JCSE The Journal of Corrosion Science and Engineering
ISSN 1466-8858 Volume 13, Preprint 32 submitted 14 July 2010

Mild Steel Corrosion Inhibition by *Ricinus Communis* Seed Husk Extract in Hydrochloric Acid

K.P.Vinod Kumar[a], , M. Sankara Narayana Pillai[b], G. Rexin Thusnavis[c]*
Department of Chemistry, University College of Engineering, Nagercoil, Anna University Tirunelveli, Nagercoil-629004, Tamil Nadu, India. nanjilvino@rediffmail.com, Mob: 009443104640; Ph: 91-4652-260510 Fax: 91-4652- 260511

[b]Department of Chemistry, Noorul Islam University, Kumaracoil, Nagercoil, Tamilnadu, India. msankars@yahoo.com

[c] Department of Chemistry, St. Xavier's Catholic College of Engineering, Chunkankadai, Nagercoil-629003, Tamil Nadu, India. Corresponding Author: grt_rexin@yahoo.co.in Mob: 009443104490; Ph: 91-4652-232560

Abstract

The seed husk of *Ricinus communis* has been studied for mild steel corrosion inhibition in acid medium. Thermodynamic parameters such as heat of adsorption of the inhibitor on the metal surface (Q), change in free energy of the reaction (ΔG), corrosion rate and energy of activation for corrosion reaction of mild steel (E) were evaluated from the weight loss data. The increase in adsorption with increase in concentration of inhibitor is substantiated using the adsorption isotherm. The functional groups responsible for inhibition were analyzed through infra red spectra. Electrochemical parameters were obtained by potentiodynamic Tafel polarization and impedance spectral studies. SEM images were photographed to study the surface morphology. All the above studies illustrated the effectiveness of seed husk extract of *R. communis* as an eco-friendly and an alternate corrosion inhibitor for mild steel in acid medium.

Key words: *R. communis,* steel, corrosion, polarization, impedance, eco-friendly

Introduction

Ricinus communis (commonly known as castor) belongs to the family Euphorbiaceae (figure 1). *R. communis* is a native of the southeastern mediterranean basin, Eastern Africa, and India. In recent days it is widespread throughout tropical regions. In areas with a suitable climate, castor propagates itself easily as a native plant and can often be found on wasteland. It is grown normally for the oil contained in the seed (figure 2), which is primarily used for surface coating formulations, lubricant, cosmetics and many other industrial applications. The oil contained in the leaves, stem and seeds is marketed as castor oil.

Figure 1 ***R. communis*** **plant with dry fruits**

Figure 2 ***R. communis*** **seeds**

Mild steel is a well-known cost effective alloy, extensively used in the petrochemical and other industries due to its good mechanical, relatively easy fabrication and corrosion resistant properties. However, it is prone to corrosion in adverse conditions particularly in acid medium. HCl is used as a cleaning and pickling agent for steel alloys. But it initiates corrosion in mild steel. Thus it is mandatory to indentify suitable corrosion inhibitors, which should be economic and eco-friendly. Traditionally organic compounds having heteroatoms were used as inhibitors for corrosion of mild steel in acid medium [1-6]. Following this plant extracts with molecules having heteroatoms were also studied for corrosion inhibition and the results were found to be hopeful [7 & 8]. *Prunus cerasus* [9], *Ficus Exasperata* [10], *Eclipta Alba* [11], *Nyctanthes arbortristis* [12], *Musa acuminate* [13], *Azadirachta indica* [14], *Andrographis paniculata* [15], *Acacia seyal* [16], Beet root [17] and tea wastes [18] were also evaluated for corrosion control properties. In the present study, the acid extract of the seed husk of *Ricinus communis* is examined for the corrosion inhibition effect on mild steel in hydrochloric acid medium.

Experimental

Mild steel specimen

The entire study was carried using Mild Steel (MS) of composition Fe = 99.51%, P = 0.08%, Mn = 0.034% and C = 0.01%. For weight loss and SEM studies MS specimens of size 4.0 x 2.0 x 0.19 cm were used. MS specimens with an exposed area of 1 cm^2 were used for electrochemical studies and MS powder was used for IR studies. These specimens were polished mechanically by different grades of emery paper and then degreased with trichloroethylene. For the acidic environment, pure HCl (Merck-61752605031730) and double distilled water as solvent were used.

Preparation of the extract and corrosive environment

50g of dried powder of *R. communis* seed husk was refluxed with 100 ml of 5% HCl for one hour. The extract obtained is cooled, filtered off and the filtrate is made up to 100 ml using double distilled water.

5% (v/v) HCl solution and double distilled water were used for preparing the corrosive environment. From this stock solution, 100 ml each of standard solutions were prepared with and without different concentrations of *R. communis* seed husk extract.

Weight loss and thermodynamic studies

Test solutions of 100 ml with and without different concentrations of inhibitor were prepared. Degreased and polished mild steel specimens of known weight were immersed in the test solutions separately for a period of one hour at four different temperatures viz., 303, 308, 313, and 318K. Then these specimens were washed, dried and weighed using Schimadzu AUX220 balance.

Infra Red studies

FTIR spectra were separately recorded for *R. communis* liquid extract and the dried product formed between finely powdered MS specimen and concentrated solution of the extract with a frequency ranging from 4000cm^{-1} to 400cm^{-1} using Bruker FTIR model-Tensor27.

Surface characterisation studies

The electrochemical parameters were studied in HCl medium and also with different concentrations of natural inhibitors. Potentio-dynamic Tafel polarization studies were made using platinum electrode, calomel electrode and MS specimen as auxiliary, standard and working electrodes respectively. Polarization studies were carried out potentio-dynamically at a sweep rate of 1mV/sec. Potential (E) versus current (I) plots are then recorded. Impedance measurements were carried out in the frequency Range of 10 KHz to

JCSE The Journal of Corrosion Science and Engineering
ISSN 1466-8858 Volume 13, Preprint 32 submitted 14 July 2010

10 mHz. All these measurements were carried out using Solartron model SI1280B electrochemical measurement unit.

SEM photographs were recorded at 10K using Hitachi S-3000H model Scanning Electron Microscope for polished mild steel specimen, specimen exposed to 2% HCl corrosive environment and specimen immersed in 10% inhibitor concentration in 5% HCl.

Results and discussion

Table 1 Weight loss data

% Conc. (v/v) of the inhibitor	Weight loss, g				Inhibition efficiency, %			
	303 k	308 k	313 k	318k	303 k	308 k	313 k	318k
0	0.0874	0.0953	0.1072	0.1156	--	--	--	--
2	0.0031	0.0042	0.0051	0.0068	96.45	95.59	95.24	94.12
4	0.0023	0.0032	0.0041	0.0053	97.37	96.64	96.17	95.42
6	0.0019	0.0026	0.0034	0.0042	97.82	97.27	96.82	96.37
8	0.0014	0.0019	0.0026	0.0032	98.39	98.01	97.55	97.23
10	0.0011	0.0016	0.0020	0.0026	98.74	98.32	98.13	97.75

The weight loss data and the corresponding inhibition efficiency values at four different temperatures are given in table 1. The data clearly show that increase in concentration of the inhibitor increases IE. At higher concentrations, IE reaches limiting values (figure 3). However the inhibition efficiency is found to decrease with rise in temperature at higher concentrations.

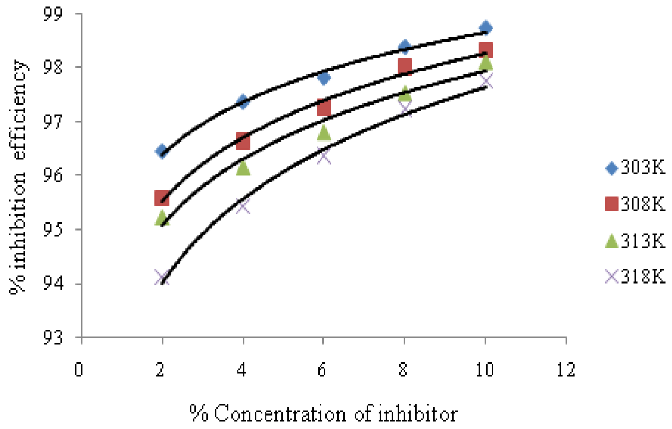

Figure 3 Effect of concentration of the inhibitor on inhibition efficiency

Thermodynamic parameters of *R. communis* extract

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

% Conc. (v/v) of the inhibitor	Q in KJ	ΔG in KJ			
		303K	308K	313K	318K
2	9.15	-16.69	-16.39	-16.45	-16.12
4	10.69	-15.73	-15.34	-15.24	-14.98
6	10.11	-15.19	-14.85	-14.68	-14.55
8	10.18	-15.24	-14.94	-14.63	-14.53
10	11.82	-15.31	-14.81	-14.58	-14.50

A negative slope is obtained that is equivalent to $-\ Q/2.303R$ from which Q, the heat of adsorption is calculated when a graph was plotted between $log\ \theta/1-\theta$ against $1/T$. θ is the fraction of the metal surface covered by the inhibitor at temperature T. ΔG, the free energy change for the adsorption was calculated using the formula [19]

$$\Delta G\ =-2.303RT\ log\ 55.5K, \text{ where } K=\ (\theta/1-\theta)/\ C \qquad \text{------(1)}$$

The values of Q and ΔG were given in table 2. The Q values range from 9.15 KJ for 2% to 11.82 KJ for 10% concentration of inhibitor. The low values of Q indicate the

JCSE The Journal of Corrosion Science and Engineering
ISSN 1466-8858 Volume 13, Preprint 32 submitted 14 July 2010

physisorption of the inhibitor on the metal surface which decreases the corrosion reaction with increase in inhibitor concentration. The values of change in free energy for the adsorption process were around -14 KJ. The negative free energy change values indicate that the adsorption of the heterocyclic chemical constituents of the extract on the metal surface is spontaneous with increased stability of the adsorbed inhibitor layer on the mild steel surface. It was already reported that the Gibbs free energy values between -49 KJ and -58 KJ are indicative of chemisorption [20]. Hence it is obvious from the low free energy change values that the adsorption is physical in nature.

Table 3 Corrosion rate and energy of activation data

% Conc. (v/v) of the inhibitor	Corrosion rate, mpy				E in KJ for the range (K)		
	303K	308K	313K	318K	303-308	308-313	313-318
0	53.35	58.18	65.44	70.56	13.43	18.84	12.47
2	1.89	2.56	3.11	4.15	47.08	31.18	47.79
4	1.40	1.95	2.50	3.24	51.41	39.81	42.95
6	1.16	1.59	2.08	2.56	48.90	43.05	34.39
8	0.85	1.16	1.59	1.95	48.23	49.80	33.81
10	0.67	0.98	1.22	1.59	58.99	60.92	43.88

The corrosion rate in mmpy was calculated using the formula

$$Corrosion\ rate\ =\ 87.6xW/\ DAT \qquad \text{------(2)}$$

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].

E, energy of activation was obtained using the formula

$$log\ S_2\ /\ S_1\ =\ E/2.303R\ x\ (1/T_1 - 1/T_2) \qquad \text{------(3)}$$

JCSE The Journal of Corrosion Science and Engineering
ISSN 1466-8858 Volume 13, Preprint 32 submitted 14 July 2010

where $S_1$and S_2 are the corrosion rates at temperatures T_1 and T_2 respectively [21, 22]. The values of corrosion rate and E were given in table 3.

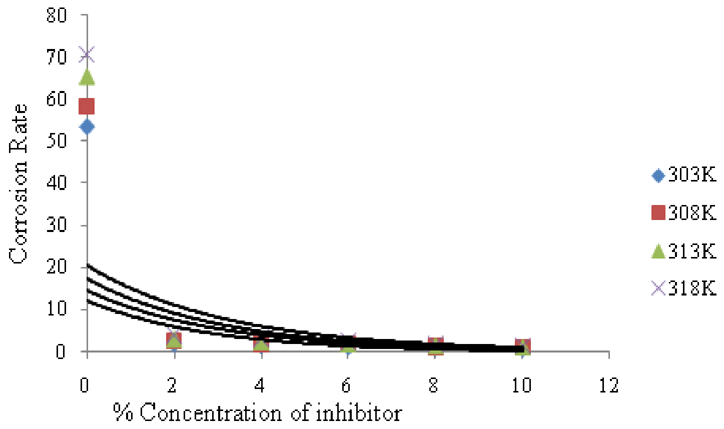

Figure 4 Effect of concentration of inhibitor on corrosion rate

The corrosion rate is decreased reasonably even at the lowest concentration of the *R. communis* extract. A tremendous decrease in corrosion rate from the blank value is noted at 10% inhibitor concentration as shown in figure 4. The 'E' values are found to increase regularly with increase in concentration of the inhibitor. The energy of activation E is very high for 10% inhibitor concentration than the blank value. This indicates that more energy is required for the corrosion reaction to occur at higher concentrations of inhibitor [23].

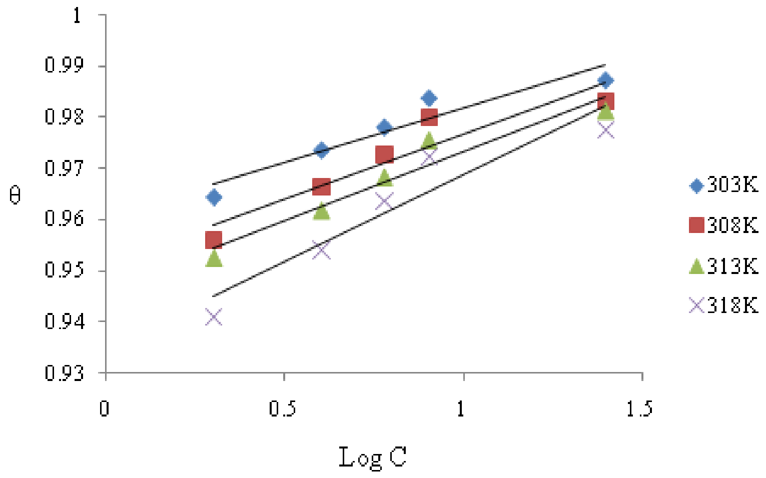

Figure 5 Adsorption isotherm

A graph (figure 5) plotted between log C, (where 'C' is the concentration of the inhibitor) versus θ gives a straight line, which obeys Temkin's adsorption isotherm. It reveals the enhanced adsorption of the inhibitor on the metal surface as the inhibitor concentration is increased [24].

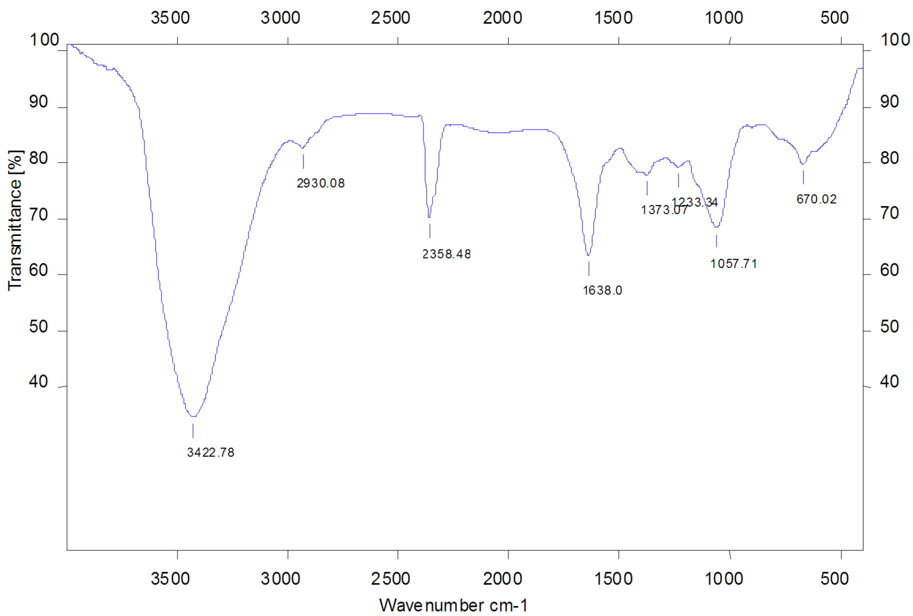

Figure 6 IR spectra of the *R. communis* extract

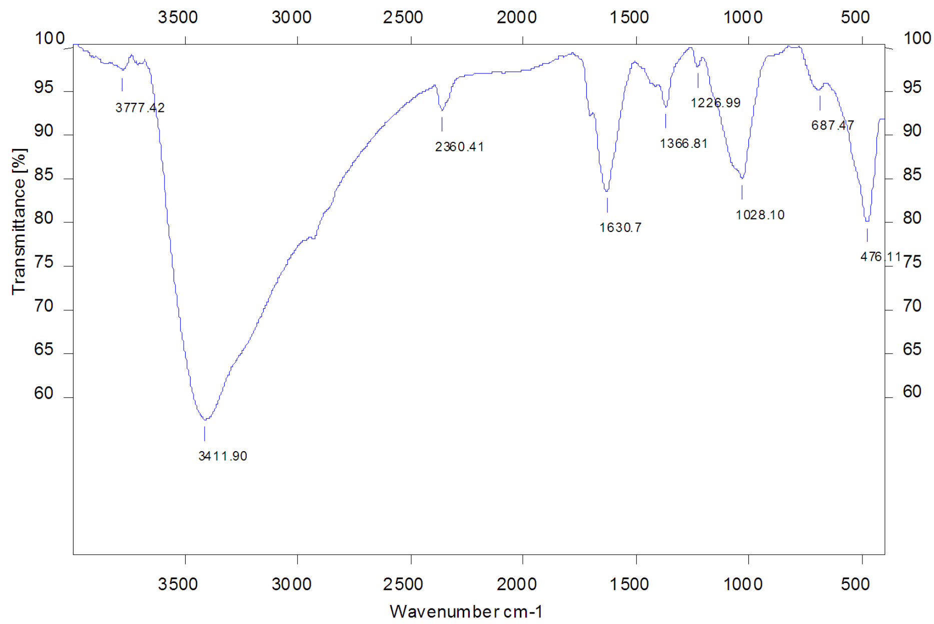

Figure 7 IR spectra of the reaction product between *R. communis* extract and MS powder

It was reported earlier that the seed husk extract contains Ricin. It is a glycoprotein, which consists of two polypeptide chains joined by a disulphide bond [25]. The comparison of IR spectra obtained for the extract and the product formed between the extract and MS powder reveals changes in amide N-H stretching, amine N-H stretching, amide carbonyl stretching, carboxylic acid -O-H bending, C-S stretching and disulphide stretching frequencies. These changes in the IR frequencies bring to light the involvement of the functional groups with hetero atoms in the adsorption process.

Table 4 Electrochemical parameters of corrosion inhibition by *R. communis* extract

% Conc. (V/V) of the inhibitor	OCP (mV)	E_{corr} (mV)	I_{corr} (μA)	b_a (mV/dec)	b_c (mV/dec)	R_{ct} (Ohm/ cm^2)	C_{dl} (μA/cm^2)	%IE
Blank	-0.5151	-0.4939	0.002678	150.91	226.11	5.8037	6.09 X 10^{-5}	-
2	-0.5512	-0.5526	2.53X 10^{-4}	125.47	332.72	207.21	3.53X 10^{-5}	90.57
4	-0.5490	-0.5571	1.57X 10^{-4}	99.33	191.44	111.20	2.12 X 10^{-5}	94.15
6	-0.5419	-0.5657	1.53X 10^{-4}	106.29	191.09	132.60	2.34X 10^{-5}	94.28
8	-0.5417	-0.5559	1.45X 10^{-4}	107.56	204.38	185.44	2.73X 10^{-5}	94.57
10	-0.5412	-0.5523	1.06X 10^{-4}	95.15	181.40	196.61	2.75X 10^{-5}	96.03

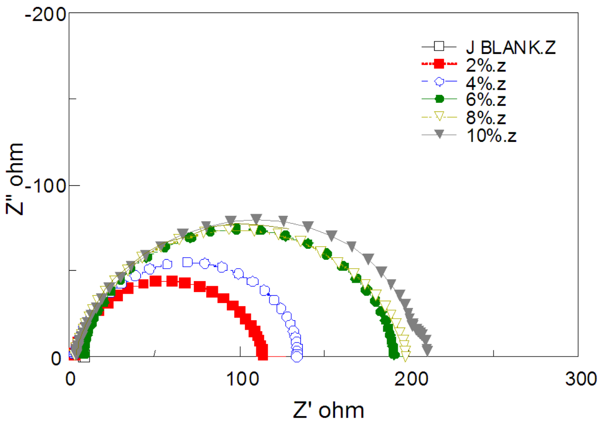

Figure 8 Impedance spectra

JCSE The Journal of Corrosion Science and Engineering
ISSN 1466-8858 Volume 13, Preprint 32 submitted 14 July 2010

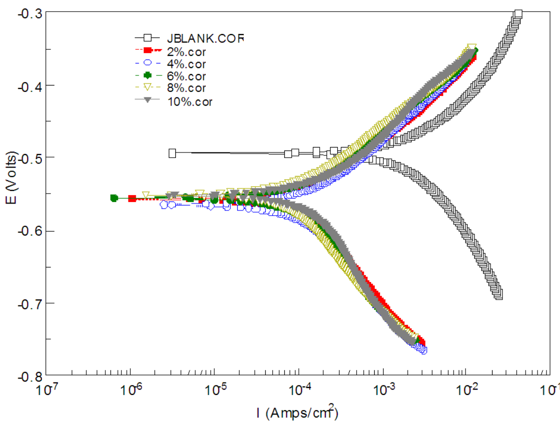

Figure 9 Tafel polarization plots

The open circuit potential (OCP), corrosion potential (E_{corr}), corrosion current (I_{corr}), anodic and cathodic Tafel slopes (b_a and b_c), charge transfer resistance (C_{dl}), corrosion rate and IE values obtained from electrochemical measurements were given in table 4. It is noted that the E_{corr} values do not increase or decrease in a regular manner from the blank value. This confirms mixed mode of inhibition of the inhibitor. The steady decrease in the Icorr values from the blank with increase in concentration of the inhibitor further authenticates the decrease in corrosion. As corrosion current is proportional to the magnitude of corrosion reaction, the decrease in the I_{corr} values reflect the decrease of reaction (figure 10). The b_a and b_c values do not fluctuate very much substantiating the decreased rate of corrosion reaction as well as mixed mode of inhibition [26].

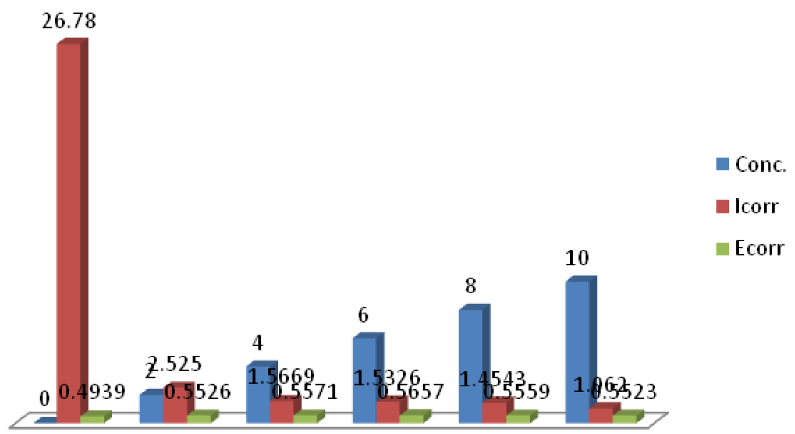

Figure 10 Effect of concentration on E_{corr} and I_{corr}

JCSE The Journal of Corrosion Science and Engineering
ISSN 1466-8858 Volume 13, Preprint 32 submitted 14 July 2010

The increased level of adsorption of the inhibitor on the metal surface is again supported by the decreased C_{dl} values from the blank as the concentration of the inhibitor is increased. This adsorption on the electropositive metal surface is attributed to the electronegative hetero atoms present in the organic constituents of the extract which is also evident from IR data. Higher R_{ct} values are observed for higher inhibitor concentrations when compared with the blank value proving the resistance towards the charge transfer reaction viz., corrosion reaction. Hence it is proved from the electrochemical parameters that the corrosion control depends on the concentration of the inhibitor as is validated from the figures 8 and 9.

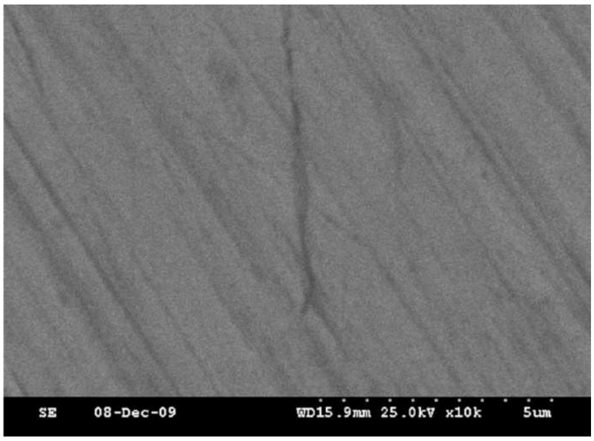

Figure 11 Polished mild steel surface

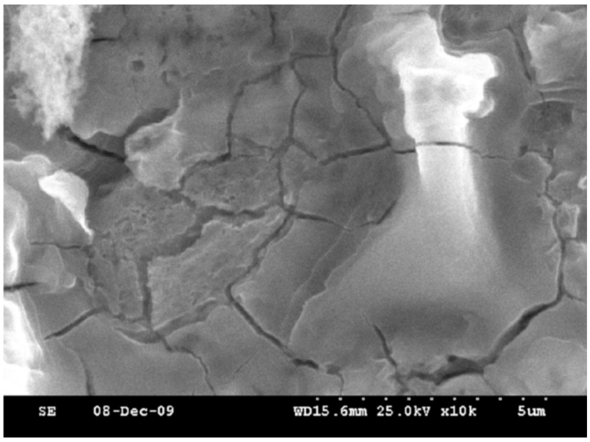

Figure 12 Mild steel exposed to 5% HCl alone

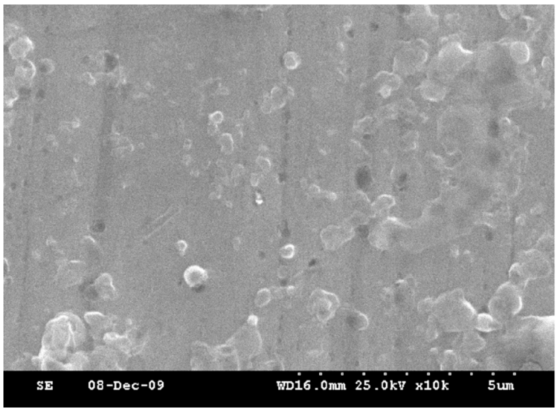

Figure 13 Mild steel sample exposed to 5% HCl having 10% inhibitor

The SEM photographs were recorded for polished metal surface (figure 11) and MS surface with (figure 13) and without inhibitor (figure 12) in hydrochloric acid medium using scanning electron microscopy to study the surface morphology of mild steel surface. The SEM studies reveal the protection of the MS surface from corrosion by the inhibitor. However this slight change on the MS surface (figure 13) is due to the formation of a protective layer on the metal surface [27].

Conclusion

The increase in concentration of the seed husk extract of *R. communis* is found to decrease the rate of corrosion enormously. However the efficiency is found to decrease with rise in temperature. The spontaneity of the reaction of the inhibitor on the metal surface is revealed by the thermodynamic parameters. From the electrochemical parameters studied, it is established that the inhibitor exhibits mixed mode of inhibition. Temkin adsorption isotherm clearly shows the increased adsorption of the inhibitor on the metal surface with increase in concentration. The adsorption may be due to the lone pair of electrons present in the hetero atoms of the *R. communis* extract which is further verified from IR spectral data. The SEM photographs clearly highlight the protective nature of the mild steel by the extract. All these results authenticate that the seed husk extract of *R. communis* can be used as an alternate eco-friendly corrosion inhibitor for mild steel in HCl medium.

Acknowledgement

We, the authors are grateful to the Director, CECRI, Karaikudi, India, for extending the laboratory facilities. The authors profusely thank Dr. S. Muralidharan, Mr. Ravi Shankar and Mrs. Nalini, CECRI, Karaikudi, India and Dr. S. Athimoolam, Anna University, Tirunelveli, for useful suggestions and other help.

References

[1] ‘Pyrimidine derivatives as corrosion inhibitors for carbon-steel in 2M hydrochloric acid solution’, Elewady, G.Y., *Int. J. Electrochem. Sci*., **3**, pp1149 – 1161, 2008.

[2] '2.5-Difuryl-N-methylpyrrole as corrosion inhibitor for steel in 1 M HCl', Krim, O.; Bouachrine, M.; Hammouti, B.; Elidrissi, A and Hamidi, M.*Portugaliae Electrochimica Acta*, **26**, pp283-289, 2008.

[3] 'Evaluation of ethylenediaminetetra-acetic acid di-sodium salt as corrosion inhibitor for mild steel in 1M hydrochloric acid', Musa, A. Y.; Kadhum, A. A. H.; Takriff, M. S.; Daud, A. R and Kamarudin, S. K., *Australian Journal of Basic and Applied Sciences*, **2**, 4, pp 956-960, 2008.

[4] 'Inhibition of acid corrosion of mild steel by Pyridoxal and Pyridoxol hydrochlorides', James, A. O.; Oforka, N. C and Abiola, O. K., *Int. J. Electrochem. Sci.*, **2**, pp278 – 284, 2007.

[5] 'Corrosion inhibition of mild steel in sulphuric acid solution by using polyethylene glycol methyl ether (pegme)', Dubey, A.K. and Singh, G., *Portugaliae Electrochimica Acta*, **25**, pp221-235, 2007.

[6] 'The effect of molecular structure on hydrogen permeation and the corrosion inhibition of mild steel in acidic solutions', Muralidharan, S.; Quraishi, M.A.; and Iyer, S.V.K., *Corrosion Science*, **37**, pp17-39, 1995.

[7] '*Strychnos nux-vomica* an eco-friendly corrosion inhibitor for mild steel in 1M sulfuric acid medium', Raja, P.B. and Sethuraman, M.G., *Materials and Corrosion*, **60**, 1, pp22 – 28, 2008.

[8] 'Inhibitory action of *Phyllanthus amarus* on the corrosion of mild steel in acidic medium', Okafor, P.C.; Ikpi, M.I.; Uwah, I.E.; Ebenso, E.E.; Ekpe U.J. and. Umoren, S.A, *Corrosion Science*, **50**, 8, pp2310 – 2317, 2008.

[9] 'The inhibition of steel corrosion in hydrochloric acid solution by juice of Prunus cerasus', Ashassi-Sorkhabi, H. and Seifzadeh D., *Int. J. Electrochem. Sci.*, **1**, pp92-98, 2006.

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

[11] 'Eclipta Alba as corrosion pickling inhibitor on mild steel in hydrochloric acid', Shyamalay, M. and A. Arulanantham, *J. Mater. Sci. Technol.*, **25**, 5, pp633-636, 2009.

[12] 'Inhibition of mild steel corrosion in 1N H_2SO_4 medium by acid extract of *Nyctanthes arbortristis* leaves', Saratha, R. and Vasudha, V.G., *e-J. Chem.*, **6**, 4, pp1003-1008, 2009.

[13] Ethanol extract of Musa acuminate peel as an eco-friendly inhibitor for the corrosion of mild steel in H_2SO_4', Eddy, N.O.; Odoemelam, S.A. and Odiongenyi, A.O., *Advances in Natural and Applied Sciences*, **2**, 1, pp35-42, 2008.

[14] 'Inhibitive and adsorption properties of ethanol extract of seeds and leaves of *Azadirachta indica* on the corrosion of mild steel in H_2SO_4', Eddy, N. O. and Mamza, P. A. P., *Portugaliae Electrochemica Acta*, **27**, 4, pp443-456, 2009.

[15] 'Extract of *Andrographis paniculata* as corrosion inhibitor of mild steel in acid medium', Ramesh, S.P.; Vinod Kumar, K.P. and Sethuraman, M.G., *Bull Electrochem.* **17**, 3, pp141-144, 2001.

[16] 'Natural products as a source of environmentally friendly corrosion inhibitors: The case of gum exudate from *Acacia seyal* var. seyal', Buchweishaija, J. and Mhinzi, G.S., *Portugaliae Electrochimica Acta*, **26**, pp257-265, 2008.

[17] 'Corrosion inhibition by beet root extract', J. A. Selvi; S. Rajendran; V.G. Sri; Amalraj, A. J. and Narayanasamy, B., *Portugaliae Electrochemica Acta*, **27**, 1, pp1-11, 2009.

[18] 'Tea waste as corrosion inhibitor for mild steel in acid medium', M.G. Sethuraman; Vadivel, P.and Vinod Kumar, K.P., *J. Electrochem. Soc. India*, **50**, 3, pp143-146, 2001.

[19] 'Corrosion inhibitive properties and adsorption behaviour of ethanol extract of *Piper guinensis* as a green corrosion inhibitor for mild steel in H_2SO_4', Ebenso, E. E.; Eddy, N. O. and Odiongenyi, A. O., *African J. of Pure and Appl. Chem.*, **2**, 11, pp107-115, 2008.

[20] 'The inhibitory effect of diethanolamine on corrosion of mild steel in 0.5M sulphuric acidic medium', Singh, M. R.; Bhrara, K. and Singh, G., *Portugaliae Electrochimica Acta*, **26**, 6, pp479-492, 2008.

[21] 'Inhibition behaviour of organic amino compounds for carbon steel in a citric acid based descaling formulation', Das, C.and Gadiyar, H.S., *J. Electrochem. Soc. India*, **42**, 4, pp225-231, 1993.

[22] 'Inhibition of corrosion of mild steel in sulphuric acid medium by *Calotropis procera*', Raja, P.B. and Sethuraman, M.G., *Pigment & Resin Technology*, **38**, 1, pp33-37, 2009.

[23] 'Corrosion inhibition of mild steel in acid media by quinolinyl thiopropano hydrazone', Adhikari, V. and Saliyan, V. R., *Ind. J. Chem. Tech.*, **16**, pp162-174, 2009.

[24] 'Investigation of *Citrus aurantiifolia* leaves extract as corrosion inhibitor for mild steel in 1M HCl', Saratha, R.; Priya, S.V. and P. Thilagavathy, *e-J. Chem.*, **6**, 3, pp785-795, 2009.

[25] 'Ricin (from *Ricinus communis*) as undesirable substances in animal feed, Scientific Opinion of the Panel on Contaminants in the Food Chain', *The EFSA Journal*, **726**, pp1-38, 2008.

[26] 'Ceftriaxone: a novel corrosion inhibitor for mild steel in hydrochloric acid', Shukla, S. K.and Quraishi, M. A., *J. Appl. Electrochem.* **39**, pp1517–1523, 2009.

[27] 'Carmine and Fast green as corrosion inhibitors for mild steel in hydrochloric acid solution', Prabhu, R.A.; Venkatesha, T.V. and. Shanbhag, A.V, *J. Iran. Chem. Soc.*, **6**, 2, pp353-363, 2009.