

Electrochemical and morphological investigation on Corrosion Inhibition of Mild steel in 1N HCl by leaf extract of *Pongamia pinnata*

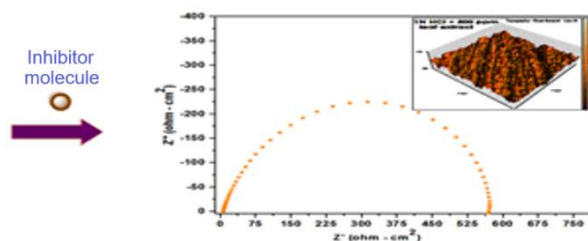
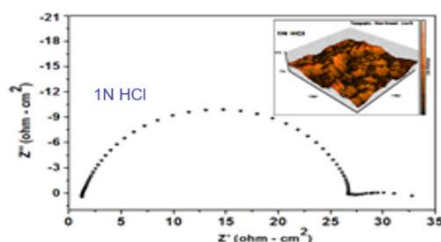
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Submitted on: 27-Sept-2022), Accepted and Published on: 11-Nov-2022

Research Article

ABSTRACT



Higher charge transfer resistance and lesser surface roughness values showed the formation of barrier film on the mild steel surface

The corrosion inhibition potential of *Pongamia pinnata* (*P. pinnata*) was investigated for mild steel corrosion in 1N HCl using electrochemical methods viz., Potentiodynamic Polarization and AC Impedance Spectroscopy (EIS). Spectroscopic techniques such as UV-Vis, FT-IR, GCMS, SEM and AFM techniques were used for characterization and morphology studies. From the results of potentiodynamic polarization, it is found that inhibition efficiency (I.E %) increases while increasing the concentration of leaf extract molecules, the highest inhibition efficiency of 95.5% is observed at 300ppm leaf extract. Tafel curves showed mixed type behaviour of inhibitor and results obtained from EIS studies confirmed the single charge transfer reaction of corrosion process. The inhibitor molecules obey Langmuir adsorption isotherm. FTIR, SEM and AFM results also supported the effectiveness of *P. pinnata* as good corrosion inhibitor for mild steel corrosion in acid medium.

Keywords: AC Impedance Spectroscopy; Atomic Force Microscopy; FTIR; Green inhibitor; Potentiodynamic polarization;

INTRODUCTION

Corrosion is an undesirable - unavoidable natural and common phenomenon that is playing a critical as well as crucial role. Since earlier times corrosion causes enormous harm not only to materials of humans use but also to the other living things in general. The impact of corrosion is viewed from both environmental and economic point of view. There are several methods and approaches to control or minimize the impact of corrosion, amongst the most adopted and accepted methods of combating corrosion is the usage of corrosion inhibitors like soluble organic or inorganic chemical substances. Corrosion inhibitors are chemical substances that are added in small proportions to the corrosive medium in order to minimize the proportion of metals or alloys to be degraded or deteriorated. The

use of common organic and inorganic corrosion inhibitors is sometimes limited, because of their toxic nature.¹⁻³

Now-a-days because of environmental stand point; researchers take advantage of organic compounds that can be obtained from plant extracts otherwise termed as “Green Inhibitors” for combating corrosion. Since the ease of availability, ease of extraction, biodegradability and eco-friendly nature make these plant derived materials suitable for corrosion mitigation process of material from corrosive environment.⁴⁻⁶ It is well reported in the literature that the plant extracts contain numerous soluble phytochemicals like flavonoids, catechins, alkaloids, amino acids, terpenoids, plant proteins and carbohydrate-based compounds, that are safe for the environment.⁷⁻⁹

These phytochemicals consist of larger organic functional groups such as aliphatic and aromatic heterocyclic rings with heteroatoms such as sulfur, nitrogen, oxygen and phosphorus in their polar functional groups that can act as reactive centers and minimize the rate of corrosion. The high potential of the plant extracts is mainly because of the presence of a numerous simple as well as complex phytochemicals and the organic functional groups that contain enormous electron rich polar functional groups and multiple bonds that speed up their adsorption on

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surface of the metallic materials like conventional organic corrosion inhibitors.¹⁰⁻¹²

When these compounds are adsorbed on the surface of the metal, it creates a protective barrier, which separates the metal surface from the aggressive environment.

The different parts of the plant extracts such as seeds, roots, stem portions, leaves, flowers and fruits have been tested and found as good corrosion inhibitor in acidic media for different materials, i.e: ferrous and non-ferrous materials. Many recent studies on mild steel corrosion inhibition in acid media using the extracts of the plant are discussed herewith. Plant (leaves) extract of *Xanthium strumarium*¹³ *Haematostaphis barteri* Leaves extract¹⁴ were taken into consideration as they possess conducive corrosion inhibition potentials for mild steel in HCl. The role of ethanolic extract of *Stachys byzantina*'s leaves for mitigation of mild-steel corrosion in the acidic solution was studied by M.H. Shahini et.al, the results suggested that the formed complex (barrier film) exhibited affinity towards the metal surface resulting in corrosion prevention¹⁵. Anti-corrosive properties of Parsley extract¹⁶, sweet melon peel extract¹⁷, *Tagetes erecta* (Marigold flower)¹⁸ and *Ficus tikoua* leaf extract¹¹ for mild steel in acid medium were reported and found that all these plant extracts acted as a good corrosion inhibitor for mild steel in aggressive medium.

In this present study, *Pongamia pinnata* (*P. pinnata*) leaves extracts has been taken as the candidate materials for mild steel corrosion in 1N HCl. *P. pinnata* belongs to legume tree in a pea family, fabaceae. It is an economically and medically important family of plants, and it is a readily available plant species. It is found all over India in different names, viz., in English it is called by the name Indian beech tree, in Hindi it is Karanj and its Tamil name is Pongam tree.¹⁹ *P. pinnata* is a tropical plant and it can be present or grown in almost all parts of Tamilnadu. *P. pinnata* have been used as a traditional medicine, cattle fodder, green manure, timber, fuel (bio-diesel – alternate and renewable energy source) in India and in neighboring countries^{20, 21}.

The plant extract (*P. pinnata*) contains number of phytochemicals with π - electrons system, larger organic molecules with N and O as heteroatom in their structure accompanied with aromatic / heterocyclic rings. Literature survey tells only few reports on the corrosion inhibition behavior of *P. pinnata* for mild steel corrosion in acid media.^{22, 23}

Earlier we have investigated and reported the corrosion inhibition potential of *P. pinnata* for mild steel corrosion in sulphuric acid.²⁴ In this present work we have given the outcomes that supported the inhibition potential of *P. pinnata* for mild steel corrosion in hydrochloric acid medium. Though both are acids, the inhibition performance of *P. pinnata* is prominent in HCl compared to H₂SO₄.

The present study involves the synthesis and evaluation of *Pongamia pinnata* leaf extract as competent corrosion inhibitor for mild steel in hydrochloric acid medium using techniques such as UV-Visible spectroscopy, FT-IR, GCMS, Electrochemical techniques, SEM and AFM, also compare the inhibition efficiency of *Pongamia pinnata* with other reported green inhibitors.

EXPERIMENTAL PROCEDURE

Pongamia pinnata leaves extract preparation

Pongamia pinnata leaves were collected, they were dried in shade, grind to powder; the powdered leaves were packed into Soxhlet apparatus. The powdered leaves were extracted using methanol at 60°C, the resulting residue was concentrated using rotary evaporator so as to get thick extract of leaves. This extract has been taken for the present investigation, stock solution was prepared, from stock solution, and working standards of concentrations 50 to 300 ppm inhibitor were prepared in corrosive medium taken for analysis.

Materials and Corrosive medium

Mild Steel sample taken for the present investigation has the following composition: Fe = 99.3%, C = 0.13%, with other alloying elements such as Ni, Mo, Cr, S, P, Mn, and Si. These mild steel specimens were picked and washed sufficiently with water so that it is free from acid; then samples have been taken for polishing using different grade emery papers (220-1200 grits), washed with distilled water and then degreased with acetone.

The AR grade hydrochloric acid has been used for preparing the corrosive media in the present study. An aliquant of the acid was exactly diluted using distilled water for the preparation of 1N HCl, for each set of experiments. These acid solutions were prepared fresh to avoid the effect of contamination.

Characterization

UV, FTIR and GCMS spectral studies have been carried out to find out the functional – phytochemical constituents of *Pongamia pinnata* leaf extract. The UV experiments have been carried out in the wavelength range 200 to 800nm using “ANTECH – AN-UV 7000 spectrophotometer. Similarly, IR system - Perkin-Elmer (version 10.03.09) spectrophotometer have been used for FT-IR spectral studies for leaf extract and the corrosion product(s) (i.e. inhibitor film on the mild steel surface was taken for analysis).

For this experiment, mild steel specimens of size 5×3×0.2 cm were placed in hydrochloric acid of concentration 1N with leaf extract concentration of 300 ppm for the duration of 5 hours, then taken out, washed gently with water and then dried. The film formed on the mild steel surface was scrapped carefully, mixed with KBr then it was made into pellets, the resulting samples were taken for FTIR analysis in the IR range between 400 and 4000 cm⁻¹. GCMS analysis has been carried out as per the procedure discussed in our earlier report.^{24, 25}

Corrosion testing: Electrochemical Investigation

The electrochemical analyzer (Model: CH-608E) with a conventional three electrode cell setup has been used to carry out potentiodynamic polarization and AC Impedance measurements. The working electrode was the mild steel specimen, counter electrode used was platinum electrode and saturated calomel electrode (SCE) was reference electrode. Before the starting of electrochemical experiment, the working electrode was immersed in the corrosive medium and set aside for 30 minutes to attain constant open circuit potential (OCP).

Potentiodynamic polarization measurements have been carried out in the potential range from ±200mV with scan rate 1 mV/s.

various corrosion parameters such as E_{corr} , i_{corr} , b_a and b_c have been calculated from the polarization curves. Equations (1) and (2) can be used to calculate rate of corrosion (mmpy) and the inhibition efficiency (IE %).

$$\text{Corrosion rate (CR)} = 3.2 \times i_{\text{corr}} \times \text{Eq. wt} / \text{Density} \quad (1)$$

$$\text{Inhibition Efficiency (IE \%)} = (i_{\text{corr}} - i_{\text{corr}}^{\text{in}} / i_{\text{corr}}) \times 100 \quad (2)$$

Where, i_{corr} & $i_{\text{corr}}^{\text{in}}$ are the corrosion current densities in the absence and presence of inhibitor

Similarly, AC Impedance measurements have been carried out with a frequency of 100 KHz to 10 mHz with a.c amplitude of 5 mV. The real part (z') was plotted against the imaginary part (z'') in Nyquist plots. From Nyquist plots, the corrosion parameters such as R_{ct} (the charge transfer resistance) and C_{dl} (double layer capacitance) values have been deduced. The difference between R_s (solution resistance) and R_t (total resistance) gave the charge transfer resistance (R_{ct}) values. Equation (3) can be used to calculate the inhibition efficiency (IE %), equations (4) & (5) can be used to arrive C_{dl} values and the θ values (surface coverage).

$$\text{Inhibition Efficiency (IE \%)} = \{R_{\text{ct}}^{\text{in}} - R_{\text{ct}} / R_{\text{ct}}^{\text{in}}\} \times 100 \quad (3)$$

$$\text{Double layer capacitance (} C_{\text{dl}}) = 1/2\pi \cdot f_{\text{max}} \times R_{\text{ct}} \quad (4)$$

$$\text{Surface Coverage } (\theta) = C_{\text{dl}} - C_{\text{dl}}^{\text{in}} / C_{\text{dl}} \quad (5)$$

Where,

$R_{\text{ct}}^{\text{in}}$ and R_{ct} are the charge transfer resistance with and without inhibitor

f_{max} is frequency at z'' value is maximum

C_{dl} & $C_{\text{dl}}^{\text{in}}$ are double layer capacitance values in the absence and presence of inhibitor

Adsorption Parameters

The adsorption isotherms give better idea about the interaction between the inhibitor molecules and the mild steel surface. The surface coverage (θ) values can be calculated using the equation (6). From the surface coverage (θ) values various isotherms were tested by plotting (θ) vs. Inhibitor concentration (C) and it was found that the adsorption isotherm model best suited in this present study is Langmuir isotherm (equation 7)

$$\text{Surface coverage } (\theta) = (\text{IE \%} / 100) \quad (6)$$

$$\text{Langmuir isotherm} = \theta / (1 - \theta) = K_{\text{ads}} \cdot C \quad (7)$$

Where,

C is the concentration of inhibitor

K_{ads} is equilibrium constant for adsorption – desorption process,

θ is surface coverage

Surface Analysis (SEM and AFM)

The analysis of mild steel surface (morphology) using SEM and AFM techniques have been carried out as per the procedure adopted in our earlier report.²⁵

RESULTS AND DISCUSSION

Characterization of *Pongamia pinnata* leaf extract : UV, FTIR and GCMS analysis

“ANTECH – AN-UV-7000 spectrophotometer have been used for taking the UV spectrum (the wavelength range is 200 to

800nm). Figure.1 (a) shows the UV spectrum of leaf extract of *P. pinnata*. From the results it is noticed that UV graph exhibited the characteristic peak of flavonoid glycoside at λ_{max} at 238, 315nm characteristic peak for chlorophyll at λ_{max} at 660nm.^{24, 25, 26}

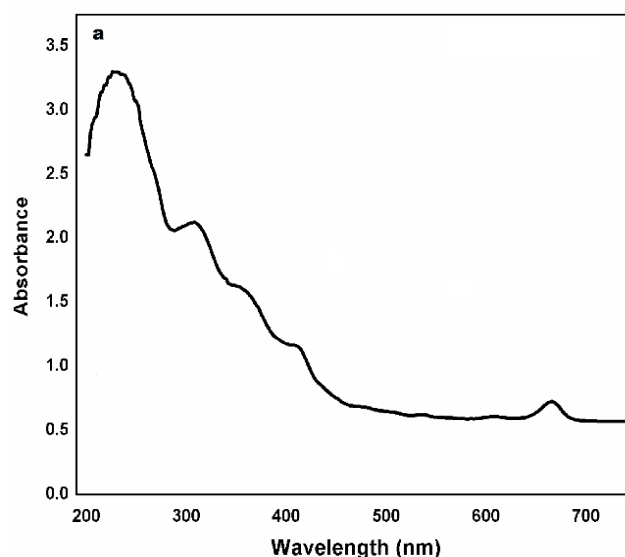


Figure: 1 (a) UV curve for leaf extract of *P.pinnata*

FT-IR experiment of *Pongamia pinnata* leaf extract and corrosion product in the presence of *P.pinnata* leaf extract are shown in figure.1 (b, c). From FTIR results, it has been found that the characteristic bands of aromatic N – H (s) and C=O stretching is observed at 3384 cm^{-1} and 1630 cm^{-1} respectively. The weak band near 2927 cm^{-1} is mainly due to the aromatic C – H (s) vibrations. The absorption band of C = O (s) vibration at about 1630 cm^{-1} in the plant extract reveal the presence of heteroatom (oxygen) of carboxylic group which may play a crucial role in adsorption of inhibitor molecules on the metal surface. The peaks at 1385 , 1115 and 1074 cm^{-1} are owing to the presence of C–H, C-O and –C–N (s) functional groups. Also, the band at 1046 cm^{-1} is due to the presence of C–N(s) in amine.²⁷

Figure 1c shows the interaction of *Pongamia pinnata* on mild steel surface in 1N HCl. From the figure, it is noticed that there is not big variation in peak values that shows the presence of inhibitor (leaf extract) molecules in adsorbed protective barrier. Some of the bands in the protective barrier are missing which is accredited to the reaction between functional groups of inhibitor molecules and the mild steel electrode surfaces in 1N HCl which is reason for corrosion inhibition. Hence, on the basis of the results obtained it is clear that the functional groups present in plant extracts are actively involved in protection of mild steel surface from aggressive acid solution.^{25, 27}

The GC-MS analysis was carried out for leaves extract of *P. pinnata* to identify the presence of phytochemicals, the respective spectrum was shown in Figure.2; it was found that, 38 phytochemicals were present in the leaf extract of *P. pinnata*. The predominant components present are already mentioned in our earlier investigation.²⁴

The presence of bigger organic components, carbonyl – aromatic functional groups, presence of hetero-atoms and the C = C bonds present in the leaf extract are very much influential in protecting mild steel from corrosive HCl medium.^{28, 29}

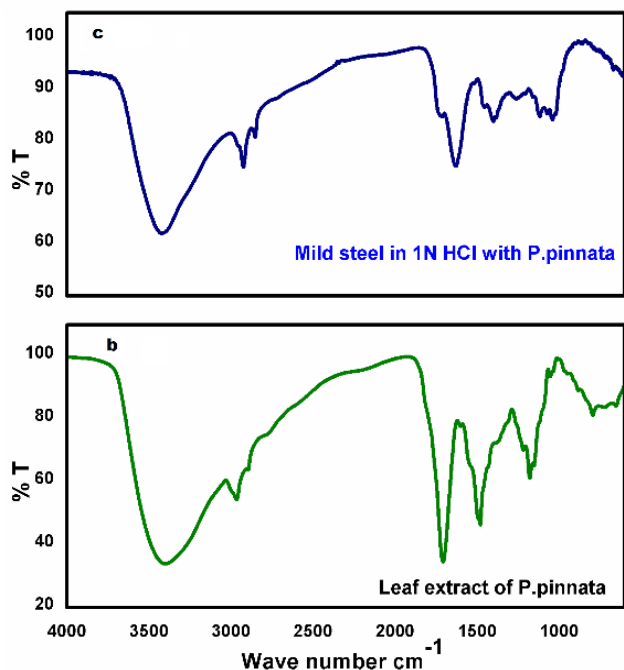


Figure: 1 FTIR curves for (b) Leaf extract of *P.pinnata* (c) FTIR spectra : Mild steel with *P.pinnata* inhibitor in 1N HCl

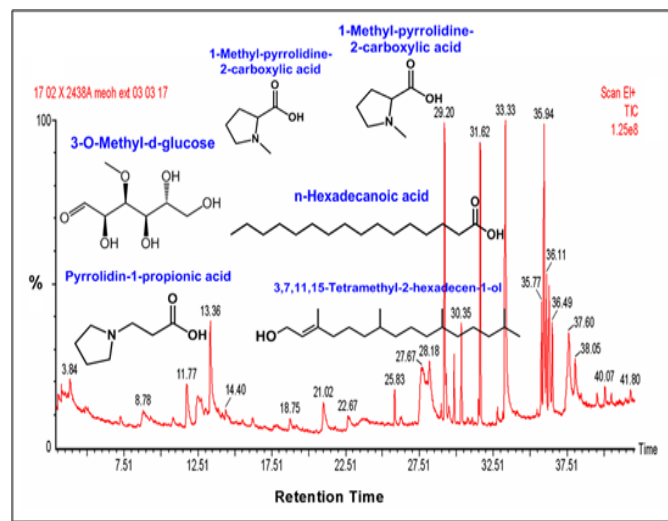


Figure: 2 GC-MS graph of *Pongamia pinnata* leaf extract

Corrosion Testing

Potentiodynamic polarization

Figure.3 shows the tafel graphs of mild steel in 1N HCl with various concentrations of *P.pinnata* leaves extract. The polarization data's such as i_{corr} , E_{corr} , b_a and b_c are derived from tafel curves and tabulated in Table.1. From table and figure, it has

been observed that progressive addition of *P.pinnata* leaf extract remarkably reduces the rate of metal dissolution in 1N HCl.³⁰ The corrosion current density (i_{corr}) decreased considerably from 3695 $\mu\text{A}\cdot\text{cm}^{-2}$ to 217 $\mu\text{A}\cdot\text{cm}^{-2}$ resulted in IE 94%, 300ppm of leaf extract was found to be the optimum concentration, beyond which there is not much changes in corrosion current density with further increase of the leaf extract concentrations.

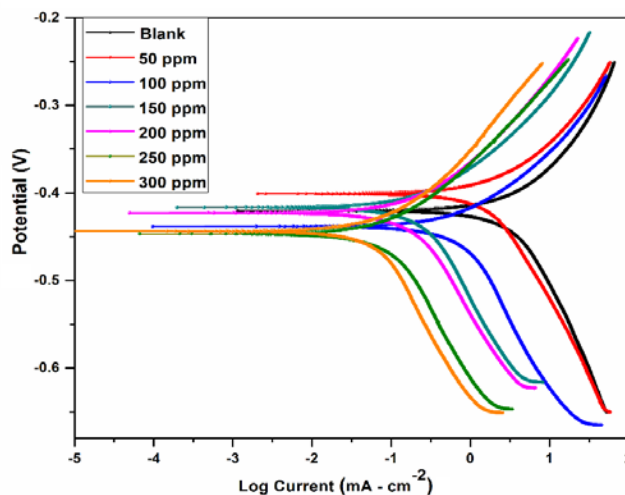


Figure: 3 Tafel curves for mild steel in 1N HCl with different concentrations of inhibitor

Also, it is observed that the leaf extract have a strong influence on both anodic metal dissolution and cathodic hydrogen evolution reactions, and moreover the variation in corrosion potential is less than 85mV – confirms the mixed type nature of inhibitor³¹.

Table.1 Corrosion parameters deduced from potentiodynamic polarization (Mild steel in 1N HCl with *Pongamia Pinnata*)

Inhibitor Conc. (ppm)	E_{corr} (mV)	i_{corr} ($\mu\text{A}\cdot\text{cm}^{-2}$)	b_a ($\text{mV}\cdot\text{dec}^{-1}$)	b_c ($\text{mV}\cdot\text{dec}^{-1}$)	IE (%)
Blank	-422	3695	118	187	--
50	-407	1991	88	165	46.0
100	-437	766	76	173	79.0
150	-414	571	86	158	85.0
200	-409	362	79	161	90.0
250	-455	298	93	160	92.0
300	-416	217	74	155	94.0

AC Impedance Spectroscopy (EIS)

Figure.4 shows Nyquist plots for mild steel without and with different concentrations of the *pinnata* leaves extract. The graph exhibited single semicircle, which reveals that the corrosion of mild steel in 1N HCl solution was mainly inhibited by charge-transfer process. The shape of the semi-circle does not change with the addition of inhibitor and the larger the diameter of semi-circle of Nyquist plot indicates higher charge transfer resistance and is thus attributed to greater corrosion inhibition efficiency.³²

The electrochemical impedance parameters (R_{ct} and C_{dl}) derived from the Nyquist plots are tabulated in Table.2. From the

table, it has been noticed that the presence of *P.pinnata* leaf extract enhances the values of charge transfer resistance (R_{ct}); this could be ascribed to the higher resistance exerted by the adsorbed components of inhibitor at the metal – solution interface. Likewise, the decrease in double layer capacitance (C_{dl}) is ascribed to increase in thickness of electrical double layer as a consequence of adsorption of extract components.

From R_{ct} values, it is noticed that leaves extract molecules slowly replace water molecules by means of adsorption of inhibitor at the metal/solution interface which induce the formation of a protective film on the mild steel electrode surface, and minimize metal dissolution. The IE % deduced from EIS measurements are in good agreement with the results obtained from Tafel polarization technique. The one time constant of bode plot supports single charge transfer mechanism, also showed that there is increase in inhibition efficiency with rise of inhibitor concentration (Figure 5).³³

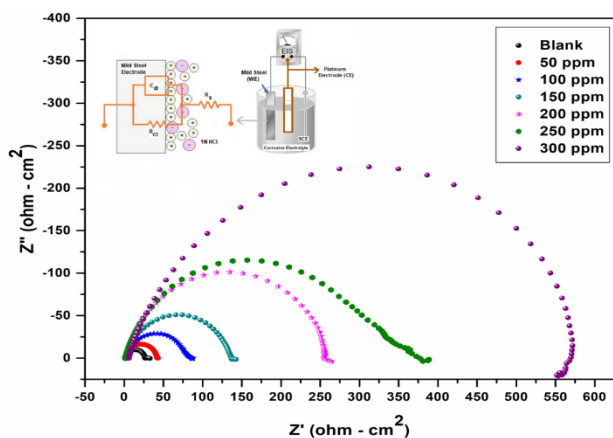


Figure: 4 Nyquist plots : Mild steel in 1N HCl (in the absence and presence of leaf extract)

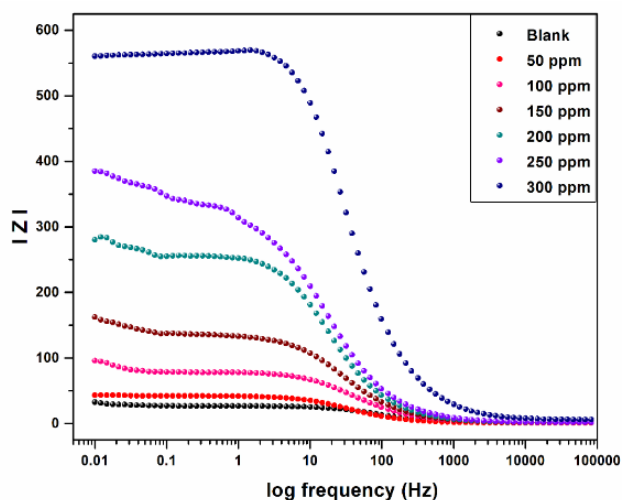


Figure: 5 Bode plot for mild steel in 1N HCl with *Pongamia pinnata* inhibitor

From figure 4-6 it is observed that the impedance parameter and the phase angle increase with the inhibitor addition as the adsorption of the inhibitor onto the steel surface is intensified. To analyze the corrosion inhibition of leaf extract, Nyquist plot is

verified with RC circuits where capacitors (C) and resistors (R) are in parallel or in series. C_{dl} is used to represent the electrical charge transfer at the metal/electrolyte interface and it is known as the capacitance of a double layer (measured in terms of farads), and that is present in all corroding aqueous systems. R_{ct} is the charge transfer resistance and R_s is the solution resistance. The combination of these three elements (R_s , R_{ct} , C_{dl}) provides a simple equivalent electrical circuit for a uniformly corroding material and the experimental system of the same is shown in figure 4 itself.³⁴

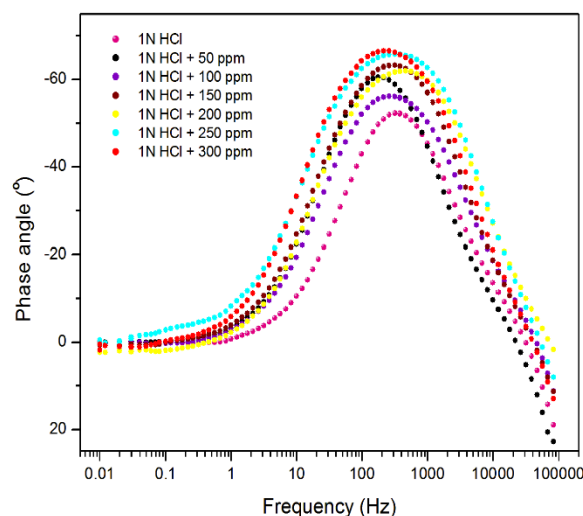


Figure: 6 Bode plot (phase angle vs. Frequency) for mild steel in 1N HCl with *Pongamia pinnata* inhibitor

Table.2. EIS parameters of mild steel in 1N HCl with leaf extract of *P.pinnata*

Conc. (ppm)	OCP (mV)	R_{ct} (ohm.cm ²)	C_{dl} (μf.cm ⁻²)	I.E (%)	(θ)
Blank	-447	27	1.0488E-04	--	-
50	-448	45	7.5902E-05	40.0	0.4000
100	-446	82	6.1066E-05	67.1	0.6707
150	-453	140	2.4397E-05	80.7	0.8071
200	-464	250	1.1327E-05	89.2	0.8920
250	-484	380	8.9884E-06	92.9	0.9289
300	-471	560	6.0993E-06	95.2	0.9518

Surface Examination

SEM Analysis

SEM images are used to determine the reaction of organic molecules (present in extract) with the metal surface.³⁵ The uniform and polished surface of mild steel (with scratch lines occurred during polishing) ahead of immersion in 1N HCl is given in Figure.7 (a).

The damaged and roughened mild steel surface (Figure.7 (b)) infers severity of corrosion of mild steel when it was immersed in 1N HCl (i.e: absence of inhibitor).³⁶ Besides, comparatively smooth surface film over mild steel surface was seen in figure.7 (c), which clearly explain the corrosion inhibition potential of

P.pinnata i.e.: the leaf extract formed a protective barrier upon mild steel surface, protecting the surface from further corrosive attack. This protective action may be due to adsorption of leaves extract constituents on mild steel surface, and corrosion process was inhibited.

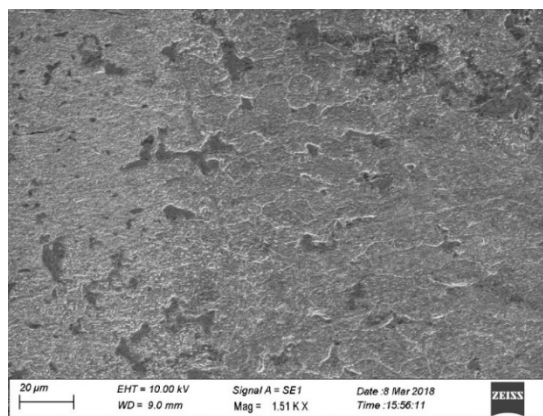
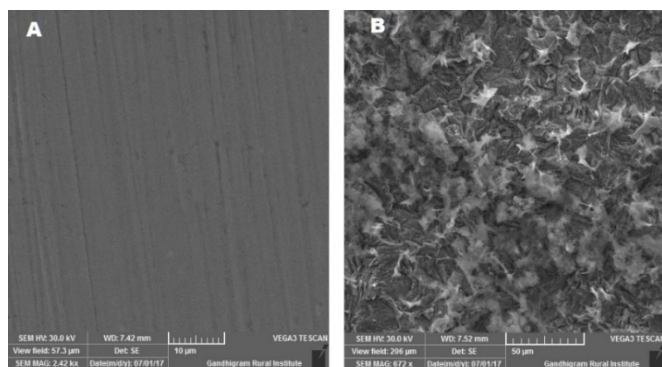


Figure: 7 SEM images of (a) Polished mild steel (b) Mild steel immersed in 1N HCl (c) Mild steel in 1N HCl with 300 ppm *P. pinnata*

AFM analysis

Atomic Force Microscopy is a new technique used to examine the surface morphology at nano-to micro-scale levels and now this technique has become a new alternative or addition to investigate the influence of corrosion inhibitors on the progress of the corrosion (mitigation) at the metal - solution interface. Figure.8 (a) showed the AFM image of polished Mild steel specimen, Figure. (8 b) revealed the AFM images of mild steel specimen after immersion in 1N HCl Figure.(8 c) showed the AFM images of mild steel in 1N HCl with 300 ppm of *P.pinnata* extract. While comparing the figures i.e. 8 (a–c), figure 8(c) showed smooth surface compared to figure 8 (b) which was confirmed by the surface roughness values.³⁷

Table.3 exhibits the AFM data of the present system, from the table, it is clear that addition of leaf extract reduced the surface roughness. The roughness values and the AFM images are similar to SEM images, which support that the leaf extract molecules adsorb on the mild steel surface and protect mild steel surface from corrosion.^{38, 39}

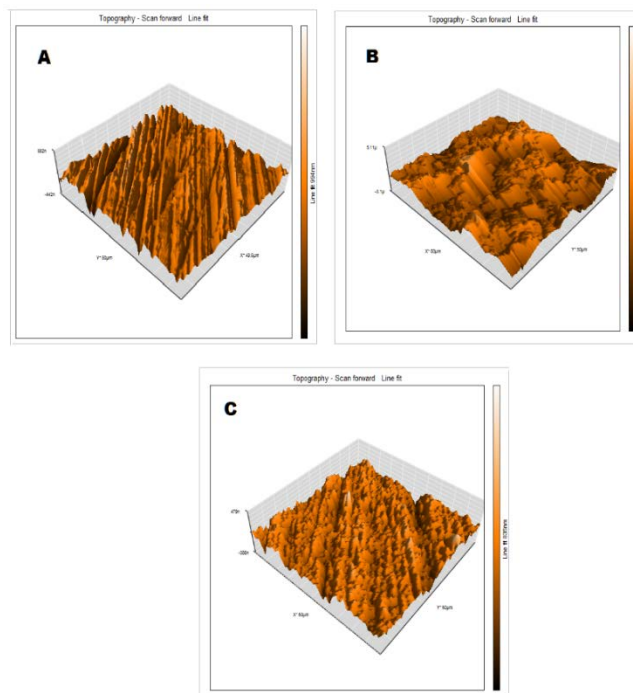


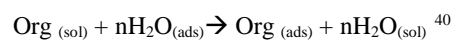
Figure: 8 AFM images (a) Polished mild steel (b) Mild Steel in 1N HCl (c) Mild Steel immersed in 1N HCl with 300 ppm *P. pinnata*

Table. 3 AFM data for mild steel surface immersed in 1N HCl

Samples	Average Roughness (Ra) (nm)	RMS Roughness (Rq) (nm)	Maximum Peak-to valley Height (nm)
Polished Mild Steel	46.597	62.308	123.05
Mild Steel in 1N HCl	367.18	465.77	1167.3
Mild Steel in 1N HCl + 300 ppm <i>P.pinnata</i>	50.684	65.912	186.79

Adsorption Isotherm

The adsorption isotherm clearly explains the basis of information on the reaction between mild steel and inhibitor molecules (leaf extract), it can be well explained by adsorption isotherms. The assimilation or adsorption of an inhibitor (organic) molecules on the metal-solution interface was mainly accredited by a substitutional adsorption process between protonated organic molecules in the corrosive medium and water molecules on metal surface viz.



Where, $\text{Org}_{(\text{sol})}$ - organic molecules in the aqueous solutions, $\text{Org}_{(\text{ads})}$ - adsorbed inhibitor on the metallic surface, $\text{H}_2\text{O}_{(\text{ads})}$ is the water molecules on the metallic surface, “n” is the size ratio represents number of water molecules replaced by one molecule of organic inhibitor molecule.

Based on the results, it has been found that the inhibitor obeys Langmuir adsorption isotherm (Figure 9), the plot of inhibitor concentration vs. surface coverage gave a straight line with regression coefficient value closer to 1, and this adsorption isotherm supported that the inhibition behavior of *Pongamia pinnata* is mainly due to adsorption process.⁴¹

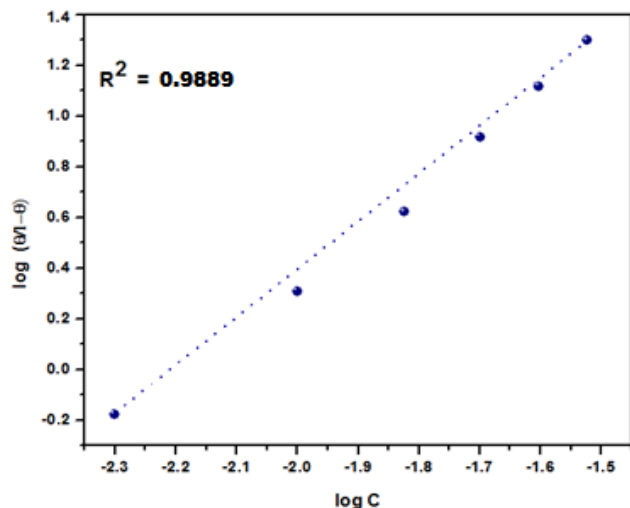


Figure: 9 Langmuir isotherm for mild steel in 1N HCl

Corrosion Inhibition Mechanism

The general criteria of organic corrosion inhibitors are: the inhibitor molecules may be adsorbed on the metal/acid solution interface by one or more of the following manner such as

- (i) electrostatic interaction between the protonated inhibitor molecule and metal surface containing negatively charged (Cl^-) ions,
- (ii) donor-acceptor interactions between the π -electrons of the aromatic ring and/or unshared e- pair of polar functional groups with unoccupied d-orbital of iron.⁴²

The corrosion inhibition and adsorption behavior of *Pongamia pinnata* in 1N HCl has been examined using electrochemical, spectral and surface morphological methods, and from the results it is observed that inhibition efficiency has been found to increase with increase of inhibitor concentration. From the literature it is well clear that when mild steel is immersed in acid medium, the immediate reactions are metal dissolution and hydrogen evolution reactions.⁴² The results obtained from electrochemical investigations also revealed that the leaf extract controls both anodic and cathodic corrosion process and acted as mixed type inhibitor, EIS results supported the single charge transfer mechanism. The adsorption of inhibitor molecules on mild steel surface was confirmed by surface analytical methods such as SEM and AFM.

When added to acid medium, these phytocompounds might be protonated and they are attracted towards the negatively charged (Cl^-) mild steel surface. So, the initial stage of adsorption is due

to negatively charged chloride ions of HCl.⁴³ followed by adsorption of protonated inhibitor molecules on the negatively charged surface through electrostatic interactions. It is well known (and reported in the literature) that Cl^- ions have stronger adsorption behaviour towards mild steel compared that of other ions⁴⁴ and the adsorption of protonated inhibitor molecules on these negatively charged surface through electrostatic interactions is the foremost reason for pronounced inhibition effect in HCl solution.⁴⁵

Therefore, the adsorption of leaf extract molecule on mild steel corrosion in 1N HCl is stronger, which results in higher inhibition efficiency. UV, FT-IR and GC-MS analysis showed the presence of larger organic molecules with oxygen and nitrogen atoms in their structures, which meet the general criteria of typical organic corrosion inhibitors. So, these phytocompounds of the studied leaf extract(s) may also get adsorbed on the mild steel electrode surface via donor-acceptor interactions of π – electrons of leaves extract components and vacant d-orbital of iron (steel) surface. The possible inhibition mechanism is given in figure.10.

So, the initial stage of inhibition may perhaps fast physical adsorption of leaf extract on the metal surface⁴⁶ followed by slow chemisorption process due to charge sharing from inhibitor molecules to the metal surface, leading to co-ordinate type bond formation, resulting protection of mild steel surface from further corrosion and the maximum inhibition efficiency obtained was 95.2%.

Comparative analysis

The inhibition efficiency of leaf extract of *P. pinnata* is compared with that of other green corrosion inhibitors derived from plants origin reported earlier in the literature^{11, 30, 47 - 51} and is given in Table 4. To evaluate the corrosion inhibition efficiency of various plant extracts, several methods such as weight loss method, electrochemical studies viz., potentiodynamic polarization and electrochemical impedance measurements were employed. By comparing the corrosion inhibition efficiency of *P. pinnata* with other plant extracts, it is noticed that *P. pinnata* showed comparatively better inhibition efficiency. Electrochemical studies showed the inhibition efficiency of 92.5% and, surface analysis techniques such as AFM, SEM exhibit the presence of smooth surface which support the protective film formed on the metal surface. As a whole, it has been observed that *P. pinnata* has good competency (as an efficient corrosion inhibitor) to minimize mild steel corrosion in hydrochloric acid like other reported plant extracts.

CONCLUSIONS

The inhibition of corrosion of mild steel by *Pongamia pinnata* in 1N HCl acid media has been examined by electrochemical, spectral and surface analytical techniques, based on the results obtained the following points disclose the conclusions:

- Polarization measurements also revealed that the corrosion current density (i_{corr}) values decreased as the leaf extract(s) concentration increased; also the tafel graphs supported the mixed type behaviour of leaf extract.
- The results obtained from EIS studies are in good agreement with the results obtained from polarization.

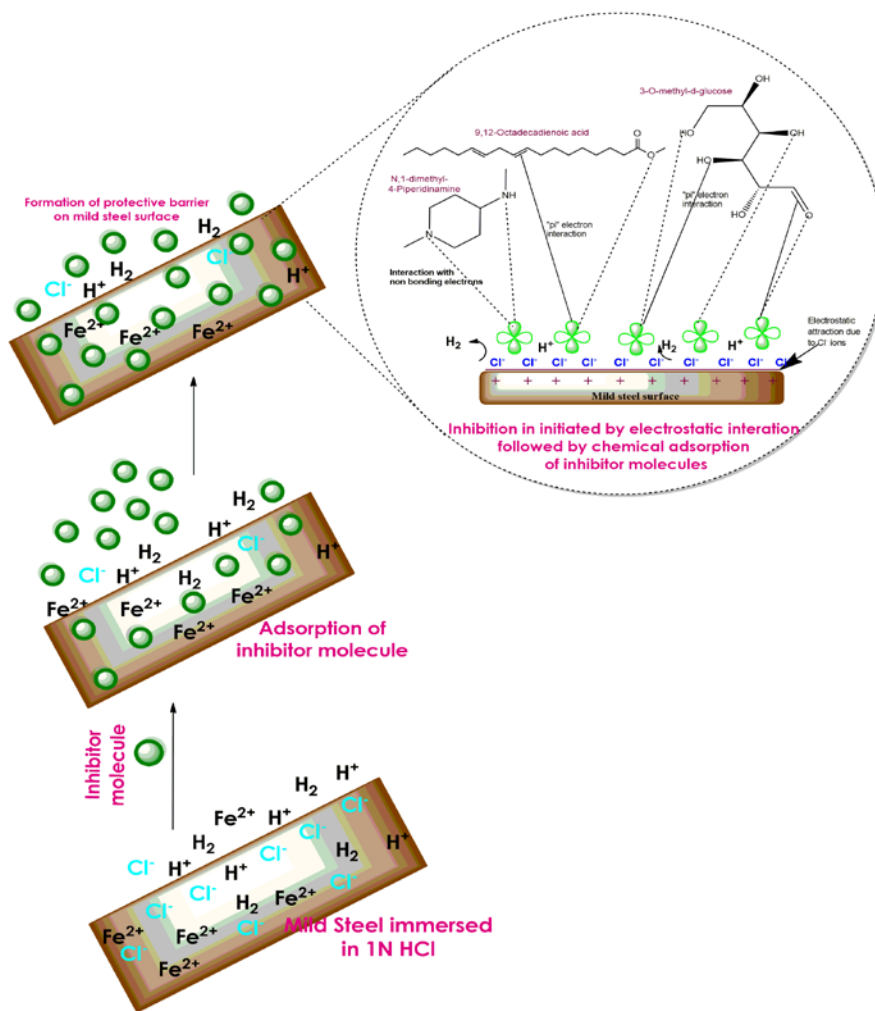


Figure: 10 Inhibition Mechanisms

Table.4 Comparison of Inhibition potential of *P.pinnata* with other plant extracts (for hydrochloric acid medium)

Plant Extract	Methods Adopted	Inhibitor Conc. (ppm)	IE (%)	Adsorption Isotherm / Type of inhibitor	Ref.
Pongamia pinnata	Electrochemical, SEM, AFM	300	95.2	Langmuir, mixed type	Present study
Eucalyptus leaf extract	Electrochemical, SEM, AFM	800	88.0	Langmuir	30
Ficus tikoua leaf extract	WL, electrochemical, SEM	200	95.8	Mixed type	11
Ananas comosus stem extracts	WL, electrochemical, SEM	1000	97.6	Langmuir	47
Dioscorea septemloba	Electrochemical, SEM, FT-IR	200	72.1	mixed type	48
Ziziphora leaf extract	Electrochemical, SEM, FT-IR	800	93.0	Langmuir, mixed type	49
Pisum sativum (Peel)	Electrochemical, SEM, FT-IR	400	91.0	Mixed type	50
(Phoenix dactylifera) Seed extract	WL, SEM electrochemical,	1500	84.1	Langmuir, mixed type	51

- The maximum inhibition efficiency of 95.2% is observed at 300ppm inhibitor concentration.
- The impedance parameter and the phase angle increases with addition of inhibitor shows the adsorption of inhibitor onto the steel surface is intensified.
- The adsorption of *P. pinnata* leaf extract is found to obey Langmuir
- SEM and AFM images for mild steel in presence of *P. pinnata* in 1N Hydrochloric acid showed the protective barrier formation.
- From the results it has been concluded that - the initial stage of inhibition may be due fast physical adsorption of leaf extract on the metal surface followed by slow chemisorption process due to sharing of charge from inhibitor molecules and metal surface, leading to coordinate type bond formation, thus protecting the mild steel surface from further corrosion reaction.
- From comparative evaluation with other reported plant inhibitors, *P. pinnata* performed equally well in inhibiting mild steel corrosion and offered a maximum inhibition of 95.2%.

ACKNOWLEDGMENTS

The authors would like to extend their sincere thanks to Gandhigram Rural Institute, Gandhigram, Dindigul for providing SEM facility. The authors would extend their sincere thanks to the St. Joseph's College, Tiruchirappalli for providing FTIR facility and Centre for Advanced Research in Indian System of Medicine (CARISM) Sastra University, Thanjavur for providing GC-MS facility.

DECLARATIONS

- (i) **Funding:** This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.
- (ii) **Conflict of interest:** All authors states that there is **no conflict of interest** for publication of this work.

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