



Mimusops Elengi Linn Plant Extract as an Efficient Green Corrosion Inhibitor for Mild Steel in Acidic Environment

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Abstract

Corrosion inhibition of mild steel in 1 N HCl by *Mimusops Elengi Linn* (MEL) leaves extract was studied using Weight Loss Method, Potentiodynamic Polarization and Electrochemical Impedance Spectroscopy (EIS) measurements techniques at room temperature. It was found that the inhibition efficiency of the MEL extract obtained from impedance and Polarization measurements was in a good agreement and increases with increasing concentration of MEL extract. The inhibition was found to be highest (97.63 %) at a concentration 20 ppm of the extract. The results obtained showed that the MEL extract could serve as an effective inhibitor for the corrosion of mild steel in acid media.

Keywords: Electrochemical Impedance Spectroscopy (EIS); FTIR spectroscopy; Green Inhibitor; *Mimusops Elengi Linn* (MEL); Potentiodynamic Polarization; Scanning Electron Microscopy (SEM).

1. INTRODUCTION

Corrosion can be defined as the destruction of metals or alloys by the surrounding environment through chemical or electrochemical changes. It is a serious environment problem in the oil, fertilizer, metallurgical and other industries (Eddy *et al.* 2010). Corrosion is a fast process and accompanied by number of reactions that change the composition and properties of both metal surface and local environment. The study of corrosion of mild steel and iron is of tremendous importance as they have wide usage domestically and industrially. Acid solutions like HCl and H₂SO₄ are used in the industrial processes, acid cleaning, acid descaling, acid pickling and oil well acidizing, require corrosion inhibitor to prevent the corrosion of metal. (Manoj Acharya *et al.* 2013). The main problem of using mild steel in acidic solution is that of uniform corrosion (Srikanth *et al.* 2006). Hence efforts for developing more efficient methods to prevent corrosion have been ongoing throughout this century (Sitaram *et al.* 1997).

Organic compounds which have different hetero atoms such as N, O, S and aromatic rings in their structure are reported as effective inhibitors (Shukla *et al.* 2009). The most effective and widely used organic compounds for corrosion inhibition of mild steel in acid medium (Lagrenée *et al.* 2002) are due to the presence of the electron donating heteroatom namely, Nitrogen, Sulphur, and Oxygen. They are known to be excellent complex or chelate forming substances with metals of transition series. Their adsorption is generally explained by the formation of an adherent film on the metal surface (El Azhar *et al.* 2002). It is noticed that organic compounds show higher inhibition efficiency as compared to Inorganic. Also, inorganic inhibitors are used in a very specific area due to their hazardous effect on human and the environment.

In recent years, plant extracts have been explored as corrosion inhibitors due to their bio-degradability, non toxicity, environment friendly nature and easy availability (Cotton *et al.* 1967) *Mimusops Elengi Linn* exhibits various biological

and pharmacological activities such as antiviral, antibacterial, antifungal, anthelmintic, anticariogenic, antihyperlipidemic, antihyperglycemic, diuretic free radical scavenging, antioxidant, cognitive enhancing, cytotoxic activities etc. due to presence of a variety of active phytochemicals (Prakash Chandra Gupta, 2013).

In a bid to inspire and sustain these efforts, practical attempts have been made by several researchers to investigate the effect of using green inhibitors to combat corrosion of metals in acid media (Okafore et al. 2008). Now a days, these investigations have shown that green inhibitors represent a veritable source of eco friendly resource.

The aim of the study to investigate in the inhibition effect of **Mimusops Elengi Linn (MEL) leaves extract as a cheap, raw and non-toxic corrosion inhibitor on corrosion of the mild steel 1N HCl**. Corrosion behaviour was studied using weight loss method, Potentiodynamic polarization and electro chemical impedance Spectroscopy (EIS) measurements. The morphology of inhibited mild steel was analyzed by scanning electron microscope technology and the protective film formed was analyzed by Fourier Transform – Infrared (FTIR) spectroscopy.



Fig. 1: Leaves of *Mimusops Elengi Linn*

2. MATERIALS & METHODS

2.1 Preparation of Extract

The fresh leaves of *Mimusops Elengi Linn* (MEL) were collected washed and shade dried and powdered. From this, 10 g of the sample was refluxed in 100 ml distilled water for five hours and kept overnight. The refluxed solution was then filtered and the filtrate was made up to 250 ml using double distilled water. This was taken as the stock solution.

The required concentrations were prepared by diluting the stock solution.

2.2 Preparation of Specimen

Weight loss and electrochemical experiments were conducted on mild steel specimens of dimensions 4 cm X 2 cm X 0.1 cm and having the area of 0.1 cm² having the composition C: 0.030 %, Mn: 0.169 %, Si: 0.015 %, P: 0.031 %, S: 0.029 %, Cr: 0.029 %, Ni: 0.030 %, Mo: 0.016 %, Cu: 0.017 % and the remainder being Fe were used for weight loss studies.

2.3 Weight Loss Method

Mass loss measurements were carried out using a balance SHIMADZU BL-220H model. The specimens were immersed in beaker containing 200 ml acid solution without and with different concentrations of MEL extract using glass hooks and rods for a predetermined time period (24 hrs) at room temperature. The corrosion inhibition Efficiency was then calculated using the equation,

$$IE \% = \frac{W_0 - W_i}{W_0} \times 100$$

Where, W_i and W_0 are the Weight loss of the mild steel with and without inhibitors of MEL extract.

2.4. FT-IR Spectra

FT-IR spectrum of the MEL extract was recorded on BRUKER alpha 8400S FT-IR spectrophotometer. The film was carefully removed, mixed thoroughly with KBr made into pellets and FTIR spectra were recorded.

2.5 Potentiodynamic Polarization Studies

Potentiodynamic polarization measurements were carried out using mild steel samples with and without inhibitors in 1N HCl solution. Electrochemical experiments were carried out using three cell assembly. Mild steel specimen coated with Teflon was used as working electrode. A platinum foil was used as counter electrode and a saturated calomel electrode (SCE) as reference electrode. The polarization studies were carried out using potentiostat/galvanostat (model Electrochemical work station CHI model 660E Amp Booster) and the data obtained were analyzed using the software CHI version 13.08. The working electrode was immersed in 1N HCl solution for 30 min until a steady-state

open circuit potential (OCP) was reached. The cathodic and anodic polarization curves for mild steel with without inhibitor were recorded under potentiodynamic conditions at a scan rate of 1 mVs⁻¹. The inhibitor efficiency by Tafel method was calculated using the equation,

$$\text{Inhibitor Efficiency (\%)} = \frac{I_{\text{corr (blank)}} - I_{\text{corr (Inhibitor)}}}{I_{\text{corr (blank)}}} \times 100$$

Where,

$I_{\text{corr (blank)}}$ = Corrosion current without inhibitor,
 $I_{\text{corr (Inhibitor)}}$ = Corrosion current with inhibitor.

2.6 Electrochemical Impedance Spectroscopic (EIS) Studies

Electrochemical AC-impedance measurements were carried out at room temperature using an electrochemical work station CHI model 660E Amp Booster as described earlier. An AC sinusoid of ±10 mV was applied at corrosion potential (E_{corr}). The frequency range of 100 KHz to 1 Hz was employed. The mild steel samples having surface area 0.5 cm² with and without inhibitor were used as the working electrodes. The percent inhibition efficiency (% I.E) was calculated as follows (Quraishi *et al.* 2002):

$$\text{I.E (\%)} = \frac{R_{\text{ct}}^{-1} - R_{\text{ct}}^{-1}(\text{inhibitor})}{R_{\text{ct}}^{-1}} \times 100$$

Where, $R_{\text{ct}}^{-1}(\text{inhibitor})$ and R_{ct}^{-1} are the charge transfer resistance values with and without inhibitors of MEL extract.

2.7 Scanning Electron Microscopy (SEM)

To understand the nature of the film in the absence and presence of inhibitors and the extent of corrosion of mild steel, the SEM micrographs of the surface are examined. The mild steel specimens were immersed in 1 N HCl in the absence and presence of the optimum concentration of MEL extract for one day at room temperature. After 2 hrs, the specimens were taken out, dried and kept in desiccators. The formation of protective film of MEL extracts on them was studied by JEOL computer controlled SEM observations.

3. RESULTS & DISCUSSION

3.1. Weight Loss Method

Weight loss method was done for mild steel in 1N HCl with various concentrations of MEL extract

ranging from 5 to 20 ppm, and the corresponding values of inhibition efficiency and corrosion rate are given in Table 1. It is observed from the table that the corrosion rate decreased and thus the inhibition efficiency increases with increasing concentration of MEL extract (5 ppm to 20 ppm.). The maximum inhibition efficiency of about 97.63 % was achieved at 20 ppm of MEL extract. This result indicated that MEL 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 MEL extract.

S.No	Conc. of MEL Extract (ppm)	Corrosion Rate (mmpy)	Inhibition Efficiency (%)
1	0	0.2948	*
2	5	0.0644	78.15
3	10	0.0766	74.02
4	15	0.0081	97.24
5	20	0.0069	97.63

3.2 FT-IR Spectra

FT-IR spectrum was recorded for MEL leaves extract in order to confirm the presence of various compounds which contributed in effective working of the inhibitor is shown in Fig. 2.

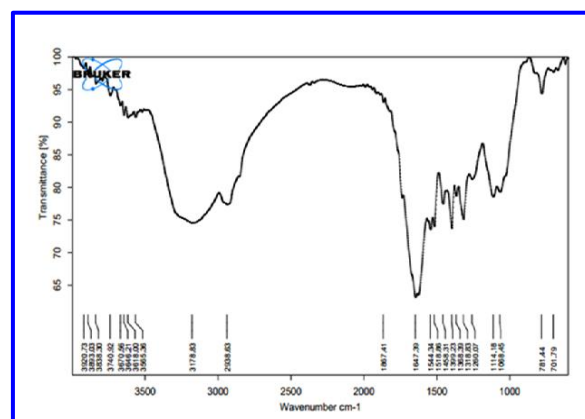


Fig. 2: FT-IR spectrum of Mimusops Elengi Linn leaves extract.

The Free O-H stretching was observed at 3500-3700 cm⁻¹ (Alcohol). The broad peak obtained at 3178 m⁻¹ can be assigned to N-H or O-H stretching (Alcohol or Amine). Another peak obtained at 2938 cm⁻¹ may be strong C-H stretching (Acid). Adsorption peak obtained at 1867.41 cm⁻¹ and 1647.39 cm⁻¹ may be due to stretching of C=O (aldehyde or Ketone).

The peaks observed at 1554.34 cm⁻¹ may be N-O bending vibration (Nitro). Few peaks can also be observed at 1518.86 cm⁻¹, 1458.31 cm⁻¹, 1399.23 cm⁻¹, which correspond to C=C stretching vibration (Aromatic ring). One of the basis of the result it can be said that MEL extract contain Nitrogen and Oxygen (N-H, N=C=S, C=N, C-N, O-H, C=O, C-O) in various functional group and aromatic ring, which make this extract attractive for being used as inhibitor.

3.3. Potentiodynamic Polarization Studies

The potentiodynamic polarization curves for mild steel in 1N HCl with and without inhibitor (extract) are shown in Fig. 3.

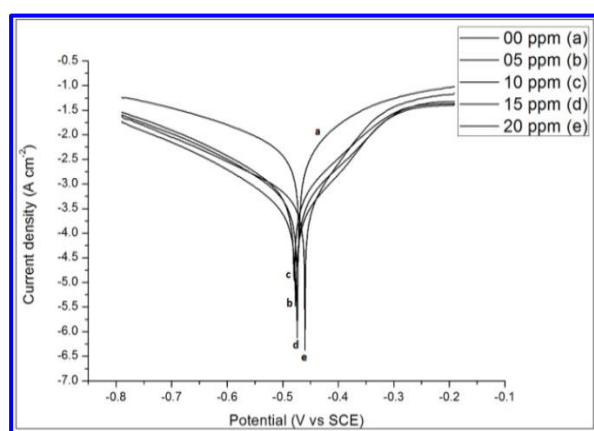


Fig. 3: Potentiodynamic polarization curves for mild steel in 1N HCl solution in the absence and presence of different concentrations of MEL leaves extract.

It is evident from the figure that the anodic and cathodic curves for mild steel inhibited with extract were shifted towards positive potential region compared to the blank metal immersed in 1N HCl. The corrosion parameters such as corrosion potential (E_{corr}) and corrosion current density (I_{corr}), obtained from Tafel plots are given in Table 2. From the table, it is observed that the I_{corr} values are found to decrease with increase in the inhibitor concentrations, ranging from 5 to 20 ppm. However, the shift in the values of corrosion potential (E_{corr}) for MEL extract is not significant (Pandian *et al.* 2009). 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. The corrosion rates calculated for the mild steel specimens with different concentrations of the inhibitor are also given in Table 2. As can be seen, the mild steel with 20 ppm concentration of the inhibitor showed excellent resistance than when compared to other concentrations of the inhibitor. For instance, the corrosion rate for mild steel without

inhibitor (blank) was found to be 0.235 mm yr⁻¹ and it was minimized by inhibitor with different concentrations like 5, 10, 15 and 20 ppm to lower values of 0.051, 0.061, 0.006 and 0.005 mm yr⁻¹, respectively. The inhibition efficiency values in the Table 2 showed that the MEL extract acted as very effective corrosion inhibitor for mild steel in HCl solution and its capacity of inhibition increased with increasing concentration.

The inhibitor efficiency by Tafel method was calculated using the equation,

$$\text{Inhibitor Efficiency (\%)} = \frac{I_{corr(\text{blank})} - I_{corr(\text{Inhibitor})}}{I_{corr(\text{blank})}} \times 100$$

Where,

$$I_{corr(\text{blank})} = \text{Corrosion current without inhibitor,}$$

$$I_{corr(\text{Inhibitor})} = \text{Corrosion current with inhibitor.}$$

The corrosion rate was determined from the measured corrosion current density values using the relation (Srikanth *et al.* 2007).

$$\text{CR (mmpy)} = \frac{87.6 \times W}{D \times A \times T}$$

where, CR is Corrosion Rate (millimeter per year), W is weight loss of the specimen (mg), D is Density (g cm⁻³), T is Time in (hours).

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

Conc. of MEL (ppm)	E_{corr} (mV) vs. SCE	I_{corr} (mA cm ⁻²)	CR (mmpy)	b_c (mV/dec)	b_a (mV/dec)	IE (%)
0	-471	5.220	0.235	199	140	*
5	-460	0.452	0.051	173	70	91.33
10	-479	0.615	0.061	146	94	88.21
15	-474	0.464	0.006	145	91	91.10
20	-477	0.230	0.005	136	74	95.57

3.4 Electrochemical Impedance spectroscopy (EIS) Studies

Electrochemical Impedance spectroscopy (EIS) techniques provide information about the kinetics of the electrode processes and simultaneously about the surface properties of the investigated systems. The shape of impedance gives mechanistic information. Nyquist plots of mild steel in uninhibited and inhibited acid solution containing various

concentrations of MEL extract are presented in Fig. 4. It followed from Fig. 4 that the impedance of the inhibited mild steel increases with increase in the inhibitor concentration and consequently the inhibition efficiency increased (Gunavathy *et al.* 2013). The presence of a single semi circle 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.

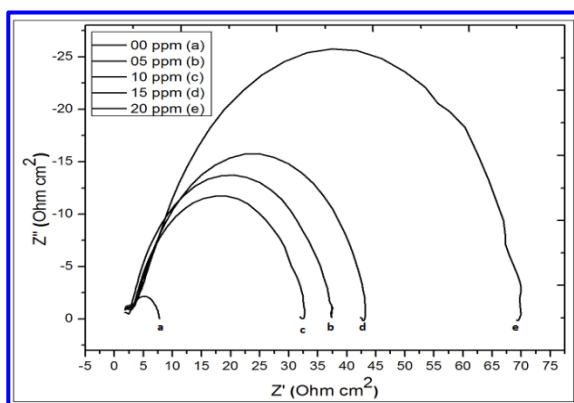


Fig. 4: Nyquist plots of mild steel immersed in 1 N HCl in absence and presence of different concentrations of MEL leaves extract.

The impedance parameters derived from EIS measurements for mild steel in 1M HCl with and without inhibitors are given in Table 3. The charge transfer resistance (R_{ct}) value calculated for blank Mild steel exhibited $5.556 \Omega\text{cm}^2$ and the double layer capacitance (C_{dl}) was $1.306 \times 10^2 \mu\text{F}/\text{cm}^2$. 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 results from a decrease in local dielectric constant and/or an increase in the thickness of the double layer, suggested that inhibitor molecules inhibit the mild steel corrosion by adsorption at the metal/acid interface. Further, the adsorption may also 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.

$$\text{Inhibitor Efficiency (\%)} = \frac{R_{ct(\text{blank})} - R_{ct(\text{Inhibitor})}}{R_{ct(\text{blank})}} \times 100$$

where, $R_{ct(\text{Inhibitor})}$ = Charge transfer resistance with inhibitor, $R_{ct(\text{blank})}$ = Charge transfer resistance without inhibitor (Srikanth *et al.* 2007).

3.5 Scanning Electron Microscopy (SEM)

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 MEL extract are shown in Fig. 5a and 5b. From SEM images, It can be concluded that MEL 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. Examination of Fig. 5a revealed that the specimen immersed in 1N HCl was rough and highly damaged due to the attack of aggressive acids. Fig. 5b clearly showed that the mild steel surface was covered with the protective layer formed by inhibitor which prevents the metal from further attack of acid medium thus inhibiting corrosion (Soror *et al.* 2013).

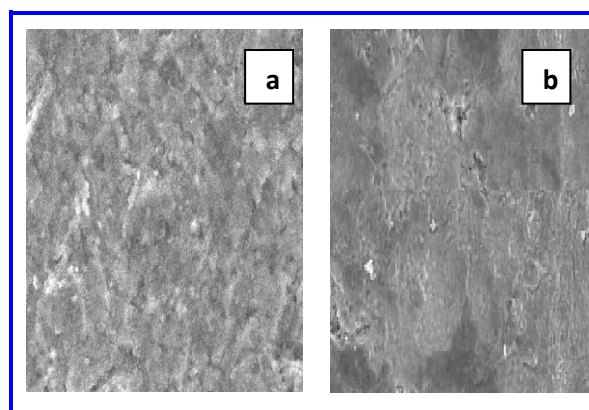


Fig. 5: SEM image of the surface of mild steel after immersion for 2 h in 1N HCl solution.(a) in the absence of inhibitor (b) in the presence of 20 ppm MEL leaves extract.

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

Conc. of MEL (ppm)	C_{dl} ($\mu\text{F cm}^{-2}$)	b_c (mV/dec)	b_a (mV/dec)	R_{ct} (Ωcm^2)	IE (%)
0	1.306×10^2	199	140	5.556	*
5	3.108×10^{-4}	173	70	37.426	85.1
10	4.237×10^{-4}	146	94	32.023	82.6
15	2.387×10^{-4}	145	91	2.985	87.0
20	8.509×10^{-5}	136	74	72.498	92.3

5. CONCLUSION

The effect of various concentrations of *Mimusops Elengi Linn* leaves extract on the corrosion

of mild steel in 1N HCl has been studied. The following conclusion can be made based on the basis of the results obtained.

The *Mimusops Elengi Linn* (MEL) leaves extract is a good, easily available and eco friendly green inhibitor for the corrosion of mild steel in 1N HCl acid solution.

The weight loss data showed that the inhibition efficiency of MEL extract increases with increase in the concentration of MEL extract and inhibit the corrosion of mild steel at the best concentration of 20 ppm.

Polarization studies showed that MEL extract acts as mixed type inhibitor and inhibition efficiency increased with the inhibitor concentration.

Protection efficiency of the extract, calculated from EIS was found to increase with increasing in concentration of the inhibitor showing maximum efficiency of 97 % at 20 ppm.

The inhibition efficiencies obtained from polarization, EIS and weight loss measurements are still in acceptable agreement.

SEM examination showed that there was improvement in the surface morphology of the as-corroded inhibited mild steel compared to uninhibited samples.

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CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest.

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