ISSN: 0975-833X

Available online at http://www.journalcra.com

International Journal of Current Research
Vol. 6, Issue, 05, pp.6571-6575, May, 2014

INTERNATIONAL JOURNAL OF CURRENT RESEARCH

RESEARCH ARTICLE

INHIBITION OF MILD STEEL CORROSION IN SULPHURIC ACID USING *CEIBA PENTANDRA* SEED EXTRACT

Priya, V. S., *Ali Fathima Sabirneeza, A. and Subhashini, S.

Department of Chemistry, Avinashilingam Institute for Home Science and Higher Education for Women,
Coimbatore, Tamil Nadu, India

ARTICLE INFO

Article History:
Received 07th February, 2014
Received in revised form
26th March, 2014
Accepted 19th April, 2014
Published online 20th May, 2014

Key words:
Ceiba Pentandra,
Mild steel,
Corrosion inhibitor.

ABSTRACT

The inhibitive effect of *Ceiba Pentandra* (CP) seed extract on the corrosion of mild steel in Sulphuric acid was investigated using gravimetric, potentiodynamic and electrochemical impedance spectroscopy (EIS) techniques. The results showed that CP seed extract could serve as effective inhibitor for corrosion of mild steel in Sulphuric acid. The percentage inhibition increased with increasing concentration of the extract at room temperature. Maximum inhibition efficiency of 90% was obtained with 0.5% v/v concentration. The inhibition efficiencies obtained from impedance and polarization measurements were in good agreement. Poteniodynamic polarization studies clearly revealed the mixed behaviour of the CP seed extract. The studies showed that the inhibition efficiency was significantly affected by the temperature of the medium.

INTRODUCTION

The corrosion of metallic materials in acidic solution causes considerable loss. In order to reduce the corrosion of metals several techniques have been adopted. The use of inhibitors during acid pickling procedure is one of the most practical methods for protection against corrosion in acidic media. Currently there is public criticism of the synthetic inhibitors for their hazardous effect. Plants are rich recourses of naturally synthesized chemicals. Plant extracts contains several organic compounds which have corrosion inhibiting abilities. The extracts from the leaves, seeds, bark of plants have been reported to inhibit metallic corrosion in acidic media. A summary of plants extracts used as corrosion inhibitors have been recently given by Okafor, *et al*. (2008) and Raja, *et al*. (2008). The plant products are rich sources of organic compounds with hetero atoms and hence involved in adsorption through electron donation to the metal atom thereby blanketing the surface from the attack of the aggressive environment (Yadav *et al*., 2013; Bouyanzer *et al*., 2006; Hmamou *et al*., 2012; Akalezi *et al*., 2012). The present work was designed to investigate the corrosion inhibition of mild steel by *Ceiba Pantandra* seed as a cost effective and environmentally benign corrosion inhibitor.

MATERIALS AND METHODS

Mild steel of 2mm thickness with a composition of Mn-0.271, C-0.143, Si-0.041, P-0.035, S-0.030, Mo-0.018, Ni-0.006, Cr-0.002 and Fe-99.454 % was obtained from local market. The sheet was press-cut into 1x5cm^2 coupons. The coupons were degreased with ethanol, polished with emery paper, dried and stored in moisture free desiccators prior to use. 1M H_2SO_4 solution prepared from reagent grade H_2SO_4 and was employed as the corrodent for the study.

Extraction of *Ceiba Pentandra* Seeds

CP seeds were collected from a local farm and dried. 5% stock solution of the seed extract of CP was prepared as reported by Abiola, *et al*. (2009). 5 g of powdered seed was reflexed with 100 ml of 1M H_2SO_4 for 3h. The solution was allowed to stand for 8h, filtered and stored. The filtrate was diluted with appropriate quantity of 1M H_2SO_4 to obtain inhibitor test solution of 0.05 to 0.5% v/v concentrations.

RESULTS

Gravimetric Measurements

The gravimetric measurements were carried out as previously described ASTM standard Procedure (ASTM, 1994). Pre weighed mild steel coupons were immersed in triplicate in test solutions with and without varying concentrations of the CP

***Corresponding author: Ali Fathima Sabirneeza, A.**
Department of Chemistry, Avinashilingam Institute for Home Science and Higher Education for Women, Coimbatore, Tamil Nadu, India

Table 1. Kinetic and Thermodynamic factors for mild steel corrosion in presence of CP Seed extract

Conc of CP seed Extract (%)	Activation energy E_a kJ/mol	Free energy of adsorption ΔG_{ads} (kJ/mol)					ΔH_{ads} kJ/mol	ΔS_{ads} kJ/Kmol
		30^o C	40^o C	50^o C	60^o C	70^o C		
Blank	42.02	-	-	-	-	-	-	-
0.1	57.38	-20.49	-20.84	-21.04	-21.37	-20.17	-21.0797	-0.0009
0.2	52.14	-19.36	-19.87	-20.33	-20.60	-20.09	-12.7573	-0.0219
0.3	48.81	-18.54	-19.04	-19.75	-20.23	-19.59	-8.4743	-0.0329
0.4	44.91	-17.93	-18.51	-19.29	-19.79	-19.59	-6.7040	-0.0460
0.5	47.39	-17.85	-18.58	-19.02	-19.43	-19.31	-6.2839	-0.0377

Table 2. Electrochemical Parameters for mild steel corrosion in presence of CP seed extract

Conc of CP seed extract (%)	LPR Method		TEM Method					EIS Method	
	R_p Ω	IE (%)	b_a mV/dec	b_c mV/dec	E_{corr} mVvs.SCE	I_{corr} mA/cm^2	IE (%)	R_{ct} Ω	IE (%)
Blank	4.88	-	263	167	475.3	6.84	-	5.17	-
0.1	6.42	23.92	187	104	468.0	4.66	31.86	24.58	78.96
0.2	6.75	27.63	168	100	470.6	4.13	39.61	26.96	80.82
0.3	8.85	44.76	174	95	475.5	2.57	62.42	29.33	82.37
0.4	9.31	47.50	154	92	472.9	2.50	63.45	32.96	84.31
0.5	9.77	49.97	138	86	472.3	2.15	68.56	35.44	85.41

extract using glass hooks. They were removed after a particular period (1, 3, 6, 12 and 24 h) of immersion, washed with alkali dried and reweighed. Experiments were also conducted at 30, 40, 50, 60 and 70^o C by immersing the coupons for half an hour. From the weight loss data the Corrosion Rates (CR) were calculated from equation,

$$CR(mpy) = \frac{534w}{dat}$$

where w is the weight loss in g, d is the density of the metal in gcm^{-3}, a is the surface area of the specimen in cm^2 and t is the immersion time in hours. From the corrosion rate the inhibition efficiencies were determined using the relation,

$$IE\ (\%) = \frac{CR_{blank} - CR_{inh}}{CR_{blank}} x100 \quad (1)$$

where CR_{blank} and CR_{inh} are the corrosion rate in the absence and presence of inhibiting CP extract respectively.

Electrochemical Techniques

For electrochemical measurements, the mild steel coupon coated with commercially available lacquer with an exposed area of 1 cm^2 were used and the experiments were carried out in a conventional three electrode cell assembly consisting of a mild steel coupon of the size 1 cm^2 as a working electrode, a large rectangular platinum foil as counter electrode and Saturated Calomel Electrode (SCE) as reference electrode. All electrochemical measurements were carried out using potentiostat/Galvanostat (Solatron 1280 B). The polarization studies were carried out in the potential range -0.1 mV to -1mV against the corrosion potential at a sweep rate of 2mV/s to study the effect of inhibition on the corrosion of mild steel. The linear Tafel segments of anodic and cathodic curves were extrapolated to corrosion potential to obtain the corrosion current densities, I_{corr}. The inhibition efficiency was evaluated from the measured I_{corr} values using the relationship,

$$IE(\%) = \frac{I^o_{corr} - I_{corr}}{I^o_{corr}} x100 \quad (2)$$

where I^o_{corr} and I_{corr} are the corrosion current density values in the absence and presence of inhibitor respectively. The linear polarization studies were carried out from cathodic potential of – 0.02V Vs corrosion potential to an anodic potential of +0.02V corrosion potential at a sweep rate 0.125mV/s to study polarization resistance (R_p). Electrochemical impedance measurements were performed using AC voltage amplitude 10mV in the frequency range of 0.1 Hz to 20 kHz. The values of charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}) were obtained using Nyquist and Bode plots. The inhibition efficiency was calculated from the charge transfer resistance using the following equation,

$$IE(\%) = \frac{R_{ct} - R^o_{ct}}{R_{ct}} x100 \quad (3)$$

where, R^o_{ct} and R_{ct} are the charge transfer resistance with and without inhibitor, respectively.

RESULTS AND DISCUSSION

Gravimetric Measurements

The corrosion of mild steel in different concentrations CP seed extract in molar sulphuric acid at 30^o C was investigated. Figure 1 shows the plot of inhibition efficiency against inhibitor concentration. The figure showed that the extract actually inhibited the sulphuric acid induced corrosion to an appreciable extent. Inhibition efficiency increased with increase in inhibitor concentration. It is obvious that the inhibition efficiency varied linearly with immersion period in plain acid and inhibited acid, showing the absence of insoluble product on steel surface (Singh and Quraishi, 2009). Also inhibition efficiency increased with increase in immersion time. The increase with increase in immersion time may be due to the increase in adsorption of the inhibitor as time passes on. The maximum inhibition efficiency was observed for 12 h of immersion. Effect of temperature on the corrosion behavior of mild steel was studied by immersing the coupons for half an hour in the stagnant solution with and without inhibitor. Figure 2 shows the variation of inhibition efficiency with immersion temperature of the system. Inspection of the figure revealed that inhibition efficiency increases with increase in concentration of the inhibitor at all the temperature studied (30-70°C). Also inhibition efficiency decreased with increasing temperature of the system. A decrease in inhibition efficiency with increasing temperature suggested the physical adsorption mechanism. The decrease may be due to the fact that most effects at elevated temperatures are adverse to corrosion inhibition by increasing the corrosion rate and decreasing the tendency of the inhibitor to be adsorbed on the metal surface (Umoren *et al.*, 2007).

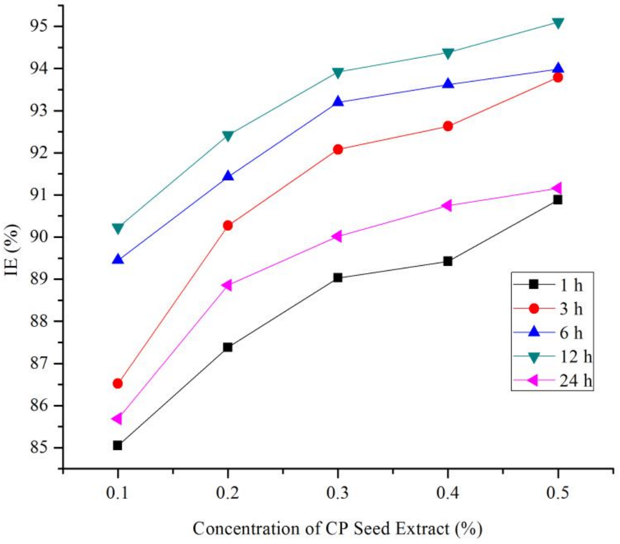

Figure 1. Variation of inhibition efficiency with concentration for different immersion time

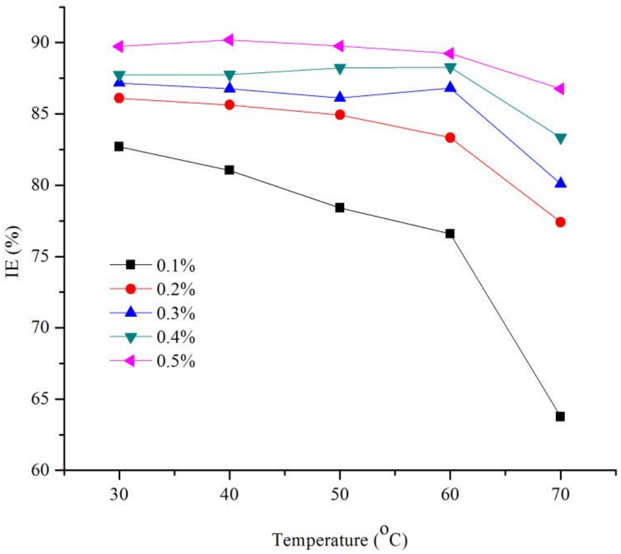

Figure 2. Variation of inhibition efficiency with temperature of different concentrations of CP Seed extract

Adsorption Studies

The mechanism of the corrosion inhibition of mild steel with the CP seed extracts proceeds by the simple adsorption mode. The adsorption of any substrate on the surface of the metal is regarded as substitution process between the compound in solution and the water molecule adsorbed on the surface (Fouda and Ellithy, 2009). To describe adsorption process a number of mathematical relations have been suggested some being empirical and other theoretical. The simplest theoretical equation is that due to Langmuir and given by the equation (Khamis *et al*., 2000).

$$\theta = \frac{bC}{1+bC}$$

(4)

The plots of log(θ/1-θ) vs logC yields straight line (figure 3), where C is the inhibitor concentration. The mean correlation coefficient is close to unity, confirming that the present system obeyed Langmuir isotherm model suggesting monolayer adsorption on the energetically uniform heterogeneous metal surface with interactions in the adsorbed layer (Daouadji and Chelali, 2004).

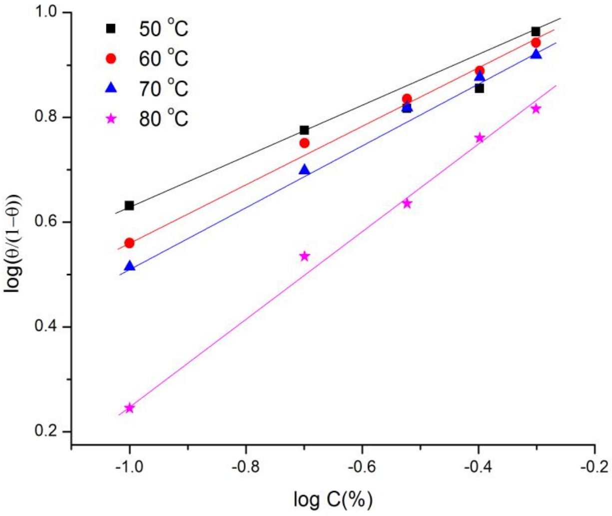

Figure 3. Langmuir Adsorption Isotherm for Adsorption of CP seed Extract on mild Steel at various temperatures

Kinetic and Thermodynamic Factors

The log of corrosion rate is a linear function with 1/T (Arrhenius equation) (Quraishi and Khan, 2005)

$$\log CR = -\frac{E_a}{2.303RT} + \lambda \qquad (5)$$

where E_a is the apparent effective activation energy, R the general gas constant expressed in J/Kmol and λ is the Arrhenius pre-exponential factor. A plot of log of corrosion rate obtained by weight loss measurement vs. 1/T gave a straight line as shown in figure 4 with a slope of −Ea/2.303R. The values of activation energy are listed in Table 1. The free energy of adsorption (ΔG_{ads}) at different temperatures was calculated using the following equation (Mu *et al.*, 2004) and presented in Table 1.

$$\Delta G_{ads} = -RT\ \ln(55.5K)\ ;\ K = \frac{\theta}{C}(1-\theta) \qquad (6)$$

where θ is degree of coverage on the metal surface, C is the concentration of the inhibitor and K is equilibrium constant. The negative values of free energy of adsorption indicate spontaneous adsorption of inhibitor molecules on the mild steel surface. The value of $-\Delta G_{ads}$ for inhibited system is less than 40 kJ mol^{-1} indicates that the inhibitor molecules are physically adsorbed on the surface of mild steel (Benabdellah *et al.*, 2007). The ΔG_{ads} values are used to calculate enthalpy and entropy of adsorption process by using the thermodynamic relation, $\Delta G_{ads} = \Delta H_{ads} - T\Delta S_{ads}$. The obtained values of ΔH_{ads} snd ΔS_{ads} are also presented in Table 1. The negative ΔH_{ads} values indicate that the adsorption of inhibitor molecules is an exothermic process. The negative ΔS_{ads} values are attributed to the adsorption process which is accompanied by an increase in order of the system resulting from the associated complex of inhibitor and mild steel (Migahed *et al.*, 2011).

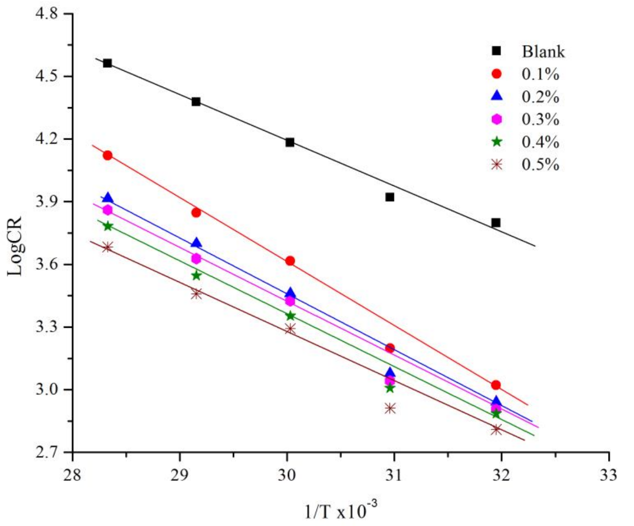

Figure 4. Arrhenius Plots for MS corrosion in presence of CP Seed Extract

Electrochemical Measurements

Potentiodynamic Polarization

Electrochemical measurements were carried out using the electrochemical analyzer Solartron 1280 B. Electrochemical techniques such as linear polarization, Tafel intercept method and electrochemical impedance spectroscopy were carried out. The values of Tafel constants ba and bc, corrosion current density (i_{corr}) and corrosion potential (E_{corr}) and IE are given in Table 2. The Potentiodynamic polarization curves are depicted in Figure 5. It is inferred that i_{corr} decreases with increase in concentration of CP seed extract in acid medium. The result confirms the inhibitive action of CP seed extract in 0.5M H_2SO_4. Inhibition efficiency calculated using i_{corr} was found to be maximum at 0.5% concentration. The values of Tafel constants b_a and b_c with respect to the blank, indicate that the inhibitor under study behave like a mixed type inhibitor (Abdel-Rehim *et al.*, 2006). Linear polarization resistance (LPR) in the presence and absence of CP seed extract calculated using Stern – Geary theory are presented in the Table 2. It is clear that the value of R_p increases with increase in concentration of the CP seed extract. Results of Tafel polarization and LPR infer the effectiveness of extract on corrosion inhibition of mild steel.

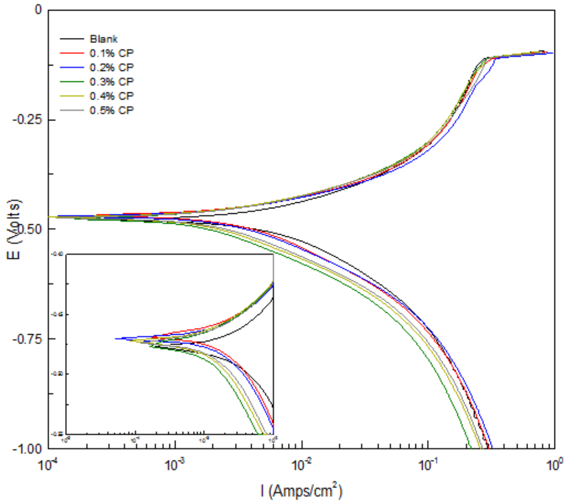

Figure 5. Potentiodynamic Polarization Plots for mild steel in 1M H_2SO_4 containing various concentrations of CP extract

Electrochemical Impedance Spectroscopy

The corrosion behavior of mild steel in 1M H_2SO_4 in the absence and presence of various concentrations of CP seed extract was investigated by electrochemical impedance technique at room temperature. Impedance diagrams shown in Figure 6 have a semicircular appearance and it indicated that the corrosion of mild steel is controlled by charge transfer process.

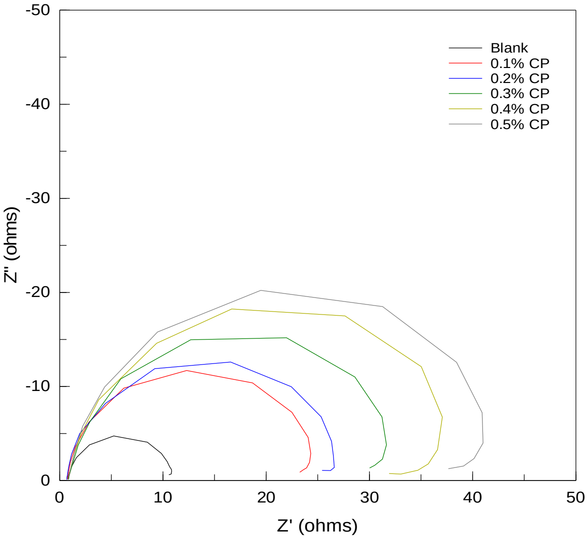

Figure 6. Nyquist representations for mild steel corrosion in 1M H_2SO_4 containing various concentrations of CP extract

It was clear that CP seed extract is acting profoundly as an excellent inhibitor to reduce acid corrosion of mild steel. The values of charge transfer resistance (R_{ct}), double layer capacitance (C_{dl}), IE are also represented in Table 2. With increase in concentration of CP seed extract the charge transfer resistance value increased. The maximum IE was found to be 85.41% at 0.5% concentration in the presence of the extract. The decrease in C_{dl} with increase in concentration of CP seed extract indicates the adsorption of the compounds on the metal surface.

Conclusions

CP seed extract has shown a remarkable performance as an inhibitor for mild steel in H_2SO_4 solution. The inhibitor used in the present study followed Langmuir adsorption isotherm which indicated the monolayer formation. Thermodynamic parameters confirm the strong interaction between the compounds present in the extract and the mild steel surface. The free energy values indicate spontaneity and the physical nature of the adsorption process. Strong adsorption of the inhibitor on the active sites of the metal surface suppresses the dissolution process and leads to the formation of a protective film. Polarization curves obtained in the presence of the extract indicate that it controls both anodic and cathodic reactions and behave as a mixed type inhibitor. Electrochemical impedance spectroscopy studies also revealed that the corrosion of the mild steel in H_2SO_4 is controlled by charge transfer process.

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