SEED EXTRACT OF *SYZYGIUM JAVANICUM* AS ECOFRIENDLY CORROSION INHIBITOR FOR MILD STEEL IN HYDROCHLORIC ACID MEDIUM

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Abstract **-** The corrosion inhibition characteristics of the extract obtained from the seeds of *Syzygium javanicum* (syn. *Eugenia javanica*) on mild steel corrosion in hydrochloric acid were investigated by weight loss, electrochemical, IR spectral and SEM studies. The inhibition efficiency increased with increase in inhibitor concentration, but decreased with increase in temperature. Thermodynamic parameters and adsorption behavior were evaluated to reveal the spontaneity of the adsorption process. The polarization measurements indicated that the inhibitor is a mixed type. The confirmation of the passive layer formation was done by Fourier transform infrared (FTIR) spectra and scanning electron microscopy (SEM).

Key words: *S. javanicum*, steel, corrosion, polarization, impedance, eco-friendly

I. INTRODUCTION

S. javanicum (**Fig. 1 & 2**), known to be wax apple is a member of Myrtaceae family. The tree is native of Malaya and common in Thailand, Cambodia, Laos, Vietnam and Taiwan, frequently cultivated in India. Primarily the plant is grown as an ornamental, as the fruits are not much valued for food [1]. Even though the uses of seeds are not very much reported, the leaves are found to have medicinal uses.

Corrosion of metals and certain alloys of industrial use have sensed a substantial magnitude of attention of researchers. Because corrosion is a world-wide scientific as well industrial problem as it affects the metallurgical, chemical and oil industries. Mild steel, an alloy of iron finds a number application in above mentioned and other industries. Because of its ease of fabrication is widely used in making vessel, tanks, boilers, pipeline and so on. However it suffers from severe corrosion in aggressive environments, particularly in acidic conditions. In most of the above concerns HCl is used often as a cleaning agent, for acidification, descaling agent, etc. It is customary to make use of corrosion inhibitors to minimize the dissolution of metals by acidic medium. A number of synthetic organic inhibitors having hetero atoms, especially N, S and O are reported to control corrosion of mild steel in acidic solution [2-6]. As most of them are synthetic chemicals, expensive, and hazardous to environments, the use of environmentally safe inhibitors for the metals and alloys is of emerging practice. *Penicillin V Potassium* [7], *Vegetal Tannins* [8], *Parthenium Hystophrous* [9], *Ficus Exasperata* [10] *Citrus aurantiifolia* [11], *Prunus cerasus* [12], *Solanum Tuberosum* [13], *Azadirachta indica* [14], *Andrographis paniculata* [15], *Fenugreek Leaves* [16], Beet root [17] and *Acacia seyal* [18] are also evaluated for anticorrosion properties. In this study the extract obtained from the seeds of *S. javanicum* is evaluated for corrosion inhibition characteristics

Fig. 1. *S. javanicum* plant

Fig. 2. *S. javanicum* seeds

II. MATERIALS AND METHODS

A. Mild steel specimen:

Mild Steel (MS) specimens of composition Fe = 99.51%, P = 0.08%, Mn = 0.034%, Si = 0.6% and C = 0.16%, polished with different grades of emery paper and then degreased with trichloroethylene is used for the entire study. Weight loss and SEM studies are carried out with MS specimens of size 4.0 x 2.0 x 0.19 cm are employed. MS powder for IR and specimens with an exposed area of 1 cm^2 are used for electrochemical studies.

B. Preparation of the extract and corrosive environment:

The extract is prepared by refluxing 100 ml of 5% HCl with 50g of dried powder of *S. javanicum* seed for one hour. The extract is cooled, filtered off and made up to 100 ml using double distilled water.

A corrosive environment of 5% (v/v) HCl solution is prepared using HCl and double distilled water. From this stock solution, 100 ml each of standard solutions are prepared with and without the addition of different concentrations of *S. javanicum* seed extract.

Reagent grade, pure HCl (Merck-61752605031730) and double distilled water are used for the entire study.

C. Weight loss study and thermodynamic studies:

Polished and degreased mild steel specimens of known weight are immersed in 100 ml of test solutions with and without different concentrations of inhibitor separately for one hour at four different temperatures viz., 303, 308, 313, and 318K. Afterwards, these specimens are washed with double distilled water, dried well and weighed using Schimadzu AUX220 balance.

D. Infra-Red Spectroscope studies:

FTIR spectra for *S. javanicum* liquid extract and the dried adsorption product formed between MS powder and concentrated solution of the extract is recorded separately using Bruker FTIR model- Tensor27.

E. Surface characterization studies:

Electrochemical parameters such as potentio-dynamic polarization and Impedance measurements are carried out. Tafel polarization plots are recorded potentio-dynamically using platinum electrode, calomel electrode and MS specimen as auxiliary, standard and working electrodes respectively. Polarization studies are carried out at a sweep rate of 1mV/sec. Potential (E) versus log current (log I) plots are then recorded. Impedance measurements are carried out at a frequency range of 10 KHz to 10 mHz. The electrochemical parameters are studied in HCl medium and also with different concentrations of natural inhibitor using Solartron model SI1280B electrochemical measurement unit.

Polished mild steel specimen, specimen exposed to 5% HCl corrosive environment and specimen immersed in 10% inhibitor concentration in 5% HCl are scanned at 10K and recorded using Hitachi S-3000H model Scanning Electron Microscope.

III. RESULTS AND DISCUSSION

Weight loss studies of *S. javanicum* extract:

The corrosion inhibiton studies are carried out at four different temperatures and the weight loss data obtained for different concentrations of inhibitor and the IE values are listed in **Table 1**. From the table, it is

observed that weight loss is not much pronounced at higher inhibitor concentrations implying the increase in IE (**Fig.3**). However, when the temperature is raised, weight loss is much pronounced, even though the inhibition efficiency is not found to decrease considerably **(Fig 4)**. It is also noted that when the exposure time is increased above one hour, the IE decreases and is drastic beyond three hours.

Table 1 Weight loss data

% Conc. of the inhibitor	Weight loss, g				Inhibition efficiency, %			
	303 k	308 k	313 k	318k	303 k	308 k	313 k	318k
0	0.0666	0.0746	0.0853	0.0912	--	--	--	--
2	0.0097	0.0109	0.0126	0.0141	85.44	85.39	85.23	84.54
4	0.0079	0.0091	0.0106	0.0120	88.14	87.80	87.57	86.84
6	0.0057	0.0072	0.0091	0.0098	91.44	90.35	89.33	89.25
8	0.0043	0.0059	0.0070	0.0077	93.54	92.09	91.79	91.56
10	0.0031	0.0038	0.0047	0.0055	95.35	94.91	94.49	93.96

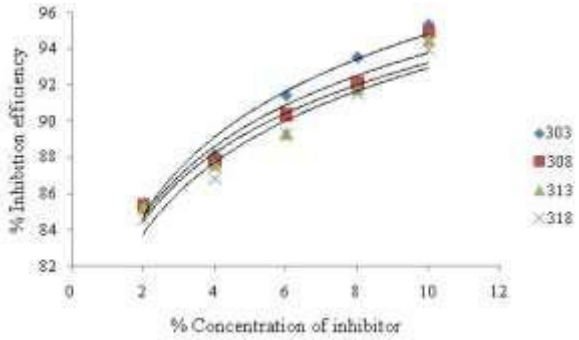

Fig.3. Plot between % IE against % concentration the *S. javanicum* extract

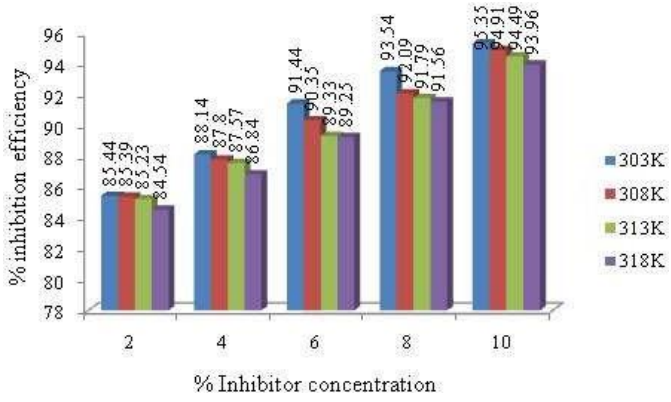

Fig. 4. Effect of temperature on inhibition efficiency of the *S. javanicum* extract

Thermodynamic parameters of *S. javanicum* extract:

The heat of adsorption (Q) was obtained by plotting log θ/1-θ against 1/T, where θ is the fraction of the metal surface covered by the inhibitor. Q values were calculated from the slope obtained that is equivalent to – Q/2.303R. The Q values are found to be negative (**Table 2**), which is an indication of decrease in corrosion reaction with increase in inhibitor concentrations and also the exothermic nature of the adsorption process.

A graph was plotted between $log\ (corrosion\ rate/T)$ against $1/T$ to find out the entropy change (ΔS) for the adsorption process. ΔS is calculated from the intercept, which is equivalent to $[log\ (R/Nh) + (\Delta S/2.303R)]$. The increased adsorption of the inhibitor on the MS surface with increase in concentration is revealed by the increased negative values of ΔS. Generally adsorption results in order from disorder of the natural inhibitor on the metal surface.

The ΔG, free energy change for the adsorption process is calculated using the following formula [19]

ΔG = -2.303RT log 55.5K, where K= (θ/1-θ)/ C ----------(1)

Chemisorption is accompanied by the change in free energy values between -49 KJ/mol and -58 KJ/mol [20]. The change in free energy (**Table 3**) for this adsorption process is in the order of -11KJ/mol, which reveals physisorption of inhibitor on MS surface. The negative free energy change values reveal the spontaneity of the adsorption of the chemical components on the metal surface.

The corrosion rate in mmpy is calculated using the formula

Corrosion rate (CR) = 87.6xW/ DAT ---------- (2)

where 'W' is the weight loss in mg, 'D' is the density of mild steel, 'A' is the area of exposure in $(cm)^2$ and 'T' is the time in hours [9]. A sudden fall in the rate of corrosion reaction with the addition of a small quantity of inhibitor shows that, even at the lowest concentration, the *S. javanicum* extract is capable of bringing down the corrosion reaction considerably. The maximum concentration of 10% inhibitor is found decrease the corrosion rate enormously from the blank value. The graph obtained (**Fig. 5**) between corrosion rate and % concentration of inhibitor also confirms that the corrosion rate is decreased tremendously with increase in inhibitor concentration irrespective of the temperature.

E, energy of activation is obtained using the formula

$$\log CR_2 / CR_1 = E/2.303R \times (1/T_1 - 1/T_2) \quad (3)$$

Where $CR_1$and CR_2 are the corrosion rates at temperatures T_1 and T_2 respectively [21&22]. The values of corrosion rate and E are given in table 3. The 'E' values are not found to vary much for a particular range of temperatures (303-318 K) even though the concentration of the inhibitor is changed. The energy of activation E is very high for 10% inhibitor dose which is found to be higher than the blank value indicating the requirement of more energy for corrosion reaction to occur at higher concentrations of inhibitor [23].

The adsorption isotherm was obtained between log C andθ, where 'C' is the concentration of the inhibitor (**Fig. 6**). The increased level of adsorption of the inhibitor on the metal surface with increase in inhibitor concentration is revealed from the graph [11].

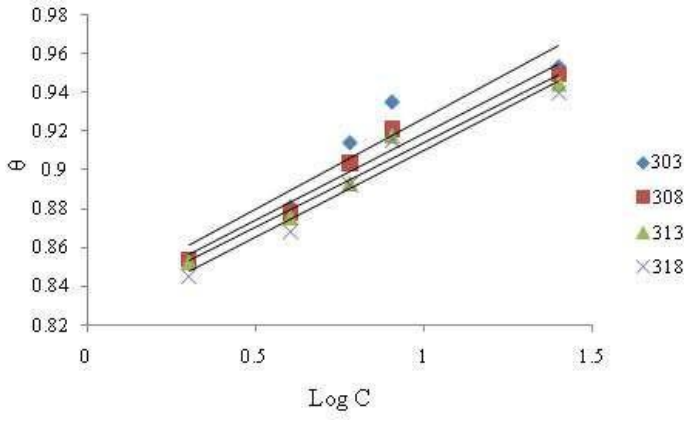

Fig. 5. Adsorption isotherm

Table 2 Heat of corrosion reaction and change in free energy data

% Conc. of the inhibitor	Q in KJ/mol	ΔS in J/mol	ΔG in KJ/mol			
			303K	308K	313K	318K
2	-3.52	-244.91	-12.83	-13.03	-13.21	-13.28
4	-6.01	-249.64	-11.68	-11.79	-11.93	-11.94
6	-14.34	-264.52	-11.57	-11.43	-11.32	-11.48
8	-15.28	-274.03	-11.61	-11.25	-11.32	-11.43
10	-14.76	-280.98	-11.93	-11.88	-11.86	-11.79

Table 3 Corrosion rate and energy of activation data

% Conc. of the inhibitor	Corrosion rate, mmpy				E in KJ/mol for the range (K)		
	303K	308K	313K	318K	303-308	308-313	313-318
0	40.66	45.54	52.07	55.67	17.58	21.47	11.07
2	5.92	6.65	7.69	8.61	18.30	23.28	18.72
4	4.82	5.56	6.47	7.33	11.57	24.29	20.67
6	3.48	4.39	5.56	5.98	36.04	37.86	12.06
8	2.62	3.60	4.27	4.70	49.29	27.35	15.89
10	1.89	2.32	2.87	3.36	31.80	34.09	26.11

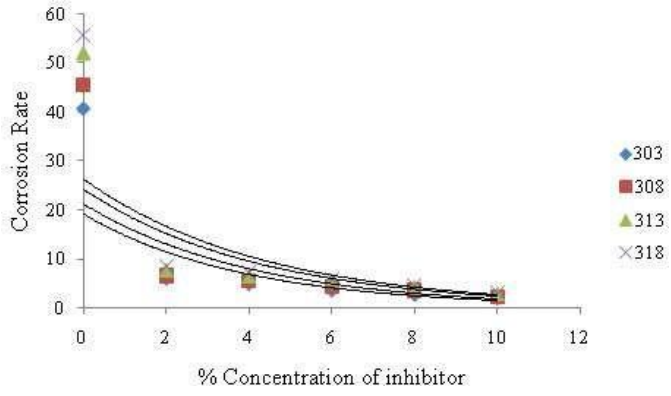

Fig. 6. Correlation between corrosion rate and % concentration of the *S. javanicum* extract

IR Spectral studies of *S. javanicum* extract:

The IR spectra of S. javanicum extract and the adsorption product between extract and MS powder are shown in **Figs. 7 and 8.**When the spectra are compared, the hydroxyl/amine stretching frequency increases from 3421.14 to 3431.16 cm-1, but the carbonyl group frequency of amide decreases significantly from 1633.30 to 1630.01 cm-1. There is also a shift in alcohol group frequency from 1371.24 to 1370.14 cm-1. These variations in group frequency indicate the adsorption of functional groups found in the S. javanicum extract via these groups, which are responsible for corrosion prevention.

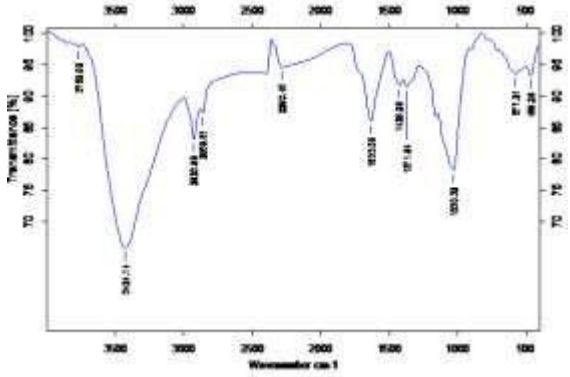

Fig. 7. IR spectra of the *S. javanicum* extract

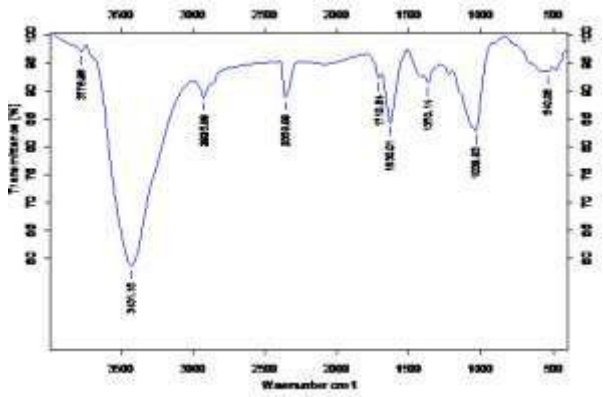

Fig. 8. IR spectra of the adsorption product between *S. javanicum* extract and MS powder

Electrochemical Studies:

The values of various electrochemical parameters were tabulated in **Table 4.** There is no regular change in corrosion potential (E_{corr}) values from the blank indicating that the inhibitor follows mixed type of inhibition. A steady decrease in the corrosion current (I_{corr}) values with ascending concentration of the inhibitor implies the retardation of corrosion reaction when compared to blank. In general, corrosion current is proportional to the magnitude of oxidation reaction associated with corrosion. The values of anodic and cathodic Tafel slopes (b_a and b_c) also do not increase or decrease in a regular manner inferring the mixed mode of inhibition.

The decrease in double layer capacitance (C_{dl}) values (**Table 4**) from the blank with increase in concentration of the inhibitor confirms the increased density of adsorption of the inhibitor on the electropositive metal surface. The adsorption is due to the electronegative hetero atoms present in the constituents of the inhibitor. The better charge transfer resistance (R_{ct}) values when inhibitor concentration is increased highlights the resistance towards the charge transfer reaction viz., corrosion reaction. It should be also noted that the IE values do not vary appreciably when compared with the conventional weight loss method. All the electrochemical parameters show that the corrosion control proceeds through the adsorption of electronegative hetero atoms present in the organic constituents of the extract on the electropositive metal surface. The

inhibition property greatly depends on the concentration of the inhibitor that is evident from the **Fig. 9 and 10.**

Table 4 Electrochemical parameters of corrosion inhibition by *S. javanicum* extract

% Conc. of the inhibitor	OCP (V)	E_{corr} (V)	I_{corr} (A)	b_a (V/dec)	b_c (V/dec)	R_{ct} (Ohm/ cm^2)	C_{dl} (A/cm^2)	%IE
Blank	-0.5151	-0.4939	0.002678	150.91	226.11	5.80	6.08×10^{-5}	
2	-0.5325	-0.5143	3.42×10^{-4}	99.22	156.28	55.93	2.52×10^{-5}	87.26
4	-0.5210	-0.5115	2.95×10^{-4}	94.87	169.04	70.94	3.95×10^{-5}	89.00
6	-0.5231	-0.5116	1.85×10^{-4}	94.48	155.72	102.45	2.66×10^{-5}	93.08
8	-0.5184	-0.5037	1.84×10^{-4}	72.25	158.24	88.73	4.39×10^{-5}	93.14
10	-0.5078	-0.5112	1.73×10^{-4}	106.44	173.47	145.11	4.79×10^{-5}	93.54

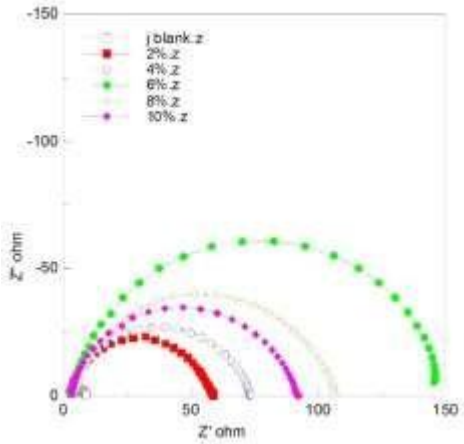

Fig. 9. Impedance spectra

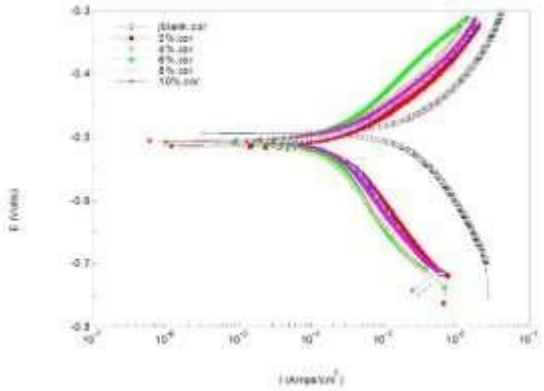

Fig. 10. Tafel polarization plot

The surface morphology of mild steel surface (**Fig. 11**), MS exposed corrosive medium (**Fig. 12**) and MS immersed in 10% inhibitor in corrosive medium (**Fig. 13**) are studied using scanning electron microscopy. The SEM photographs show that in the presence of inhibitor, the pits and corrosion products are not formed on the mild steel surface the mild steel surface. It indicates the formation of passive layer on the metal surface which [24] is clearly seen in **Fig.13.**

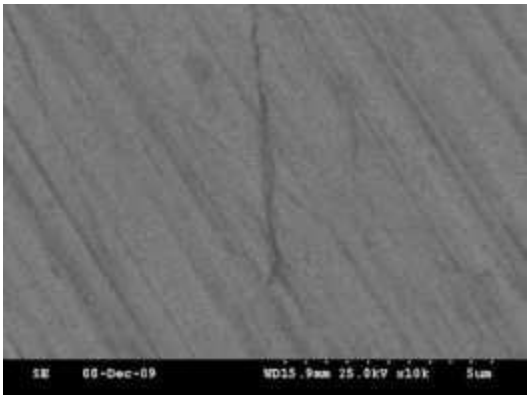

Fig. 11. Polished mild steel surface

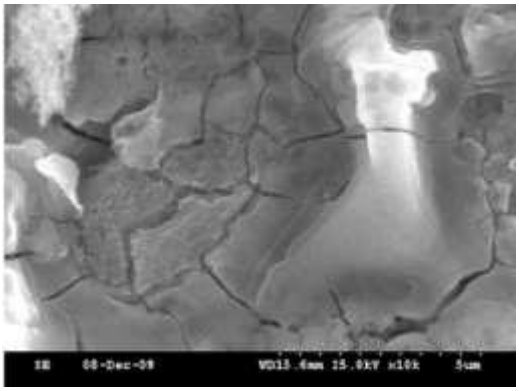

Fig. 12. Mild steel exposed to 5% HCl alone

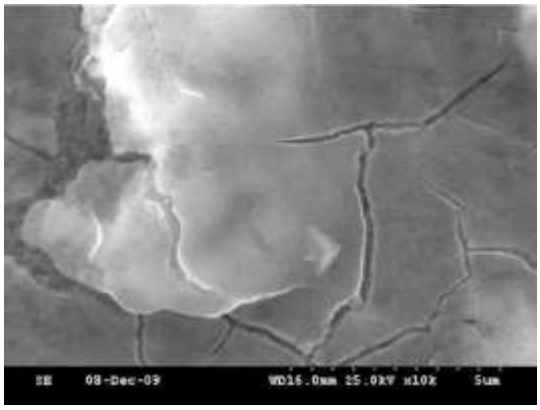

Fig. 13. Mild steel sample exposed to 5% HCl having 10% inhibitor

IV. CONCLUSION

The corrosion inhibition efficiency of *S. javanicum* extract increases along with the increase in inhibitor concentration and decreases as the temperature is raised as substantiated from the Weight loss studies. Thermodynamic analysis highlights the spontaneity of the adsorption reaction of the inhibitor on the metal surface. The enriched adsorption of the inhibitor on the metal surface with increase in concentration of the inhibitor is evolved from the adsorption isotherm plotted between log C andθ. The adsorption is assigned to the lone pair of electrons present in the hetero atoms of the *S. javanicum* extract as is revealed from IR spectral studies. The electrochemical parameters such as E_{corr}, b_a and b_c indicate the mixed mode of inhibition. The SEM photographs noticeably emphasize the protective nature of the mild steel by the extract. All these results acquaint with the fact that the seed extract of *S. javanicum* can be utilized as a nontoxic, alternate, green corrosion inhibitor for mild steel in HCl medium.

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REFERENCES

[1] Julia F. Morton, "Java Apple", *In: Fruits of warm climates* 1987, pp. 381–382..

[2] P. Lowmunkhong, D. Ungthararak, P. Sutthivaiyakit, "Tryptamine as a corrosion inhibitor of mild steel in hydrochloric acid solution" *Corrosion Science*, ,52, 2010 ,pp 30–36.

[3] A.O.James, N. C. Oforka, O. K. Abiola, B. I.Ita, "Corrosion inhibition of mild steel in hydrochloric acid by 2-Benzoylpyridine and Pyridoxolhydrochloride", *e-Journal of Chemistry* ,6 (2) ,2009.pp 385-394.

[4] N. O. Eddy, P. Ekwumemgbo, S. A. Odoemelam, "Inhibition of the corrosion of mild steel in H_2SO_4, by 5-amino-1-cyclopropyl-7-[(3*R*, 5*S*) 3, 5-dimethylpiperazin-1-YL] -6, 8-difluoro-4-oxo-uinoline-3-carboxylic acid (ACPDQC)", *International Journal of Physical Sciences*, 3 (11) 2008, pp 275-280.

[5] A.K. Dubey, G.Singh, "Corrosion inhibition of mild steel in sulphuric acid solution by using polyethylene glycol methyl ether (pegme)", *Portugaliae Electrochimica Acta*. 25, 2007, pp 221-235.

[6] B.M. Praveen, T.V. Venkatesha, Metol as corrosion inhibitor for steel, *Int. J. Electrochem. Sci*. 4, 2009, pp 267 – 275.

[7] N.O. Eddy, S.A. Odoemelam, "Inhibition of the Corrosion of Mild Steel in Acidic Medium by *Penicillin V Potassium*", *Advances in Natural and Applied Sciences*, 2 (3), 2008, pp 225-232.

[8] Afidah A. Rahim, Jain Kassim, "Recent Development of *Vegetal Tannins* in Corrosion Protection of Iron and Steel", *Recent Patents on Materials Science*, 1, 2008, pp 223-231.

[9] B. M. Muhamath,.Ali, Kulanthai, Kannan, "Inhibition effect of *Parthenium hystophrous* L. Extracts on the corrosion of mild steel in sulphuric acid", *Journal of Applied Sciences & Environmental Management*. 13, 2009, pp 27-36.

[10] N. S. Patel, S. Jauhari, G. N. Mehta, "Inhibitive effect by acid extract of *Ficus exasperata* leaves on the sulphuric acid corrosion of mild steel", *e-J. Chem.* 6(S1), 2009, pp 89-94.

[11] R. Saratha, S.V. Priya, P. Thilagavathy, "Investigation of *Citrus aurantiifolia* leaves extract as corrosion inhibitor for mild steel in 1M HCl". *E-J. Chem.* 6(3), 2009, pp 785-795.

[12] H. Ashassi-Sorkhabi, D. Seifzadeh, "The inhibition of steel corrosion in hydrochloric acid solution by juice of *Prunus cerasus*", *Int. J. Electrochem. Sci*., 1, 2006, pp 92-98.

[13] P.B Pandian, M.G Raja, "Sethuraman, *Solanum tuberosum* as an inhibitor of mild steel corrosion in acid media", *Iran. J. Chem. Chem. Eng.* 28(1), 2009, pp 77-84.

[14] N. O. Eddy, P. A. P. Mamza, "Inhibitive and Adsorption Properties of Ethanol Extract of seeds and leaves of *Azadirachta indica* on the corrosion of mild steel in H_2SO_4" , *Portugalete Electrochemical Acta*, 27(4), 2009, pp 443-456.

[15] S.P. Ramesh, K.P. Vinod Kumar, M.G. Sethuraman, "Extract of *Andrographis paniculata* as corrosion inhibitor of mild steel in acid medium", *Bull Electrochem.* 17(3), 2001, pp 141-144.

[16] Ehteram A. Noor, "Temperature Effects on the Corrosion Inhibition of Mild Steel in Acidic Solutions by Aqueous Extract of *Fenugreek Leaves*", *Int. J. Electrochem. Sci.*, 2, 2007, pp 996 – 1017.

[17] J. A. Selvi, S. Rajendran, V.G. Sri, A. J. Amalraj, B. Narayanasamy, "Corrosion inhibition by beet root extract", *Portugaliae Electrochemica Acta*. 27(1), 2009, pp 1-11.

[18] J. Buchweishaija and G.S. Mhinzi, "Natural products as a source of environmentally friendly corrosion inhibitors: The case of gum exudate from *Acacia seyal* var. seyal", *Portugaliae Electrochimica Acta*, 26, 2008, pp 257-265.

[19] E. E. Ebenso, N. O. Eddy, A. O. Odiongenyi, "Corrosion inhibitive properties and adsorption behaviour of ethanol extract of *Piper guinensis* as a green corrosion inhibitor for mild steel in H_2SO_4 ", *African J. of Pure and Appl. Chem.* 2 (11), 2008, pp 107-115.

[20] M. R. Singh, K. Bhrara, G. Singh,. "The inhibitory effect of diethanolamine on corrosion of mild steel in 0.5M sulphuric acidic medium", *Portugaliae Electrochimica Acta*. 26(6), 2008, pp 479-492.

[21] C. Das, H.S. Gadiyar, "Inhibition behaviour of organic amino compounds for carbon steel in a citric acid based descaling formulation", *J Electrochem. Soc. India.* 42(4), 1993, pp 225-231.

[22] P.B. Raja, M.G. Sethuraman, "Inhibition of corrosion of mild steel in sulphuric acid medium by *Calotropis procera*", *Pigment & Resin Technology*. 38(1), 2009, pp 33-37.

[23] V. Adhikari, V. R. Saliyan, "Corrosion inhibition of mild steel in acid media by quinolinyl thiopropano hydrazine", *Ind. J. Chem. Tec*h. 16, 2009, pp 162-174.

[24] R.A. Prabhu, T.V. Venkatesha, A.V. Shanbhag, "Carmine and Fast green as corrosion inhibitors for mild steel in hydrochloric acid solution", *J. Iran. Chem. Soc*. 6(2), 2009, pp 353-363.