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Ziziphus Jujuba Leaves Extract as Green Corrosion Inhibitor for Mild Steel in 1N Hydrochloric Acid Medium

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ABSTRACT

The effect of Ziziphus Jujuba (ZJ) leaves extract on the corrosion inhibition of mild steel in 1N HCl solution was studied using chemical and electrochemical techniques. It was found from the results of weight loss method that the inhibition efficiency increased with increase in the ZJ extract up to 15 ppm. It indicates that 15 ppm is the optimum concentration to get maximum corrosion protection for mild steel in 1N HCl. The results obtained from the chemical and electrochemical measurements are in good agreement. Organic moieties present in the extract are found responsible for effective performance of inhibitor which was well supported by FTIR studies. The potentiodynamic polarization studies revealed that the ZJ extract acts as mixed type inhibitors. The surface characteristics of the inhibited and uninhibited mild steel were investigated by Scanning Electron Microscopic studies.

Keywords: Mild steel, Corrosion inhibitors, ZJ leaves extract, EIS, SEM.

INTRODUCTION

Mild steel is a structural material widely used in automobiles, pipes and used in most of the chemical industries. Mild steel suffers from severe corrosion in aggressive medium of acids and pickling process. Hydrochloric acid is widely used for pickling, descaling and chemical cleaning processes of mild steel. 90% of pickling problems can be solved by introducing appropriate pickling inhibitor to the medium. Generally organic compounds containing O, N and S atoms are normally used as inhibitors to reduce the corrosion of mild steel in hydrochloric acid medium [1,2]. Environmental concerns worldwide are increasing and are likely to influence the choice of corrosion inhibitors in the present and in the future. Environmental requirements are still being developed, but some elements have been established. One of the methods to protect metals against corrosion is addition of species to the solution in contact with the surface in order to inhibit the corrosion rate. Unfortunately, many of the inhibitors used are inorganic salts or organic compounds with toxic properties or limited solubility. Increasing awareness of health and ecological risks has drawn attention to find more suitable inhibitors which are nontoxic. Accordingly, greater research efforts have been directed towards formulating environmentally acceptable inhibitors.

Due to diversity of the structures, many extracts of common plants have been used as corrosion inhibitors for materials in pickling and cleaning processes. Plant materials contain proteins, polysaccharides, polycarboxylic acids, tannins, alkaloids and so forth. These compounds are potential acid corrosion inhibitors for many metals [3]. The cost of using green inhibitors is very low when compared to that of organic inhibitors which require a lot of chemicals and also time for its preparation. Chemical inhibitors are more expensive and cause more hazard effects. Nowadays due to strict environmental legislation, emphasis is being focused on usage of natural products that are corrosion inhibitor. The recent and growing trend is using plant extracts as corrosion inhibitor. Recently, many plant extracts have been reported as effective corrosion inhibitors within India and outside India [4-20]. In this study, leaf extracts of Ziziphus Jujuba plant have been selected to study the corrosion of mild steel in 1N hydrochloric acid medium using weight loss method, the potentiodynamic polarization method, and electrochemical impedance method and scanning electron microscopic method.

MATERIALS AND METHODS

Preparation of Leaves Extract: The leaves of medicinal plant Ziziphus Jujuba collected were taken and cut into small pieces, and they were shade dried in room temperature for few days and ground well into powder. From this, 25 g of sample was refluxed in 200 mL distilled water for 3 h and kept overnight. The refluxed was then filtered carefully, the filtrate volume was made up to in 500 mL using double distilled water which was the stock solution, and the concentration of the stock solution was expressed in terms of ppm.

Preparation of Mild Steel Specimen: Mild steel strips containing the composition of (C-0.030%, Cr-0.029%, Ni-0.030%, Mb-0.016%, Cu-0.017%), and the reminder Fe, were mechanically cut into 4cm x 2cm x 0.1cm and were used for weight loss studies. For electrochemical studies, the mild steel strips of the same composition but with an exposed area of 1cm^2 were used, subsequently degreased with acetone and finally washed with deionized water, and stored in the desiccators.

Weight Loss Method: Mild steel specimens were immersed in 200 mL of 1N HCl solution containing various concentration of the inhibitor in the absence and presence of mild steel for 24 h. The weights of the specimens before and after immersion were determined using four digit model (shimadzu ay220).
From the mass loss measurements, the corrosion rate was calculated using the following relationship.

$$\text{CR (mmpy)} = \frac{\text{K x Weight loss}}{\text{D x A x t (in hours)}} \qquad 1$$

Where, K = 8.76x10^4 (constant), D is density in gm/cm^3 (7.86), W is weight loss in grams and A is area in cm^2.
The inhibition efficiency (%) was calculated using equation (2) respectively,

$$\text{IE\%} = \frac{W_0 - W_i}{W_0} X100 \qquad 2$$

Where, W_0 and W_i are the weight loss in the absence and presence of the inhibitor.

Fourier Transform Infrared (FTIR) Spectrum: FTIR spectra were recorded BRUKER ALPHA 8400S spectrometer. The film was carefully removed, mixed thoroughly with KBr made into pellets and FTIR spectra were recorded.

Potentiodynamic Polarization Method: Potentiodynamic polarization measurements were carried out using CHI608D electrochemical work station analyzer. The polarization measurements were used to evaluate the corrosion current, corrosion potential and Tafel slopes. The experiments were carried out in conventional three electrode cell assembly with working electrode as mild steel specimen 1 cm^2. Platinum electrode was used as counter electrode and calomel electrode was used as reference electrode. A time interval of 10-15 min was given for each experiment to attain the study state open circuit potential. The polarization was carried out from cathodic potential to anodic potential at a sweep rate of 1 mV per second. From the polarization curves, Tafel slopes, corrosion potential and corrosion current were calculated. The inhibitor efficiency was calculated using the formula:

$$IE\% = \frac{I_{Corr} - I^{*}_{Corr}}{I_{Corr}} X100 \qquad 3$$

Where I_{corr} and I^{*}_{corr} are corrosion current in the absence and presence of inhibitors.

Electrochemical Impedance Method: Experiments were carried out in three cells assembly as that used for potentiodynamic polarization studies. A sine wave is with amplitude 10 mV on the steady state open circuit potential. The real part (z') and the imaginary part (z'') were measured at various frequencies in the range of 100 kHz to 10 MHz. Plot of z' versus z'' was made. From the plot the charge transfer resistance (R_{ct}) was calculated and double layer capacitance (C_{dl}) was calculated using formula:

$$C_{dl} = 1/2\pi f_{max} Rct \qquad 4$$

Where R_{ct} is charge transfer resistance and C_{dl} is double layer capacitance. The experiments were carried out in the absence and presence of different concentration of inhibitor.

$$IE\% = \frac{R_{ct} - R^{0}_{ct}}{R_{ct}} X100 \qquad 5$$

Where R_{ct} and R^{0}_{ct} are the charge resistance values in the inhibited and uninhibited solution respectively.

RESULTS AND DISCUSSION

Weight Loss Method: The weight loss method was done with concentrations of ZJ extract ranging from 5 to 25 ppm for mild steel in 1N HCl with various concentrations and the corresponding values of inhibition efficiency and corrosion rate are given in table 1. The inhibition efficiency and corrosion rate of mild steel are with without different ranging of ZJ extract was determined after 24 h room at temperature, and the results are given in Table 1. It was observed from the table that the corrosion rate decreased and thus the inhibition efficiency increases with increasing concentration of ZJ extract (5 ppm to 25 ppm). The maximum inhibition efficiency of about 95.90% was achieved at 15 ppm of ZJ extract. This result indicated that ZJ extract could act as an excellent corrosion inhibitor.

Table 1. Data from Weight Loss Method for MS corroding in 1N HCl solutions at various concentrations of ZJ extract

Conc. of ZJ Extract (ppm)	Corrosion Rate (mmpy)	Inhibition Efficiency (%)
Blank	0.0348	*
5	0.0125	80.06
10	0.0127	89.45
15	0.0133	95.90
20	0.0145	90.68
25	0.0116	73.13

FTIR Spectra: FT-IR spectrum was recorded for ZJ leaves extract in order to confirm the presence of various compounds which contributed in effective working of the inhibitor is shown in figure 1. It is observed the Free O-H stretching was observed at 3500-3700 cm^{-1}. Broad peak obtained at 3916 cm^{-1} may be N-H or C-H stretching. C-H stretching was observed at 2000 cm^{-1} to 2300 cm^{-1}. Other strong peak obtained at 1670 to 1820 cm^{-1} correspond to C=O band. Strong peaks obtained at 1550 to 1633 cm^{-1} and 1629 cm^{-1} are due to N-H bending vibration. Absorption band at 1110 cm^{-1} can be assigned to C-O bending. Peaks observed at 1348 cm^{-1}, 1325 cm^{-1} and 1159 cm^{-1} are due to C-N and C-O stretching vibration. Few weak peaks can also observed at 1550 cm^{-1}, 1525 cm^{-1}, 1472 cm^{-1} 1438 cm^{-1}, which correspond to C=C stretching vibration of aromatic ring.

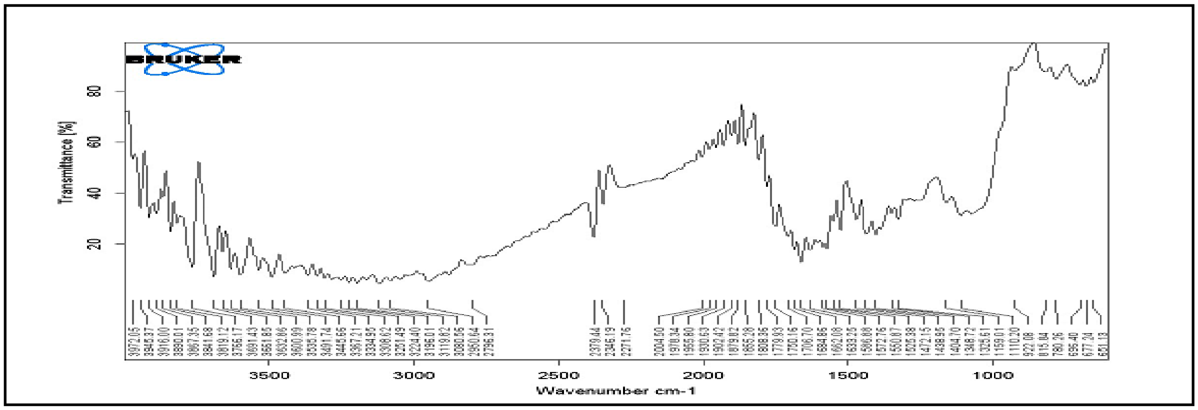

Figure 1. FT-IR spectrum of Ziziphus Jujuba leaves extract

Potentiodynamic polarization Studies: The electrochemical parameter like corrosion potential (E_{corr}), corrosion current density (I_{corr}), cathodic Tafel slopes (b_c), anodic Tafel slope (b_a) and percentage of inhibition efficiency for mild steel in the absence and presence of various concentrations of ZJ extract in 1N HCl is given in Table 2 and their polarization curves are shown in figure 2. It was noted from the table that the addition of green inhibitor decreases the dissolution rate of mild steel in 1N HCl acid media. However, the shift in the values of corrosion potential (E_{corr}) for ZJ leaves extract was not significant. This observation clearly showed that the inhibition of mild steel in the presence of the extract control both cathodic and anodic reactions and thus the inhibitor acts like mixed type inhibitors. However, the maximum inhibition efficiency of 96.97% was achieved at 15ppm. From these findings, it is concluded that 15ppm is an optimum concentration of the inhibitor where the rate of corrosion is found to be maximum.

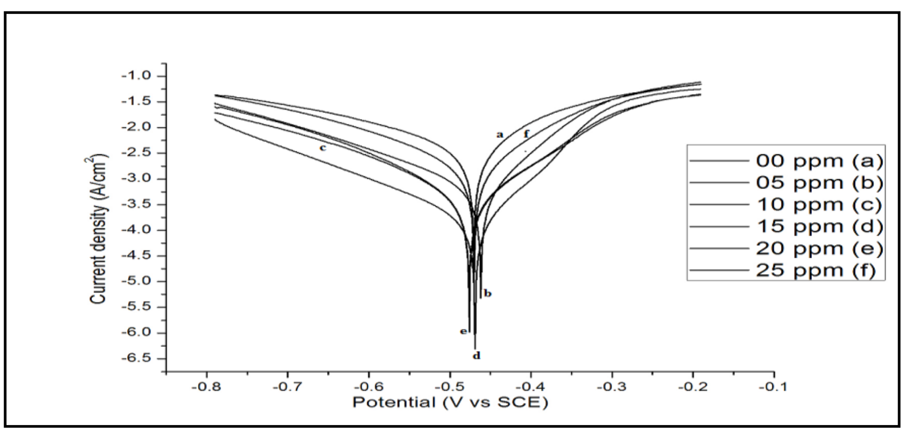

Figure 2. Potentiodynamic polarization curves for mild steel in 1N HCl solution in the absence and presence of different concentrations of ZJ leaves extract

Table 2. Potentiodynamic polarization parameter for mild steel in 1N HCl solution containing various concentrations of ZJ leaves extract

Conc. of ZJ (ppm)	E_{corr} (mV) vs. SCE	I_{corr} (mA cm^{-2})	CR (mmpy)	b_c (mV/dec)	b_a (mV/dec)	IE (%)
Blank	-471	4.706	0.0278	208	153	-
5	-462	0.656	0.0130	171	80	86.06
10	-476	0.4021	0.0102	142	97	91.45
15	-469	0.1425	0.0106	159	63	96.97
20	-476	0.3912	0.0116	131	101	91.68
25	-470	1.7350	0.0092	166	111	63.13

Electrochemical Impedance spectroscopy (EIS) Studies: To ensure complete characterization of the interface and surface processes, EIS measurements were made at OCP in a wide frequency range. Figure 3 shows Nyquist plots for mild steel electrode immersed in 1N HCl solution in absence and presence of various concentrations of the Ziziphus Jujuba extract. The presence of a single semicircle in the blank and for different concentrations of the inhibitor systems corresponds to the single charge transfer mechanism during dissolution of mild steel, which is unaltered by the presence of inhibitor components.

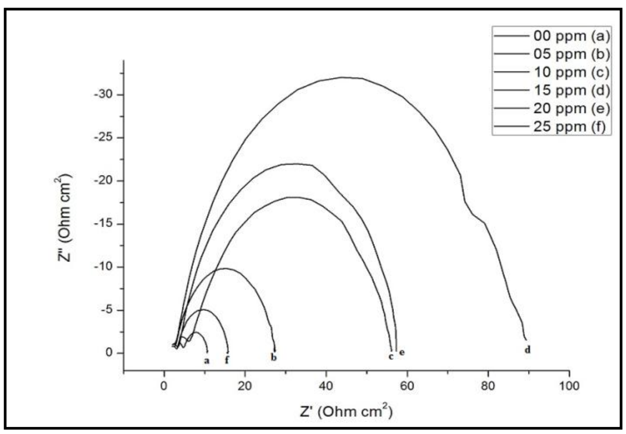

Figure 3. Nyquist plots of mild steel immersed in 1N HCl in absence and presence of different concentrations of ZJ leaves extract

The impedance parameters were calculated for mild steel in 1N HCl with and without inhibitors are given in table 3. The higher R_{ct} value obtained for higher inhibitor concentration suggests that a protective film is formed on the surface of the metal. The decreased in the C_{dl} values from the blank as the increased in the concentration of the inhibitor confirm the enhancement of the adsorption of the inhibitor on the metal surface. The decrease in C_{dl} is attributed to an increase in thickness of the electronic double layer due to adsorption. The adsorption is due to the electronegative hetero atoms present in the organic constituents of the extract on the electropositive metal surface. All the electrochemical parameters clearly proposed that the corrosion control depends on the concentration of the inhibitor.

Table 3. The electrochemical parameters (EIS) for mild steel corrosion rate in 1N HCl solution in different concentrations of ZJ leaves extract

Conc. of ZJ (ppm)	C_{dl} (μF/cm^2)	b_c (mV/dec)	b_a (mV/dec)	R_{ct} (Ωcm^2)	IE (%)
Blank	9.728	208	153	6.454	*
5	6.159	171	80	26.36	75.53
10	1.591	142	97	54.619	88.20
15	5.402	159	63	92.426	93.02
20	1.281	131	101	56.345	88.55
25	2.288	166	111	13.275	51.39

Bode Plot: Bode plots of mild steel in uninhibited and inhibited acid solution containing various concentrations of ZJ extract are presented in figure 4. It is apparent that the mild steel specimens with ZJ extract showed increase in maximal phase angle value, which indicated the inhibition property on the surface mild steel. The linear portion observed in the low frequency region indicated that the diffusion process controlled the metal dissolution rate at the surface of mild steel.

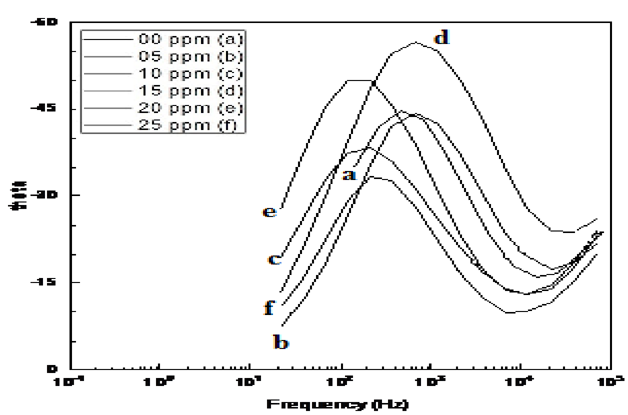

Figure 4. Bode plots of mild steel immersed in 1N HCl in absence and presence of different concentrations of ZJ leaves extract

Surface Examination Studies: Some scratches can be noticed on the surface, which are the results of grinding of the mild steel surface with emery paper. Scanning electron microscopy was used to examine the morphology of the inhibited mild steel specimens in 1N HCl. SEM images for the mild steel specimens exposed to 1N HCl in the absence and presence of ZJ extract are shown in figure.5 (A and B). It should be noted from the figure 5A that the mild steel specimen immersed in 1N HCl was rough and highly damaged due to severe attack of aggressive acid. Figure 5B clearly showed that a smooth and pits free surface which prevents the metal and inhibiting corrosion. From SEM images, It can be concluded that ZJ leaves extract inhibited mild steel dissolution in acid by covering the surface area with protective film which has found absent in case of acid interaction with mild steel.

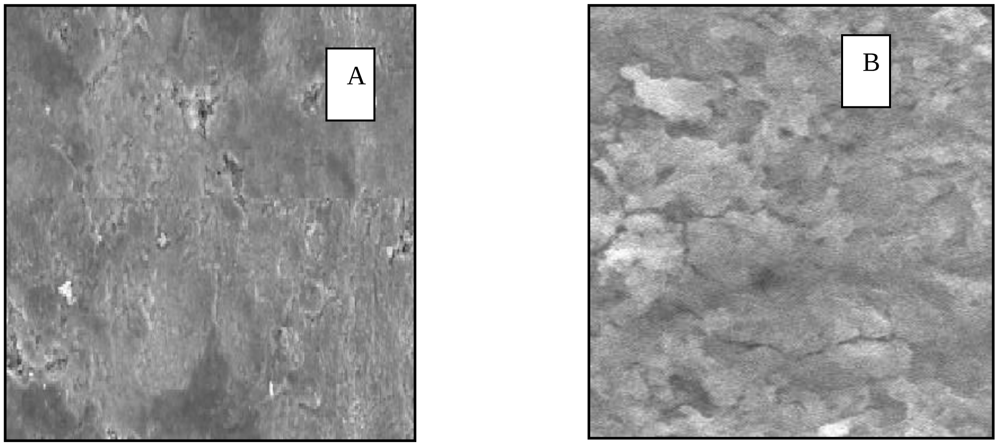

Figure 5. SEM image of the surface of mild steel after immersion for 24 h in 1NHCl solution (A) in the absence of inhibitor (B) in the presence of 20ppm ZJ leaves extract

Phytochemical Screening Method: Phytochemical screening of the aerial parts of plant's powder (aqueous) extract was tested in order to find the presence of various chemical constituent included Sterols, Carbohydrates, Proteins & Amino Acids, Alkaloids, Glycosides, Tannins, Saponins the results are listed in table4.

Table 4. Phytochemical screening of leaves extract of ZJ

S.No	Phytochemical Test	Aqueous extract of ZJ
1	Sterols	+
2	Carbohydrates	+
3	Proteins & Amino Acids	+
4	Alkaloids	+
5	Glycosides	-
6	Tannins	+
7	Saponins	+

+ is Present - is absent

APPLICATIONS

The ZJ leaves extract exhibit excellent corrosion resistance to the mild steel in HCl medium. The ZJ inhibitor that has little or no impact on the environment i.e. the inhibitor is Ecofriendly, safe and some extent good corrosion resistance with temperature. Therefore this inhibitor can be used for the corrosion protection of mild steel in acid medium for various industries.

CONCLUSIONS

In this study, the aqueous extract of ZJ leaves as inhibitor was tested for mild steel in 1N HCl. Present study showed that the investigated ecofriendly inhibitor had a high inhibitory effect to corrosion process of mild steel. The inhibition efficiency increased with increase in inhibitor concentration. E_{Corr} values shifted to more positive potential direction. The adsorption of ZJ leaves extract on mild steel obeys Temkin adsorption isotherm. Adsorption of inhibitor on mild steel was further confirmed by SEM .

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