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Research Article

Adsorption of Extract of *Milletia pinnata* on Mild Steel: A Green Inhibitor for Protection of Steel Surface at Different Corrosive Environments

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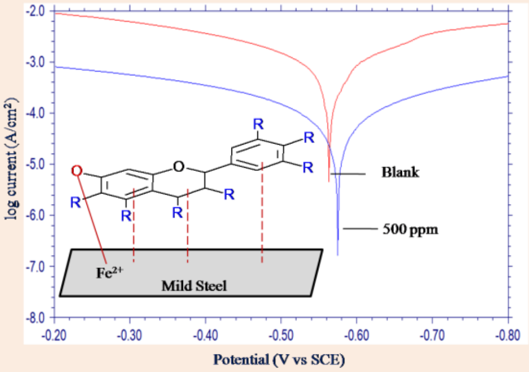
Abstract

Green inhibitors from renewable natural resources have been demonstrated as potential candidates for inhibition of corrosion in different chemical and physical environments. The scientific investigations on the underlying principles of 'Green Chemistry' utilizing plant sources for industrial problems can pave way to development of cost effective and eco-friendly solutions. The ethanolic extract of *Milletia pinnata* leaves was evaluated for its inhibitive properties as a green inhibitor for corrosion of mild steel in hydrochloric acid medium. The inhibitor was studied by means of weight loss measurements involving in different corrosive environments such as different concentrations of inhibitor, acid, and at elevated temperatures. 94.5% inhibition efficiency was showed by 500 ppm of inhibitor at 298 K. Langmuir isotherm suggested that the inhibitor protects the metal predominantly via physisorption. Electrochemical studies revealed that the inhibitor affects both anodic and cathodic reactions. Morphological examination by SEM added evidence for adsorption of inhibitor on the surface of mild steel.

Keywords: Milletia pinnata, corrosion, inhibition, green inhibitor, isotherm

The present study reveals that the ethanolic exract of *Milletia pinnata* greatly inhibits (~94.5%) the corrosion of mild steel in hydrochloric medium. Inhibitor exhibited significant efficiency in protecting the mild steel surface at different environments such as at elevated temperatures, higher acid concentration, and prolonged exposure of mild steel to corrosive medium.



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Introduction

Corrosion of metals is a spontaneous destruction during the course of their chemical, electrochemical, or biochemical interaction with their environment. Economically, the loss due to corrosion is comparable to any natural disasters of a country. Different methods have been developed to protect the metals from corrosion. Corrosion inhibitors play crucial role in protecting the metals. Inhibitors based on chromium were found to be effective against the corrosion. Due to the toxic nature of the chromium inhibitors, in recent years, researches were carried out on exploration of eco-friendly inhibitors. The natural products extracted from different parts of plants are reportedly eco-friendly and exhibit significant inhibition properties. Plant extracts contains mixture of organic compounds ranging from terpenoids to flavonoids, which have electronegative atoms such as oxygen and nitrogen [1,2].

Several eco-friendly or green inhibitors were reported for their potential for inhibition of steel corrosion [1,2]. Our research group has evaluated inhibitors derived from plants as well as synthetic organic molecules for inhibition of mild steel corrosion in different corrosive environments [3-9]. *Millitia pinnata* (MP) is a commonly available tree in tropical regions such as India, Malaysia, China, Australia, and Japan. MP belongs to Leguminosae family and involves in nitrogen fixation. In recent years it has been examined as a potential candidate for production of biodiesel [10]. In view of plentiful availability, eco-friendliness, and economy, the present study examines the inhibitive characteristics of MP against the corrosion of mild steel in aqueous hydrochloric acid solution. The inhibition potential of MP is studied by means of weight loss measurements and electrochemical studies. The adsorptive nature of the inhibitor was observed under scanning electron microscopy (SEM) and the results are discussed in the following sections.

Experimental

The extraction of the inhibitor was performed by means of conventional distillation method. The detailed experimental procedure is given in the following sections. An electrochemical analyzer (CH 6043b) was used to perform polarization and impedance studies using the mild steel specimen. The mild steel specimens used for both inhibited and uninhibited (blank) measurements along with fresh MS were observed under a scanning electron microscope (Hitachi 3000H).

Inhibitor Preparation

Fresh leaves (1 kg) of MP were collected from Salem, Tamil Nadu, India and dried under shade for 5 days. The dried leaves were crushed into powders and soaked in 95% ethanol for 3 days. The extract was filtered and reduced *in vacuo* to yield green colored oily product (30 g). The inhibitor solutions were prepared by dissolving known quantity of inhibitor in 1 M HCl.

Weight Loss Measurements

The mild steel specimens having C, 0.10 %; Mn, 0.34 %; P, 0.08 %; and remainder being Fe were used for the studies. The specimens were abraded using different grades of emery sheets and degreased using acetone. Then the specimen was immersed in 100 mL of 1 M HCl both in presence and absence of inhibitor for 2 hr at 298 K. The experiments without application of inhibitor were set as blank measurements. All the experiments were performed in triplicate and the average values were taken for further calculation. The weight differences before and after experiments were noted and surface coverage (θ) and the inhibition efficiency were calculated as gives in equations 1 and 2

$$IE\% = \frac{W_o - W}{W_o} \times 100 \qquad (1)$$

$$\theta = IE\,\% / 100 \qquad (2)$$

The corrosion rate (CR) was calculated according to ASTM standard [11] and it is given by equation 3.

$$CR = \frac{W_o}{AtD} \qquad (3)$$

Electrochemical Studies

A platinum electrode was used as an auxiliary electrode whereas standard calomel electrode was used as a reference for electrochemical measurements. A mild steel specimen with an exposed area of 1 cm^2 was used as working electrode. Prior to each electrochemical measurement, the working electrode was polished. All measurements were carried out at room temperature (300 K). The corrosion current densities were obtained from the extrapolation of anodic and cathodic curves of Tafel polarization results. The polarization curves were recorded at a sweep rate of 0.01 mVs^{-1}. The IE% from polarization studies were calculated as given in equation 4.

$$IE\% = \frac{I'_{corr} - I_{corr}}{I'_{corr}} \times 100 \qquad (4)$$

EIS measurements were carried out at the range of 1 to 10,000 Hz at amplitude of 0.01 V using an equivalent circuit (**Figure 1**). The impedance diagrams were represented by means of Nyquist plots. The IE% was calculated using the values of charge transfer resistance (R_{ct}) as shown in equation 5.

$$IE\% = \frac{R_{ct} - R'_{ct}}{R_{ct}} \times 100 \qquad (5)$$

where, R_{ct} and R'_{ct} are the charge transfer resistances in the absence and presence of inhibitor.

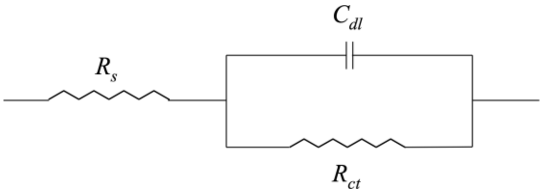

Figure 1 Electrical Equivalent circuit model for EIS measurements, where, R_s – solution resistance, R_{ct} – charge transfer resistance, and C_{dl} – double layer capacitance

Results and Discussion

Weight loss measurements

Effect of Inhibitor Concentration

The effect of inhibitor concentration on inhibition process was examined by using 1 M HCl solution containing 100 – 500 ppm of MP. The corrosion parameters such as surface coverage, percentage inhibition efficiency (IE%) and corrosion rates are given in **Table 1** and **Figure 2**. It is obvious from the results that the IE% increases by increasing the inhibitor concentration. The IE% gradually increased between 100 ppm to 500 ppm inhibitor solutions. The inhibitor showed a maximum of 94.5% at 500 ppm. Further increase in inhibitor's concentration did not show any significant change in IE%.

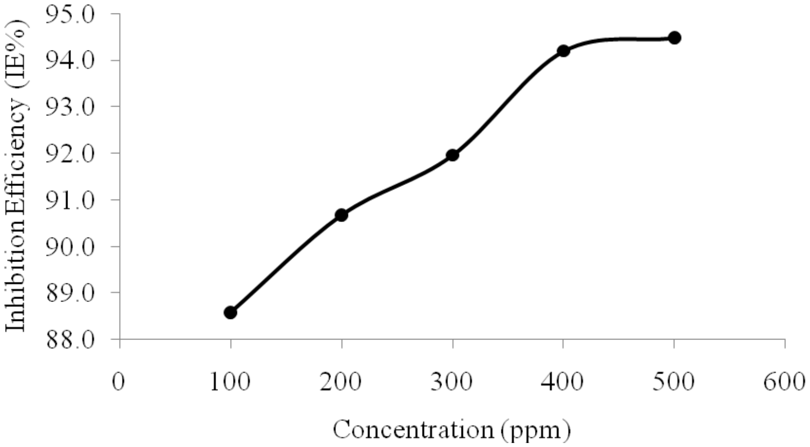

Figure 2 Effect of inhibitor concentration on inhibition efficiency at 300 K

Table 1 Weight loss data of mild steel both in presence and absence of inhibitor and thermal parameters for adsorption of inhibitor on metal surface

Concentration (ppm)	IE%	θ	CR (mmpy)	K_{ads} (KJ/mol)	ΔG_{ads} (KJ/mol)
0 (Blank)	-	-	2.96		
100	88.6	0.886	0.34	7.75	-22.30
200	90.7	0.907	0.28	4.85	-21.17
300	92.0	0.920	0.24	3.80	-20.57
400	94.2	0.942	0.17	4.05	-20.72
500	94.5	0.945	0.16	3.42	-20.30

Effect of Time

The mode of interaction between metal surface and the inhibitor molecules can be understood by examining the effect of immersion time. As shown in **Figure 3**, the IE% is inversely proportional to the immersion time. These results suggested that, the mechanism of inhibition may be adsorption and possibly physisorption. Physisorption is due to weak van der Waals force of attraction between inhibitor molecules and the mild steel surface [11].

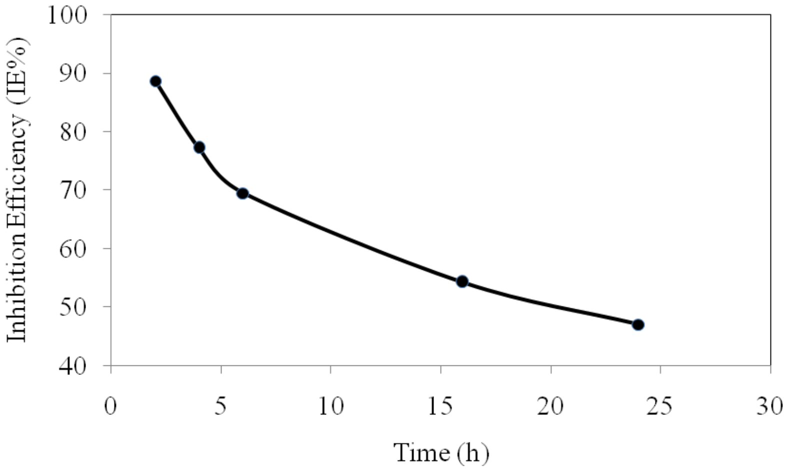

Figure 3 Effect of time concentration on inhibition efficiency at 300 K

Effect of Temperature

Figure 4 showed that the temperature and corrosion rates (CR) are directly proportional, which means that the IE% decreases at elevated temperatures. This is attributed to the increased activity of the acid and partial desorption of the inhibitor molecules from the metal surface. In general, weak attraction forces disappear at elevated temperatures. From the effect of immersion time and the temperature, it is obvious that the inhibitor molecules were adsorbed on the metal surface via physical adsorption [12,13].

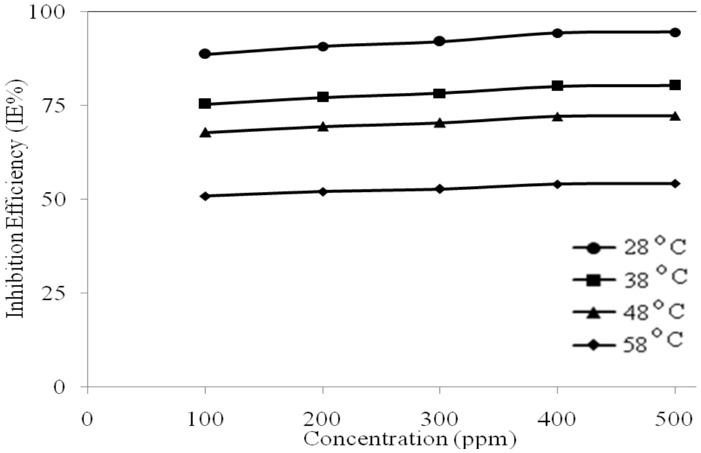

Figure 4 Effect of temperature on inhibition efficiency at 300 K

Effect of Acid Concentration

The inhibition characteristics of the inhibitor were examined under different corrosive circumstances. The concentration of the corrosive medium was varied from 1 M to 3 M HCl. The increased aggressiveness of the acid resulted in decrease of IE% as shown in **Figure 5**. About 65% of IE was achieved at 3 M HCl with 500 ppm of inhibitor. The results suggested that the inhibitor is effective in protecting the metal surface even at 3 M HCl.

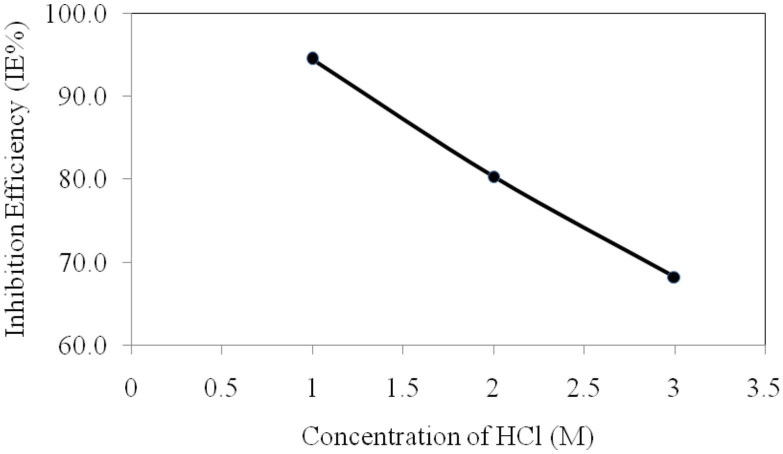

Figure 5 Effect of acid concentration on inhibition efficiency at 300 K

Tafel Polarization

In general, a Tafel polarization of MS reveals the effect of inhibitor on cathodic and anodic reactions. Depending on the changes observed, the inhibitor can be classified as anodic, cathodic, or mixed type. **Figure 6** shows the polarization curves for mild steel in 1 M HCl both in absence and presence of inhibitor. Various polarization parameters such as anodic (b_a) and cathodic (b_c) Tafel slopes, corrosion potential (E_{corr}), current density (I_{corr}) were calculated from the Tafel curves (Figure 6) and the results were given in **Table 2**. It was observed that increase in MP concentration decreases the corrosion potential and increase in IE%. Despite small shift in the E_{corr} in presence of MP, the displacement is not more than ±85 mV with respect to blank Tafel curve [14]. Therefore MP is classified as mixed type inhibitor, which suggests that the inhibitor affects both anodic and cathodic reactions.

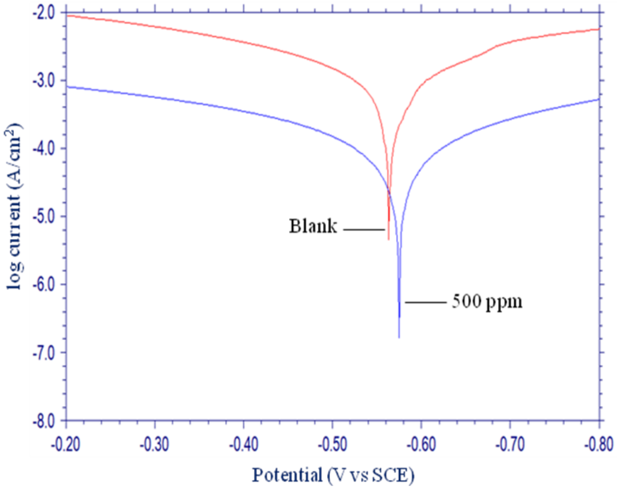

Figure 6 Tafel polarization curves of mild steel in 1 M HCl in the presence and absence of inhibitor

Table 2 Tafel polarization parameters

Inhibitor	Concentration (ppm)	b_c (mV/ decade)	b_a (mV/ decade)	-E_{corr} (mV vs SCE)	I_{corr} ($\mu A/cm^2$)	ϴ	IE%
Blank	0	5.663	4.426	0.563	995.7	-	-
MP	500	5.070	5.272	0.520	42.1	0.958	95.8

Electrochemical Impedance Spectroscopy (EIS)

Nyquists plots of mild steel in the presence and absence inhibitor MP are shown in Figure 8. Various impedance parameters such as charge transfer resistance (R_{ct}), double layer capacitance (C_{dl}) and percentage inhibition efficiency (IE%) were given in **Table 3**. The plots contain semicircles with its center under the real axis (Z'). The size of semicircle or the value of R_{ct} increases in the presence of inhibitor, which indicates that the corrosion of mild steel is controlled mainly by charge transfer process (**Figure 7**). Addition of 500 ppm of inhibitor decreases the C_{dl} value from 307 $\mu F\ cm^{-2}$ to 11 $\mu F\ cm^{-2}$. C_{dl} values suggest that the phytochemical compounds of MP are adsorbed on the mild steel surface resulting in formation of a surface protective film [15]. The results obtained from both polarization and EIS measurements were well-correlated with the weight loss measurements.

Table 3 Impedance parameters

Inhibitor	Concentration (ppm)	R_{ct} ($\Omega\ cm^2$)	C_{dl} ($\mu F\ cm^{-2}$)	ϴ	IE%
Blank	0	16.82	307	-	-
MP	500	293	11	0.943	94.3

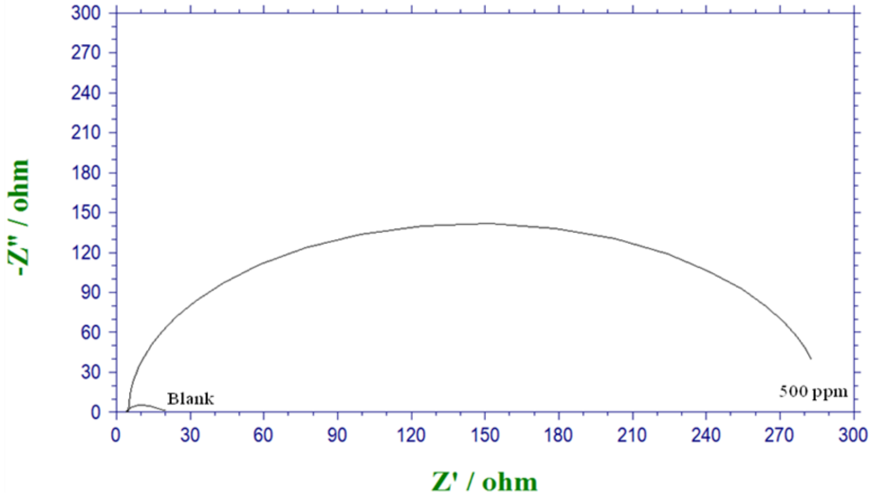

Figure 7 EIS of mild steel in 1 M HCl in the presence and absence of inhibitor

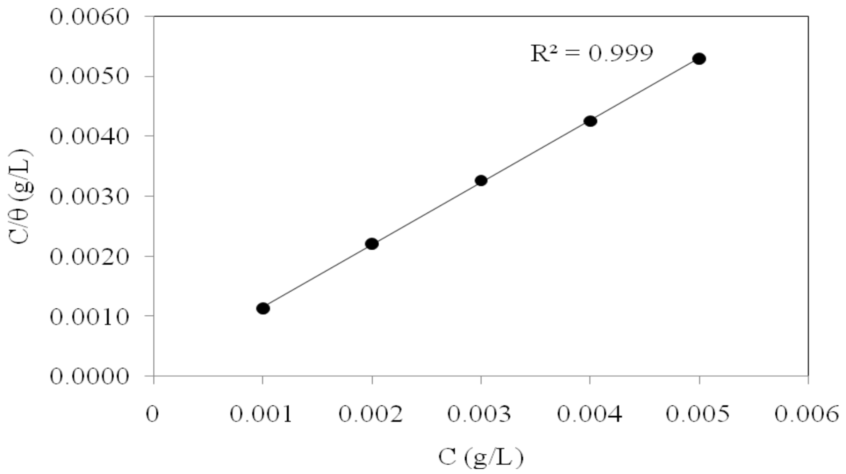

Figure 8 Langmuir isotherm for adsorption of inhibitor on mild steel surface

Adsorption Isotherm

The weight loss measurements and electrochemical studies indicated that inhibition mechanism involves in adsorption of **MP** on mild steel surface. Further, the weight loss data were subjected to adsorption isotherms. Different isotherms were fitted and the data were found to obey Langmuir adsorption isotherm (**Figure 8**).

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \qquad (1)$$

Langmuir isotherm is represented as given in equation 1, where C is concentration of inhibitor molecules, θ is surface coverage, and K_{ads} is equilibrium constant of adsorption process.

The correlation coefficient value of the plot was almost unity (R^2 = 0.999). This indicates the inhibition process proceeds via physical adsorption of inhibitor on the mild steel. K_{ads} values were calculated for all the inhibitor concentrations from equation 6 and presented in Table 1. From K_{ads} values ΔG_{ads} were calculated as shown in equation 2.

$$\Delta G_{ads} = -RT \times ln(55.5K_{ads}) \quad (2)$$

Where ΔG_{ads} is Gibbs free energy of adsorption process, R is gas constant and T is temperature. The negative sign of the ΔG_{ads} indicated the adsorption process is spontaneous and exothermic. Generally, any adsorption process having ΔG_{ads} is ≤ 20 kJ mol^{-1}, is known to have electrostatic interaction between inhibitor molecules and the metal surface (physisorption). Whereas, if $\Delta G_{ads} \geq 40$ kJ mol^{-1}, the adsorption involves in charge-transfer mechanism (chemisorption). In the present study, ΔG_{ads} was between -20.3 to -22.2 kJ mol^{-1} indicating that the adsorption of inhibitor molecules on mild steel surface was due to both electrostatic and charge-transfer processes. The ethanolic extract of the leaves were reported to consist of mainly consists of flavonoids. In **Figure 9**, adsorption modes of flavonoid on mild steel surface are proposed using the general structure of flavonoid.

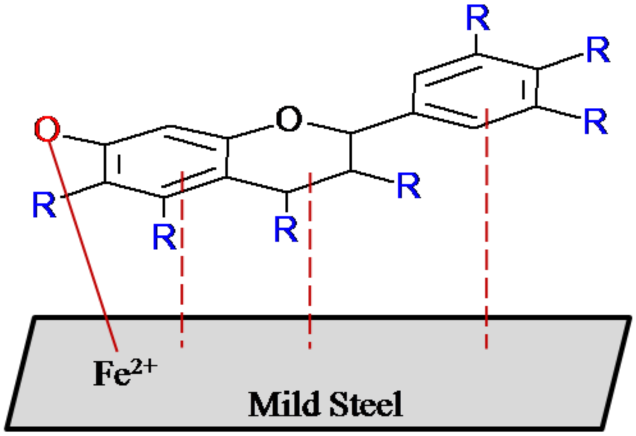

Figure 9 Schematic illustration of adsorption modes of inhibitor using the general structure of flavonoids

Surface Analysis

The morphologies of polished MS, MS treated 1 M HCl, and MS immersed in 1 M HCl with 500 ppm of inhibitor were observed under scanning electron microscope (**Figure 10**). It is obvious that the raw MS shows the characteristics of abraded surface with scratches arose during polishing. The specimen immersed in 1 M HCl exhibits rough surface and covered with corrosion products. Meanwhile, the specimen treated with 1 M HCl + inhibitor exhibits smoother surface since the inhibitor molecules reduced the aggressiveness of acid by forming organic film on the mild steel surface.

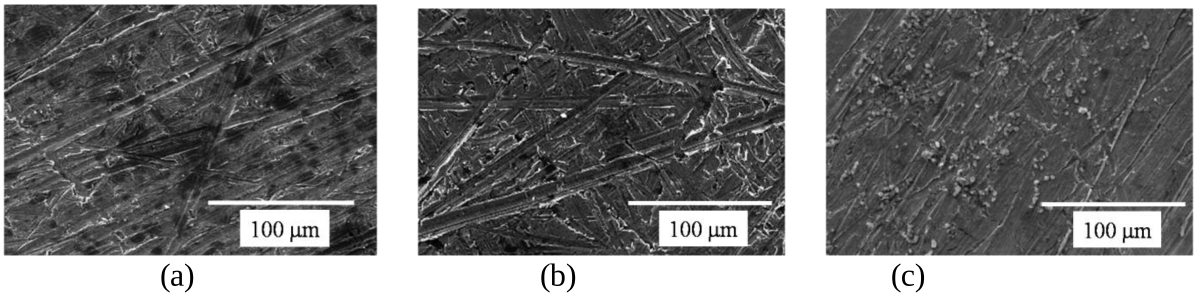

Figure 10 SEM images (a) Mild Steel, (b) Mild Steel in Acid, and (c) Mild Steel in Acid with Inhibitor

Conclusions

The *Milletia pinnata* was extracted with ethanol and the extract was evaluated for its corrosion inhibitory properties. The inhibitor exhibited a maximum IE% of 94.5 in 500 ppm of concentration at 300 K. Weight loss measurements indicated that MP is a versatile inhibitor, which can be employed under conditions such elevated temperatures, different acid concentrations and prolonged immersion time. Electrochemical studies revealed that MP is a mixed type inhibitor and acts by forming surface protective film on the mild steel surface. The results obtained from weight loss measurements obey Langmuir adsorption isotherm indicates that the mode of adsorption is predominantly physisorption. In conclusion, MP is a cost effective and eco-friendly inhibitor for corrosion of mild steel in hydrochloric acid medium.

Abbreviations

MP: *Milletia pinnata*; MS: Mild steel; SEM: Scanning Electron Microscopy; EIS: Electrochemical impedance spectroscopy.

Competing Interest

The authors declare that they have no competing interests.

Authors' Contribution

DK: designed the research, RK: performed the experiments, DK & AS: guidance for research, RK & DK: analysis of results and writing paper. All authors read and approved the final manuscript.

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