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Pericarp of the Fruit of *Garcinia Mangostana* as Corrosion Inhibitor for Mild Steel in Hydrochloric Acid Medium

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Abstract

The corrosion inhibition effect of acid extract of the pericarp of the fruit *Garcinia mangostana* on mild steel in hydrochloric acid medium is studied. Using weight-loss data, corrosion rate (CR) and thermodynamic parameters such as energy of activation for corrosion of mild steel (E), heat of adsorption of the inhibitors on the metal surface (Q) and change in free energy (ΔG) are calculated. Adsorption isotherm is also recorded between log C and θ. Electrochemical parameters are evaluated from AC impedance and Tafel polarization studies in the presence and absence of different concentrations of inhibitor. Infra-red spectra are recorded for the extract and the adsorption product to find out the changes in the functional group frequencies of the organic components of the extract. The surface morphological changes are analysed using the SEM images. The entire study shows that the pericarp extract of the fruit *G. mangostana* is a non-toxic, cost-effective corrosion inhibitor for mild steel in acid medium.

Keywords: corrosion; mild steel; *G. mangostana;* Tafel polarization; impedance; SEM.

Introduction

Research has been aimed throughout the globe to find out more eco-friendly green products that can serve as a substitute for the substances that are presently applied for various industries and domestic needs. The present work is focused to find out an alternative green corrosion inhibitor for mild steel in acid medium. Mild steel finds a wide range of applications in construction and petrochemical industries. But mild steel has a high tendency to corrode easily, especially in acid, alkali and other aggressive environments. HCl is widely used in chemical, petrochemical and in many other industries. Mild steel is severely prone to

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corrosion in HCl medium and hence several protective attitudes are being adopted. Corrosion inhibitor is one among them.

Recently, plant extracts containing organic compounds having heteroatoms are evaluated for corrosion inhibition [1-6]. Azoles and N-methyl-p-aminophenol sulphate have been proved as excellent inhibitors of corrosion for mild steel in acid medium [7, 8]. Beet root [9] and *Ficus Exasperata* [10] are also reported to be effective acid corrosion inhibitors. Also acid extracts of *Citrus aurantiifolia* [11], *Nyctanthes arbortristis* [12] and *Solanum Tuberosum* [13] have also been investigated for anticorrosion properties. Recent studies on *Azadirachta indica* [14] and tea wastes [15] have also proved to be efficient corrosion inhibitors. The corrosion inhibition effects of *Andrographis paniculata* [16] and *Withania somnifera* [17] have been also studied.

In the present study, the corrosion inhibition effect of acid extract of the pericarp of the fruit of *G. mangostana* on mild steel in hydrochloric acid medium is studied.

G. mangostana, colloquially known as "the mangosteen", is a tropical evergreen tree. Mangosteen fruit (Fig. 1) first appears as pale green in colour. As the fruit enlarges, the colour of the exocarp of the pericarp (Fig. 2) deepens to darker green. On ripening it will become purple in colour.

Figure 1. *G. mangostana* fruit.

Figure 2. Pericarp of *G. mangostana*

Experimental

Mild steel (MS) of composition, Fe=99.51%, C=0.01%, P=0.08%, Mn=0.034% are used for the entire study. MS specimens of size 4.0×2.0×0.19 cm are used for weight loss and SEM studies. Powdered MS is used for IR studies and MS specimen with an exposed area of 1 cm^2 is used for electrochemical studies. These specimens are polished mechanically followed by different grades of emery paper and then degreased with trichloroethylene. Analar grade HCl and double distilled water are used for the entire study.

Preparation of extract

50 g of dried powder of the pericarp of the fruit of *G.* mongostana are mixed with 100 mL of 5% HCl and refluxed for one hour and the extract is filtered off and made up to 100 mL.

Preparation of corrosive environment

The corrosive environment of 5% (w/v) HCl solution is prepared using double distilled water. From this stock solution 100 mL each of standard solutions are prepared with and without different concentrations of the inhibitor.

Weight loss study

Mild steel specimens are immersed in 100 mL test solutions with and without different concentrations of inhibitor for a period of one hour at four different temperatures viz., 303, 308, 313, and 318 K using a thermostat. Then the specimens are washed and dried well. The weights of the specimens before and after studies are determined using a Schimadzu AUX220.

Electrochemical studies

Pt electrode, calomel and MS specimens are used as auxiliary, reference and working electrodes, respectively. Impedance measurements are carried out in the frequency range of 10 KHz to 10 mHz for mild steel in HCl and also with different concentrations of the green inhibitor. Potentio-dynamic Tafel polarization studies are carried out at a sweep rate of 1 mV/sec. Potential (E) versus log current (log I) plots are then recorded. The electrochemical parameters are measured in HCl medium and also with different concentrations of inhibitor.

Both impedance and polarization studies are carried out using a Solartron model SI1280B electrochemical measurement unit.

Infra red spectroscopic studies

Finely powdered MS specimen is immersed in a saturated solution of the extract for 1 hour to form the adsorption product of MS and extract. FTIR spectrum is recorded for the extract and the adsorption product using a Nexus 670(FTIR) Centraurms 10X (Microscope), Thermo Electron Corporation, USA.

Scanning electron microscope studies

Mild steel specimens are immersed in a corrosive environment of 5% HCl having 25% concentration of the extract for one hour. The specimen is dried and scanned using a Hitachi S-3000H model Scanning Electron Microscope.

Results and discussion

The extract of the pericarp of *G.* mangostana contains oxygenated prenylated xanthones, 8-hydroxycudraxanthone G and mangostingone [7-methoxy-2-(3-methyl-2-butenyl)-8-(3-methyl-2-oxo-3-butenyl)-1,3,6-trihydroxyxanthone,

along with other xanthones such as cudraxanthone G, 8-deoxygartanin, garcimangosone B, garcinone D, garcinone E, gartanin, 1-isomangostin, α-mangostin, γ-mangostin, mangostinone, smeathxanthone A, and tovophyllin A [18, 19].

Weight loss analysis

The corrosion rate (CR) in mmpy is calculated using the formula

$$CR = 87.6 \times W / DAT \qquad (1)$$

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 [20]. The weight loss values and corrosion rate (CR) at four different temperatures are given in Table 1. The above table clearly reveals that, even at the lowest concentration, the *G. mangostana* extract is able to bring down the corrosion rate substantially. The corrosion rate has decreased drastically from the blank value irrespective of the variation in temperature and also at different concentrations of the inhibitor.

Table 1. Weight loss data and corrosion rate.

% Conc. of the extract	**Weight loss / g**				**Corrosion rate / mmpy**			
	303 K	**308 K**	**313 K**	**318 K**	**303 K**	**308 K**	**313 K**	**318 K**
0	0.0822	0.0901	0.0963	0.1012	50.18	55.00	58.79	61.78
5	0.0085	0.0097	0.0108	0.0120	5.19	5.92	6.59	7.33
10	0.0064	0.0075	0.0086	0.0094	3.91	4.58	5.25	5.74
15	0.0041	0.0052	0.0061	0.0070	2.50	3.17	3.72	4.27
20	0.0025	0.0033	0.0041	0.0048	1.53	2.02	2.50	2.93
25	0.0021	0.0027	0.0032	0.0037	1.28	1.65	1.95	2.26

Thermodynamic studies

The inhibition efficiency (IE) obtained from weight loss data is given in Table 2. From the table it is obvious that the IE increases with increase in inhibitor concentration. The inhibition efficiency is found to decrease with rise of temperature for higher range of concentrations. However, the decrease in IE values is not significant.

E, energy of activation is obtained using the formula

$$\log CR_2 / CR_1 = E / 2.303 \times (1/T_1 - 1/T_2) \qquad (2)$$

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 2.

The 'E' values are almost constant for a particular range of temperatures (308-318 K) even at different concentrations of the inhibitor (Table 3). The higher E values for various inhibitor concentrations when compared to blank indicate the slowness of corrosion reaction on the metallic surface [22].

Q, the heat of adsorption, is obtained by plotting log θ/1-θ against 1/T (Fig. 3), where θ is the fraction of the metal surface covered by the inhibitor at temperature T.

The free energy change, ΔG, for the adsorption is calculated using the formula [23]

$$\Delta G = -2.303 RT \log 55.5K \ \text{ where } K = (\theta / 1 - \theta) / C \qquad (3)$$

Table 2. Inhibition efficiency and thermodynamic parameters of corrosion inhibition effect of *G. mangostana extract.*

% Conc. of the extract	Inhibition efficiency, %				E in kJ/mol for the range (K)		
	303 K	308 K	313 K	318 K	303-308	308-313	313-318
0	-	-	-	-	14.225	10.661	8.201
5	89.66	89.23	88.78	88.14	20.442	17.192	17.622
10	92.21	91.68	91.07	90.71	24.548	21.877	14.799
15	95.01	94.23	93.66	93.08	36.845	25.640	22.847
20	96.96	96.34	95.74	95.26	43.135	34.162	26.279
25	97.45	97.00	96.67	96.34	39.419	26.784	24.449

The very low Q values (Table 3) show that the adsorption is physical in nature. The values of free energy change for blank at four different temperatures are around -11 kJ/mol. The lesser ΔG values, around -10.5kJ/mol, for various inhibitor concentrations (Table 3) reveal the decreased rate of corrosion reaction, which is also substantiated by other studies. The negative free energy change values substantiate that the adsorption of the chemical components on the metal surface is spontaneous, and the high stability of the adsorbed layer on the mild steel surface. It has been already reported that Gibbs free energy values between -49 kJ/mol and -58 kJ/mol are indicative of chemisorption [24]. The low free energy change values in the present case further confirm the physical nature of adsorption.

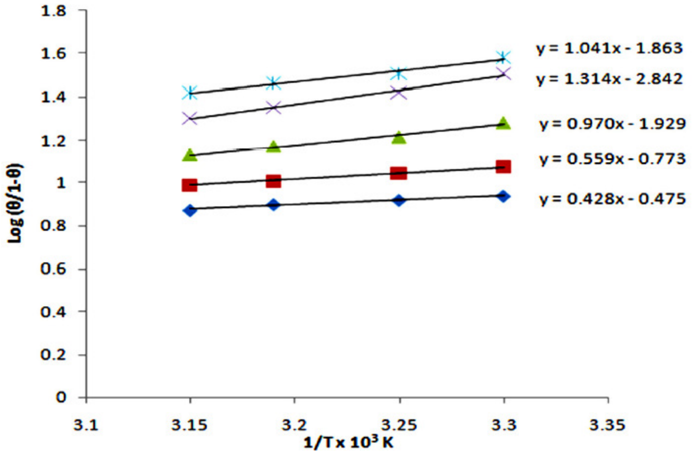

Figure 3. Graphical representation between log θ/1-θ and 1/T.

Table 3. Enthalpy and free energy change parameters.

% Conc. of the extract	Q in KJ/mol	ΔG in kJ/mol			
		303 K	308 K	313 K	318 K
5	-8.1949	-11.5069	-11.5799	-11.6481	-11.6686
10	-10.7033	-10.5444	-10.5349	-10.5046	-10.5574
15	-18.5727	-10.7208	-10.5043	-10.4141	-10.3321
20	-25.1593	-11.2446	-10.9902	-10.7569	-10.6335
25	-19.9322	-11.1889	-10.9448	-10.8426	-10.7571

Adsorption studies

The surface coverage values are tested graphically by plotting θ versus log C, where 'C' is the concentration of the inhibitor. A straight-line plot (Fig. 4) is obtained and it is found to fit exactly Temkin adsorption isotherm, which is mathematically given by

$$\theta = a + b \log C \tag{4}$$

where 'a' and 'b' are intercept and slope, respectively [10]. This isotherm reveals the increased adsorption of the inhibitor on the MS surface with increase in its concentration, and thus the increased protection.

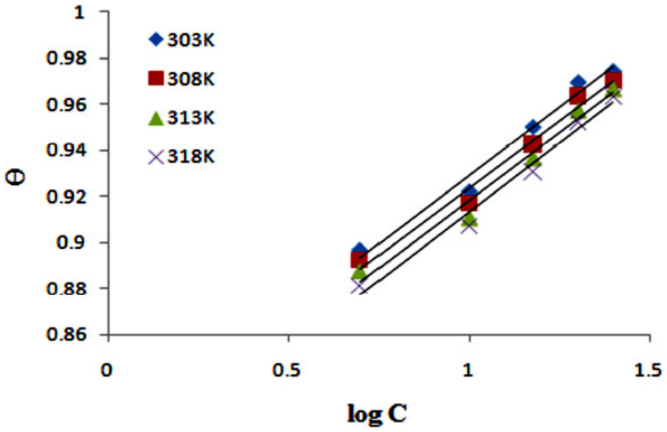

Figure 4. Temkin adsorption isotherm.

Electrochemical studies

The values of 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 (R_{ct}), double layer capacitance (C_{dl}), and IE as obtained from electrochemical measurements are given in Table 4. It is obvious from the Tafel plot (Fig. 5), that both anodic and cathodic curves are shifted to lower current densities in the presence of the inhibitor.

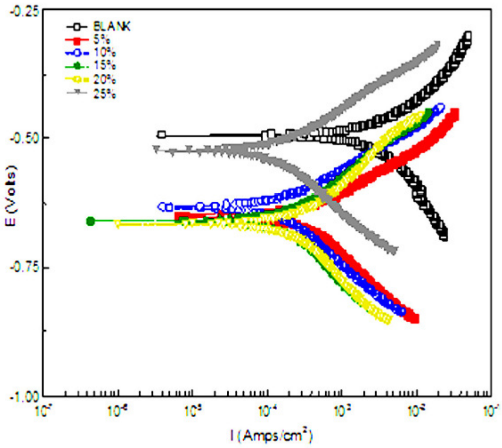

Figure 5. Tafel curves of mild steel in the absence and presence of various concentrations of *G. mangostana* extract.

This indicates a remarkable decrease in corrosion reaction. The steady decrease in I_{corr} values with increase in concentration of the inhibitor is an indication of decrease in corrosion as compared to blank. The inhibitor acts through mixed mode of inhibition, as is evident from the values of E_{corr}, which do not increase or decrease in a regular manner from the blank value. The shift in values of b_a and b_c in the presence of inhibitor indicates the drastic slow down of anodic and cathodic reactions. The changes in the value of b_a and b_c reflect the mixed mode of inhibition but retards predominantly through cathodic reaction. It is obvious from the IE values that the corrosion control is dependent upon the concentration of the inhibitor.

Table 4. Electrochemical parameters of corrosion inhibition by *G. mangostana* extract.

Concn. of *G. mangostana* extract (mL/100mL)	**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	26.78×10^{-4}	150.9	226.1	5.804	6.08×10^{-5}	-
5	-0.6540	-0.6501	2.92×10^{-4}	87.2	156.6	62.53	3.93×10^{-5}	89.08
10	-0.6559	-0.6641	1.52×10^{-4}	114.7	161.9	149.84	3.15×10^{-5}	94.32
15	-0.5223	-0.5249	1.43×10^{-4}	102.9	156.9	163.44	3.83×10^{-5}	94.67
20	-0.6477	-0.6324	1.37×10^{-4}	87.5	143.3	98.72	3.89×10^{-5}	94.88
25	-0.6519	-0.6596	9.74×10^{-5}	93.9	124.8	156.08	3.59×10^{-5}	96.36

The Nyquist illustrations of impedance plot of mild steel in HCl with and without addition of various concentrations of the inhibitor are given in Fig. 6 and the equivalent circuit used for the impedance studies is given in Fig. 7. The presence of a single semi circle in the plot showed the single charge transfer process during the oxidation of the metal, which is unchanged when the inhibitor is added to the acid medium.

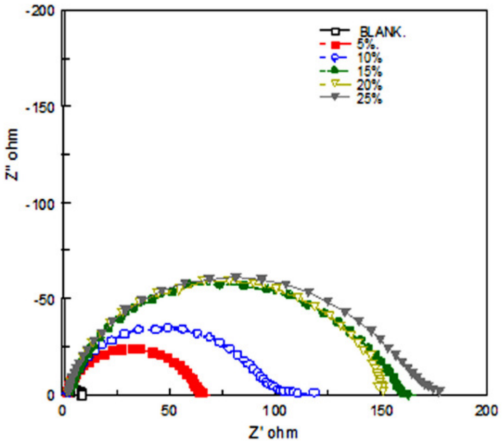

Figure 6. Impedance spectra of mild steel in the absence and presence of different concentrations of *G. mangostana* extract.

The values of C_{dl} (Table 4) are found to be lower than those from the blank value as the concentration of the inhibitor is increased, which confirms the adsorption of the inhibitor on the metal surface forming an electronic double layer [22]. The adsorption on the metal surface may be due to the hetero atoms present in the organic constituents of the extract [18, 19]. The higher values of R_{ct} for higher inhibitor concentrations indicate the resistance towards charge transfer reactions responsible for corrosion process, through the formation of a protective film on the metal-acid medium interface.

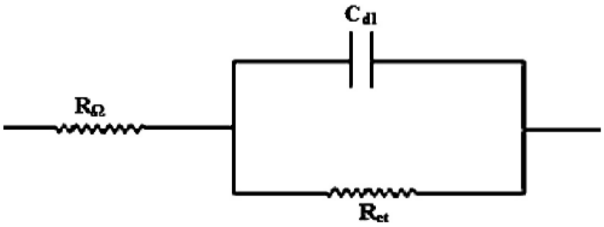

Figure 7. Equivalent circuit for impedance studies

IR analysis

The IR spectra of the extract of *G. mongostana* fruit pericarp (Fig. 8) contain bands corresponding to phenolic hydroxyl groups (3432.7 cm^{-1}), carbonyl groups (1632.3 cm^{-1}) and alcoholic hydroxyl groups (1379.4 cm^{-1}). The dried adsorption product of the extract with mild steel powder (Fig. 9) has IR spectral bands at different wave numbers, corresponding to phenolic hydroxyl groups (3389.1 cm^{-1}), carbonyl groups (1629.7 cm^{-1}) and alcoholic hydroxyl groups (1369.1 cm^{-1}). These changes in adsorption bands suggest that adsorption between extract and mild steel has taken place through these functional groups.

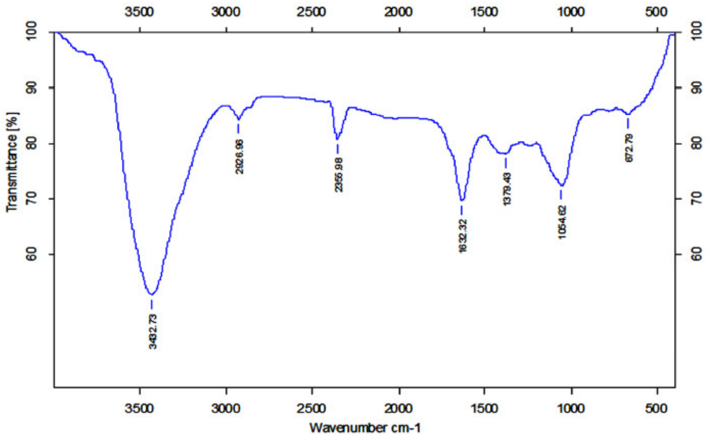

Figure 8. IR spectra of the *G. mongostana* extract in the liquid state.

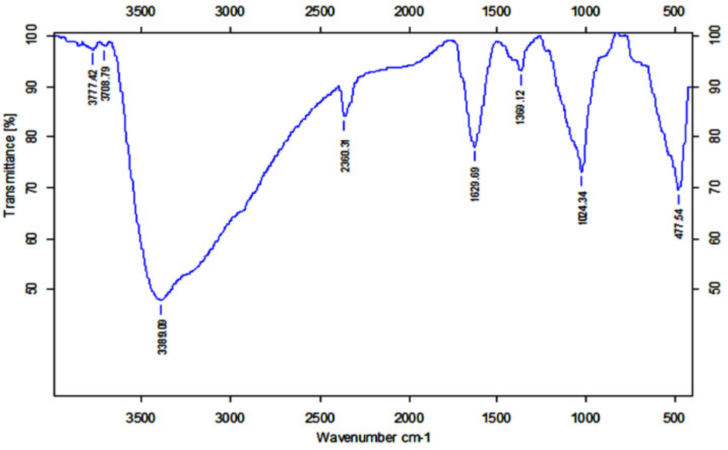

Figure 9. IR spectra of the dried solid adsorption product of *G. mongostana* extract and mild steel powder.

Scanning electron microscope studies

The SEM photographs were recorded for polished metal surface (Fig. 10), MS surface exposed to corrosive environment (Fig. 11), and MS exposed to 25% concentration of the extract in corrosive environment (Fig. 12), respectively, in hydrochloric acid medium using scanning electron microscopy to study the surface morphology of mild steel surface. The SEM photograph showed that the surface of the metal has pits, pores and cracks when exposed to 5% HCl solution. In the presence of inhibitor, the photograph reveals that they are minimized on the metal surface, which indicates the formation of a protective layer of the inhibitor on the metal surface [8].

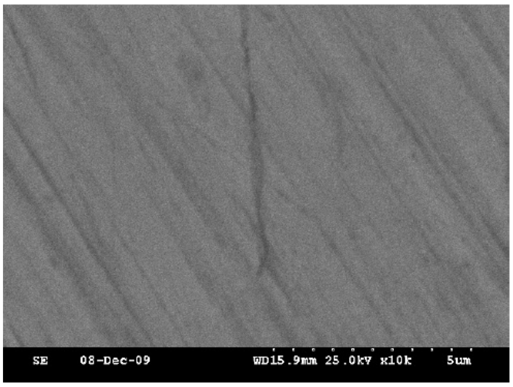

Figure 10. SEM image of polished mild steel surface.

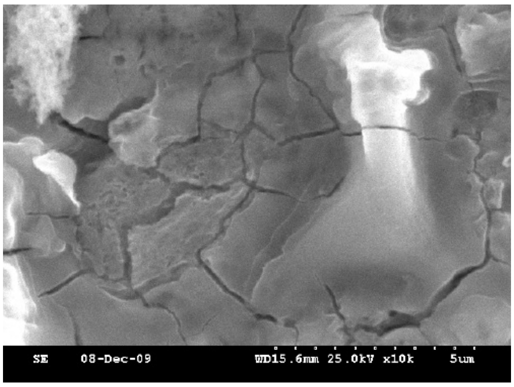

Figure 11. SEM image of mild steel exposed to 5% HCl alone.

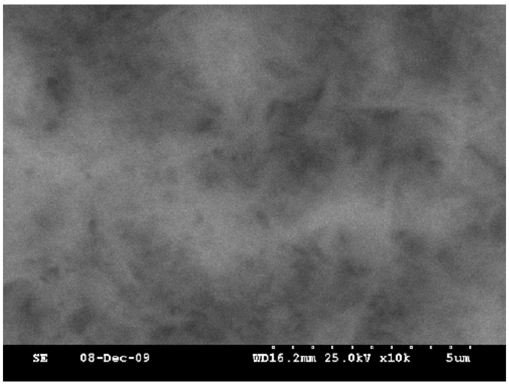

Figure 12. SEM image of mild steel sample exposed to 5% HCl having 25% inhibitor.

Conclusion

The entire study reveals that the corrosion inhibition efficiency of G. mangostana extract increases with increase in inhibitor dosage and decreases as the temperature is raised. A plot of θ versus log C gives a straight line and is found to follow Temkin adsorption isotherm. The decreased rate of corrosion reaction with increased dosage of the inhibitor is reflected from the I_{corr} values. Electrochemical parameters such as E_{corr}, b_a and b_c indicate the mixed mode of inhibition, but predominantly cathodic. IR analysis and impedance studies indicate that the adsorption on the metal surface is due to the hetero atoms present in the organic constituents of the extract of G. mangostana. SEM studies reveal the protection of the metal from corrosion in acid medium by the inhibitor. The above results confirm that G. mangostana extract can be used as an effective eco-friendly corrosion inhibitor for mild steel in HCl medium.

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References

1 V. Adhikari, V.R. Saliyan, *Ind. J. Chem. Tech.* 16 (2009) 162-174.

2 A.K. Dubey and G. Singh, *Port. Electrochim. Acta* 25 (2007) 221-235. 10.4152/pea.200702221

3 R.A. Prabhu, T.V. Venkatesh, A.V. Shanbhag, *J. Iran. Chem. Soc.* 6 (2009) 353-363.

4 S.L. Granese, B.M. Rosales, C. Ovido, J.O. Zarbino, *Corr. Sci.* 33 (1992) 1439-1453. 10.1016/0010-938X(92)90182-3

5 S. Muralidharan, M.A. Quraishi, S.V.K. Iyer, *Corr. Sci.* 37 (1995) 1739-1750. 10.1016/0010-938X(95)00068-U

6 Z. Zhang, S. Chen, Y. Feng, Y. Ding, J. Zhou, H. Jia, *J. Serb. Chem. Soc.* 74 (2009) 407-415. 10.2298/JSC0904407Z

7 K. Ajmal, A.S. Mideen, M.A. Quraishi, *Corr. Sci.* 36 (1994) 79-84. 10.1016/0010-938X(94)90110-4

8 B.M. Praveen, T.V. Venkatesha, *Int. J. Electrochem. Sci.* 4 (2009) 267-275.

9 J.A. Selvi, S. Rajendran, V.G. Sri, A.J. Amalraj, B. Narayanasamy, *Port. Electrochim. Acta* 27 (2009) 1-11. 10.4152/pea.200901001

10 N.S. Patel, S. Jauhari, G.N. Mehta, *e-J. Chem.* 6 (2009) S189-S194.

11 R. Saratha, S.V. Priya, P. Thilagavathy, *e-J. Chem.* 6 (2009) 785-795.

12 R. Saratha, V.G. Vasudha, *e-J. Chem.* 6 (2009) 1003-1008.

13 Pandian, P.B. Raja, M.G. Sethuraman, *Iran. J. Chem. Chem. Eng.* 28(1) (2009) 77-84.

14 N.O. Eddy, P.A.P. Mamza, *Port. Electrochim. Acta* 27 (2009) 443-456. 10.4152/pea.200904443

15 M.G. Sethuraman, P. Vadivel, K.P.V. Kumar, *J. Electrochem. Soc. India* 50 (2001) 143-146.

16 S.P. Ramesh, K.P.V. Kumar, M.G. Sethuraman, *Bull. Electrochem.* 17 (2001) 141-144.

17 S.P. Ramesh, K.P. Vinod Kumar, M.G. Sethuraman, Proc. Ninth National Congress on Corrosion Control, Goa, India, (1999). p.139.

18 H.-A. Jung, B.-N. Su, W.J. Keller, R.G. Mehta, A.D. Kinghorn, *J. Agric. Food Chem.* 54 (2006) 2077–2082. 10.1021/jf052649z

19 W. Mahabusarakam, P.Wiriyachitra, W.C.Taylor, *J. Natural Products* 50 (1987) 474-478. 10.1021/np50051a021

20 Muhamath, B.M. Ali, Kulanthai, Kannan, *J. Appl. Sci. Environ. Management* 13 (2009) 27-36.

21 C. Das, H.S. Gadiyar, *J. Electrochem. Soc. India* 42 (1993) 225-231.

22 R.T. Vashi, V.A. Champaneri, *Bull. Electrochem.* 13 (1997) 353-360.

23 E.E. Ebenso, N.O. Eddy, A.O. Odiongenyi, *African J. Pure Appl. Chem.* 2 (2008) 107-115.

24 M.R. Singh, K.Bhrara, G. Singh, *Port. Electrochim. Acta* 26 (2008) 479-492. 10.4152/pea.200806479