ELECTROCHEMICAL STUDIES OF MILD STEEL CORROSION INHIBITION IN ACID MEDIUM BY *MUKIA MADERASPATANA* LEAVES EXTRACT

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Abstract: The corrosion behaviour of mild steel in acid medium under the inhibiting action of various concentrations of *Mukia maderaspatana* was studied using the weight loss and electrochemical techniques. The efficiency of the inhibitor increased with increase in the inhibitor concentration. The results obtained reveal that the *Mukia maderaspatana* performed effectively as a green corrosion inhibitor. The adsorption mechanism indicates spontaneous and of physisorption type. The adsorption of the inhibiting compound was found to obey Langmuir and Temkin adsorption isotherms.

Keywords: Mild steel, acid corrosion, *Mukia maderaspatana*, HCl medium, Potentiodynamic polarisation, Impedance.

1. INTRODUCTION

Mild steel finds application in many industries due to its easy availability, ease of fabrication, low cost and good tensile strength besides various other desirable properties. It suffers from severe corrosion when it comes in contact with acid solutions during acid cleaning, transportation of acid, de-scaling, storage of acids and other chemical processes. The heavy loss of metal as a result of its contact with acids can be minimised to a great extent by the use of corrosion inhibitors. Inorganic compounds like chromates, phosphates, molybdates *etc*. And a variety of organic compounds containing hetero atoms like nitrogen, sulphur and oxygen are being investigated as corrosion inhibitors [1-6].

Pure synthetic chemicals are costly, some of them are not easily biodegradable and their disposal creates pollution problems. Plant extracts are environmentally friendly, bio-degradable, non-toxic, easily available and of low cost. Most of the naturally occurring substances are safe and can be extracted by simple procedures. Recent days the researches are mainly focussed on the application of green inhibitors for inhibiting corrosions. The examples are numerous such as *Fenugreek* [7], *Henna* [8,9], *Olive* [10], *Jojoba* [11], *Black pepper* [12], *Occimum viridis* [13], *Andrographis paniculata* [14], *Phyllanthus amarus* [15], *Onion, Garlic* [16], *Eugenia jambolans* [17], *Pongamia glabra* [18], *Opuntia* [19] and *Eugenol* [20] *etc*. Many of these naturally occurring substances proved their ability to act as corrosion inhibitors for the corrosion of different metals and alloys in different aggressive media. *Hibiscus sabdariffa* [21], *Apricot juice* [22], *Azadirachata indica* [23], *Dodonaea viscosa* [24] and *Carica papaya* [25] have also been used for the corrosion inhibition study for mild steel. The aim of the present work is to investigate the corrosion inhibition effect of the leaves of *Mukia maderaspatana* as a cheap and environmentally friendly corrosion inhibitor for mild steel in 1 M HCl medium by weight loss and polarisation and impedance measurements.

2. EXPERIMENTAL METHODS

2.1 Collection and extraction of plant material

Figure 1: *Mukia maderaspatana plant*

Green leaves of *Mukia maderaspatana* plant were collected and authenticated by Dr. John Britto, The Rapient Herbarium and Centre for Moduler Systematics, St.Joseph's college, Trichirappallli, Tamilnadu, India. *Mukia maderaspatana* powder (10g) was boiled with 100 ml double distilled water and condensed to 50 ml. The extract was left to cool down and then filtered using Whatman filter paper. From that various concentrations were prepared [26].

2.2 Specimen preparation

Mild steel specimens with the composition Carbon = 0.07%; Sulphur = 0%; Phosphorus = 0.008%; Silicon = 0%; Manganese = 0.34% and Iron = Reminder and size of 4 × 1 cm were used for weight loss, same composition embedded in polytetrafluoroethylene (PTFE) with exposed measurements. The electrode was polished using a sequence of emery papers and the thickness of mild steel specimens and the radius of the holed were determined with the help of Vernier Caliper of high precision and the surface areas of the specimens were calculated.

2.3 Determination of inhibition efficiency

Weight loss measurements were done according to the method described previously [27-29]. Weight loss measurements were performed at 303 ± 1K for 2h by immersing the mild steel specimens in 1M HCl solutions (100 mL) without and with various concentrations of inhibitor (0.2%-1.0%) concentrations respectively. After the elapsed time, the specimen was taken out, washed, dried, and weighed accurately. All the concentrations of the inhibitor for weight loss and electrochemical study were taken in percentage concentration (%).

$$\text{Corrosion Rate (mpy)} = 87.6 \times W/ADT \text{ --- (1)}$$

W= Weight loss in mg, A=Area of the mild steel sample in cm^2, D=Density of the mild steel g/cm^3; T= Exposure time in hrs.

The surface coverage (θ) and inhibition efficiency (IE %) were determined by following equations.

$$\theta = W_0 - W_1/W_0 \text{ --- (2)}$$

$$\text{I.E (\%)} = W_0 - W_1/W_0 \times 100 \text{ --- (3)}$$

Where, W_1 and W_0 are the weight loss value in presence and absence of inhibitors, respectively.

2.3.1 Weight loss method at different temperatures

The loss in weight was calculated at different temperatures from 303K to 333K. Each experiment was duplicated to get good reproducibility. Weight loss measurements were performed in 1M HCl with and without the addition of the inhibitor at their best inhibiting concentration (1.0%). Percentage inhibition of the inhibitor at various temperatures was calculated.

2.3.2 Potentiodynamic polarisation measurements

Potentiodynamic polarisation studies have been performed for mild steel specimen both in the presence and the absence of the inhibitors.

Potentiostatic polarization studies were carried out using a CHI electrochemical impedance analyzer, model 660 A. A three-electrode cell assembly was used. The working electrode was a rectangular specimen of carbon steel with one face of the electrode (1 cm^2 area) exposed and the rest shielded with red lacquer. A saturated calomel electrode (SCE) was used as the reference electrode and a rectangular platinum foil was used as the counter electrode. Polarization curves were recorded using IR compensation. The results, such as Tafel slopes, and I_{corr}, E_{corr} and LPR values were calculated. During the polarization study, the scan rate (v/s) was 0.01; hold time at E_f (s) was zero and quit time(s) was 2.

2.3.3 AC-Electrochemical impedance spectroscopy

A CHI electrochemical impedance analyzer (model 660A) was used for AC impedance measurements. A time interval of 5 to 10 minutes was given for the system to attain its open circuit potential. The real part Z' and imaginary part Z" of the cell impedance were measured in ohms at various frequencies. The values of the charge transfer resistance R_t, double layer capacitance C_{dl} and impedance value were calculated.

$$C_{dl} = \frac{1}{2} \pi R_t f_{max} \text{ -------------- } (4)$$

Where f_{max} = maximum frequency AC impedance spectra were recorded with initial E (v) = 0; high frequency (Hz) = 1; amplitude (v) = 0.05; and quiet time(s) = 2.

RESULTS AND DISCUSSION

3.1 Weight Loss measurements:

The weight loss studies for the various concentrations of *Mukia maderaspatana* leaves extract have been carried out in the concentration range 0.2% to 1.0% at 303 ± 1K in 1M HCl to understand the influence of various concentrations of MM extract on the corrosion inhibition of mild steel for a period of 2 hours. The corrosion parameter obtained from weight loss measurements for mild steel in 1M HCl solution containing various concentrations of MM extract are shown in Table-1. It was found that the increase in the concentration of the MM extract, the corrosion rate was decreased and the inhibition efficiency increased from 46.15 to 71.79%. These results indicated that the best inhibiting concentration was obtained at 1.0% concentration. The effect of inhibition efficiency with various concentrations of MM extract on mild steel in 1M HCl is shown in table-1[30].

Table-1 Corrosion rate, inhibition efficiency and surface coverage of mild steel immersed in 1 M HCl for various concentrations of MM obtained by weight loss method at 303 ± 1K

S. No.	Concentration of inhibitor (v/v %)	Corrosion Rate (mpy)	Inhibition Efficiency (%)	Surface Coverage (θ)
1.	Blank	54.33	-	-
2.	0.2	29.25	46.15	0.4615
3.	0.4	25.07	53.84	0.5384
4.	0.6	22.29	58.97	0.5897
5.	0.8	20.89	61.53	0.6153
6.	1.0	15.32	71.79	0.7179

The effect of temperature on the performance of MM extract clearly indicated that the inhibition efficiency decreases with increase in temperature. We know that the adsorption and desorption of inhibitor molecules continuously occur at the metal surface and equilibrium exists between two processes at a particular temperature. But, with the increase of temperature, the equilibrium between adsorption and the desorption processes is shifted to a higher desorption. It explains the lower inhibition efficiency at higher temperature. Decrease in performance of compounds with increase in temperature is due to the weakening of bonds between metal surface and the inhibitors.

The effect of temperature on the rate of corrosion process was studied in different temperatures ranging from 303K to 333K (30°C to 60°C) at their best protecting concentration on 1.0%. The extract of MM is able to maintain an inhibition of about 67.79% up to 313 K and the inhibition is found to decline to 61.22% at 333 K in 1M HCl medium and the results are presented in Table - 2.

Table-2 Values of corrosion rate, inhibition efficiency and surface coverage for different temperatures in the presence of 1.0% concentration of MM in 1M HCl.

S. No.	Temperature (K)	Corrosion Rate (mpy)	Inhibition efficiency (%)	Surface coverage (θ)
1.	303	15.32	71.79	0.7179
2.	313	52.93	67.79	0.6779
3.	323	61.29	65.89	0.6589
4.	333	79.40	61.22	0.6122

3.2 Adsorption Isotherm:

Basic information on the interaction between the inhibitor and the mild steel surface can be provided by the adsorption isotherm. The degree of surface coverage (θ) for different concentrations of inhibitors in 1M HCl has been evaluated using weight loss. The data were graphically fit to Temkin's isotherms. Figure - 2 shows the plot of surface coverage (θ) versus 2+logC and the expected linear relationship is obtained for MM in 1M HCl. The strong correlation is obtained which confirms the validity approach.

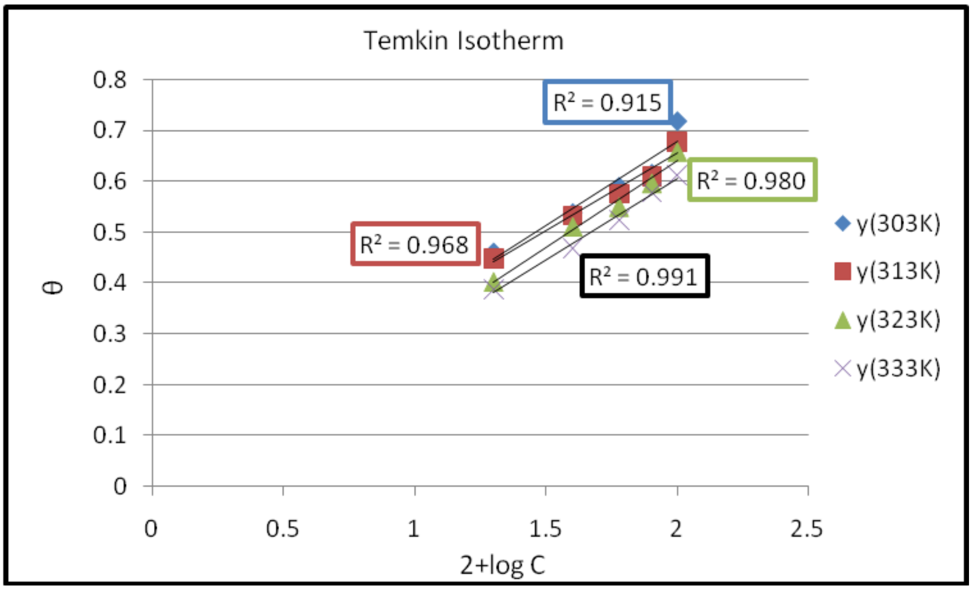

Figure2: Temkin adsorption isotherm for mild steel in 1M HCl in the presence of MM at different temperatures.

The use of adsorption isotherm provides useful insight into the corrosion inhibition mechanism. Figure - 3 shows the plot of C/θ versus 2+logC and the expected linear relationship is obtained for MM in 1M HCl suggesting that the adsorption of MM extract on the surface of mild steel in 1M HCl solution follows Langmuir adsorption isotherm [31-33].

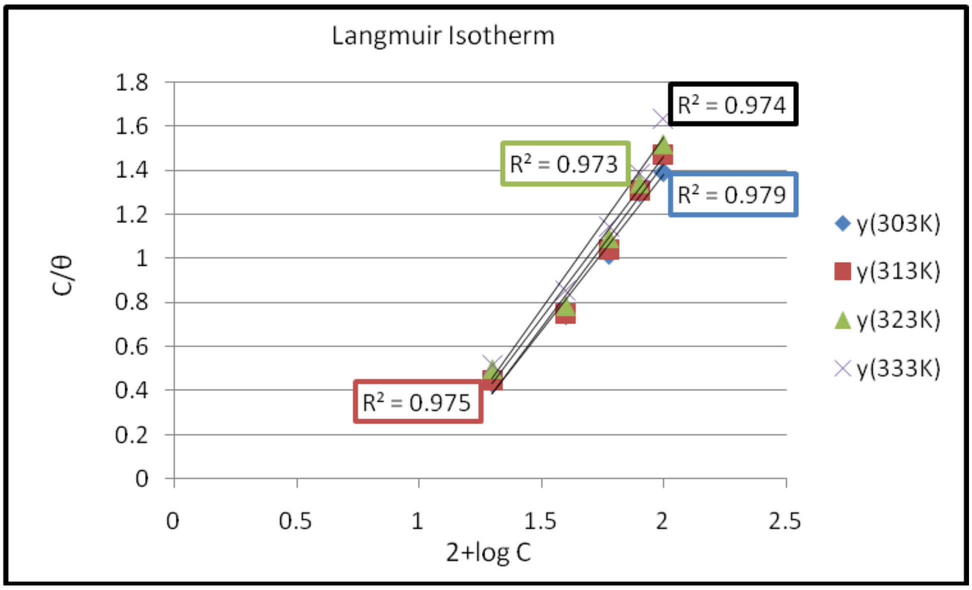

Figure 3: Langmuir adsorption isotherm for mild steel in 1M HCl in the presence of MM at different temperatures.

3.3 Potentiodynamic polarisation measurements

Electrochemical corrosion kinetic parameters such as corrosion potential potential (E_{corr}), corrosion current (I_{corr}), anodic and cathodic tafel slopes (b_a and b_c) and percentage of IE for the corrosion of mild steel in 1M HCl at 30°C in the absence and presence of different concentrations of the inhibitor are given in Table - 3 and its corresponding polarisation curves are shown in Figure - 4. It is seen from the tables that the corrosion current density (I_{corr}) markedly decreased with the addition of the inhibitor and corrosion potential shifts to less negative values upon addition of the inhibitor. Moreover, the values of anodic and cathodic Tafel slopes (b_a and b_c) are slightly changed indicating that this behaviour reflects the acid dissolution of the inhibitor ability to inhibit the corrosion of mild steel in 1M HCl via adsorption of its molecules on both anodic and cathodic sites and consequently, it act through mixed mode of inhibition [34-39].

Table - 3 Potentiodynamic polarization measurements for the corrosion of mild steel in 1M HCl in the absence and presence of different concentrations of MM

S. No	**Concentration, v/v%**	**-E_{corr},** mV vs SCE	**I_{corr},** A/cm^2	**b_c,** mV/decade	**b_a,** mV/decade	**LPR** ohm cm^2	**% I.E**
1.	Blank	0.471	6.058x10^{-4}	0.1447	0.1040	43.5	-
2.	0.2	0.479	3.179x10^{-4}	0.1204	0.0598	55.0	47.52
3.	1.0	0.461	2.005x10^{-4}	0.1272	0.0558	84.0	66.90

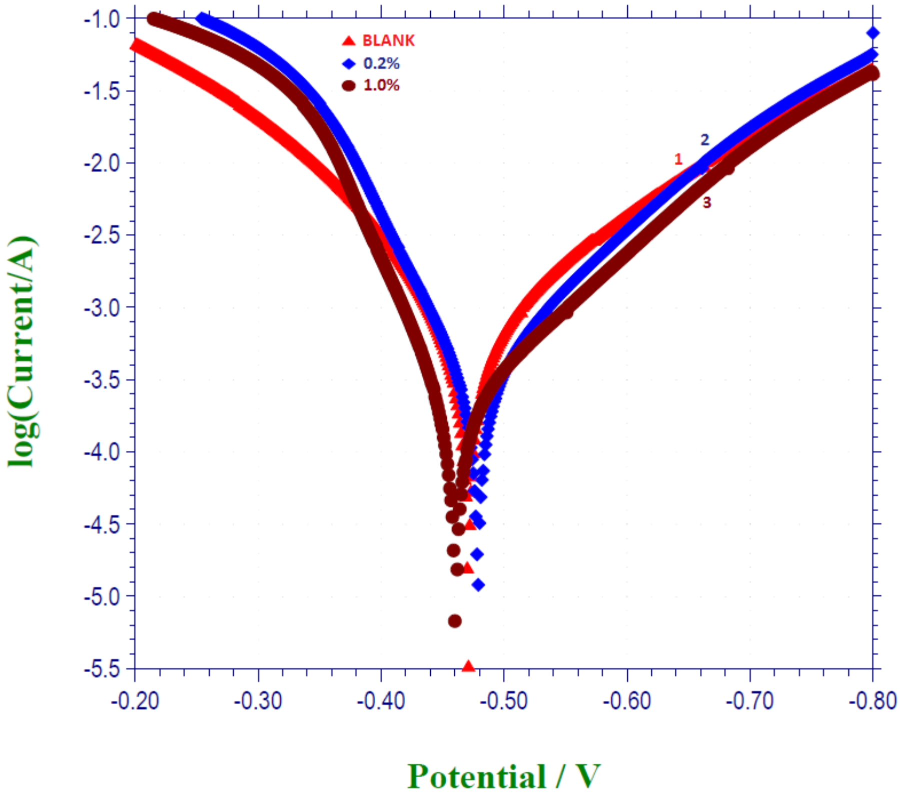

Figure 4: Potentiodynamic polarization curve for mild steel in 1M HCl in the absence and presence of various concentrations of MM.

3.4 AC-Electrochemical impedance spectroscopy

Impedance spectra (Nyquist plots) of mild steel in 1M HCl containing various concentrations of the inhibitor at 30°C are shown in Figure - 5. It is apparent from the plots that the impedance of the inhibited solution has increased with an increase in the concentration of the inhibitor. The experimental results of EIS measurements for the corrosion of mild steel in 1M HCl in the absence and presence of the inhibitor are given in Table - 4. It can be concluded that the charge transfer resistance (R_{ct}) value increased with an increase in the concentration of the inhibitor, where as values of the double-layer capacitance (C_{dl}) of the interface start decreasing, with an increase in the inhibitor concentration, which is most probably due to the decrease in local dielectric constant and/or increase in thickness of the electrical double layer [40-44].

Table - 4 Impedance measurements for the corrosion of mild steel in 1M HCl in the absence and presence of different concentrations of MM

S. No.	Concentration, v/v%	R_{ct}, ohm cm^2	C_{dl}, F/cm^2	Imp log z/ohm	P.A	% I.E
1.	Blank	2.280	7.22×10^{-7}	0.58	23.29	-
2.	0.2	4.859	3.38×10^{-7}	0.94	41.31	53.19
3.	1.0	6.253	2.63×10^{-7}	1.02	49.98	63.57

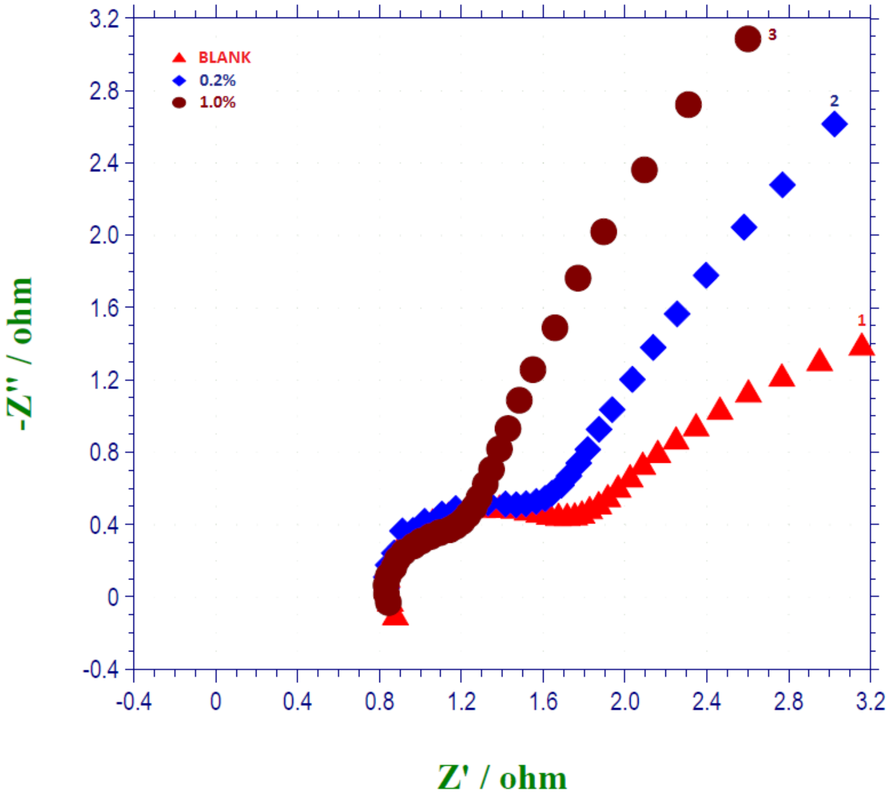

Figure 5: Impedance diagram for mild steel in 1M HCl in the absence and presence of various concentrations of MM.

4. CONCLUSIONS

The inhibitive influence of *Mukia maderaspatana* levaes extract on the corrosion of mild steel in 1.0 M HCl was studied by weight loss method, polarisation and impedance measurements.

- The *Mukia maderaspatana* leaves extract has good inhibition efficiency for preventing the corrosion of mild steel in 1 M hydrochloric acidic medium.
- *Mukia maderaspatana LE* extract formed a protective layer on the surface of the mild steel and improved surface condition, due to adsorption, for the corrosion protection.
- The adsorption isotherms reveal that in HCl, Langmuir and Temkin isotherms show best fit results.
- The corrosion process was inhibited by adsorption of the active components on the mild steel surface.
- AC impedance studies reveal that a protective film was formed on the metal surface.
- These results suggest *Mukia maderaspatana* is a best green inhibitor.

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