

International Journal of Scientific Research and Reviews

Green Approach to Corrosion Inhibition of Mild steel using Pongamia Pinnata Leaf Extract in 1M H₂SO₄ Medium

J.Thiruppathy* and M.Keerthana

Department of Chemistry, Thiagarajar College, Madurai-625009, Tamilnadu, India.

ABSTRACT

The inhibition of the corrosion of mild steel in 1M sulphuric acid medium by the leaf extract of pongamia pinnata has been studied using weight loss, electrochemical impedance spectroscopy, potentiodynamic polarisation. Inhibition has been found to increase with increasing concentration of the leaf extract. Values of inhibition efficiency calculated from weight loss, potentiodynamic polarisation and electrochemical impedance spectroscopy are in good agreement. The SEM micrographs revealed that there was adsorption of the inhibitor on the mild steel surface. From the Infrared spectrum confirmed that the presence of functional groups in pongamia pinnata leaf extract.

KEYWORDS: Corrosion, Mild steel, Pongamia Pinnata, Sulphuric acid, Surface Morphology, Electrochemical Impedance Spectroscopy, Weight loss.

***Corresponding author**

Dr. J.Thiruppathy,
PG and Research
Department of chemistry
Thiagarajar College,
139-140, Kamarajar Salai
Madurai-625009, Tamilnadu, India.
E Mail - chemwin3@gmail.com,
Mob Mo. - 96984 31052

INTRODUCTION

Mild steel is an important material which is extremely useful because of its low cost to manufacture reaction vessels, cooling towers and pipelines. In particular, its application in steam generators and ballast tanks are worthy to mention. Because of the extreme corrosive environment in industries its usefulness in strategic applications is much affected by corrosion phenomena. The corrosion process is controlled by protective coatings. Corrosion problems are also solved by adding suitable substances which will reduce the corrosion rate. We already know that the use of inhibitors is one of the most practical methods for protection against corrosion in acidic media. Inhibitors are used to prevent metal dissolution as well as acid consumption. As acidic media, HCl and H₂SO₄ are widely used in the treatment of steel and ferrous alloys. Corrosion inhibitors are substances which when added in small concentrations to corrosive media decreases or prevent the reaction of the metal with the media¹. The use of inhibitors is one of the most practical methods for protecting metals or alloys from corrosion. Compared with organic and inorganic salt corrosion inhibitors, using organic corrosion inhibitors is an effective, inexpensive and less pollution means of reducing the degradation of metals or alloys in many fields of applications and which has been extensively investigated during the last decade²⁻⁸.

The inhibition of the corrosion in acid solutions can be effected by the addition of variety organic compounds which act as very good inhibitors, mainly contain the nitrogen, sulphur and oxygen atoms along with unsaturated bonds and extensive aromatic ring systems favour the adsorption of inhibitors on the metal surface. An earlier study has shown that the nitrogen atom and large molecular size of inhibitors ensure greater coverage on the metallic surface. It is known that the structure of the inhibitor molecule is not the only factor affects the efficiency of the organic inhibitor but also the parameters such as temperature and time duration. The corrosion of mild steel in acid solution causes considerable loss. In order to reduce the corrosion of mild steel several techniques have been adopted. The use of inhibitors during acid pickling procedure is one of the most practical methods for protection against corrosion in acidic media. Currently there is public criticism of the synthetic inhibitors for their hazardous effect. Plant extracts contains several organic compounds which have corrosion inhibiting abilities. The extracts from the leaves, seeds, bark of plants have been reported to inhibit mild steel corrosion in acidic media. A summary of plants extracts used as corrosion inhibitors have been recently given⁹. The plant products are rich sources of organic compounds with hetero atoms and hence involved in adsorption through electron donation to the metal atom there by blanketing the surface from the attack of the aggressive environment¹⁰⁻¹⁴. The green inhibitors are significant that they do not contain any heavy metal in their composition¹⁵.

Several authors also reported that the use of natural products as the potential corrosion inhibitors for various metals and alloys under different environments¹⁶⁻²¹. The present work was designed to investigate the corrosion inhibition of mild steel by pongamia pinnata leaf extract in 1M H₂SO₄ as a cost effective and environmentally benign corrosion inhibitor using electrochemical impedance spectroscopy, (EIS) weight loss and potentiodynamic polarisation. Inhibition has been found to increase with increasing concentration of the leaf extract.

2. EXPERIMENTAL SECTION

2.1 Materials and Methods

Specimen Preparation

Corrosion tests are carried out on electrodes cut from sheets of mild steel strips containing 0.01%Al, 0.05% Mn, 0.21% C, 0.05%S and the remaining of the iron is used for the measurement. In the present study mild steel is used as the specimen for determining corrosion rate. Mild steel 1cm × 1cm is abraded with emery paper washed with conductivity water.

2.2 Preparation of Pongamia Pinnata leaf extract

The leaf was dried and ground to powder form. Dried (5 g) powder was soaked in double distilled water (500 mL) and refluxed for 5 hours. The aqueous solution was filtered and concentrated to 100 mL. This extract was used to study the corrosion inhibition properties.

2.3 Weight loss measurements

Weight loss is a non-electrochemical technique for the determination of corrosion rates and inhibition efficiency which provides more reliable results when compared with electro chemical techniques under experimental conditions. After accurate weighing, the specimens are immersed in a 100 ml beaker which contained 50 ml of H₂SO₄ with and without addition of different concentrations of inhibitor. After one hour the specimens are taken out washed, dried and weighed accurately. Then the tests are repeated at different temperatures, different concentrations of inhibitor. In all cases duplicate experiments were performed and the mean values are reported.

Weight loss allowed us to calculate the mean corrosion rate as expressed in mmpy.

The corrosion rate and inhibition efficiency IE (%) were calculated according to the Equations (1) and (2) respectively.

$$\text{Corrosion rate (mmpy)} = 534 W / \rho A t \quad (1)$$

Where W is the weight loss (mg), ρ is the density of the specimen (gcm⁻³), A is the

area of the specimen (cm^2), and t is the exposure time (hours).

Inhibition efficiency is defined as follows

$$\text{IE (\%)} = ((\text{CR}^0 - \text{CR}) / \text{CR}^0) \times 100 \quad (2)$$

Where CR^0 - Average weight loss without inhibitor, CR - Average weight loss with inhibitor

2.4 Electrochemical measurements

Electrochemical measurements were performed in a conventional three electrode cell consisting of mild steel as working electrode (WE), platinum as counter electrode (CE) and a saturated calomel electrode (SCE) as the reference electrode. To minimize ohmic contribution the Luggin capillary was close to working electrode (WE) which was in the form of a square embedded in a PVC holder using epoxy resin so that the flat surface was only surface in the electrode. By using emery paper, the mild steel (WE) surface was abraded and degreased with acetone at room temperature before used. The area of the working electrode surface is 1 cm^2 . The anodic and cathodic potentiodynamic polarization curves of mild steel specimen were obtained in the inhibited and uninhibited solution. Measurements were carried out in $1\text{M H}_2\text{SO}_4$ solution having different concentrations of the present inhibitor by changing electrode potential automatically from -600 to -300 mV. The current density curves are obtained by linear extrapolation of the anodic and cathodic branches of the Tafel plots. Electrochemical Impedance Spectroscopy (EIS) studies were carried out in a frequency range of 100 kHz to 10 mHz with amplitude of 10 mV using AC signals at open circuit potential (OCP) with scan rate of 1 mVs^{-1} . Computer programs automatically control the measurements performed at rest potentials after 30 minutes of exposure. Before recording the curves the test solution is de-aerated and magnetically stirred for few minutes in the cell with nitrogen. Nyquist plots were drawn from these experiments and the best semicircle can be fitted through the data points in the Nyquist plot.

The charge transfer resistance (R_{ct}) values have been obtained from the diameter of semicircles of Nyquist plots. The inhibition efficiency has been calculated by using the following equation

$$\text{IE (\%)} = [(R_{\text{ct}} - R_{\text{ct}}^0) / R_{\text{ct}}] \times 100 \quad (3)$$

R_{ct} - charge transfer resistance with inhibitor, R_{ct}^0 - charge transfer resistance without inhibitor

2.5 Scanning electron microscopy (SEM)

The mild steel specimen immersed in 1M H₂SO₄ for 1 hour was taken out and washed with distilled water, dried and taken SEM micrograph. Similarly the mild steel specimen immersed in leaf extract solution containing acid for 1 hour was taken out, rinsed with double distilled water, dried and subjected to surface examination by scanning electron microscopy (SEM) using HITACHI S-3000H instrument.

3. RESULTS AND DISCUSSION

3.1 Weight loss studies

The weight loss method of obtaining corrosion rate and inhibition efficiency is useful because of its simple nature and reliable results. Weight loss data of mild steel in 1M H₂SO₄ in the absence and presence of various concentrations of the inhibitor are listed in Table 1. The data shows that corrosion rate decreases and inhibition efficiency increases with the increase in the inhibitor concentration. The values of corrosion rate and inhibition efficiency are obtained by the equations (1) and (2) in the corrosion of mild steel at different concentrations in 1M H₂SO₄ after one hour immersion are given in Table 1.

Table 1 Variation of corrosion rate of mild steel and inhibition efficiency (%) with increasing concentration of inhibitor Pongamia Pinnata in 1M H₂SO₄

S.No	Inhibitor concentration (mM)	Corrosion rate (mmpy)	Inhibition efficiency (%)
1	2	906	50.5
2	6	726	59.8
3	10	690	68.7
4	14	624	81.3
5	18	594	91.2

3.2 Electrochemical studies

Table 2 Potentiodynamic polarization parameters in different concentrations of Pongamia Pinnata at 303 K for the corrosion of mild steel in 1M H₂SO₄

Conc. mM	E _{corr} (mv/SCE)	I _{corr} (mA/cm ²)	β _c (mv/dec)	β _a (mv/dec)	IE %
0	-540	3.48	11.01	11.05	
2	-534	2.31	3.73	5.30	28.16
6	-523	2.02	2.57	3.51	41.95
10	-540	1.92	1.50	2.73	44.82
14	-556	1.12	1.19	2.53	67.81
18	-553	0.31	1.13	2.90	91.09

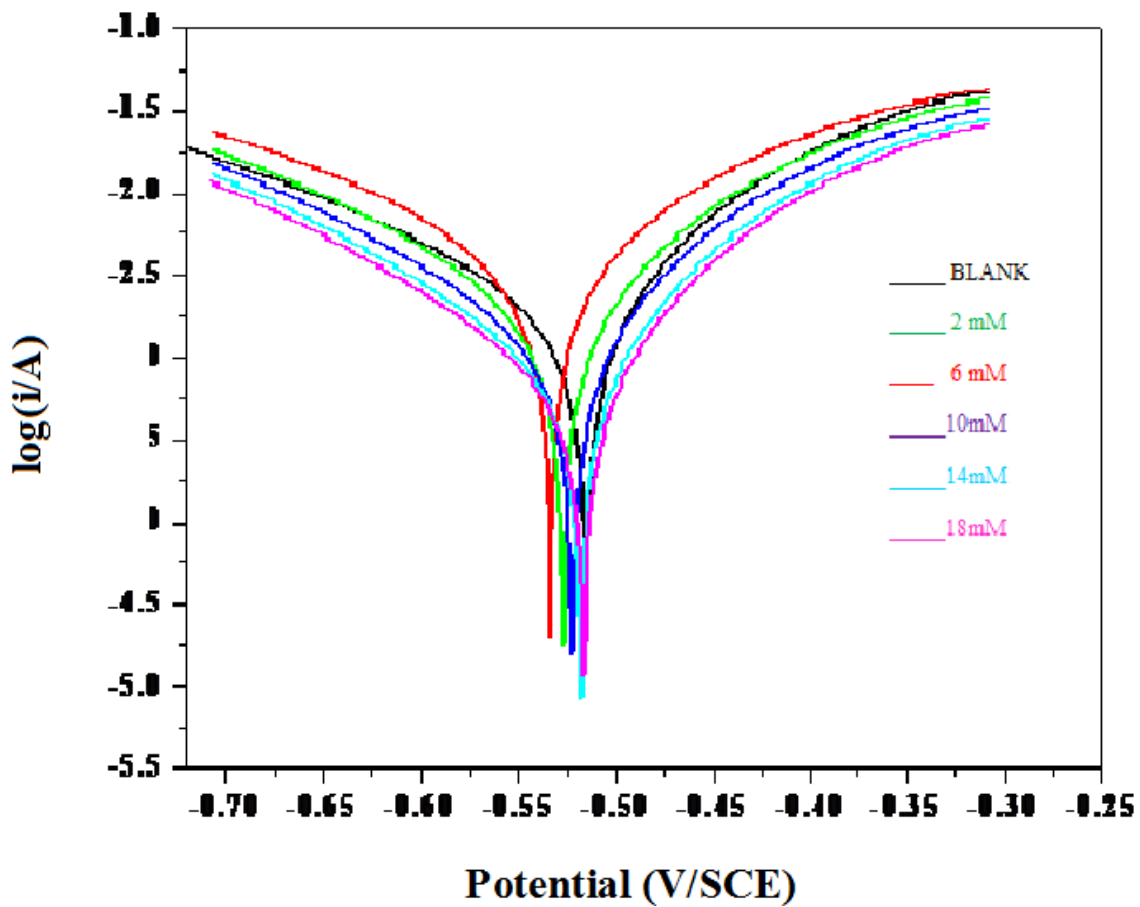


Figure 2 Polarization curves of mild steel in 1M H₂SO₄ with and without pongamia pinnata at various Concentrations

Electrochemical measurements are performed in a conventional three electrode cell consisting of a mild steel working electrode (WE), platinum counter electrode (CE) and saturated calomel electrode as the reference electrode. By using emery paper, these electrodes are degreased and dried at room temperature before used. The area of the working electrode is 1 cm². The current density (I_{corr}) curves obtained by extrapolation of the Tafel lines.

Potentiodynamic polarization measurements were carried out for this system and the details are given Table 2. The kinetic parameters obtained by this method Figure 2 such as E_{corr} , I_{corr} , anodic and cathodic tafel slopes (β_a & β_c) are given in Table 2. It is observed that with the increasing concentration of inhibitor the corrosion potential (E_{corr}) shifts slightly towards the cathodic direction. For the blank, E_{corr} is -540mV and at higher concentration of inhibitor 18 mM its value is -563 mV. These observations indicate that there is a dismal effect on corrosion potential with increase in the concentration of the inhibitor. However there is a progressive change in the values of anodic and cathodic Tafel slopes. This clearly shows that the mechanism of anodic dissolution of metal and cathodic hydrogen evolution steps is affected by the inhibitor. Here it is understood that the inhibition is due to the adsorption of the inhibitor on the mild steel surface. The values of β_c and β_a show increasing trend indicating the inhibitive action is of mixed type²²⁻²³. From the Potentiodynamic polarization measurements the inhibition efficiency is obtained using the equation.

$$\text{IE\%} = \frac{I_{\text{corr}} - I_{\text{corr}}(\text{inhibitor})}{I_{\text{corr}}} \times 100 \quad (4)$$

Where I_{corr} and $I_{\text{corr}}(\text{inhibitor})$ are the values of corrosion current densities of mild steel without and with the inhibitor respectively. The inhibition efficiency increases with the increase in concentration of the inhibitor

3.3 Electrochemical impedance spectroscopy (EIS)

Electrochemical impedance spectroscopy (EIS) studies were carried out in a frequency range of 100KHz to 10 MHz with amplitude of 10 mV using AC signals at open circuit potential (OCP). The charge transfer resistance (R_{ct}) values have been obtained from the diameter of semicircles of Nyquist plots.

Table 3 Electrochemical impedance parameters of mild steel at different concentrations of inhibitor pongamia pinnata in 1 M H₂SO₄

Conc.mM	R _{ct} Ω cm ²	C _{dl} μF cm ⁻² 10 ⁻⁷	IE %
0	2.82	5.64	
2	4.67	3.40	39.67
6	5.22	3.05	45.96
10	5.42	2.93	47.97
14	10.21	1.55	72.38
18	34.70	0.66	91.87

The effect of the inhibitor concentration on the impedance behaviour of mild steel in 1M H₂SO₄ has been determined Table 3 and the Nyquist plots are given in Figure 3. The impedance spectra show a single semicircle and as the concentration of inhibitor increases diameter of the semicircle increases. The results indicate that the R_{ct} significantly increases with increase in concentration of inhibitor and C_{dl} tends to decrease. This decrease in C_{dl} may be due to decrease in local dielectric constant and/or an increase in the thickness of protective layer at electrode surface which enhances the corrosion resistance of the mild steel. The increase in R_{ct} values is attributed to the formation of protective film at the metal-solution interface.

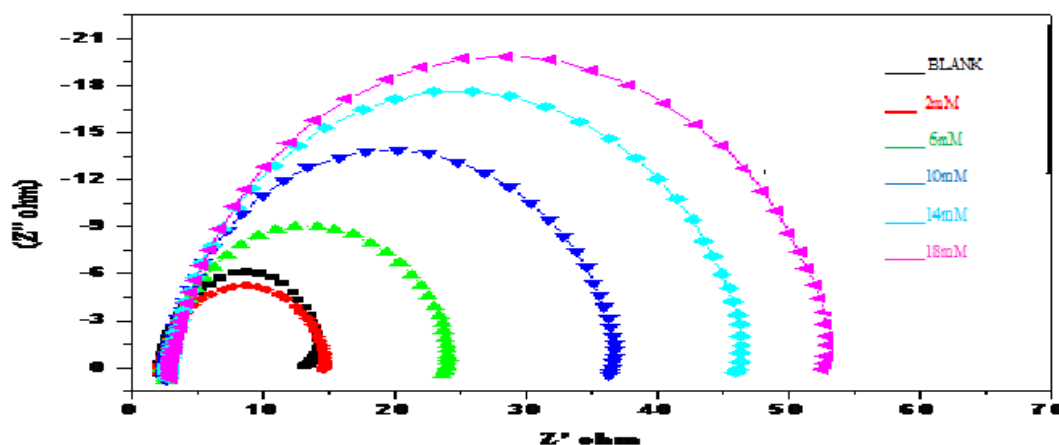


Figure 3 Nyquist plots for mild steel immersed in 1M H₂SO₄ solution without and with pongamia pinnata inhibitor at various concentrations.

3.4 Scanning electron spectroscopy (SEM)

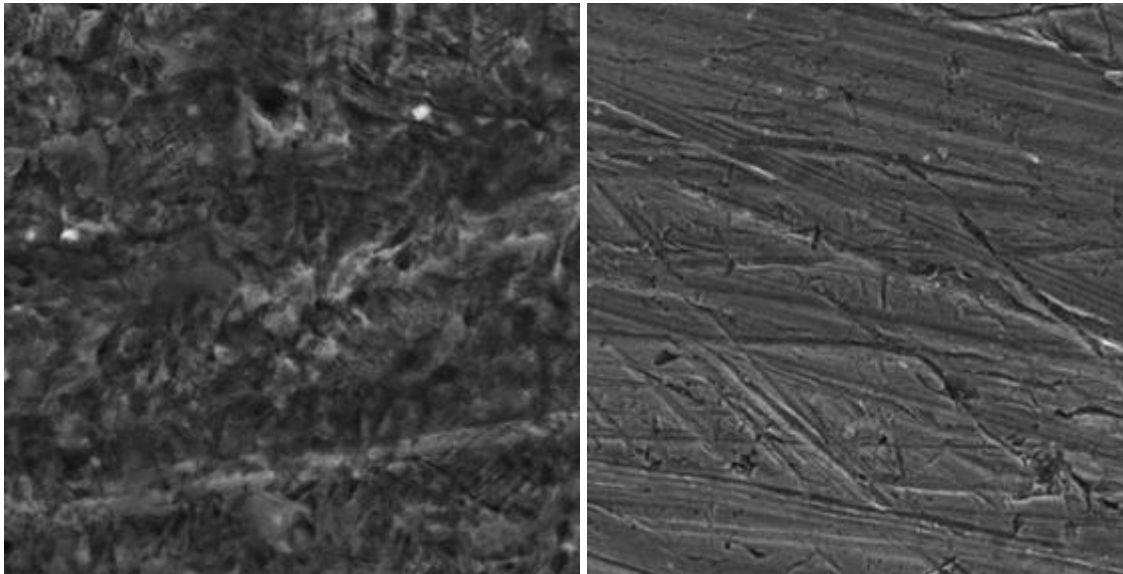


Figure 4 SEM micrograph of mild steel after 1 hour immersion in 1M H₂SO₄

SEM micrograph of mild steel after 1 hour immersion in the presence of inhibitor in 1M H₂SO₄

The mild steel specimen immersed in 1M H₂SO₄ for one hour was taken out and washed with distilled water, dried and taken SEM micrograph. Similarly the mild steel specimen immersed in inhibitor solution containing acid for one hour was taken out, rinsed with double distilled water, dried and subjected to surface examination by scanning electron microscopy (SEM) using HITACHI S-3000H instrument

3.5 IR Spectroscopy

Infrared spectrum of pongamia pinnata was taken in KBr pellet form in the region 750-4000 cm⁻¹. The mild steel specimens of size 1cm × 1cm were prepared and immersed in 100 ml of 1M H₂SO₄ solution containing 18 mM of inhibitor and were then dried. The infrared spectrum was applied to study the mild steel surface. The characteristic IR absorption bands of pongamia pinnata are as follows:

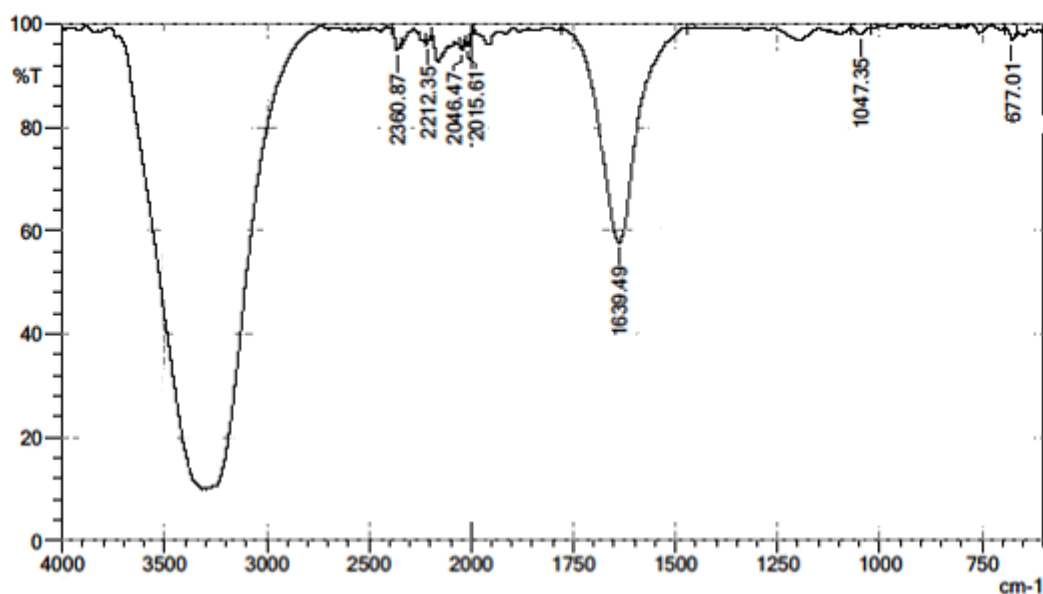


Figure 5 Infrared spectrum of pongamia pinnata leaf extract

From Infrared spectrum of the compound, a broad band 3352 cm^{-1} is attributed to O-H groups: at 1047 cm^{-1} is attributed to ether linkage groups: at 1639 cm^{-1} is attributed to C=O groups: at 677 cm^{-1} is attributed to C-F groups: at 2212 cm^{-1} C-N groups: at 2015 cm^{-1} C≡C-groups: at 2360 is attributed to C - C groups.

4. MECHANISM

Electrostatic interaction of protonated molecules with already adsorbed sulphate ions donor-acceptor interactions between the π -electrons of aromatic ring and vacant d-orbital of surface iron atoms, interaction between unshared electron pairs of hetero atoms and vacant d-orbital of iron surface atoms. Generally, two ways of adsorption are considered on the metal surface in acid media. In the first way, the neutral molecules may be adsorbed on the surface of mild steel involving the displacement of water molecules from the mild steel surface and the sharing electrons between the hetero atoms and iron. The inhibitor molecules can also adsorb on the mild steel surface on the basis of donor-acceptor interactions between π -electrons of the aromatic/heterocyclic ring and vacant d-orbitals of surface iron atoms. In second way, since it is well known that the steel surface bears positive charge in acid solution it is difficult for the protonated molecules to approach the positively charged mild steel surface due to the electrostatic repulsion²⁴. Since sulphate ions have a smaller degree of hydration, they could bring excess negative charges in the vicinity of the interface and favor more adsorption of the positively charged inhibitor molecules,

the protonated inhibitors adsorb through electrostatic interactions between the positively charged molecules and the negatively charged metal surface. Thus, there is a synergism between adsorbed sulphate ions and protonated inhibitors. Thus, inhibition of mild steel corrosion in 1M H₂SO₄ due to the adsorption of pongamia pinnata constituents on the mild steel surface. This assumption could be further confirmed by Infrared analysis of mild steel surface. The high performance of the present investigation is attributed to the presence of rich π -electrons and its large molecular size²⁵⁻²⁸.

5. CONCLUSION

- Pongamia pinnata leaf extract is a good inhibitor for mild steel corrosion in 1M H₂SO₄ solution. Inhibition efficiency increases with increasing concentration of inhibitor and IE % values obtained from different methods are in reasonable agreement.
- Polarization curves measurements indicate that pongamia pinnata leaf extract acted as mixed type inhibitor.
- The Infrared analysis showed that the inhibition of mild steel corrosion occurred due to the formation of a protective film on the metal surface through adsorption of constituents of pongamia pinnata leaf extract.

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