OPEN ACCESS JOURNAL

BIOINTERFACE RESEARCH IN APPLIED CHEMISTRY

RESEARCH ARTICLE

www.BiointerfaceResearch.com

ISSN 2069-5837

Volume 4, Issue 2, 2014, 685-693

Received: 09.01.2014 / Accepted: 15.02.2014 / Published on-line: 15.04.2014

Corrosion control of mild steel in 1.0N Hydrochloric acid medium using Pyrus pyrifolia fruit peel extract

Arumugam Petchiammal [1]*, Subbiah Selvaraj [1], Kannusamy Kalirajan [1]

ABSTRACT

The inhibitory performance of the alcoholic extract of Pyrus pyrifolia fruit peel towards the corrosion of mild steel in 1N Hydrochloric acid medium has been studied by mass loss measurement with various periods of contact and temperature. The present study revealed that the percentage of inhibition efficiency is enhanced with the increase of the inhibitor concentration and decreased with the rise in immersion time. The temperature studies reflect that the inhibitor adsorption on the metal surface takes place via chemisorption. The values ofΔH_{ads} Δ_{ads} and ΔG_{ads} suggested that the adsorption may be an exothermic and spontaneous process. It was found that the adsorption of PPFP inhibitor follows Langmuir adsorption isotherm. The protective film formed on the metal surface could also be confirmed by spectral studies.

Keywords: *Mild steel, Corrosion, Inhibition, Pyrus pyrifolia fruit peel, Mass loss, Adsorption isotherm.*

1. INTRODUCTION

Mild steel is one of the most important metal widely used for all kinds of field work in world viz. used in industries, automobiles, engineering, submarine etc. However this metal is severely affected due to the environmental pollutant such as chlorate, sulphate, nitrate, phosphate etc [1]. In order to overcome this problem, the use of inhibitors is one of the best methods to protect the metal against corrosion. Thus corrosion of mild steel and its inhibition in acid and other environments got more attention from numerous previous of investigators [2-6]. Most of the chemicals containing hetero atoms like oxygen, nitrogen and sulphur are used as corrosion inhibitors which are very toxic to all living organisms even in very small concentration, thereby green corrosion inhibitors used nowadays are biodegradable, non toxic, eco- friendly and do not contain heavy metals [6-7]. Recently numerous investigators have been studied the corrosion of metals using various plant extract as green inhibitors such as Musa acuminate peel [8], orange juice [9], Strychnos nuxvomica [10], Mango bark and leaf extract[11], Acacia seyal var. seyal [12], Uncaria gambir [13], Solanum melongena [14], Punica granatum[15], Emblica officinalis[16], Andrographis paniculata [17], Citrullus vulgaris Peel [18], Hibiscus esculenta leaves[19], Lawsonia inermis seeds [20], Anogessus leocarpus [21]. The assessment of the inhibitory and adsorption properties of Pyrus pyrifolia fruit peel extract on the corrosion of Mild steel in 1N Hydrochloric acid demonstrated that these features occur at various concentration of inhibitor using mass loss measurements at different time duration

---

[1] Post graduate and Research Department of chemistry, Sri Paramakalyani College, Alwarkurichi-627412, Tamil Nadu, India.

*Corresponding author e-mail address: ***ap_mscchem@yahoo.in***

and temperature. By utilizing the spectral studies viz. UV, SEM from which the formation of protective film on the metal surface may also confirmed.

2. EXPERIMENTAL SECTION

2.1. Specimen preparation. Mild steel specimen were mechanically pressed cut to form different coupons, each of an exact dimension of 20cm^2 (5x2x2cm), polished with emery wheel of 80 and 120, and degreased with trichloroethylene, then washed with distilled water, dried and then stored in desiccator for the present study.

2.2. Preparation of *Pyrus pyrifolia* fruit peel (PPFP) extract. Freshly available *Pyrus pyrifolia* fruits (PPF) were collected from which the peels were removed and dried well, grinded and soaked in alcohol solvent for about 48hrs, and then filtered and submitted to evaporation in order to remove the alcohol completely and the pure plant seed alcoholic extract was collected. From this extract different concentrations of 10,50,100,500,1000 ppm stock solution were prepared and used throughout the present investigation. All reagents used for this present study were Analar grade and double distilled water for their preparation.

2.3. Mass Loss measurement. In mass loss measurement, Mild steel specimens were immersed in 50ml of the test solution in the presence and absence of the inhibitor. The specimens were withdrawn from the test solutions after one hour at the temperature ranged from 303K to 333K and after 24h to 480hrs at room temperature. From this observed data, the corrosion rate (mmpy), percentage inhibition efficiency(%I.E) and surface coverage (θ) were calculated using the following formula:

$$\text{Corrosion Rate}\left(\text{mmpy}\right) = \frac{87.6\times \text{W}}{\text{DAT}} \qquad (1)$$

Where, mmpy = millimeter per year, W = Mass loss (mg), D = Density (gm/cm^3), A = Area of specimen (cm^2), T = time in hours.

$$\%\,\text{IE} = \frac{W_1 - W_2}{W_1}\times 100 \qquad (2)$$

$$\theta = \frac{W_1 - W_2}{W_1} \qquad (3)$$

Where W_1 and W_2 are the corrosion rates in the absence and presence of the inhibitor, respectively.

2.4. Surface characterization. The UV spectrum was analyzed by the instrument Model Jasco V670. The predominant elements present in the corrosion products was recorded by an EDX detector using a model Oxford Instrument Model - INCA Penta xFET. The SEM analyses of mild steel coupons after abrading and immersion in 1N HCl in the absence and presence of optimum concentration (1000 ppm) of PPFP was performed on an instrument (Model Jeol - JSM 6390) at an accelerating voltage of 20 kV and magnification of 20K.

3. RESULTS SECTION

The corrosion parameters of Mild steel in 1N Hydrochloric acid containing various concentrations of PPFP extract with different exposure times were listed out in Table 1. It could be noticed that the loss of mass increased (141mg to 1463mg) with the increase of exposure time (from 24 to 480 hrs) in the absence of the inhibitor. But in the presence of *Pyrus pyrifolia* fruit peel extract, the corrosion rate was significantly reduced from 3.273 to 0.232 mmpy for 24 hrs and 1.698 to 0.204 mmpy for 480 hrs, respectively. The maximum of 94.49% inhibition efficiency was achieved at 1000 ppm of inhibitor concentration even after 72 hrs exposure time. This was mainly due to the blocking effect of surface by film formation which reduces the corrosion rate by the attack of the acid environment. This was achieved by the hetero atoms, like nitrogen, oxygen and olefinic bonds present in the inhibitor. The observed surface coverage (θ) were constantly greater than 94%, mainly due to the formation of an insoluble stable complex between the ion in the metal surface and the hetero atom present in the phytoconstituent of the PPFP extract.

Table 1: Corrosion parameters of Mild steel in 1N Hydrochloric acid containing various concentration of PPFP extract with different exposure time.

Time immersion (hrs)	Concentration of inhibitor (ppm)	Massloss (mg)	Corrosion rate (mmpy)	Inhibition efficiency (%)
24	0	141	3.273	---
	10	39	0.905	72.34
	50	28	0.650	80.14
	100	21	0.487	85.10
	500	16	0.371	88.65
	1000	10	0.232	92.90
72	0	327	2.530	---
	10	59	0.456	81.95
	50	48	0.371	85.32
	100	35	0.270	89.29
	500	29	0.224	91.13
	1000	18	0.139	94.49
120	0	504	2.340	----
	10	115	0.534	77.18
	50	98	0.455	80.55
	100	72	0.334	85.71
	500	51	0.236	89.88
	1000	45	0.208	91.07
168	0	693	2.298	---
	10	172	0.570	75.18
	50	142	0.471	79.50
	100	109	0.361	84.27
	500	97	0.321	86.00
	1000	68	0.225	90.18
240	0	853	1.980	-----
	10	226	0.524	73.50
	50	192	0.445	77.49
	100	153	0.355	82.06
	500	126	0.292	85.22
	1000	91	0.211	89.33
480	0	1463	1.698	---
	10	415	0.481	71.63
	50	362	0.420	75.25
	100	283	0.328	80.65
	500	236	0.273	83.86
	1000	176	0.204	87.96

3.1. Effect of temperature. Table 2 reflects that the corrosion parameters of Mild steel in 1N Hydrochloric acid containing various concentration of PPFP extract with different temperature ranges from 303K to 333K. The maximum of 85.39 % and 89.36% have been attained at 303K and 333K, respectively. This was mainly due to the adsorption rate of the active molecules present in the inhibitor molecules on the metal surface superior to that of the desorption process, at higher temperature.

Table 2: Corrosion parameters of Mild steel in 1N Hydrochloric acid containing various concentration of PPFP extract with different temperature

Temperature (K)	Concentration of inhibitor (ppm)	Mass loss (mg)	Corrosion rate (mmpy)	Inhibition efficiency (%)
303	0	89	49.5954	-----
	10	32	17.8320	64.04
	50	24	13.3740	73.03
	100	21	11.7022	76.40
	500	16	8.9160	82.02
	1000	13	7.2442	85.39
313	0	264	147.1145	----
	10	87	48.4809	67.04
	50	65	36.2213	75.37
	100	53	29.5343	79.92
	500	34	18.9465	87.12
	1000	31	17.2748	88.25
323	0	582	324.3206	-----
	10	136	75.7862	76.63
	50	129	71.8855	77.83
	100	98	54.6106	83.16
	500	72	40.1221	87.62
	1000	63	35.1068	89.17
333	0	649	361.6565	----
	10	142	79.1297	78.12
	50	131	73.0000	79.81
	100	106	59.0687	83.66
	500	76	42.3511	88.28
	1000	69	38.4503	89.36

3.2. Adsorption studies. The surface coverage values (Table 3) were fitted with Langmuir adsorption isotherm (Figure 1) which was given by the following expression

$$\log C/\theta = \log C - \log K \qquad (4)$$

Where θ is the degree of surface coverage, C is the concentration of the inhibitor solution and K is the equilibrium constant of adsorption of inhibitor. This isotherm assumed that the adsorbed molecules occupied only on one site and there was no interaction with other molecules adsorbed. The linearity of Langmuir adsorption isotherm of PPFP inhibitor represents the formation of monolayer on the mild steel surface [22]. The equilibrium constant of adsorption of PPFP extract on the surface of metal is related to the free energy of adsorption (ΔG_{ads}) by the following Equation (5)

$$\Delta G_{ads} = -2.303\ RT \log (55.5\ K) \qquad (5)$$

Where R is the gas constant, T is the temperature and K is the equilibrium constant of adsorption. The negative values of ΔG_{ads} suggested that the adsorption of PPFP extract onto metal surface was a spontaneous process and the adsorbed layer was more stable one.

Table 3: Langmuir adsorption parameters for the adsorption of PPFP extract on Mild steel in 1N Hydrochloric acid.

Adsorption Isotherms	Temperature (Kelvin)	Slope	K	R^2	$-\Delta G_{ads}$ kJ/mol
Langmuir	303	0.76657	0.277141	0.997382	11.72752
	313	0.76657	0.373864	0.997382	12.69423
	323	0.76657	0.432729	0.997382	13.46385
	333	0.76657	0.440251	0.997382	13.92865

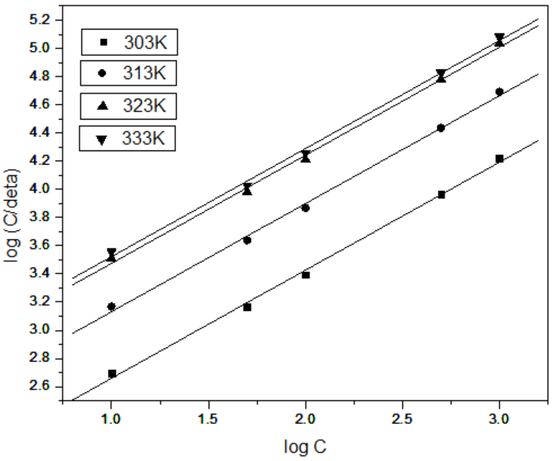

Figure 1: Langmuir adsorption isotherm of PPFP extract on Mild steel in 1N Hydrochloric acid

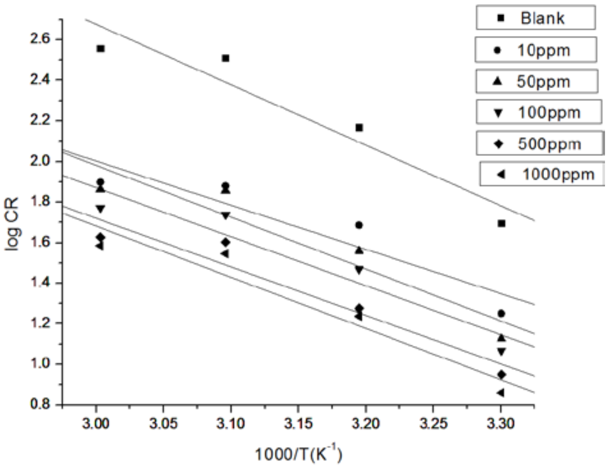

Figure 2: Arrhenius plots of mild steel in acid with and without different concentrations of PPFP

3.3. Thermodynamic parameters. A plot of log CR Vs. 1000/T gave straight lines as shown in Figure 2. The apparent activation energy (E_a) was calculated by using following relationship.

$$CR = A\exp(-E_a/RT) \qquad (6)$$

$$\log CR = \log A - E_a/RT \qquad (7)$$

Where E_a is the apparent activation energy for the corrosion of mild steel in 1N HCl solution, R the gas constant, A the Arrhenius pre-exponential factor and T is the absolute temperature. The values of E_a obtained from the slope of the lines are given in Table 4.

An alternative formula of the Arrhenius equation (6 and 7) is called transition state equation

$$CR = RT/Nh \exp(\Delta S/R) \exp(-\Delta H/RT) \qquad (8)$$

where h is the Planck's constant, N the Avogadro's number, ΔS the entropy of activation, and ΔH the enthalpy of activation. A plot of log (CR/T) Vs. 1000/T should give a straight line (Figure 3) with a slope of (−ΔH/R) and an intercept of [log(R/Nh)) + (ΔS/R)], from which the values of ΔS and ΔH were calculated and listed in Table 4. It reflects that the thermodynamic parameters (E_a and ΔH) of the corrosion of mild steel in 1N HCl solution in the presence of the inhibitors are lower than those in the free acid solution clearly indicating that less energy barrier in the reaction with inhibitor is attained. The negative enthalpy of activation reflects that the exothermic nature of mild steel dissolution process. The negative value ofΔS implies that t he activated complex is the rate determining step and represents association rather than dissociation step, meaning that a decrease in disorderness takes place during the course of the transition from reactants to the activated complex [23].

Table 4: Thermodynamic parameters for mild steel in 1N HCl solution obtained from weight loss measurements

S.No	Concentration of PPFP (ppm)	E_a (kJ mol−1)	ΔH (kJ mol−1)	-ΔS (J K−1 mol−1)
1	0	24.80349	-24.8035	1.4215
2	10	18.12252	-18.1225	1.9319
3	50	21.25757	-21.2576	0.7252
4	100	20.11522	-20.1152	1.2928
5	500	19.91037	-19.9104	1.5373
6	1000	20.9916	-20.9916	1.1548

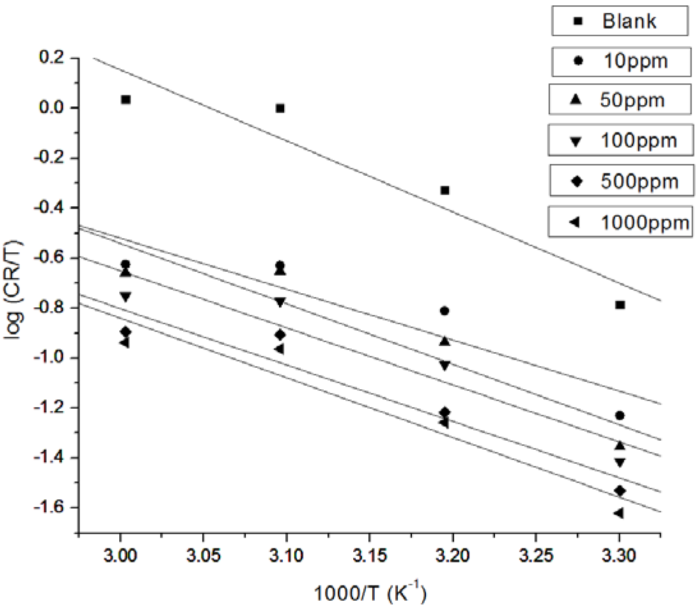

Figure 3. The relation between log(CR/T) and 1/T for different concentrations of PPFP extract

3.4. Morphology examination of mild steel

3.4.1. UV spectral analysis. Figure 4 (a) and (b) shows the UV visible spectrum of the corrosion product on the surface of mild steel in the absence and presence of PPFP inhibitor in 1.0N Hydrochloric acid. In the absence of inhibitor, the UV absorption displays maximum of two bands around 350.5nm, and in the presence of inhibitor, two bands around 396nm, 572.2nm were noticed. Thus in the presence of the inhibitor, the absorption band is shifted to longer wavelength region indicating the Bathochromic shift (or) Red shift. These results confirmed the binding between the active group present in the inhibitor and the surface of the metal.

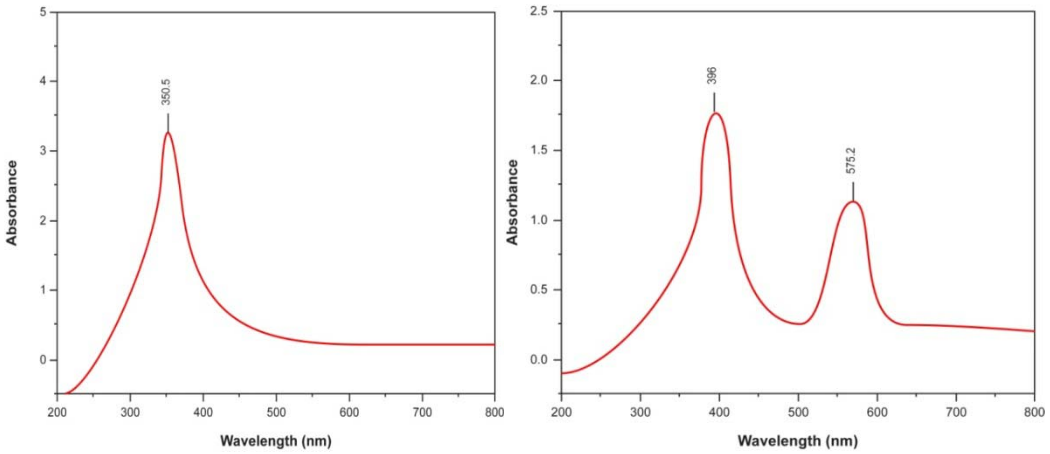

Figure 4: UV spectrum of (a) alcoholic extract of PPFP (b) corrosion product on mild steel in the presence of PPFP inhibitor in 1.0N Hydrochloric acid

3.4.2. SEM analysis

SEM Figure 5 (a-c) shows the morphological view of polished mild steel and in the absence and presence of PPFP extract in 1.0N Hydrochloric acid. The SEM micrographs of polished mild steel surface (control) in Figure 5(a) show the smooth surface of the metal and the absence of any corrosion products formed on the metal surface. The SEM micrographs of mild steel surface immersed in 1.0N Hydrochloric acid in Figure 5(b) shows the roughness of the metal surface which indicates the corrosion of metal in HCl. Figure 5(c) indicates that in the presence of 1000 ppm of inhibitor the surface coverage increases, which in turn results in the formation of an insoluble complex on the surface of the metal and the surface coverage by a thin layer of inhibitors, which effectively control the dissolution of mild steel.

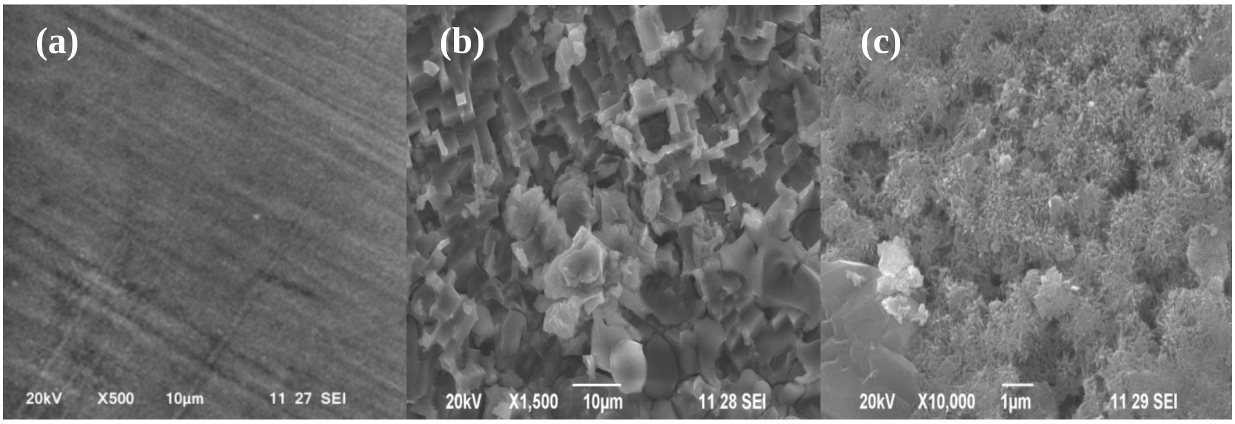

Figure 5: SEM image of polished mild steel surface a). Mild steel with 1N Hydrochloric acid alone b). SEM image of mild steel in 1.0N Hydrochloric acid having 500ppm of PPFP inhibitor (c)

4. CONCLUSIONS

Pyrus pyrifolia fruit peel has been found to be a very good inhibitor for mild steel in 1N Hydrochloric acid. The maximum inhibition efficiency attained was 94.49% and the corrosion resistance of the mild steel increased with the increase in inhibitor concentration. The inhibition efficiency decreased with the raise in temperature, i.e, 85.39% to 89.30% for 303K and 333K. This is due to the adherence of protective film on metal surface. The PPFP inhibitor is found to obey Langmuir adsorption isotherm. It follows chemical adsorption mechanism. The adsorption process is spontaneous and exothermic. The thin film formation on the metal surface may also be confirmed by UV and SEM analysis.

5. ACKNOWLEDGMENT

The authors sincerely thank to the management of Sri Paramakalyani College, Alwarkurichi, for providing all the lab facilities.

6. REFERENCES

[1] Uhlig Revie, R. Winston Corrosion handbook 2nd edition, © 2000 John Wiley & Sons

[2] Umoren S.A., Eduok U.M., Oguzie E.E., Corrosion Inhibition of Mild Steel in 1 M H_2SO_4 by Polyvinyl Pyrrolidone and Synergistic Iodide Additives, *Portugaliae Electrochimica Acta*, 26, 6, 533-546, **2008**

[3] Rafiquee M.Z.A., Khan S., Saxena N., Quraishi M.A., Influence of Some Thiadiazole Derivatives on Corrosion Inhibition of Mild Steel in Formic and Acetic Acid Media, *Portugaliae Electrochimica Acta* 25, 419-434, **2007.**

[4] Eno E. Ebenso., Taner arslan., Fatma kandemirli., Ian love., Cemil Og Rretir., Murat Saracog Lu., Saviour A. Umoren., Theoretical Studies of Some Sulphonamides as Corrosion Inhibitor for Mild Steel in Acidic Medium, *International Journal of Quantum Chemistry*, 110, 14, 2614-2636, **2010.**

[5] Siddiqi W.A., Chaubey V. M., Corrosion Inhibition Efficiency of 3-Hydroxy-2 Methylquinazoline-4-one on Mild Steel in 1 M H_2SO_4 and 1 M HCl Acid at Different Temperatures, *Portugaliae Electrochimica Acta* 26, 221-233, **2008.**

[6] Singh G., Adeyemi O.O., Galvanostatic Polarization and Resistance Studies of Acid Corrosion of Commercial Copper in the Presence of Some Heterocyclic Compounds, *J. Surf Sc. Tech*, 121-124, 1987.

[7] Adeyemi O.O., Singh G., Mechanism of Inhibition by Thiophene on Copper in 0.5 M Sulphuric Acid, *Bull. Electrochem*, 8, 12, 581-583, **1992.**

[8] Eddy N.O., Odoemelam S.A., Odiongenyi A.O., Ethanol Extract of *Musa acuminate* peel as an eco-friendly inhibitor for the corrosion of mild steel in H2SO4., *Advances in Natural and Applied Sciences,* 2, 1, 35-42, **2008.**

[9] Sanusi Kazeem Oladele., Hussein Kehinde Okoro., Investigation of corrosion effect of mild steel on orange juice, *African Journal of Biotechnology* 10, 16, 3152-3156, **2011.**

[10] Ambrish Singh., Singh V. K., Quraishi M. A., Inhibition effect of environmentally benign kuchla (*Strychnos nuxvomica*) seed extract on corrosion of mild steel in hydrochloric acid Solution., Rasayan. J.chem., 3, 4, 811-824, **2010.**

[11] Loto CA., The Effect Of Mango Bark And Leaf Extract Solution Additives On The Corrosion Inhibition Of Mild Steel In Dilute Sulphuric Acid -Scientific surveys ltd, corrosion prevention control, 48, 59-59.

[12] Buchweishaija J., Mhinzi G.S., Natural Products as a Source of Environmentally Friendly Corrosion Inhibitors: The Case of Gum Exudate from *Acacia seyal* var. *seya., Portugaliae Electrochimica Acta* 26, 257-265, **2008.**

[13] Mohd. Hazwan Hussin., Mohd. Jain Kassim., Electrochemical Studies of Mild Steel Corrosion Inhibition in Aqueous Solution by *Uncaria gambir* Extract, *Journal of Physical Science*, 21, 1, 1–13, **2010.**

[14] Nnabuk O. Eddy, Femi Awe., Eno E. Ebenso., Adsorption and Inhibitive Properties of Ethanol Extracts of Leaves of *Solanum Melongena* for the Corrosion of Mild Steel in 0.1M HCl, *Int. J. Electrochem. Sci.,* 5, 1996 – 2011, **2010.**

[15] Deepa Rani P., Selvaraj S., Inhibitive and adsorption properties of P*unica granatum* extract on brass in acid media, *Journal of Phytology*, 2, 11, 58–64, **2010**

[16] Deepa Rani P., Selvaraj S., *Emblica Officinalis* (AMLA) leaves extract as corrosion inhibitor for copper and its alloy (CU-27ZN) in natural sea water, *Archives of Applied Science Research*, 2, 6, 140-150, **2010.**

[17] Deepa Rani P., Selvaraj S., Alcoholic extract of Andrographis paniculata as corrosion inhibitor on stainless steel in Natural sea water environment, Int. J. Chem. Res, v02i1, 6-18, **2012**

[18] Petchiammal A., Deepa Rani P., Selvaraj S., Kalirajan K., Corrosion Protection of Zinc in Natural Sea Water using *Citrullus Vulgaris* peel as an Inhibitor *Research Journal of Chemical Sciences*, 2, 4, 24-34, **2012.**

[19] Petchiammal A., Selvaraj S., Kalirajan K., Influence of *Hibiscus Esculenta* leaves on the corrosion of stainless steel in acid medium International journal of universal pharmacy and bio sciences., *2*(1), 242-252, **2013.**

[20] Petchiammal A., Selvaraj S., The Corrosion Control Of Aluminium Using Lawsonia Inermis Seed Extract In Acid Medium, International Journal of ChemTech Research, 5(4), 1566-1574, **2013**

[21] Nnabuk Okon Eddy., Paul Ameh., Casmir E. Gimba., Eno E. Ebenso., GCMS Studies On *Anogessus Leocarpus* (Al) Gum and Their Corrosion Inhibition Potential for Mild Steel in 0.1 M HCl., *Int. J. Electrochem. Sci.,* 6, 5815 – 5829, **2011.**

[22] Deana Wahyuningrum., Sadijah Achmad., Yana Maolana Syah., Buchari., Bunbun Bundjali., Bambang Ariwahjoedi., The Correlation between Structure and Corrosion Inhibition Activity of 4,5-Diphenyl-1-vinylimidazole Derivative Compounds towards Mild Steel in 1% NaCl Solution, *Int. J. Electrochem. Sci,* 3, 154 -166, **2008.**

[23] Zhang Q.B., Hua Y.X., Corrosion inhibition of mild steel by alkylimidazolium ionic liquids in hydrochloric acid, Electrochimica Acta 54 1881–1887, **2009.**