

Inhibition of mild steel corrosion in hydrochloric acid by the seed husk extract of *Jatropha curcas*

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Abstract - The seed husk extract of *Jatropha curcas* has been studied for mild steel corrosion inhibition in acid medium. Traditional weight loss data obtained at four different temperatures are used to evaluate inhibition efficiency (IE) and 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). Temkin's adsorption isotherm was plotted to verify the nature of adsorption of the inhibitor on the metal surface. Infra red spectra were documented to fix the functional group responsible for inhibition. The electrochemical parameters are evaluated from the potentiodynamic Tafel polarization and impedance spectral studies. The surface morphology of the mild steel is analyzed using the SEM images. All the results obtained reflect that the seed husk extract of *J. curcas* as an effective eco-friendly and alternate corrosion inhibitor for mild steel in acid medium.

Key words: *J. curcas*, steel, corrosion, polarization, impedance, eco-friendly

1. Introduction

Jatropha curcas, an economically important plant for the production of biodiesel can grow easily in fertile and even in less fertile soil. It belongs to the family of Euphorbiaceae. *Jatropha* oil, obtained by crushing the seeds is used as biodiesel. The residue finds application as a source for generating electrical energy as well as a fertilizer. Yet another potential application of the seed husk as corrosion inhibitor for mild steel in acid medium is established through this study.

Mild steel, an alloy of iron is widely used in petrochemical, chemical and metallurgical industries. It is also used as a construction material owing to its excellent mechanical properties and cost effectiveness. However, it easily undergoes corrosion in various environmental conditions especially in acid medium. HCl find various applications in those industries as pickling, etching, descaling and cleaning agent, but it instigates corrosion in mild steel. It is already proved that organic compounds having heteroatoms can be used as effective corrosion inhibitors for mild steel in acid medium [1-5]. As most of the synthetic chemicals are found to be harmful to the environment, research works are much focused on plant extracts for corrosion inhibition and found to be successful [6, 7]. *Prunus cerasus* [8], *Parthenium hystophrous* [9], *Ficus exasperata* [10] *Citrus aurantiifolia* [11], *Musa acuminata* [12], *Solanum tuberosum* [13], *Azadirachta indica* [14], *Andrographis paniculata* [15], *Fenugreek leaves* [16], Beet root [17] and tea wastes [18] are also evaluated for anticorrosion properties. Since natural extracts obtained from plants are eco-friendly, the inhibition effect of *J. curcas* seed husk extract on mild steel corrosion in hydrochloric acid medium is analyzed in this study.

2. Experimental details

2.1. Mild steel specimen

The entire study was carried out using Mild Steel (MS) specimen of composition, Fe = 99.51%, P = 0.08%, Mn = 0.034% and C = 0.01%. MS specimens of size 4.0 x 2.0 x 0.19 cm and MS powder were used for weight loss and IR studies respectively. For SEM and electrochemical studies, specimens with an exposed area of 1 cm² were used. These specimens were degreased with trichloroethylene and polished mechanically with different grades of emery paper to obtain very smooth surface. For the entire study, pure HCl (Merck-61752605031730) and double distilled water were used.

2.2. Preparation of the extract and corrosive environment

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

5% (v/v) HCl solution prepared using double distilled water was used as corrosive environment. From this, 100 ml each of the test solutions of 2, 4, 6, 8, 10% (v/v) *J. curcas* seed husk extract in 5% HCl were prepared.

2.3. Weight loss and thermodynamic studies

Previously degreased, polished and weighed mild steel specimens were 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 318K. Then these specimens were washed with double distilled water, dried well and weighed using Shimadzu AUX220 balance.

2.4. Infra Red Spectroscopic studies

FTIR spectra for *J. curcas* liquid extract and the dried product formed between finely powdered MS specimen and concentrated solution of the extract were recorded between a frequency range of 4000cm⁻¹ to 400cm⁻¹ using Bruker FTIR model- Tensor 27

2.5. Surface characterisation studies

Potential-dynamic Tafel polarization studies were carried out with platinum, calomel and MS specimen as auxiliary, standard and working electrodes respectively. Potential-dynamic polarization studies were carried out at a sweep rate of 1mV/sec. Potential (E) versus current (I) plots were recorded. Impedance measurements were carried out in the frequency Range of 10KHz to 10mHz. The electrochemical parameters were studied in HCl medium with and without different concentrations of the extract. All these measurements were carried out using Solartron model SI1280B electrochemical measurement unit.

Scanning Electron Microscope (SEM) photographs were recorded for polished mild steel specimen, specimen exposed to 5% HCl corrosive environment and specimen immersed in 10% inhibitor test solution. Scanning was done at 10K using Hitachi S-3000H model scanning electron microscope.

3. Results and discussion

The IE values calculated from the weight loss studies carried out at four different temperatures are given in table 1. The data clearly illustrates that the IE increases with increase in concentration of the inhibitor. This increase is further confirmed from figure 1. However the inhibition efficiency is found to decrease with rise in temperature at higher concentrations. Below 2% inhibitor concentration, the IE is not so significant. When the exposure time is prolonged above one hour, IE is found to decrease and the effect is drastic after four hours as revealed in figure 2.

Table 1 Weight loss data

% Conc. (v/v) of the inhibitor	Weight loss. g				Inhibition efficiency %			
	303K	308K	313K	318K	303K	308K	313K	318K
0	0.0417	0.0488	0.0561	0.0666	--	--	--	--
2	0.0032	0.0043	0.0061	0.0079	92.32	91.19	89.13	88.14
4	0.0024	0.0036	0.0049	0.0062	94.27	92.62	91.27	90.69
6	0.0019	0.0027	0.0035	0.0048	95.44	94.46	93.76	92.79
8	0.0015	0.0021	0.0029	0.0036	96.40	95.69	94.83	94.59
10	0.0012	0.0017	0.0023	0.0032	97.12	96.52	95.90	95.19

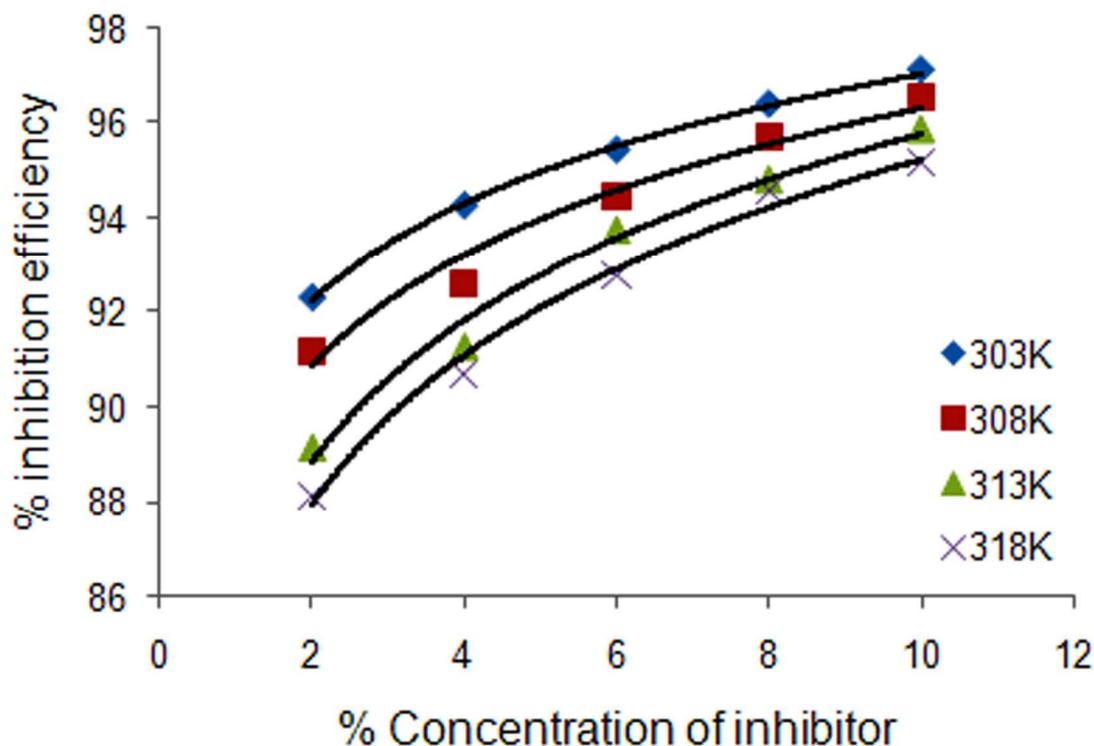


Fig. 1. Plot between % IE against % concentration of inhibitor

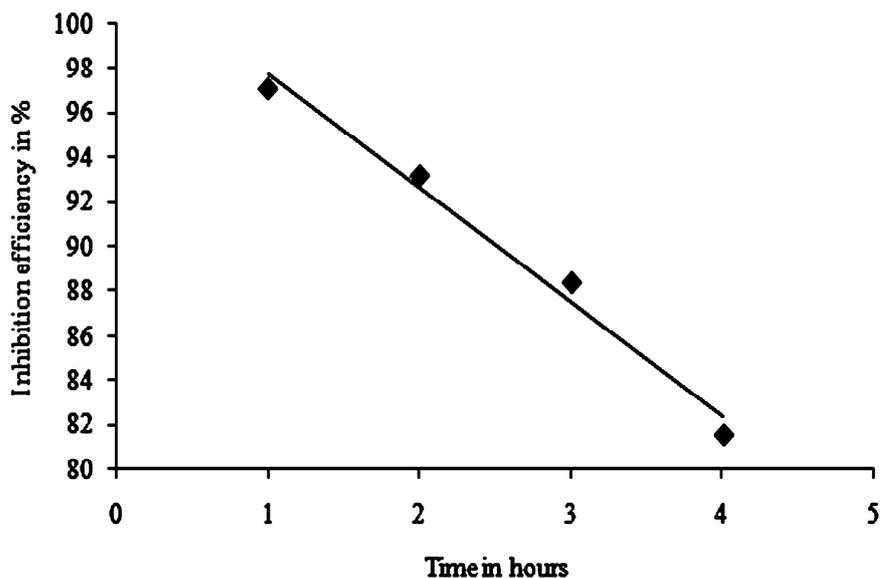


Fig. 2. Effect of time on inhibition efficiency

The heat of adsorption, Q is obtained by plotting $\log \theta/1-\theta$ against $1/T$, where θ is the fractional surface coverage area of the inhibitor on the metal at temperature, T . The obtained negative slope is equivalent to $-Q/2.303R$. From the slope value, Q is calculated [19]. The entropy change (ΔS) for the adsorption process is obtained by plotting a graph between $\log(\text{corrosion rate}/T)$ against $1/T$. The obtained intercept is equivalent to $\log(R/Nh) + \Delta S/2.303R$, from which, ΔS is calculated [20]. ΔG , free energy change [21] for the adsorption is calculated using the formula $-2.303RT \log 55.5K$, where $K = (\theta/1-\theta)/C$.

The Q , ΔS and ΔG values are given in table 2. The Q values are found to be negative and hence the adsorption is an exothermic process, which is attributed unambiguously to adsorption of the inhibitor on the metal surface [22]. The ΔS values are high and negative revealing disorder to order of the natural inhibitor through adsorption on the metal

surface. The mean ΔG value for this adsorption process is -12KJ/mol. The negative free energy change values confirm the spontaneous adsorption of the chemical components through physisorption and chemisorptions as well as the stability of the adsorbed inhibitor layer on the metal surface [21, 23].

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

% Conc. (v/v) of the inhibitor	Q in KJ/mol	ΔS in J/mol	ΔG in KJ/mol			
			303K	308K	313K	318K
2	-27.44	-236.96	-14.64	-14.49	-14.13	-14.09
4	-28.79	-217.82	-13.68	-13.22	-12.95	-12.97
6	-25.68	-198.67	-13.27	-12.96	-12.84	-12.63
8	-24.24	-179.52	-13.16	-12.90	-12.61	-12.69
10	-28.72	-160.37	-13.18	-12.89	-12.66	-12.43

The corrosion rate in mmpy is calculated using the formula

$$\text{Corrosion rate} = 87.6 \times W / DAT \quad (1)$$

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 [9].

E, energy of activation is obtained using the formula

$$\log S_2 / S_1 = E / 2.303R (1/T_1 - 1/T_2) \quad (2)$$

where S_1 and S_2 are the corrosion rates at temperatures T_1 and T_2 respectively [24, 25].

The values of corrosion rate and E are given in table 3. The corrosion rate is decreased tremendously from the blank even at the lowest concentration of the *J. curcas* extract. The corrosion rate has decreased very much from the blank value at the maximum concentration of 10% inhibitor. The 'E' values are higher from the blank value for a temperature range of 303-318 K irrespective of the concentrations of the inhibitor. This indicates the requirement of more energy for corrosion reaction to occur in the presence of inhibitor [26].

Table 3 Corrosion rate and energy of activation data

% Conc. (v/v) 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	25.46	29.79	34.25	40.66	24.36	22.36	28.42
2	1.95	2.62	3.72	4.82	45.83	56.15	21.54
4	1.47	2.19	2.99	3.78	61.84	49.88	38.83
6	1.16	1.65	2.14	2.93	54.66	41.65	52.06
8	0.92	1.28	1.77	2.19	51.23	51.94	36.35
10	0.73	1.04	1.40	1.95	54.91	47.63	54.89

Temkin's adsorption isotherm is plotted between $\log C$ and θ , where 'C' is the concentration of the inhibitor (figure 3). The graph clearly shows that the adsorption of the inhibitor on the metal surface increases as the inhibitor concentration is raised [11].

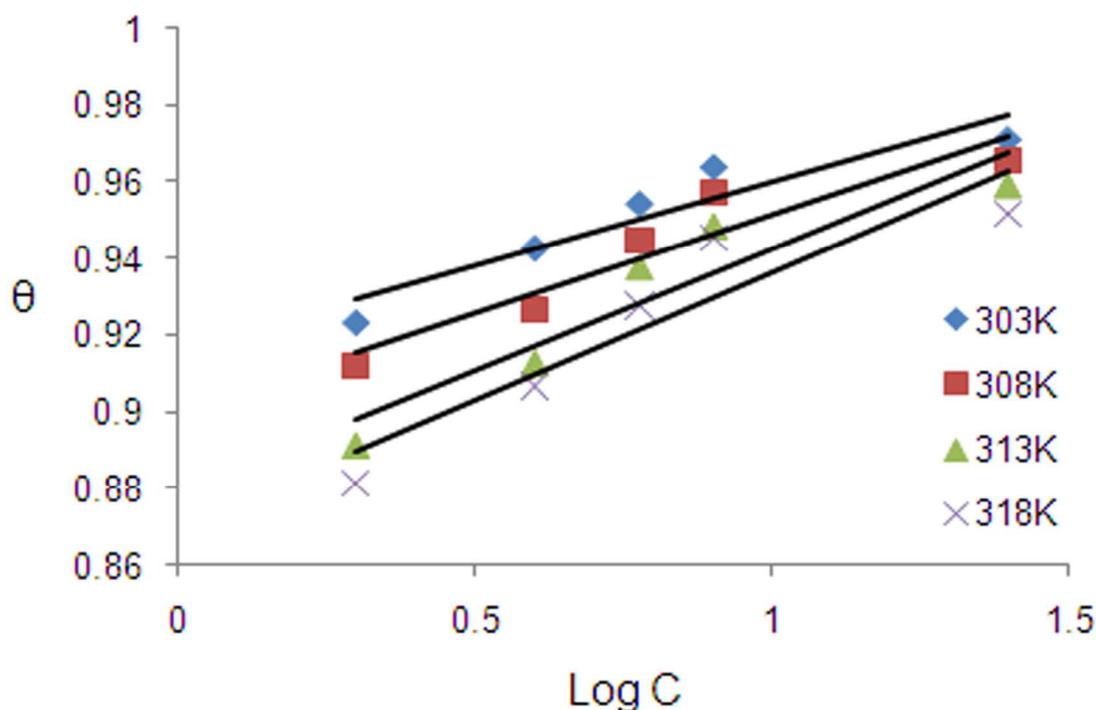


Fig. 3. Adsorption isotherm

Fig. 4 and 5 are the IR spectra of *J. curcas* seed husk extract and the product formed between extract and MS powder. IR studies reveal the functional groups responsible for the corrosion inhibition through adsorption. On comparing the spectra, there is a downshift from 3416.5 to 3410.7 cm^{-1} , which is attributed to the change in the stretching frequencies of hydroxy and amino groups. C-H stretching frequency of $-\text{CH}_2-\text{CO}-$ has downshifted from 2928.5 to 2925.9 cm^{-1} . A marked shift from 2089.9 to 2359.6 cm^{-1} is observed for N-H stretching for amino group in the presence of HCl. Carbonyl group frequency is downshifted from 1634.9 to 1629.7 cm^{-1} . A downshift from 1413.9 to 1370.6 cm^{-1} is observed for C-N of amide group. O-H in plane bending vibration has downshifted to 1030.7 from 1051.1 cm^{-1} . Hence it is obvious from the analysis that the inhibition is due to adsorption of hydroxyl, amino and amide groups of phenolic, protein, lipids and lignin molecules of the extract [27].

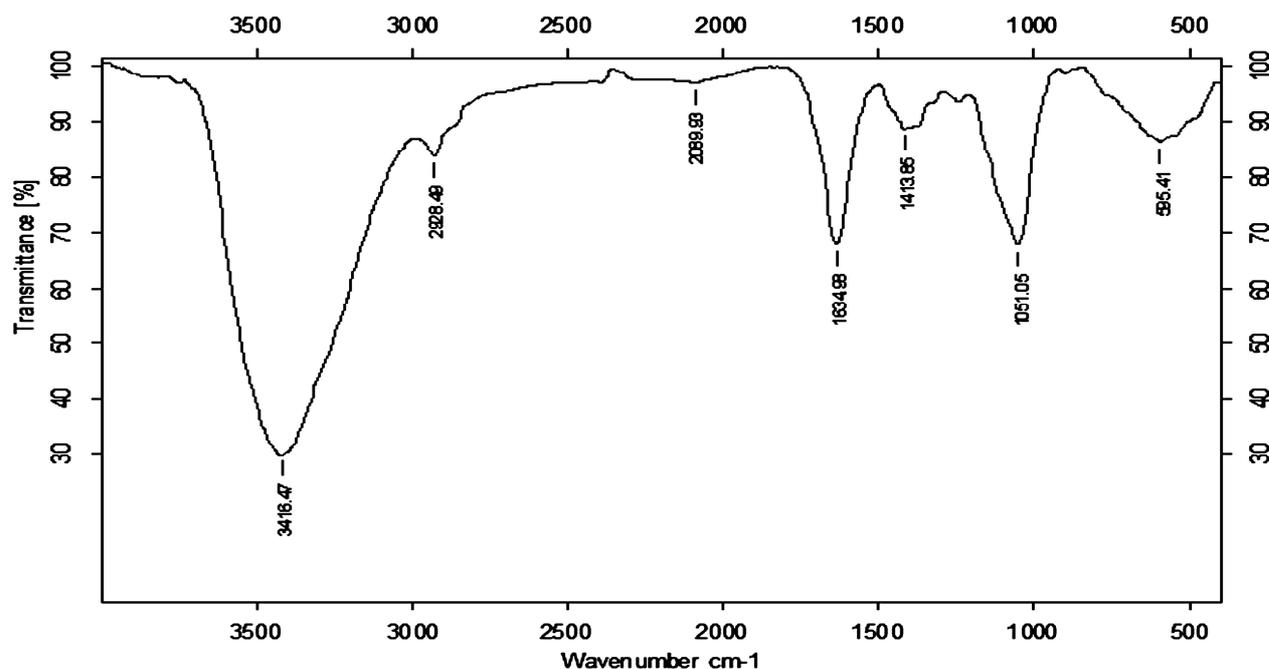


Fig. 4. IR spectra of the *J. curcas* extract

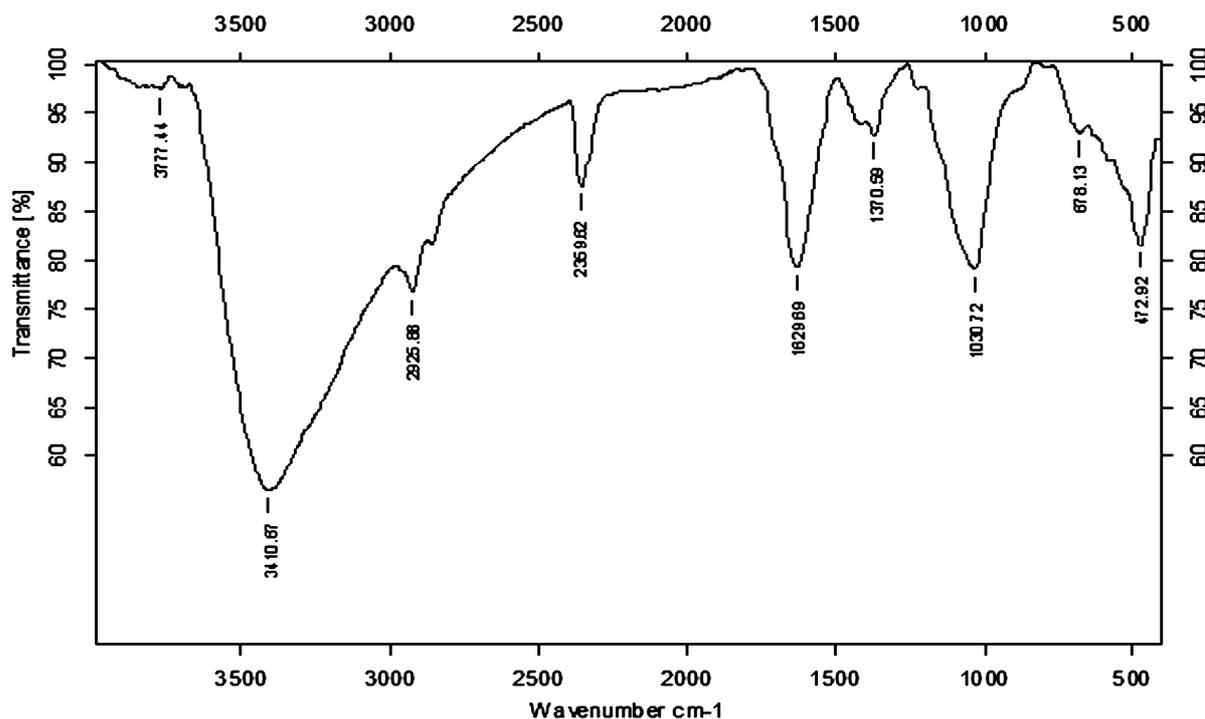


Fig. 5. IR spectra of the product between *J. curcas* extract and MS powder

The values of electrochemical parameters such as 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 obtained from electrochemical measurements are given in table 4. A mixed mode of inhibition is revealed by the E_{corr} values as they do not increase or decrease in a regular manner from the blank value. The mixed mode of inhibition is again proved by the values of b_a and b_c , which also do not increase or decrease in a regular manner. The steady decrease in I_{corr} values with increase in inhibitor concentration is an indication of decrease in corrosion reaction because corrosion current is proportional to the magnitude of corrosion reaction (figure 6).

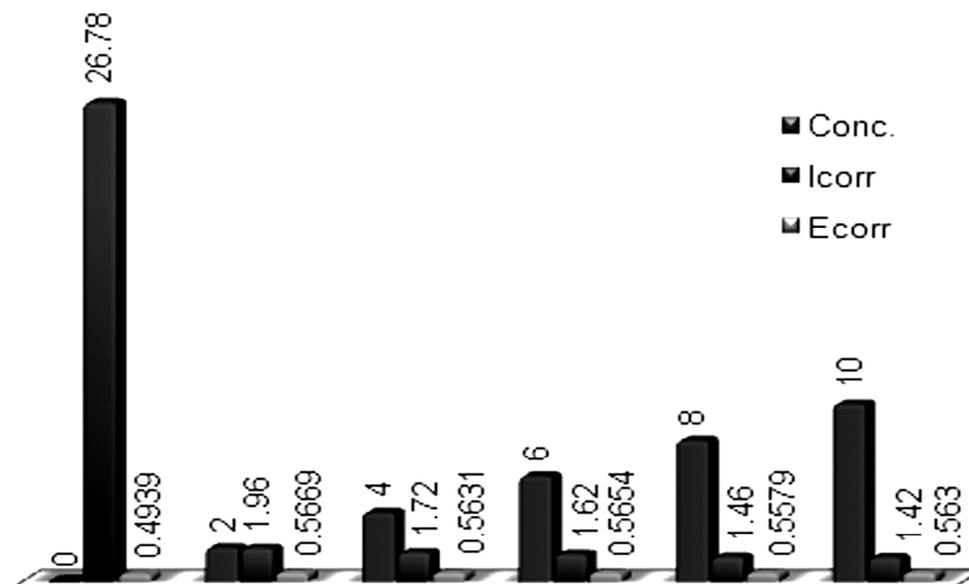


Fig. 6. Plot correlating I_{corr} and E_{corr} with concentration of the inhibitor

The C_{dl} values are found to decrease from the blank with increase in inhibitor concentration, which expose the increased level of adsorption of the inhibitor on the metal surface [28]. This adsorption is due to the electronegative hetero atoms of the organic constituents of the extract on the electropositive metal surface. This is also confirmed from the IR analysis. The increase in resistance towards the charge transfer reaction viz., corrosion reaction with increase in

inhibitor concentration is shown by the increased R_{ct} values. All the electrochemical parameters confirm that the corrosion control depends on the concentration of the inhibitor, which is evident from figures 7 and 8.

Table 4 Electrochemical parameters of corrosion inhibition by *J. curcas* extract

% Conc. (v/v)	OCP (mV)	E_{corr} (mV)	I_{corr} (μA)	b_a (mV/dec)	b_c (mV/dec)	R_{ct} (Ohm/ cm^2)	C_{dl} ($\mu A/cm^2$)	%IE
Blank	-0.5151	-0.4939	0.002678	150.91	226.11	5.8037	6.08×10^{-5}	-
2	-0.5771	-0.5669	1.96×10^{-4}	91.97	168.23	105.04	2.87×10^{-5}	92.29
4	-0.5710	-0.5631	1.72×10^{-4}	98.16	188.33	145.62	2.67×10^{-5}	93.58
6	-0.5669	-0.5654	1.62×10^{-4}	103.57	188.99	169.91	2.49×10^{-5}	93.96
8	-0.5621	-0.5579	1.46×10^{-4}	108.32	231.80	209.59	2.61×10^{-5}	94.55
10	-0.5622	-0.5630	1.42×10^{-4}	98.31	176.47	173.60	3.05×10^{-5}	94.68

In order to evaluate the surface morphology of mild steel, SEM photographs were recorded for MS surface and MS specimens exposed to test solution with and without inhibitor. The SEM photographs are given in figures 9, 10 and 11. The specimen immersed in the inhibitor solutions has apparently smooth surface when compared with that of corroded rough and uneven surface of mild steel immersed in HCl alone. This is due to the adsorption of inhibitor molecules on the metal surface forming a protective layer [29].

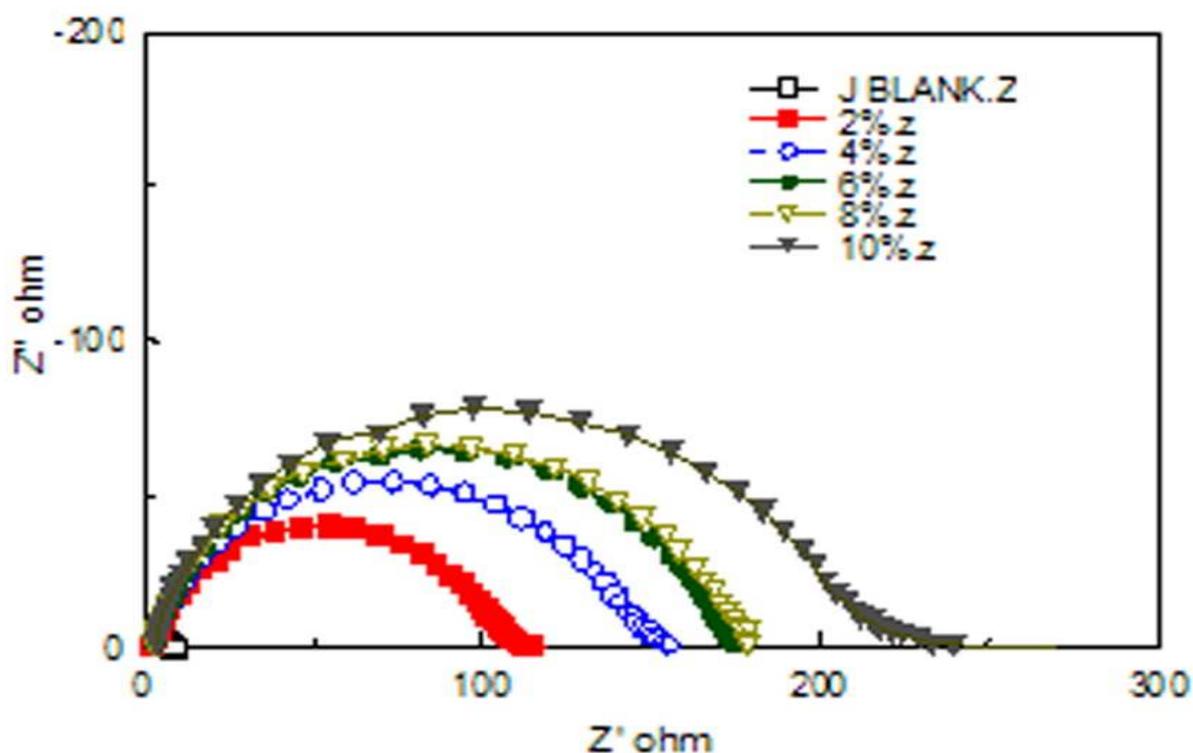


Fig. 7. Impedance spectra

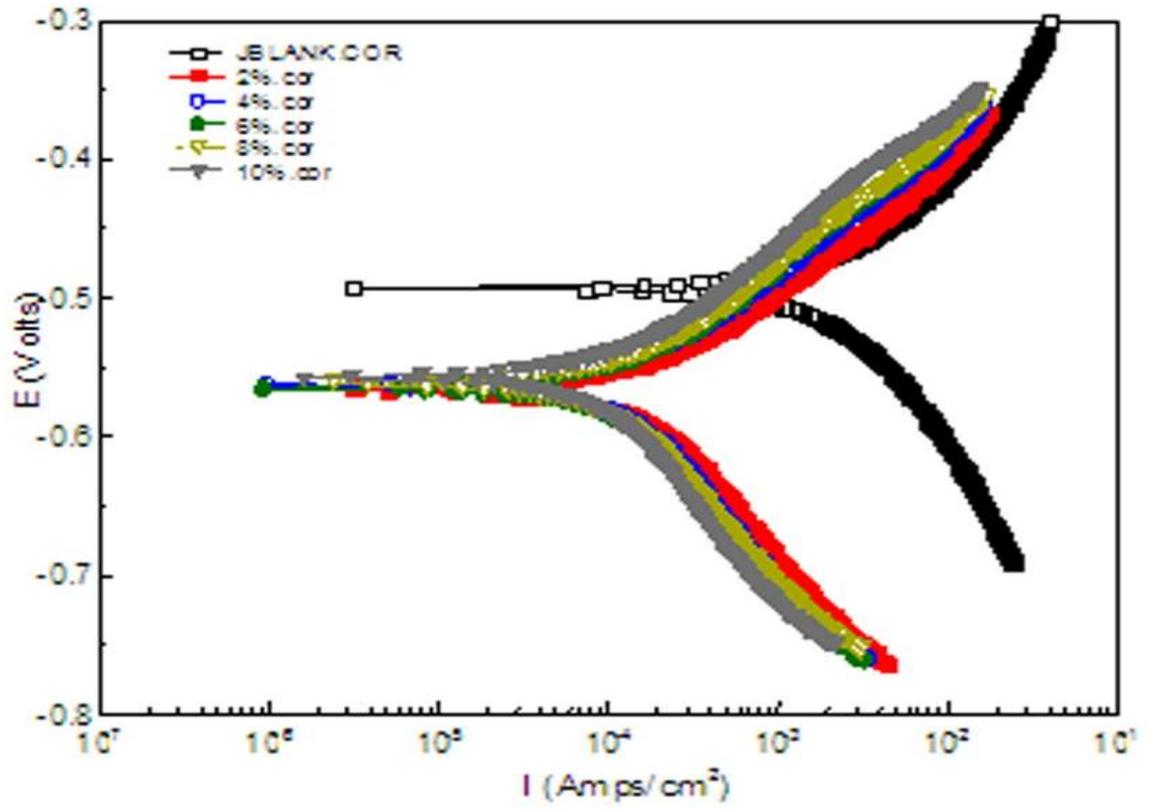


Fig. 8. Tafel polarization plots

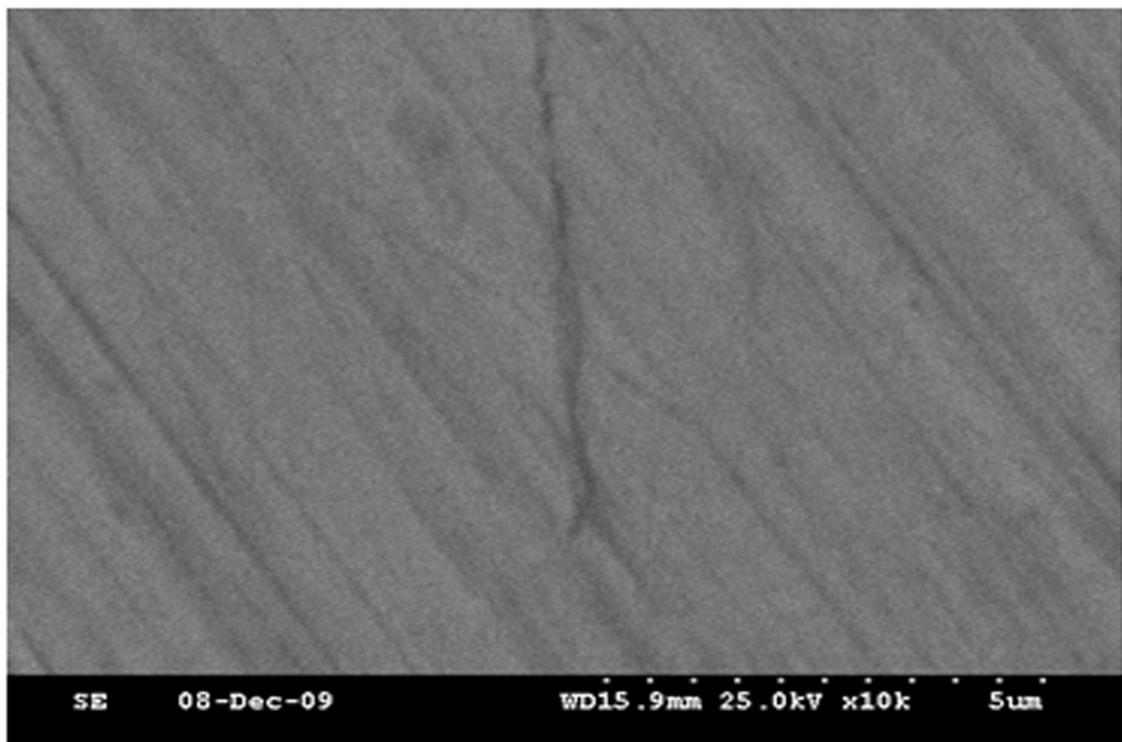


Fig. 9. Polished mild steel surface

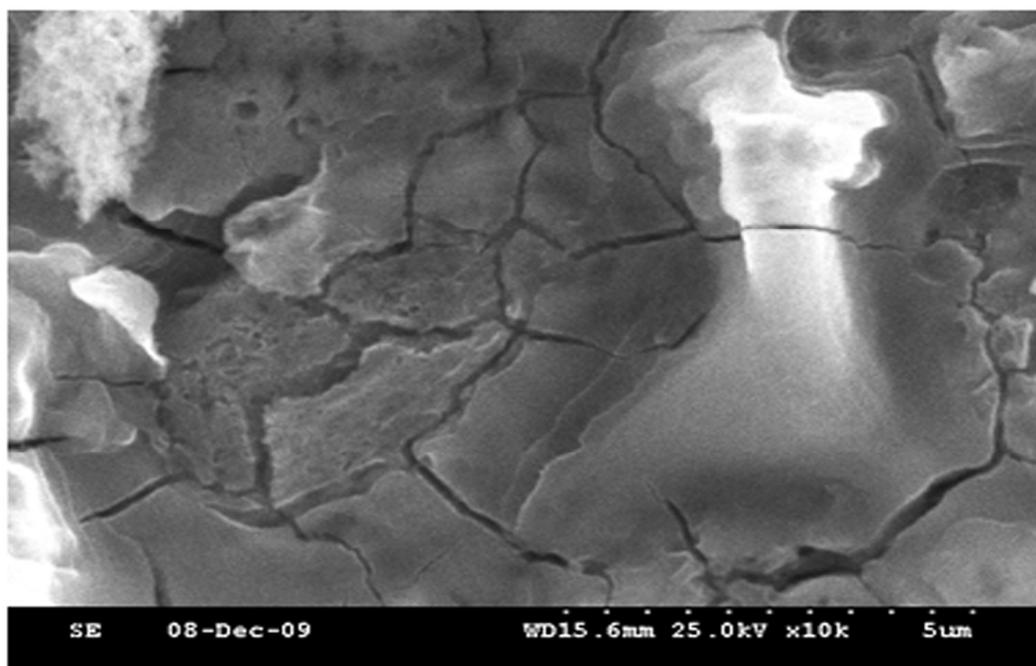


Fig. 10. Mild steel exposed to 5% HCl alone

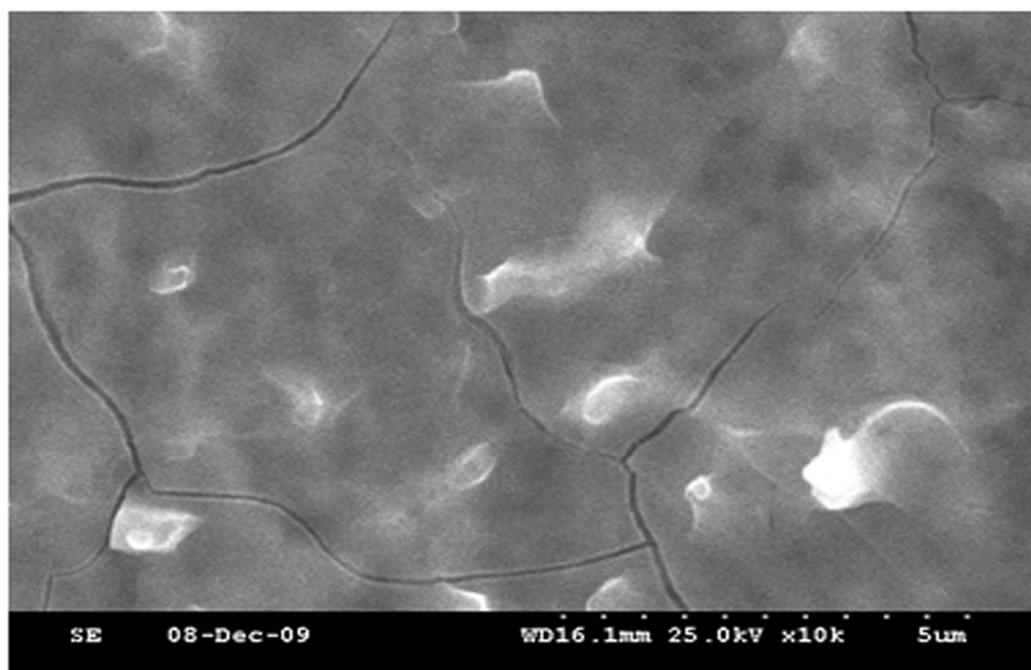


Fig. 11. Mild steel sample exposed to 5% HCl having 10% inhibitor

4. Conclusion

The weight loss study clearly depicts that corrosion inhibition efficiency of *J. curcas* extract increases with increase in inhibitor concentration and decreases only marginally as the temperature is raised. The spontaneity of the adsorption of inhibitor on the metal surface is revealed by the thermodynamic analysis. The enhanced adsorption on the metal surface by inhibitor with increase in concentration is illustrated from the various graphical studies. The adsorption of the inhibitor on the metal surface is accredited to the lone pair of electrons present in the hetero atoms of the *J. curcas* extract. This is further confirmed from IR spectral studies. The electrochemical parameters specify the mixed mode of inhibition. The photographs of the SEM study evidently focus the protective nature of the extract over mild steel. Therefore, it is obvious that the seed husk extract of *J. curcas* is an effective, eco-friendly and alternate corrosion inhibitor for mild steel in HCl medium.

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