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ASSESSMENT OF ANTI-CORROSION POTENTIAL OF *ROSA-SINENSIS* PLANT LEAVES EXTRACT ON MILD STEEL IMMERSED IN 0.5M H_2SO_4

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ABSTRACT

The anti-corrosion potential of an aqueous leaves extracts of *rosa-sinensis* plant in 0.5M H_2SO_4 **s**olution was systematically studied to control its inhibitory effect on the corrosion of mild steel by weight-loss method, potentiodynamic polarisation technique and electrochemical impedance spectroscopy (EIS). When the concentration of the inhibitor solution is increased, the inhibition efficiency of rosa-sinensis plant leaves extract on mild steel corrosion in 0.5M H_2SO_4 solution increases. The maximum inhibition efficiency has been reached by an aqueous leaves extract of *rosa-sinensis* plant inhibitor is 97.83% and the corrosion rate is decreased. This is due to the adsorption of phytochemical constituents present in the *rosa-sinensis* plant leaves extract. The effect of temperature has been studied at different temperatures ranges from 3030 K to 333 K. The corrosion rate is increased and inhibition efficiency decrease at a maximum temperature of 333 K. The adsorption of *rosa-sinensis* plant leaves on mild steel obey the tempkin and Langmuir adsorption isotherms. Potentiodynamic polarization measurement shows that *rosa-sinensis* plant leaves extract acts as an anodic type inhibitor and control the anodic reaction predominantly. The results of electrochemical impedance tests and polarization measurements were found to agree. The surface morphology of polished mild steel, mild steel was immersed in 0.5M H_2SO_4 (blank) and mild steel was immersed in 0.5M H_2SO_4 with 10% aqueous leaves extract of *rosa-sinensis* plant (inhibitor system) have been characterized by SEM and AFM. Scanning electron microscopy (SEM) and AFM studies confirmed that the inhibition of corrosion of mild steel takes place through the adsorption of the aqueous leaves extract of *rosa-sinensis* plant molecules on the surface of mild steel.

Keywords: Acid Corrosion, Acid inhibition, AFM, EIS, Mild steel and *Jasminum sambac* plant

INTRODUCTION

Corrosion inhibitor in acidic medium is one of the most challenging and thrust areas in the current research, due to its potential applications in industries such as acid pickling, industrial cleaning, acid descaling, oil-well acid in oil recovery and petrochemical processes **[1-5]**. The capability of a compound to act as a corrosion inhibitor is dependent on its ability to form a compact barrier film and the nature of adsorption of inhibitor on the metal surface. Many researchers reported the use of organic compounds as corrosion inhibitors to control the corrosion process. Organic compounds with heteroatoms, such as O, N, S, and numerous bonds, as well as inorganic compounds, make up the majority of well-known inhibitors **[6]**. Although many synthetic organic and heterocyclic compounds and inorganic compounds show good anticorrosive properties. But most of them are highly toxic to both human beings and environments so it is very difficult to use as corrosion inhibitors in controlling the corrosion of metal in acid medium **[7]**.

The dangers of most synthetic organic inhibitors, as well as stringent environmental restrictions, have prompted researchers to focus on the need to produce inexpensive, non-toxic, and environmentally acceptable inhibitors such as natural goods and plant extract leaves. Natural product extracts are regarded as a vast source of naturally generated chemical compounds that may be extracted using simple, low-cost techniques that are biodegradable. As a result, they can be employed as corrosion inhibitors to prevent the mild steel from corroding in various environments **[8]**. Environmentally friendly, ecologically acceptable, affordable, readily available, and renewable materials such as an aqueous leaves extract of the *rosa-sinensis* plant are important to study topics.

The main objective of the present study is to evaluate the anti-corrosion potential of *rosa-sinensis* plant leaves extract on the mild steel corrosion in 0.5M H_2SO_4 using weight loss, and electrochemical techniques (OCP, potentiodynamic polarization, EIS). The temperature studies have been carried out at different temperature ranges from 303 to 333 K. The adsorption of *rosa-sinensis* on mild steel obeys the tempkin and Langmuir adsorption isotherms. The attained results were confirmed by surface morphology analysis of the surface layer of the mild steel using FTIR, SEM and AFM instruments.

MATERIALS AND METHODS

The mild steel specimens were picked from the same sheet with the following composition: 0.1 % carbon, 0.026 % sulfur, 0.06 % phosphorus, 0.4 % manganese, and the balance iron. Mild steel specimens with dimensions of 1.0 4.0 0.2 cm were polished to a mirror finish, degreased with trichloroethylene, and utilized in weight-loss and surface evaluation experiments **[9]**.

In potentiodynamic polarisation tests, a mild steel rod encapsulated in Teflon with an exposed cross-section of 1 cm area was employed as the working electrode. The electrode's surface was polished to a mirror finish before being degreased using trichloroethylene. Dilution of an analytical grade sulphuric acid with double distilled water yielded the medium (0.5M H_2SO_4).

Inhibitor preparation

Double distilled water and analytical reagents-grade (AR Grade) were used for preparing solutions. *Rosa-sinensis* plant leaves were dried for 6 hours in an oven at 70^{o}C and grinding to powdery form and 10 grams of the powder of *rosa-sinensis* plant leaves was refluxed in 100 ml double distilled water for 1 hour. The extract of the plant leaves was prepared by evaporating the filtrate. The needed amounts of solution were generated using residues in a 0.5M H_2SO_4 aqueous solution.

Weight loss method

Among many experimental methods available to determine the %age of inhibition efficiency and corrosion rate, the weight loss method is the simplest and frequently used method. In this study, the experiments were carried out by varying the concentrations of the inhibitor and the immersion period was fixed as 3 hours. The difference in weight of the metal specimen before and after immersion in the corroding fluid is the weight loss calculated in grams. The findings are discussed to determine the effect of concentration.

$$IE = 100[1-(w_2-w_1)]\ \% \longrightarrow \quad (1)$$

Where w_1 is the weight loss in the absence of inhibitor and w_2 is weight loss in the presence ofinhibitor and temperature **[10]**.

The inhibition efficiency increases due to the inhibitor molecules present in plant leaves extract getting adsorbed on the mild steel surface **[11]**. The maximum inhibition efficiency and the lower corrosion rate is found at a high concentration 10% wt /v for the inhibitor system. With a further increase in inhibitor concentration above 10%, the inhibition efficiency and corrosion rate almost remained constant. So the 10% concentration is fixed as the concentration for maximum inhibition. This concentration corresponds to the attainment of a saturation value in surface coverage of mild steel.

Effect of concentrations

From the stock solution, various concentrations of the plant extract leaves were prepared in aqueous media. Different concentrations of the inhibitor used in the study are 2, 4, 6, 8 and 10 (%v/v).

Effect of temperature

The temperature effect would be high on mild steel corrosion in an acid medium. Inhibitor efficiency depends on temperature was used to determine activation energy (E_a) of corrosion of the mild steel in the presence and the absence of the inhibitors. It was used to identify the mechanism of the action of inhibitor on mild steel corrosion. The temperature factor is the most important parameter in corrosion studies and also the effect of the temperature on the inhibitive nature is examined by the weight loss method. The study of temperature effect on corrosion at different concentrations of the inhibitor in the temperatures (303, 313, 323 and 333K) for the immersion period of 3 hours has been adopted **[12]**.

Adsorption isotherm

Phyto-constituents present in the aqueous extracts are possibly adsorbed on the mild steel surface and the degree of adsorption depends on, the temperature and the electrochemical potential at the metal solution interface. Adsorption isotherms provide details about the interaction among the adsorbed molecules among themselves and also their interactions on the metal surface. The fittest isotherm was found by measuring the degree of surface covering (ϴ) concerning varied inhibitor concentrations and temperatures. The following two isotherms were used to fit the experimental data **[13]**.

Electrochemical methods

The measurements of the electrochemical impedance and potentiodynamic polarization were done using a PC-controlled electrochemical impedance analyzer model CHI6608 Microcell kit Princeton electrochemical Analyzer system with Electrochemistry software. These measurements proceeded in a classical three-cell electrode cell with an overall volume of 100 ml. The used reference and counter electrodes were a saturated calomel electrode and a cylindricalshaped graphite electrode, respectively **[14]**. Before each run, the mild steel working electrode was abraded using emery sheets of various grades and rinsed. This working electrode had a surface area of 3.14 cm2. To perform the OCP test, the working electrode was immersed in both uncontrolled and inhibited acidic solutions. The potential change began with the OCP (Eocp) during polarisation measurements in both anodic and cathodic directions, with a scan rate of 0.17 mV s–1. To give Eocp adequate time to stabilize, the electrode was submerged in the testing solution for 30 minutes.

Surface Characterization

FT-IR spectral analysis

Perkin Elmer FT –IR spectrophotometer was used to record the FT-IR spectrum from 4000 to 400 cm^{-1}. The adsorbed plant leaves extract inhibitor on the metal surface have been analyzed by FT-IR spectra. After it was scratched from the mild steel surface, which was immersed in 0.5 M H_2SO_4 in the presence of all the studied plant leaf extract inhibitors for 3 hours at room temperature **[15]**.

Scanning Electron Microscope (SEM)

It was used to investigate the differences like mild steel surfaces before and after they were in direct touch with the corrodent solution, as well as the effect of adding an inhibitor **[16]**. Thus SEM was used to analyze the topography of the mild steel surface after corroding in the presence and absence of the inhibitor. The SEM image was taken by the SEM instrument, JEOL MODEL JSM 6390.

Atomic Force Microscopy (AFM)

Surface morphology was also characterized by using an atomic force microscope. Following the inhibition test, the mild steel specimens were placed in vacuum desiccators, mounted on a sample holder beneath the objective of an atomic force microscope, and 3D images of the 100 magnified surface were captured using a computer operating program. AFM analysis was used to analyze the surface of mild steel specimens after three hours of immersion in 0.5M H_2SO_4 solution in the absence and presence of aqueous leaves extract of rosa-sinensis plant **[17]**. From the AFM cross-sectional 3D – image, the line and surface roughness parameters of the specimens such as R_a, R_q and peak to valley value were obtained for the mild steel after immersion in 0.5M H_2SO_4 in the absence and presence of the inhibitor.

RESULTS

Results of weight loss method

Table 1 shows the inhibition efficiency (IE) and corrosion rates (CR) of mild steel immersed in 0.5M H2SO4 in the absence and presence of the rosa-sinensis plant inhibitor obtained by the weight loss method. It is observed that 10% of the aqueous leaves extract of *rosa-sinensis* offers 97.83% of inhibition efficiency in an aqueous solution of 0.5M H_2SO_4.

Results effect of temperatures of *rosa-sinensis* leaves extract on mild steel corrosion

In corrosion studies, the effect of temperatures plays a major role to get an idea about the adsorption mechanism of inhibitors on mild steel surfaces. In this case, the corrosion efficiency and corrosion rate are determined for the RSPLE inhibitor system from 2 - 10% v/v with temperatures ranging from 303-333 K. The data of inhibition efficiency and the corrosion rate of RS plant leaves extract are mentioned **(Table 2)**.

Langmuir adsorption isotherm

The degree of surface coverage (Θ) for different concentrations of inhibitors (2, 4, 6, 8 and 10 % (v/v)) at different temperatures (303, 313, 323 and 333K) has been found from the weight loss method. According to Langmuir isotherm, the following equation relates the surface coverage (Θ) and the inhibitor concentration C.

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

Where,

K_{ads} is the equilibrium constant for the adsorption process.

The K_{ads} is related to ΔG^0_{ads} by the following equation,

$$K_{ads} = \frac{1}{CH_2O} \exp\left(\frac{\Delta G^o_{ads}}{RT}\right)$$

Where, R = gas constant,

T= temperature and

C H_2O = 55.55 mol. dm^{-3}. The plots of Langmuir adsorption isotherm, C/Θ Vs. C at different temperatures is shown in **(Figure 1)** for RSPLE studied inhibitor at different temperatures.

The values of adsorption parameters obtained from Langmuir adsorption isotherm, including ΔG^o_{ads}, R^2, slope, intercept of the inhibitor system RSPL on mild steel surface are enlisted **(Table 3)**.

The negative values of ΔG^o_{ads} ensure the spontaneity of the adsorption process and the stability of adsorbed layer on the steel surface. The ΔG^o_{ads} is calculated from the equation

$$-\Delta G^o_{ads} = -2.303\,RT \log(K_{ads} \times 55.55)$$

Temkin adsorption isotherm

The Temkin adsorption isotherm is based on the assumption of uniform distribution of the RSPLE inhibitor (monolayer) on the mild steel surface. The adsorption energy linearly decreases with the increase of surface coverage values (Θ). The values of surface coverage Θ, at various concentrations of RSPLE inhibitor in 0.5M H_2SO_4 solution obtained from weight loss measurements, were fitted to Temkin adsorption isotherm shown below

$$\exp(-2a\theta) = K_{ads}.C$$

$$\Theta = -2.303 \log K_{ads} / 2a - 2.303 \log C/2a$$

Where "a" denotes the lateral molecular interaction parameter. The adsorption of organic molecules at a mild steel-solution interface is a quasi-substitutional process between the inhibitor molecule (in aqueous solution) and a water molecule (on the mild steel surface).

$$Org_{sol} + H_2O_{ads} \longrightarrow Org_{ads} + H_2O_{sol}$$

Where, X is the size parameter and represents the number of adsorbed water molecules replaced by the given adsorbate (inhibitor molecule). The plot of ΘVs.log C for the mild steel in 0.5M H_2SO_4 in the absence and the presence of inhibitor system RSPLE is given in **(Figure 2)** for various temperatures.

Electrochemical analysis

The electrochemical measurements extend a way for calculating the rate of corrosion of mild steel. It permits quick evaluation of the performance of inhibitor, the durability of surface film and also the rate of corrosion.

The following techniques were used for mild steel corrosion in 0.5M H_2SO_4 in the absence and the presence of the inhibitor, aqueous extract of *rosa-sinensis* plant to know whether they are cathodic or anodic or mixed type inhibitor and also to formulate an appropriate mechanism for their inhibition action on the corrosion of mild steel.

Potentiodynamic polarization method

A polarization study has been used to confirm the formation of protective film on the mild steel surface during the corrosion inhibition process. The linear polarization resistance values (LPR) increase, the corrosion current value (Icorr) drops, and the corrosion potential increases when a protective coating is produced on the mild steel surface (Ecorr). **Figure 3** shows the potentiodynamic polarization curves of mild steel immersed in a 0.5M H_2SO_4 aqueous solution in the absence and presence of rosa-sinensis plant leaves extract.. The corrosion parameters are given in **Table 5**.

Analysis of results of AC impedance spectra

AC impedance spectra of mild steel immersed in 0.5M H_2SO_4 in the absence and presence of RSPL inhibitor system are shown in **Figure 4** (Nyquist plots) and

Figure 5 (Bode plots).

The AC impedance spectra of mild steel immersed in various solutions were recorded. The AC impedance parameters, namely, charge transfer resistance (R_t) and double-layer capacitance (C_{dl}) are given in **Table 6**.

Analysis of results of FTIR spectra

FT-IR analysis helps to identify the absorption bands for the functional groups and the alignment of inhibitor molecules on the mild steel surface. Many of the researchers have found that FT-IR studies are a major tool that can be used to predict the nature of bonding of phytochemical components of the inhibitor on the mild steel surface. The absorption bands of the functional groups present in corresponding systems are given in **Table 7**. FTIR spectrum of aqueous leaves extract of RSP is shown in **Figure 6a**. The OH stretching frequency appears at 3466.13 cm^{-1}.

SEM Analysis of mild steel surface

SEM micrographs of the mild steel surface are studied to determine the nature of the film created in the absence and presence of the aqueous extract of plant leaves inhibitor on the mild steel surface, as well as the level of mild steel corrosion. The mild steel surface is observed using a scanning electron microscope (SEM). **Figure 7 (a, b, and c)** show SEM images of mild steel specimens immersed in 0.5M H_2SO_4 for three hours in the absence and presence of an inhibitor system.

Results of Atomic force microscopy

It is a most important tool to evaluate the morphology of surfaces for different samples at nano-micro scales. In the present investigation, the effect of corrosion inhibitors on the surface of mild steel in an acid medium is analyzed with the help of AFM.

Major important parameters from the 3D images of AFM analysis are average roughness R_a, root means square roughness R_q and peak-to-valley value are observed. Among all the parameters, the average roughness R_a calculated from the average deviation of roughness, for all points from a mean line over the evaluation length, plays an important role in giving an idea about the nature of the protective adsorbed layer on the surface of the mild steel.

Figures 8a and 8b show the 3D AFM morphologies and AFM cross-sectional profiles of polished mild steel and mild steel following immersion in 0.5M H_2SO_4 for 3 hours at room temperature, respectively. **Figure 8c** shows the AFM cross-sectional pictures of the mild steel specimen after being immersed in 0.5M H2SO4 for 3 hours at room temperature in the presence of high quantities of JS plant leaves extract.

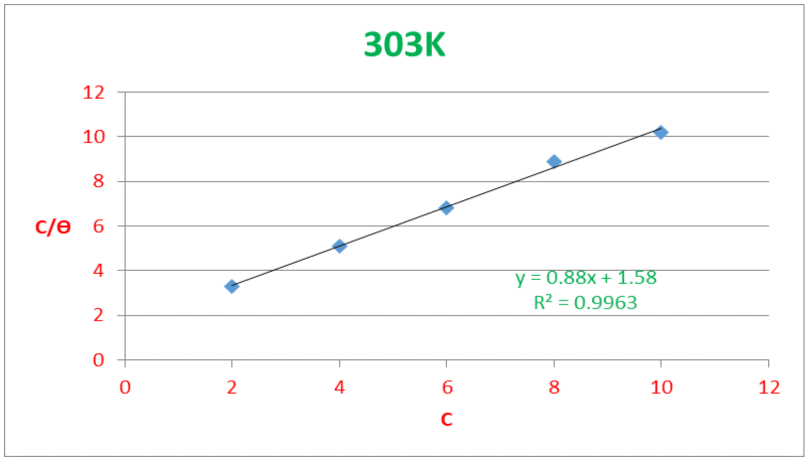
The different parameters R_q, R_a and R_y from the AFM images of mild steel surface are given in **Table 4** for the polished mild steel and that after immersion in the absence and presence 10% of inhibitor with aqueous extract of RSPL. The analysis of values from **Table 4** indicates that the average roughness R_a parameter is reached very high for the blank. The small average roughness R_a is noticed for the polished mild steel. It is found that the R_a values after the mild steel are immersed in 0.5M H_2SO_4 in the presence of the aqueous extract of RSPL inhibitor at high concentration, is in between the blank and polished mild steel. It is lower than that of the blank and greater than that of the polished mild steel surface, implying the formation of a protective film on the mild steel surface **[33-34]**. The root means square roughness R_q, is the average of the measured height deviations measured from the mean line.

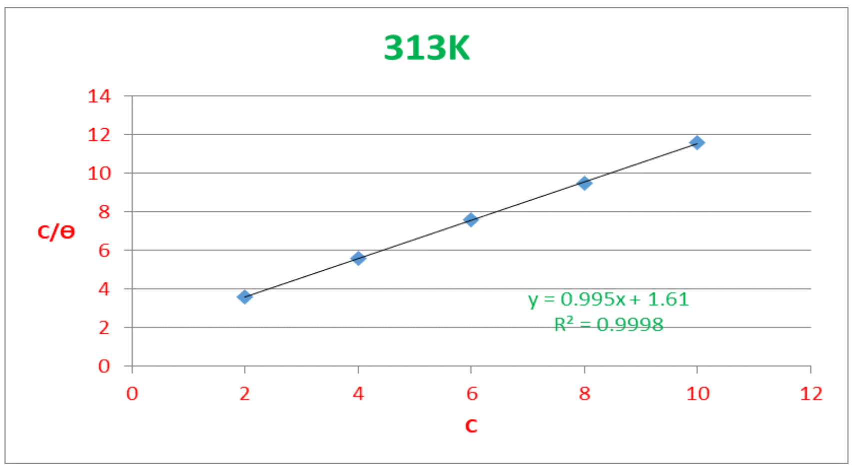
Table 1: Inhibition efficiency of aqueous leaves extract of *rosa-sinensis* plant on the corrosion of mild steel in 0.5M H_2SO_4 at room temperature (303K)

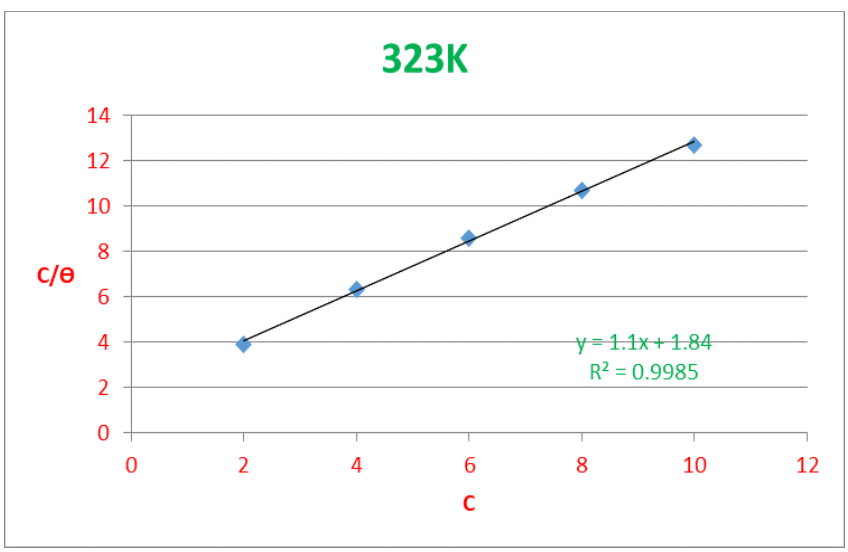
Concentration of RSPL Inhibitor (% wt/v)	Corrosion rate (mdd)	Inhibition Efficiency (%)
blank	328.13	-
2	128.42	60.87
4	71.33	78.26
6	39.23	88.04
8	32.10	90.22
10	7.13	97.83

Table 2: Inhibition efficiency of aqueous leaves extract of RSP on the corrosion of mild steel in 0.5M H_2SO_4 at different temperatures

Temperature (K)	RSPLE Inhibitor (% v/v)	Corrosion rate (mdd)	Inhibition efficiency (%)
303	Blank	328.13	-
	2	128.42	60.87
	4	71.33	78.26
	6	39.23	88.04
	8	32.10	90.22
	10	7.13	97.83
313	Blank	467.23	-
	2	206.87	55.72
	4	135.53	71.03
	6	99.87	78.65
	8	74.90	84.06
	10	64.20	86.35
323	Blank	542.13	-
	2	267.50	50.75
	4	196.10	63.84
	6	164.07	69.73
	8	135.53	75.02
	10	114.13	78.91
333	Blank	677.70	-
	2	378.10	44.24
	4	267.50	60.55
	6	228.30	66.36
	8	206.87	69.57
	10	171.20	74.74


303K
c/ө
c
y = 0.88x + 1.58
R² = 0.9963


313K
c/ө
c
y = 0.995x + 1.61
R² = 0.9998


323K
c/ө
c
y = 1.1x + 1.84
R² = 0.9985

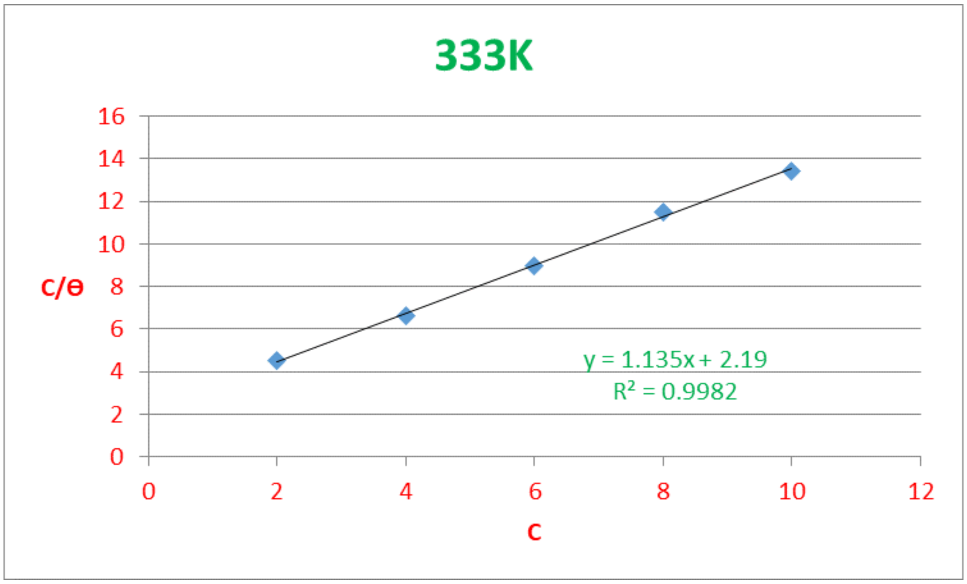


Figure 1: At different temperatures, the inhibitory effect of aqueous extract of RSPL on mild steel corrosion in 0.5M H_2SO_4 was shown using the Langmuir adsorption isotherm

Table 3: Langmuir adsorption isotherm parameters for the aqueous extract of RSPL on the corrosion of mild steel in 0.5M H_2SO_4

Inhibitor system	Temperature (K)	R^2	Slope	Intercept	K_{ads}	$-\Delta G^O_{ads}$ KJ mol^{-1}
Aqueous extract of RSPL	303	0.996	0.880	1.58	0.638	8.970
	313	0.999	0.995	1.61	0.601	9.214
	323	0.998	1.100	1.84	0.540	9.150
	333	0.998	1.135	2.19	0.452	8.950

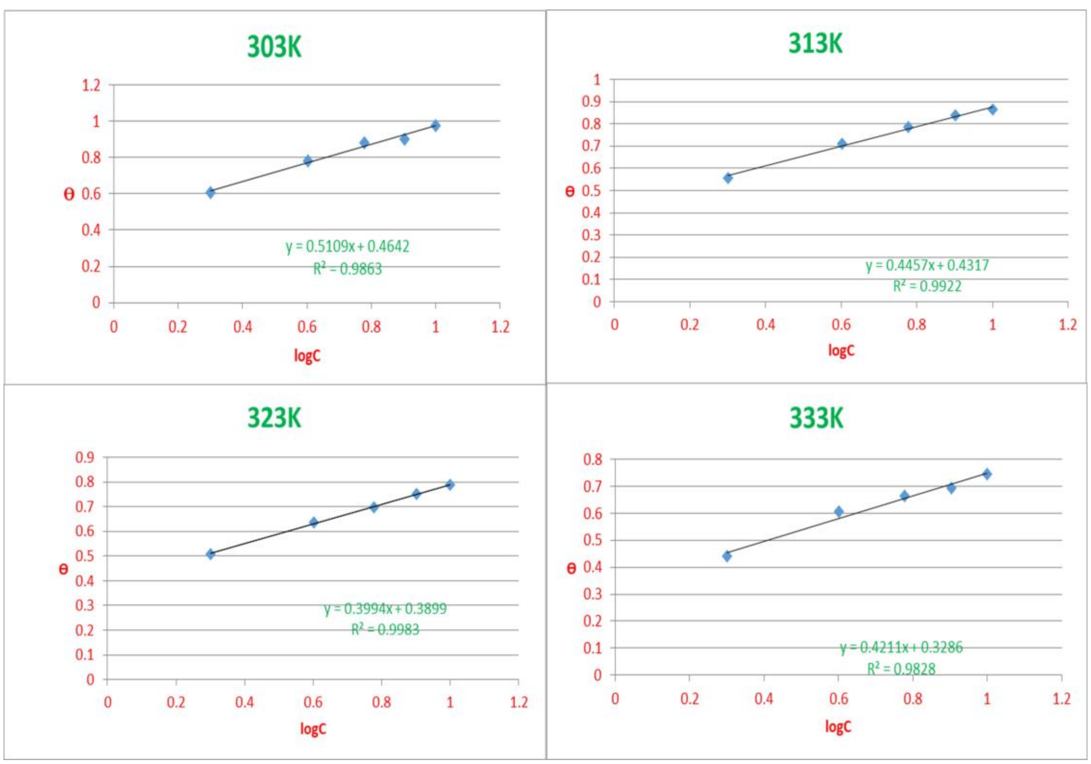


Figure 2: Temkin adsorption isotherm plot for the inhibition effect of aqueous extract of RSPL on mild steel corrosion in 0.5M H_2SO_4 at different temperatures

Table 4: Temkin adsorption isotherm parameters for the corrosion inhibitive effect of aqueous extract of RSPL on the mild steel corrosion in 0.5M H_2SO_4

Inhibitor system	Temperature (K)	R^2	Slope	Intercept	-a	K_{ads}	$-\Delta G^O_{ads}$ KJ mol^{-1}
Aqueous extract of RSPL	303	0.9863	0.5109	0.4642	2.25	8.103	15.391
	313	0.9922	0.4457	0.4317	2.58	9.306	16.259
	323	0.9983	0.3994	0.3899	2.88	9.466	16.820
	333	0.9828	0.4211	0.3286	2.73	6.032	16.097

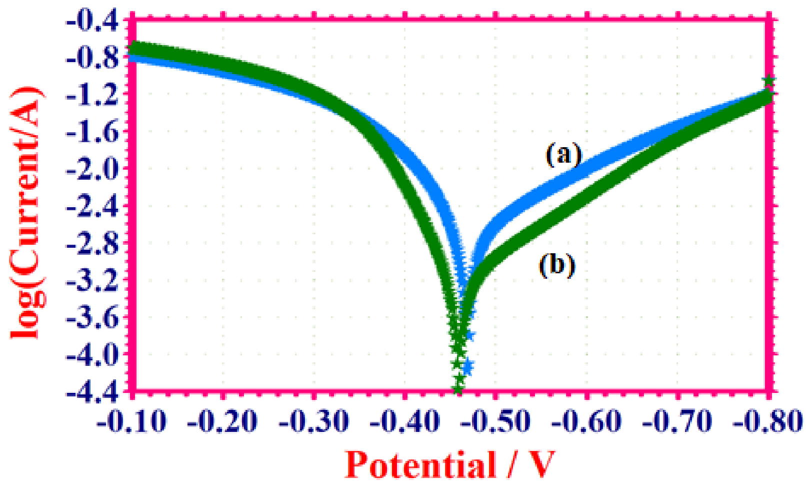


Figure 3: Potentiodynamic polarization curves for corrosion of mild steel in 0.5M H_2SO_4 in absence and presence of RSPLE inhibitor
(a) Mild steel in 0.5M H_2SO_4 (blank); b) Mild steel in 0.5M H_2SO_4 with 10% aqueous extract of RSPL

Table 5: Potentiodynamic Polarization parameters for the corrosion of mild steel in 0.5M H_2SO_4 for the aqueous extract of RSPL system

Concentration of the aqueous extract of RSPL (%V/V)	E_{corr} mV/SCE	Tafel slope		I_{corr} A / cm^2	LPR Ω/cm^2
		ba, mV/dec	bc, mV/dec		
blank	- 468	127	185	3.459×10^{-3}	9.5
10	- 459	079	157	9.335×10^{-3}	24.5

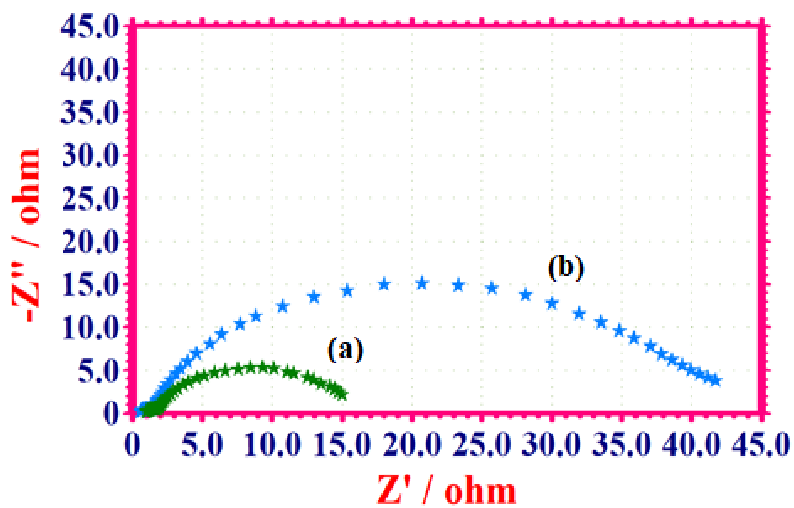


Figure 4: AC impedance spectra of mild steel immersed in to 0.5M H_2SO_4 in the absence and presence of RSPLE inhibitor (Nyquist plots)
(a) Mild steel in 0.5M H_2SO_4 without inhibitor; (b) Mild steel in 0.5M H_2SO_4 with 10% aqueous extract of RSPL

Table 6: Electrochemical impedence parameters from Nyquist plots for the corrosion of mild steel for aqueous extract of RSP leaves in 0.5 M H_2SO_4

Concentration of the aqueous leaves extract of RSP (%v/v)	Nyquist plot		Impedance Log (z/ohm)
	R_t, Ω/cm^2	C_{dl} F/cm^2	
blank	13.88	2.108026×10^{-6}	1.17248
10	40.82	6.197184×10^{-6}	1.40510

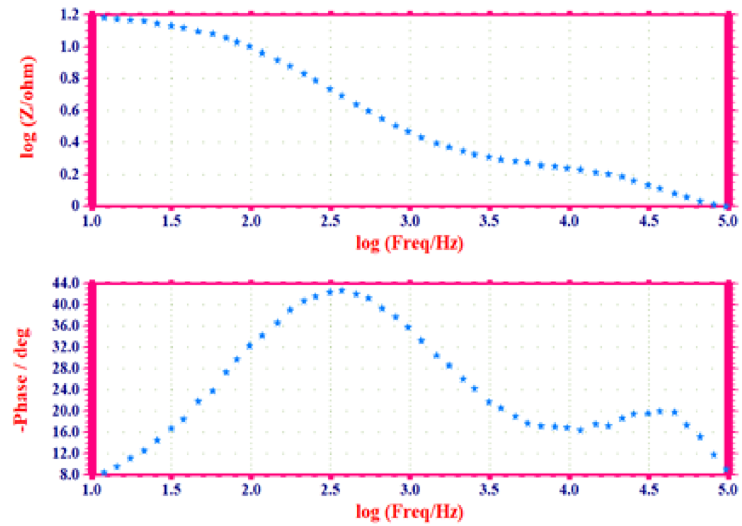


Figure 5a: AC impedance spectra (Bode Plot) of mild steel immersed in 0.5M H_2SO_4

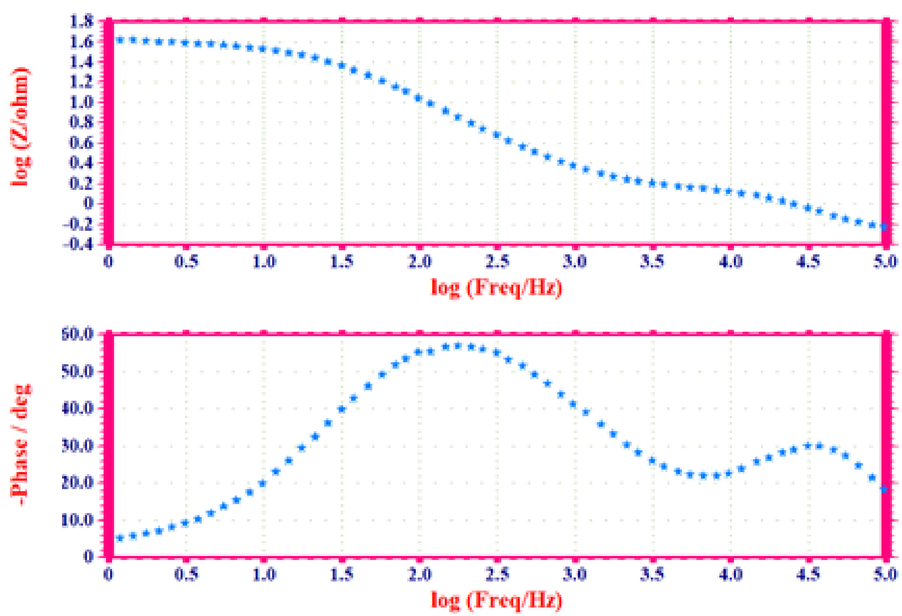


Figure 5b: AC impedance spectra (Bode Plot) of mild steel immersed in 0.5 M H_2SO_4 with 10% aqueous extract of RSPL

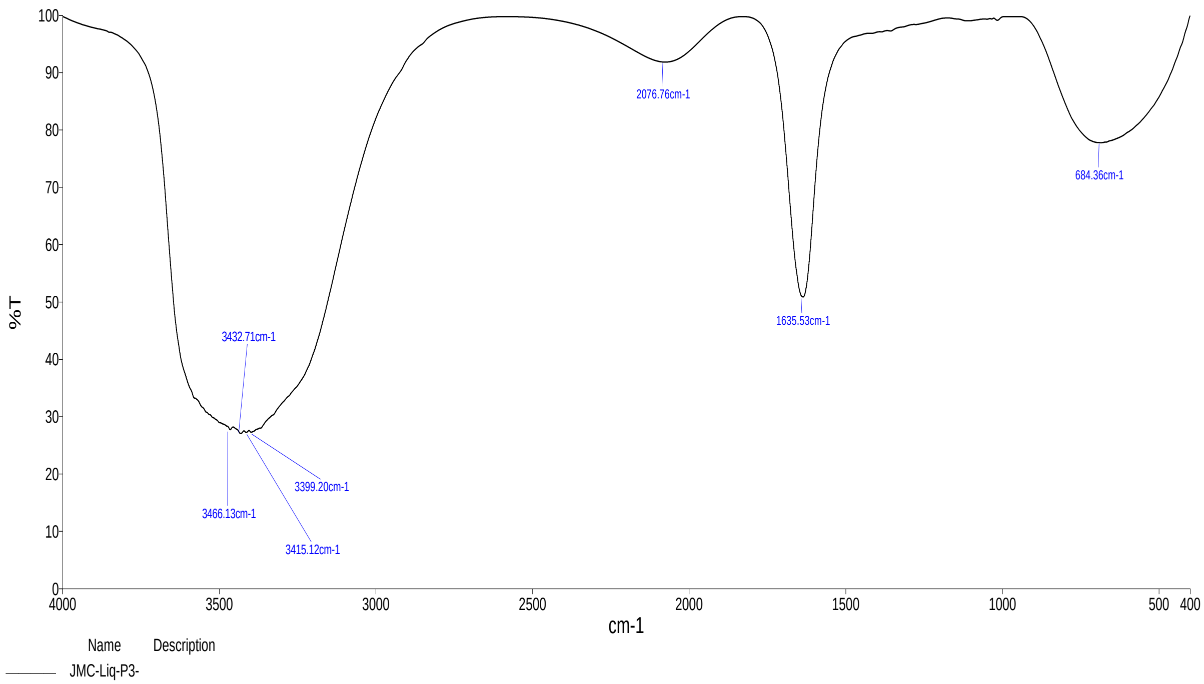


Figure 6a: FT-IR spectrum of aqueous extract of RSPL

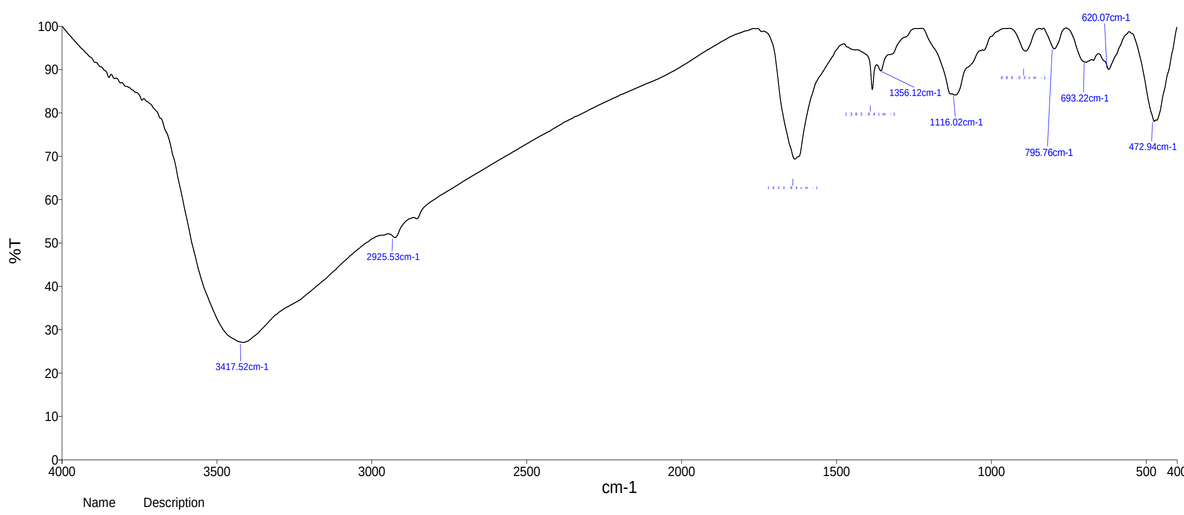


Figure 6b: FT-IR spectrum of scratched film from the mild steel surface after immersion in 0.5M H_2SO_4 with 10% aqueous extract of RSPL

Table 7: FT-IR spectral data for the crude aqueous extract of RSPL and the scratched film from mild steel surface after immersion in 0.5M H_2SO_4 with 10% RSPL inhibitor system

IR bands of crude RS plant leaves extract	IR Bands of film from mild steel surface	Frequency assignment to functional groups
3466.13	3417.52	-OH
3399.20	-	N-H stretching
2076.76	2925.53	C-H stretching
1635.53	1633.84	C-O stetching
-	1116.02	C-C stretching
-	889.03	C=C
684.36	693.22	N-H
-	620.07	CH “oop”
-	472.94	Y-Fe_20_3

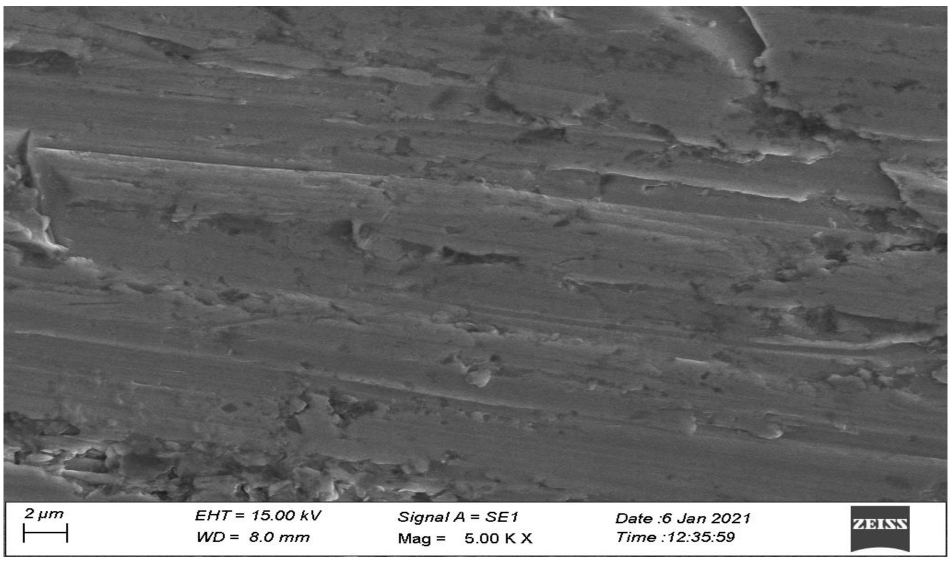


Figure 7a: SEM image of polished mild steel specimen before immersion in 0.5M H_2SO_4 (control)

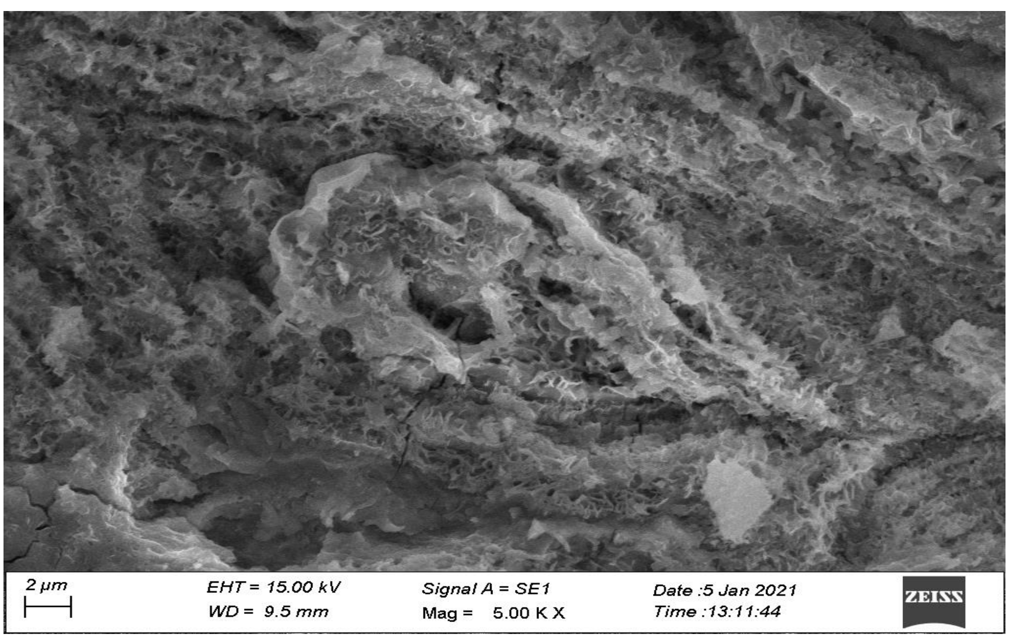


Figure 7b: SEM image of mild steel specimen after immersion in 0.5M H_2SO_4 (blank)

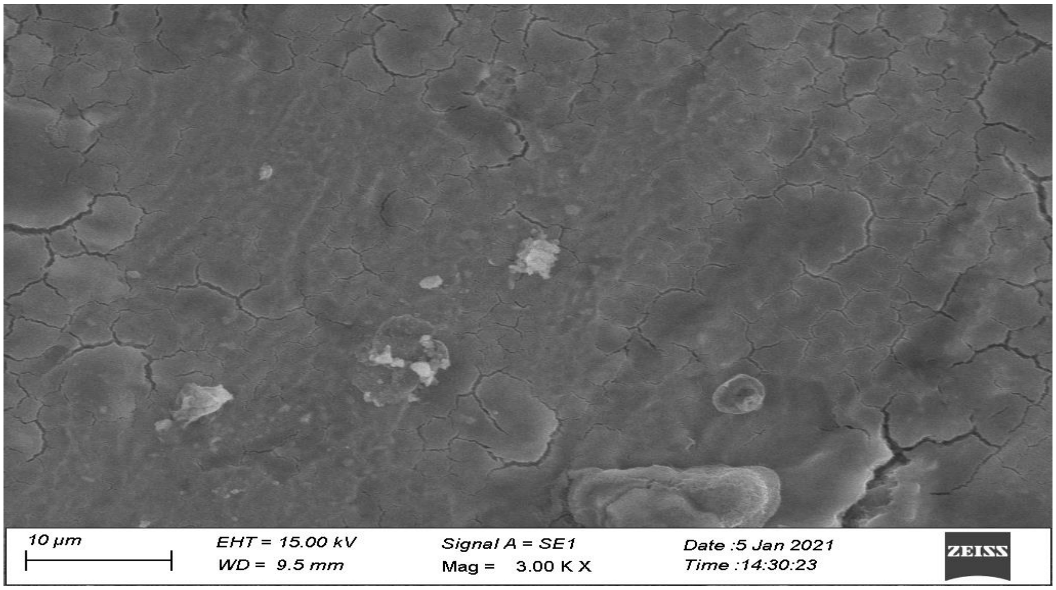


Figure 7c: SEM image of mild steel specimen after immersion in 0.5M H_2SO_4 in the presence of 10% aqueous extract of JSPL

Table 8: AFM surface and line roughness data for aqueous extract of RSPL systems

Systems	Average roughness (R_a)	Root mean Square roughness (R_q)	Maximum peak to valley (P-V) height
Polished mild steel	**180.64**	**222.09**	**1558.8**
Mild steel +0.5M H_2SO_4	**604.44**	**749.65**	**4283.3**
Mild steel + 0.5M H_2SO_4 with 10 % of aqueous extract of RSPL	**159.04**	**199.85**	**1367.6**

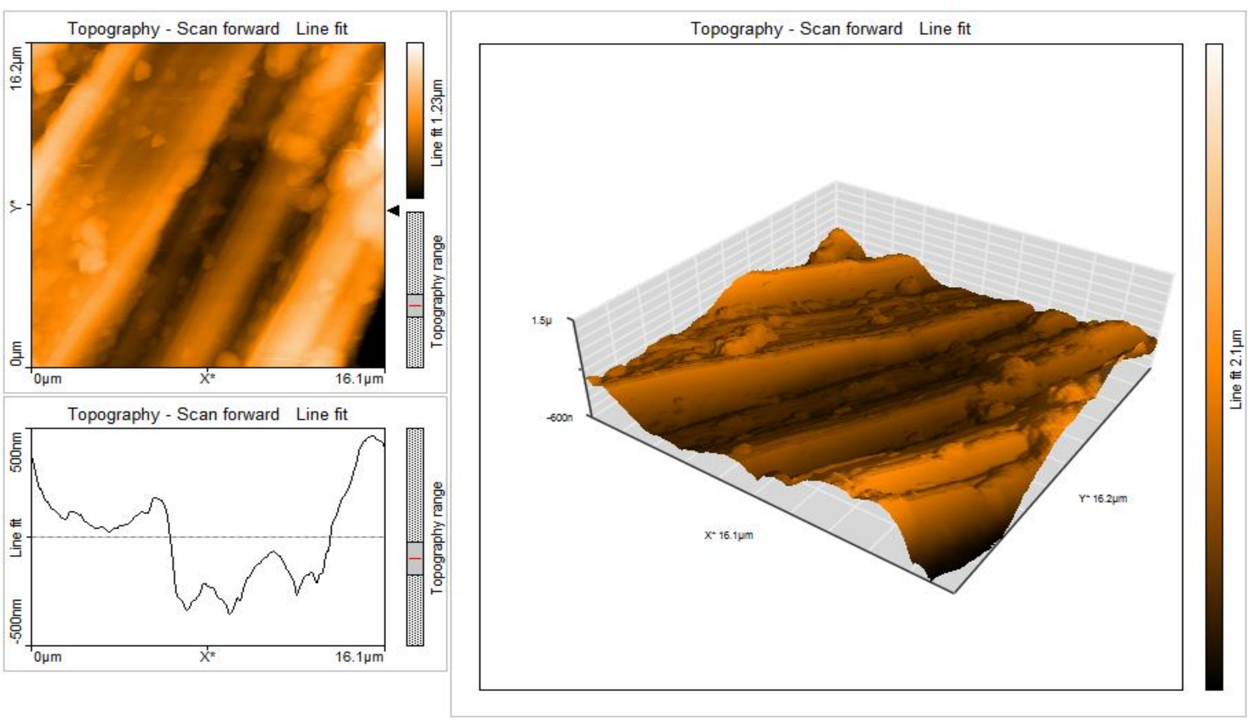


Figure 8a: AFM cross sectional image of the polished mild steel surface (control)

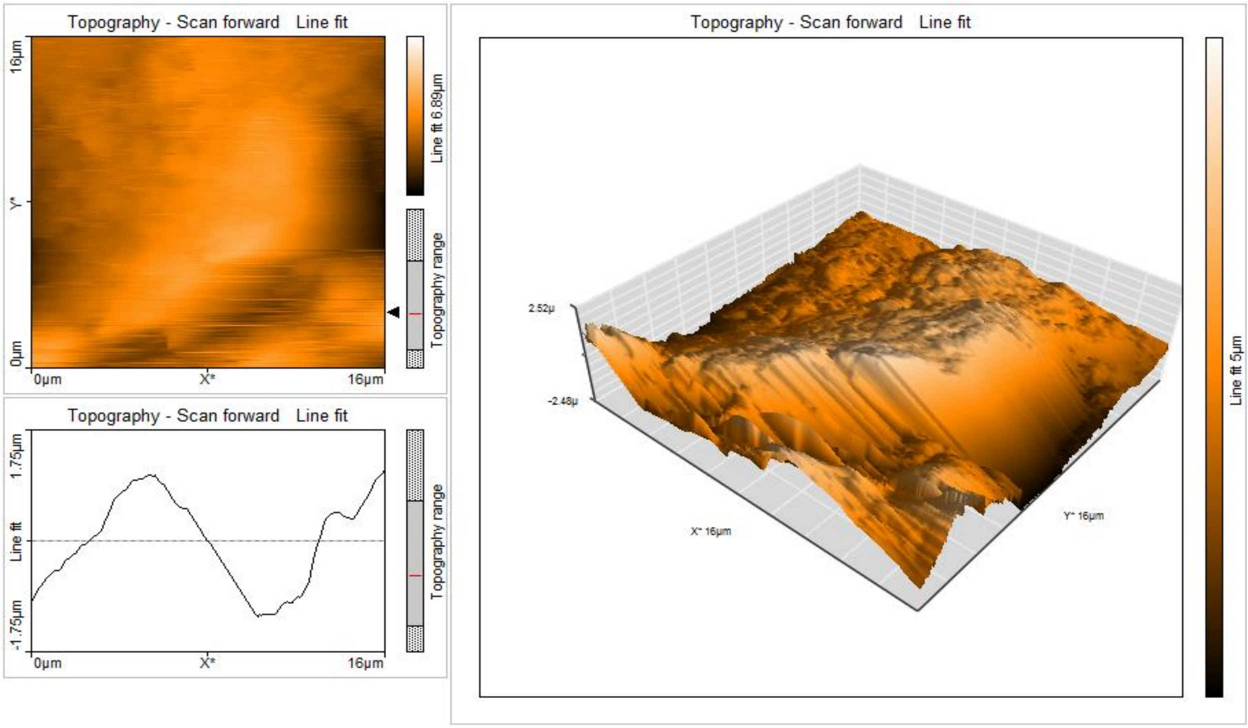


Figure 8b: AFM cross sectional image of the mild steel surface after immersion in 0.5M H_2SO_4 (blank)

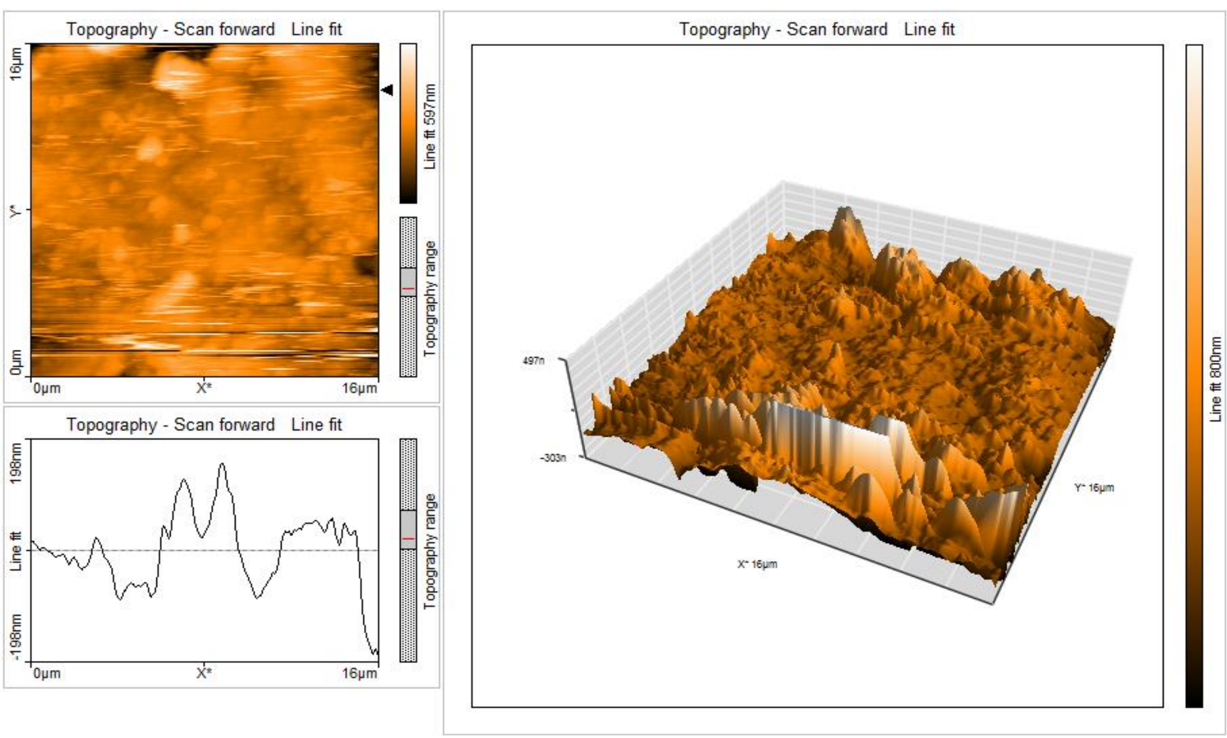


Figure 8c: AFM cross-sectional image for the mild steel surface after immersion in 0.5 M H_2SO_4 with 10% aqueous extract of RSPL

DISCUSSION

Analysis of weight loss method

It is observed from Table 1 that the aqueous extract of *rosa-sinensis* plant leaves shows good inhibition efficiency. As the concentration of the leaves extracts of *rosa-sinensis* plant increases, the inhibition efficiency increases. This is due to an increase of surface coverage at higher concentrations of the *rosa-sinensis* plant leaves which retards dissolution of mild steel **[18]**. The possibility of interaction between the heteroatoms present in the plant leaves extract and metal ions from the metal surface can be attributed to higher inhibition efficiencies. The presence of many phytochemical constituents in the plant extracts is responsible for the inhibition of mild steel corrosion. There may be reasons for the anti-corrosive actions of plant extracts. This surveillance is in good agreement with the results reported by many researchers **[19]**.

Analysis of temperatures of *rosa-sinensis* leaves extract on mild steel corrosion

The inhibition efficiency decreases from 97.83 to 74.74% and the corrosion rate is increased from 7.13 to 171.20 as the rise in temperature from 303 – 333 K in 0.5M H_2SO_4 at the higher concentration (10%) for RSP leaves extract. The effect of temperature increased with increasing inhibitor concentration on the dissolution of mild steel and the partial desorption of inhibitor molecule from the surface of the mild steel.

Langmuir adsorption isotherm

For the ideal Langmuir adsorption isotherm, the slopes of the plots are expected to be unity on the assumption that there is no interaction between the adsorbed inhibitor molecules and the surface of the mild steel **[20]**. However, the slope values depart from unity, indicating that the adsorbed inhibitor molecules on the mild steel surface are interacting. The inhibitor molecules deposited on the mild steel surface's anodic and cathodic sites interact by mutual repulsion (or) attraction **[21]**. The comparison of R^2 values obtained from Langmuir adsorption isotherm, at various temperatures shows that the isotherm fits better at 303 K than the other higher temperatures and it has been reported by many researchers. The R^2 values are greater than 0.9 showing that the Langmuir plots are linear. The K_{ads} values are high at 303 K for the inhibitor system RSPLE and decrease with the increasing temperatures, it indicates that the inhibitor is more strongly adsorbed on the mild steel surface at low temperature than at higher temperatures.

Temkin adsorption isotherm

Temkin isotherm plots, which are depicted in, are used to compute the values of intercept, slope, a, Kads, and Goads **(Table 4)**. The presence of repulsion in the adsorbed molecule layer on the mild steel surface is indicated by the negative 'a' value for the inhibitor system RSPL at various temperatures **[22]**.

The R^2 values at different temperatures are slightly < 9 for RSPL inhibitor system and approach unity. It indicates the weak correlation between Θ and log C for the inhibitor RSPL system. The value, $R^2 > 0.9$ for the inhibitor RSPL system.

The comparison of regression co-efficient, R^2 values indicates that Langmuir isotherm is highly fitting than the Temkin isotherm for the evaluated set of green inhibitors, reflecting that the studied inhibitors follow Langmuir adsorption isotherm more closely than the Temkin isotherm.

The negative ΔG^o_{ads} values indicate that the adsorption of inhibitor molecules from the aqueous extract of plant leaves on the mild steel surface is spontaneous. The ΔG^o_{ads} values up to -20 kJ $mol^{-1}$are consistent with physisorption and more than -40 kJ are consistent with chemisorptions **[23]**.

The high values of K_{ads} and low negative ΔG^o_{ads} values at a temperature ranging from 303-303K **(Table 4)** indicate that the physisorption occurs. However, chemisorption may not be excluded due to the nature of complex formation in the corrosion inhibiting process.

Results of potentiodynamic polarization method

It is observed **(Figure 3a)** that when mild steel is immersed in 0.5 M H_2SO_4, the corrosion potential is -0.468 mV Vs SCE (Saturated Calomel Electrode). The LPR value is 9.5 Ohm/cm^2. The corrosion current is 3.459 x10^{-3} A/cm^2.

When 10 % of RSPLE is added to the above environment the corrosion potential is shifted to the anodic side (-0.459 mV / SCE) **(Figure 3b)**. This indicates that the corrosion potential is shifted to the anodic side due to the formation of protective film over the mild steel surface. This film controls the anodic reaction of mild steel dissolution by forming Fe^{2+}-RSPLE complex on the anodic sites of the mild steel surface **[24-26]**. An increase in LPR and a decrease in I_{corr} values are indications of more corrosion-resistant nature.

Analysis of results of AC impedance spectra

When mild steel is immersed in 0.5M H_2SO_4, R_t value is 13.88 ohm cm^2 and C_{dl} value is 2.108026 × 10^{-6} F cm^{-2}. When 10% of RSPLE is added to 0.5M H_2SO_4, R_t value increases from 13.88 to 40.828 ohm cm^2. The C_{dl} decreases from 2.108026 × 10^{-6} to 6.197184 × 10^{-6} F cm^{-2}. The impedance value [log (z/ohm)] increases from 1.17248 to 1.40510. This suggests that a protective film is formed on the surface of the mild steel surface. Further, the phase angle increases from 42.61 to 56.80^o **[27 -28]**.

Analysis of results of FTIR spectra

The OH stretching frequency appears at 3466.13 cm^{-1}[36]. The N-H stretching frequency appears at 3399.20 cm^{-1}. The C-H stretching frequency appears at 2076.76 cm^{-1}. The peak due to C-O appears at 1635.53 cm^{-1}. The N-H frequency appears at 684.36 cm^{-1} **[29]**.

A Protective thin film is formed on the surface of the mild steel immersed in 0.5M H_2SO_4 with 10% aqueous extract of RSPL is shown in Fig.V.1.8b. A shift of the O-H stretching from 3466.13 to 3417.52 cm^{-1} indicates that molecular adsorption possibly occurs via O-H [30]. The shift in frequency from 2076.76 to 2925.53 cm^{-1} are noticed for the C-H group. The shift in frequency from 1635.53 to 1633.84 cm^{-1} are noticed for the C-O group. The N-H frequency is shifted from 684.36 cm^{-1} to 693.22 cm^{-1}. The new peaks at 1116.02 cm^{-1} and 889.03 cm^{-1} are noticed for C-C and C=C groups respectively. The peaks at 620.07 cm^{-1} are attributed to CH oop. The band 472.94 cm^{-1} considerably originates mainly from Fe-complex **[31]**. All the above bands indicate the formation of a complex on the mild steel surface.

SEM analysis of mild steel surface

The SEM micrographs of polished mild steel surface (control) in **Figure 4a** show the smooth surface of the mild steel. This shows the absence of any corrosion products / rough surface or inhibitor complex formed on the mild steel surface.

The SEM micrograph of the mild steel surface was immersed in 0.5M H_2SO_4 **(Figure 6b)** shows the roughness of the mild steel surface, which indicates the highly corroded area of mild steel**.**

However, **Figure 6c** indicates that in the presence of inhibitor (10 % of RSPLE) the rate of corrosion is suppressed, as can be seen from the decrease of corroded areas. The mild steel surface is almost free from corrosion due to the formation of the insoluble complex on the surface of the mild steel. The mild steel specimen’s smoothness show almost equal to the polished mild steel surface. In the presence of RSPLE, the surface is covered by a thin layer of inhibitor which effectively controls the dissolution of mild steel immersed in 0.5M H_2SO_4 with 10 % of aqueous extract of RSPL. Thus it is revealed that the inhibitor has increased the efficiency of adsorption at the mild steel/solution interface and thus the inhibitors tend to reduce metallic surface destruction **[32]**.

Analysis of results of Atomic force microscopy

A few pits in the corroded mild steel surface are visible in the blank system, and the polished mild steel surface has a minor roughness. When compared to the polished surface of the mild steel specimen in the blank system, it indicates that the roughness is larger **[33]**.

The measured R_q values of the JSPLE inhibitor system is lower than that of blank and higher than that of the polished system. The decrease in the R_q and R_a values reflects that the inhibitor molecules from the plant leave extract, are adsorbed on the mild steel surface, reducing the rate of corrosion and thereby increasing the efficiency of inhibition.

The values of the maximum peak-to-valley highest (P-V) is a largest single-peak-to-valley height in five adjoining sampling heights. The (P-V) height for the mild steel surface corroded in 0.5M H_2SO_4 is greater than that for the polished mild steel. The surface topography of the mild steel surfaces, in the presence of high concentrations of inhibitor, show that the (P-V) height is greater for the inhibited system compared to the polished system and less than that of the blank system.

Thus the greater surface roughness is observed for the mild steel specimen immersed in 0.5M H_2SO_4, without inhibitor than that of the polished mild steel specimen. It indicates the mild steel surface becomes rougher in acid medium, without the inhibitor. The roughness probably decreases, due to the protective barrier layer formation on mild steel surface on the addition of inhibitor and the surface becoming smoother. The parameters derived from the three-dimensional AFM morphologies and AFM cross-sectional profiles show that the R_q, R_a and R_y values for inhibitors decrease compared to those of blank studies **[35]**.

These observations prove that the surface is smoother, in presence of inhibitor due to the layer formation and also the protective film is in nanometer-scale of aqueous extract of JSPL inhibitor system in 0.5M H_2SO_4**.** It also proves the inhibitor JSPL has the maximum inhibition efficiency. The same trend is observed in weight loss as well as polarization and impedance analyses **[34]**.

CONCLUSION

The anti-corrosion potential of *rosa sinensis* plant leaves extract has been evaluated as a corrosion inhibitor in controlling the corrosion of mild steel immersed in 0.5 M H_2SO_4 solution. The maximum concentration of inhibitor is the lower corrosion rate and the higher corrosion inhibition efficiency. Weight loss experiment shows that the maximum inhibition efficiency of the high concentration of inhibitor is 97.83%. The temperature has influenced the rate of corrosion and inhibition efficiencies. At higher temperatures, the rate of corrosion is high and inhibition efficiency is low. At lower temperatures the corrosion rate is decreases and inhibition efficiency is increases. Electrochemical studies confirm the formation of a protective film over the mild steel surface. Polarization studies shows the aqueous leaves extract of *rosa sinensis* plant act as an anodic inhibitor which controls the anodic reaction preferably. FTIR was used to characterize the surface film. SEM and AFM revealed the formation of a surface film on the mild steel surface. Surface analysis such as SEM and AFM has been used to observe the microstructure of mild steel in the absence and presence of inhibitors. It showed that the *rosa sinensis* plant leaves extract to have effectiveness in preventing the corrosion of mild steel in 0.5M H_2SO_4 solution.

Conflict of Interest

The authors declare that there is no conflict of interest regarding the publication of this article.

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