increase in the concentration of the plant extract from 5 to 25 mL. The highest inhibition efficiency of about 96.94% was observed in 20 mL of the inhibitor concentration. The corrosion rate was found to be the least of about 25.62 mmpy at the same concentration. So the optimum concentration of the inhibitor was fixed at 20 mL.

Table 1. Weight loss determination of mild steel in 1N HCl solution containing Various Concentration of MLL extract.

Conc.of MLL (mL)	CR (mmpy)	IE%
Blank	838.53	-
5	109.51	86.93
10	67.42	91.95
15	56.70	93.23
20	25.62	96.94
25	41.33	95.07

Effect of immersion time: The mass loss measurement of MLL extract was done with various concentrations of the plant extracts with variations in immersion time. The results were given in table 2. It was observed that the inhibition efficiency increased with increase in time duration as well as increase in plant extract concentrations. The maximum inhibition efficiency was found to be in the highest concentration of 25 mL in each immersion time.

Table 2. Inhibition efficiency of MLL extract in various immersion time

Conc.of MLL (mL)	Inhibition efficiency (%)						
	1h	3h	5h	7h	9h	12h	24h
5	61.33	64.55	69.04	83.53	86.85	92.05	94.76
10	61.82	68.66	75.28	86.09	87.21	93.83	97.64
15	67.11	69.01	79.74	87.23	90.14	94.00	97.79
20	72.29	71.42	85.42	89.26	90.43	94.03	97.95
25	73.39	74.64	86.87	90.93	91.07	96.86	98.50

FTIR spectra: The FT-IR spectrum was used to analyze various functional groups present in the plant species. Some of the functional groups present in the MLL extract was shown in the figure1. The peak at 3616 cm^{-1} was due to the presence of O-H stretching frequency. The peak in the frequency range 2981.96 cm^{-1} could be assigned to the presence of C-H stretching frequency. The absorption band which was observed in the region 1741.72 cm^{-1} was due to aldehyde or ketonic C=O stretching vibration. The frequency at 1616.35 cm^{-1} was due to C=O bending bond. Some peaks in the range of 1369.46 cm^{-1}, 1244 cm^{-1} and 1188 cm^{-1} were in coincidence with C-N and C-O stretching bonds. The band at 1093 cm^{-1} was due to ring oxygen atom. Some of the peaks below 1000 cm^{-1} were due to aliphatic C-H group. The presence of all these groups showed that the plant extract acts as a good inhibitor by means of the adsorbed or protective layer formed on the metal surface.

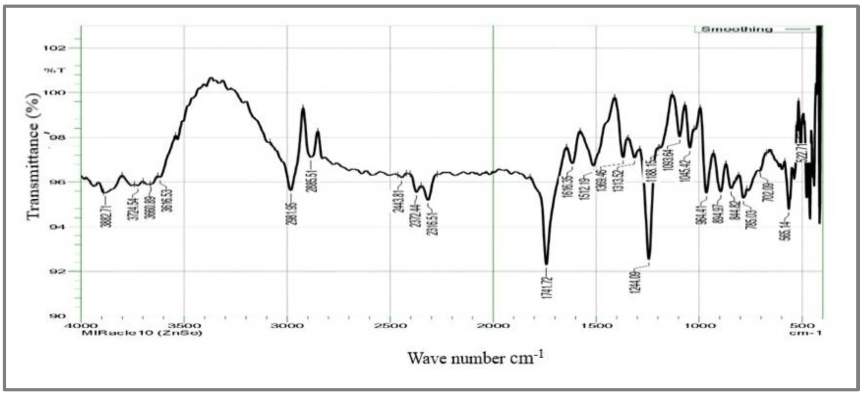


Figure 1. FTIR spectrum of *Markhamia lutea* leaves extract.

Potentiodynamic polarization method: Potentiodynamic polarization study was carried out to know the formation of protective layer on the surface of the metal. The various parameters recorded in this study were corrosion potential (E_{corr}), corrosion current density (I_{corr}), cathodic and anodic slopes(b_c and b_a) respectively. The readings were listed in the table 3. It showed that the corrosion current density was higher for 1N HCl and keep on lowering as the concentration of plant extract increased from 5 to 20 mL, only slight changes would be observed in corrosion potential values due to increase in the concentration of inhibitor which showed that the plant extract acted as a mixed type of inhibitor. The plant extracts contain lone pair of electrons on the oxygen atom which would react with the surface of the metal thereby retarded the dissolution of metal at the anode side, which retarded the corrosion rate of the mild steel [11]. The inhibition efficiency in the table 3 showed that the MLL extract act as an effective corrosion inhibitor. It was understood from the figure 2 that the curves of anode were moving towards positive potential for the mild steel dipped in the solution containing inhibitor compared with the specimen dipped in 1N HCl. The highest inhibition efficiency was found to be 93.17% where the inhibitor volume was about 20 mL which is the optimum concentration.

Table 3. The various parameters of potentiodynamic polarization for mild steel in various concentrations of MLL extract with 1N HCl

Conc. of MLL (mL)	E_{corr} (mV)vs(SCE)	I_{corr} (mA/cm^2)	CR mmpy	bc (mV/dec)	ba (mV/dec)	IE (%)
Blank	-468	1.306	0.6025	265	163	*
5	-495	0.4738	0.2185	158	179	63.72
10	-500	0.2841	0.1310	137	122	78.21
15	-506	0.2840	0.1310	128	113	78.25
20	-502	0.0890	0.04109	71	64	93.17
25	-525	0.3606	0.1663	157	160	72.38

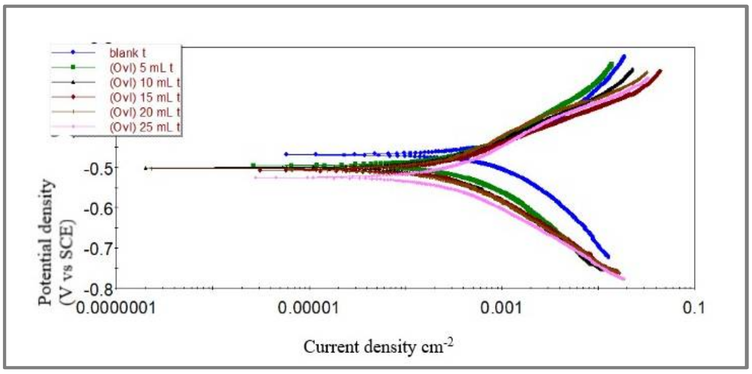


Figure 2. Tafel slope of mild steel in the blank and MLL extract of different concentration.

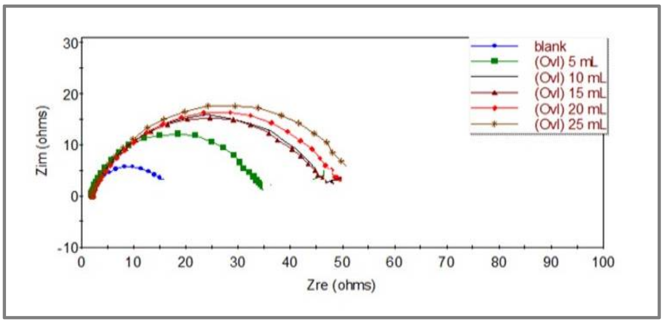
Electrochemical impedance spectroscopy: Electrochemical impedance spectroscopy was carried out to know about the formation of protective film on the metal surface [6]. This was shown by the parameters such as charge transfer resistance (R_{ct}) and double layer capacitance (c_{dl}). There would be increase in the (R_{ct}) values and decrease in (c_{dl}) values which is given in the table 4.The Nyquist plot shown in the figure 2 would be seen that the semicircle diameters were increasing with increase in concentration of inhibitors from 5 to 25 mL [12]. The lowering of (c_{dl}) values shown in the table 4 was due to the growing of electrical double layer thickness and decrease in dielectric constant. In the figure 2 the increase in concentration of the MLL extract caused the increase in value of charge transfer resistance [13]. It was evident from the Nyquist plot that the single semicircle formed controls the corrosion due to the formation of protective film on the metal surface [14].

Table 4. Measurement of impedance with various concentrations of plant extract with 1N HCl

Conc.of MLL (mL)	C_{dl} (μFcm^{-2})	R_{ct} Ωcm^2	IE (%)
Blank	$6.929x10^{-5}$	14.98	-
5	$4.741x10^{-5}$	34.16	56.14
10	$4.234x10^{-5}$	45.62	67.16
15	$3.82x10^{-5}$	50.17	70.14
20	$4.284x10^{-5}$	50.36	70.25
25	$4.177x10^{-5}$	49.52	69.74

Effect of temperature: The mild steel specimen which was immersed in 1N HCl containing the plant extract of 5,10,15,20 and 25 mL concentrations were used to know more about the effect of temperatures on the specimens by varying the temperatures from 313K to 353K in 2 h duration of each variation. It was tabulated as follows:

Figure 2. Nyquist plot of electrochemical impedance spectroscopy in the presence and absence of inhibitor



From table 5, it was understood that inhibition efficiency was increasing from the temperature 313K to 333K. This is because the metal was undergoing dissolution and the plant extract was chemically adsorbed on the surface of the metal. The corrosion rate is also keep on increasing by increasing the temperature in the blank solution. But there would be desorption takes place by increasing the temperature from 343K to 353K. This was proved that the inhibiting effect of inhibitor decreases as the temperature rises because of physical adsorption of the plant extract on the metal surface [15].

Table 5. Inhibition efficiency of MLL extracts at various temperatures

Conc. of MLL(mL)	313K		323K		333K		343K		353K	
	CR (mmpy)	IE (%)	CR (mmpy)	IE (%)	CR (mmpy)	IE (%)	CR (mmpy)	IE (%)	CR (mmpy)	IE (%)
Blank	920.16	-	999.57	-	1642.5	-	2125.91	-	3235.54	-
5	179.71	80.46	141.40	85.85	139.31	91.52	357.34	83.19	640.84	80.19
10	127.47	86.14	127.47	87.24	120.50	92.66	252.85	88.10	434.66	86.56
15	125.38	86.37	113.54	88.64	106.57	93.51	199.91	90.59	320.42	90.10
20	123.99	86.52	101.00	89.90	97.52	94.06	164.39	92.26	269.57	91.66
25	89.86	90.23	87.07	91.28	83.59	94.91	150.46	92.92	229.17	92.92

Adsorption isotherm: The word adsorption means the way in which the inhibitor is adsorbed on the surface of the metal. It was explained with the help of the graph plotted between C/θ vs C which has given a straight line in the figure 4 indicates that the inhibitor obeyed Langmuir adsorption isotherm [16]. It can be represented as,

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \qquad (5)$$

Where, K_{ads} is the equilibrium constant and C_{inh} is the concentration of the inhibitor. The plot obtained

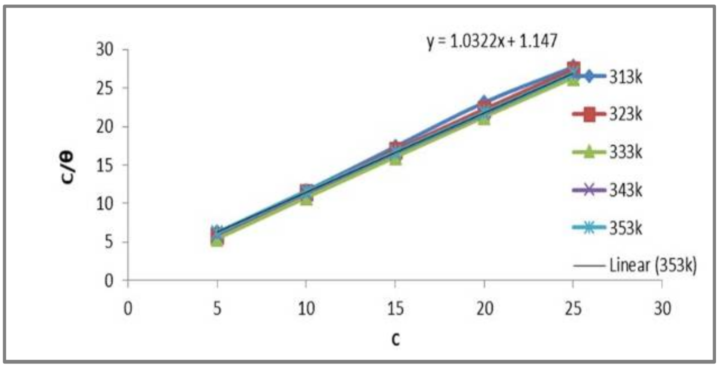


Figure 4. Langumuir adsorption isotherm of different temperatures of MLL extract.

was found to be linear, proved that the metabolites present in the extract acted as a barricade for charge and mass transfer between MS specimen and habitat, preceded by Langmuir adsorption isotherm exhibited the inhibition efficiency [17].

Scanning electron microscopy: Scanning electron microscopy was used to evaluate the surface morphology of the mild steel specimen in the presence and absence of the inhibitor. The metal was dipped in the blank solution and also in the optimum concentration of the plant extract in 1N HCl for 24 h. Then the metal was washed, dried and SEM study was carried out in MIRA3 TESCAN instrument and the images are shown in figure 5(a) and 5(b). It was clearly explained that in Figure 5(a), the metal surface was highly damaged due to the corrosive nature of acid and figure 5(b) showed that due to the plant extract a smooth protective layer was formed which controls further corrosion of the metal.

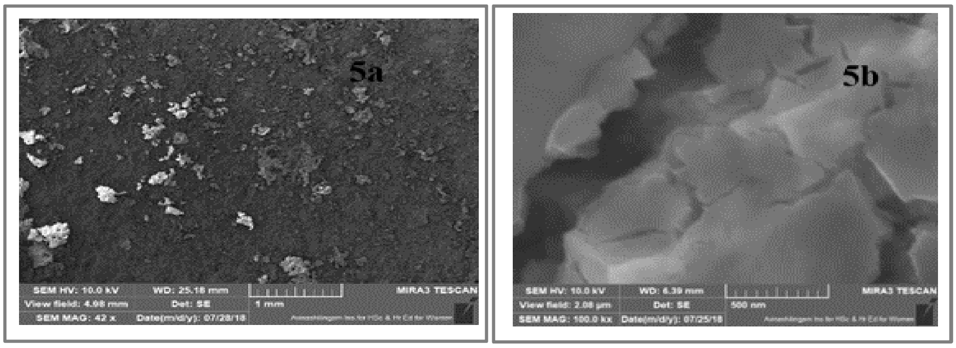


Figure 5. SEM morphology of mild steel in the absence of inhibitor (5a) presence of inhibitor (5b).

Phytochemical screening method: The plant extract acted as a good corrosion inhibitor because of the presence of phytochemical constituents present in it. The MLL extract was subjected to phytochemical screening test to find out the components such as Alkaloids, Carbohydrates, Phenolic compounds, Terpenoids, Flavanoids, Saponins, Proteins and Glycosides. The components present in MLL extract was listed in table 6.

Table 6. Phytochemical screening of MLL extract

Phytochemical Test	ML leaf extract
Alkaloids	+
Carbohydrates	+
Triterpenoids	-
Phenolic compounds	+
Flavanoids	+
Glycosides	+

(+) Presence (-) Absence

APPLICATION

The MLL extract has excellent resistance capacity over mild steel in HCl medium. The inhibitor present in MLL extract is found to be harmless, ozone friendly and safe to use even in high temperature. So this plant can be used for the protection of mild steel in acid medium in industries.

CONCLUSION

As a result of various studies carried out, it was observed that the MLL acted as a good green corrosion inhibitor in acid medium which showed that the inhibition efficiency of about 95.07% at optimum concentration. In the temperature studies the plant extract inhibits till the temperature reaches 333K because of chemisorption. In polarization techniques the cathodic and anodic reactions were retarded which showed that the inhibitor acted as a mixed type of inhibitor. The SEM study explained that the inhibitor gets adsorbed and forms a protective film on the metal surface [15].

REFERENCES

[1]. P. R. Sivakumar, K. Vishalakshi, A. P. Srikanth, Inhibitive action of *Bombax Malabaricum* leaves extract on the corrosion of Mild steel in 1N HCl Medium, *J. Applicable Chemistry,* **2016**, 5(5), 1080-1088.

[2]. K. K. Alaneme, S. J. Olusegan, A. W. Alo, Corrosion inhibitory properties of elephant grass (*Pennisetum Purpureum*) extract: Effect on mild steel corrosion in 1M HCl solution, *Alexandria Engineering Journal,* **2016**, 55, 1069-1076.

[3]. O. K. Abiola, O. J. Moriamo, P .O. Asekunowo, P. C. Okafor, O. J. Oladele,3-[(4-amino-2-methyl-5-pyrimidinyl) methyl]-5-(2-hydroxyethyl)-4-methyl thiazolium chloride hydrochloride as green corrosion inhibitor of copper in HNO_3 solution and its adsorption characteristics, *Green Chem. Let. Rev.*, **2011**, 4 (3), 273-279.

[4]. N. S. Patel, S. Jauhari, G. N. Mehta, Mild steel corrosion inhibition by *Bauhinia purpurea* leaves extract in 1N sulphuric acid, *The Arabian Journal for Science and Engineering*, **2009**, 34(2)C, 61-69.

[5]. S. Geetha, S. Lakshmi, K. Bharathi, Solanum trilobatum as a green inhibitor for aluminium corrosion in alkaline medium, *Journal of chemical and pharmaceutical Research,* **2013**, 5(5), 195-204.

[6]. S. Vidhya, A. Leema Rose, Evaluation of *Solanum nigrum* Leaf extract as a corrosion inhibitor and reductant for the green synthesis of Gold Nano particles, *International Journal of research and development in pharmacy and Life Sciences,* **2014**, 3, 1011-1021.

[7]. A. Mesbah, C. Juers, F. Locouture, S. Mathieu, E. Rocca, M. Francois, J. Steinmetz, Inhibitors for magnesium corrosion, *J. Solid State Sci.*, **2007**, 9, 322-328.

[8]. P. R. Sivakumar, A. P. Srikanth, *Ziziphus jujuba* leaves extract as green corrosion inhibitor for mild steel in 1N hydrochloric acid medium, *J. Applicable Chem.*, **2016**, 5 (5), 1080-1088.

[9]. V. Johnsirani, J. Athiyabama, S. Rajendran, J. Sathiyabama, S. Rajendran, S. M. Lydiachristy, J. Jeyasundari, The Effect of Eclipta Alba Leaves Extract on the corrosion inhibition process of carbon steel in sea water, *Porugaliae Electrochimica Acta*, **2013**, 31(2), 95-106.

[10]. P. R.Siva kumar, M. Karuppusamy, A. P. Srikanth, Corrosion inhibition of mild steel in 1N HCl media using Millingtonia Hortensis leaves extract, *IOSR Journal of Applied Chemistry,* **2017**, 10, 65-70.

[11]. M. Ramanandasingh, Prachi Gupta, Kaushal Gupta, The Litchi(Litchi Chinensis) peels extract as a potential green inhibitor in prevention of corrosion of mild steel in 0.5M H_2S0_4 solution, *Arabian Journal of Chemistry,* **2015**.

[12]. R. Saratha, V. G. Asudha, Inhibition of mild steel corrosion in 1N H_2S0_4 medium by Acid Extract of Nyctanthes arbortristis Leaves, *E-Journal of chemistry*, **2009**, 6(4), 1003-1008.

[13]. C. B. Pradeep Kumar, K. N. Mohana, Adsorption and Thermodynamic characteristics of plumeria rubra plant extracts on mild steel corrosion in industrial water medium, *International Research Journal of pure and Applied Chemistry,* **2013**, 3(4), 330-346.

[14]. P. R. Sivakumar, A. P. Srikanth, Ecofriendly green inhibitor for corrosion of mild steel in 1N Hydrochloric acid medium- A comparative study, *J. Applicable Chem.*, **2018**, 7(1), 1080-1088.

[15]. G. Malathi, N. Sridevi, S. Rani, Corrosion Inhibition of Mild steel in 1N HCl by Basella alba, *International Journal of Frontiers in science and technology,* **2015**, 210-227.

[16]. P. R. Siva Kumar, M. Karuppusamy, K. Vishalakshi, A. P. Srikanth, The inhibition of mild steel corrosion in 1N HCl solution by Melia Azedarach leaves extract, *Der Pharma Chemica,* **2016**, 8(12), 74-83.

[17]. B. B. Patel, R. T. Vashi, *Azadirachta Indica* (Neem) extract as green corrosion inhibitor for corrosion of brass in nitric acid media, *J. Applicable Chem.*, **2007**, 6 (3), 340-349.