Corrosion Inhibition of Mild Steel in Sulphuric Acid Using *Luffa Aegyptiaca* Leaves Extract

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Abstract The corrosion inhibition of mild steel (MS) in sulphuric acid using *Luffa aegyptiaca* (LA) leaves extract was investigated by weight loss studies, colorimetric measurements, potentiodynamic polarisation and electrochemical impedance spectroscopy. The adsorption of LA leaves extract was confirmed by Fourier transform infrared spectroscopy and optical profilometry. The inhibition efficiency increased with increasing concentration of the extract but decreased with rise in temperature and with the increase in acid strength. Furthermore, the inhibition efficiency synergistically increased on the addition of halide ions. Polarisation studies revealed that the LA extract acts as mixed-type inhibitor. Physical adsorption mechanism is proposed from the trend in inhibition efficiency with the change in temperature and from thermodynamic parameters. The adsorption of LA on MS surface obeys Langmuir adsorption isotherm and follows the kinetic thermodynamic model of El-Awady at all temperatures studied.

KEY WORDS: Mild steel; Adsorption; Corrosion; Thermodynamic properties; FTIR

1 Introduction

Acid solutions are widely used in industry for several processes such as acid pickling, industrial acid cleaning, acid descaling and oil well acidizing. Due to the aggressiveness of acid solution towards mild steel, the use of inhibitors for the prevention of metal dissolution is inevitable [1]. Most synthetic inhibitors are highly toxic and this has led to the investigations on the use of naturally occurring corrosion inhibitors which are not harmful to both human beings and the environment. Thus, plant extracts have attracted some attention as eco-friendly corrosion inhibitors for a few decades [2]. Plant extracts are incredibly rich source of natural chemical compounds that can be extracted by a simple

procedure at a low cost and are also biodegradable in nature. In recent years, volumes of the literature are available on the use of plant extracts as corrosion inhibitors for MS in acidic media [3–9]. Survey of the literature reveals that the leaves extract of *Luffa aegyptiaca* (LA) has so far not been tried as corrosion inhibitor. LA is an easily available plant belonging to cucurbitaceous family. The extract of LA contains numerous naturally occurring organic compounds which could get easily adsorbed on the metal surface. Hence an attempt has been made to study the inhibitive effect of acid extract of LA leaves on the corrosion of mild steel (MS) in sulphuric acid medium by weight loss measurements, colorimetric estimation, potentiodynamic polarisation and electrochemical impedance spectroscopy.

2 Experimental

2.1 Materials

The experiments were performed on MS with the following composition (in wt%): C 0.143, Ni 0.006, Mo 0.018,

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P 0.035, Si 0.041, Mn 0.271 and the balance is Fe. The aggressive solution of 0.5 mol/L H_2SO_4 was prepared by dilution of AR grade 98% H_2SO_4 with distilled water. Fresh LA leaves were picked and then cleaned with tap water to eliminate ash and mud, dried in shade and then ground to powder. The acid extract was prepared by refluxing 10 g of dried and milled LA leaves in 500 mL of 0.5 mol/L H_2SO_4 for 3 h and keeping it overnight for cooling. It was then filtered and the filtrate was stored in a standard flask. The acid extract of the LA leaves was subjected to various chemical tests using the procedure described in the literature [10] to identify the constituents present in it. It has been found that the extract contains alkaloid, saponins, terpenoids, flavonoids and glycosides as main constituents. The desired concentrations of the inhibitor were prepared by diluting the above stock solution with distilled water. The concentration range of ALA used was (0.04–0.36) vol%.

2.2 Mass Loss Measurement

The MS sheet was cut into small pieces of dimensions 1 cm × 5 cm × 0.15 cm and was abraded with a series of emery papers (grade 320, 500 and 800), washed with distilled water, degreased with acetone and dried. After weighing accurately using digital balance with sensitivity of ± 0.1 mg, specimens in triplicate were immersed in the test solutions for specified periods of immersion in the absence and presence of ALA. After a quantified interval of time, the specimens were removed, rinsed with water, dried in warm air then stored in a desiccator and then reweighed to determine the weight loss. The inhibition efficiency (IE), corrosion rate (CR) and surface coverage (θ) were obtained using the following equations:

$$\text{CR} = (K\Delta W) / (\rho At), \quad (1)$$

$$\text{IE} = ((W_0 - W) / W_0) \times 100, \quad (2)$$

$$\theta = (W_0 - W) / W_0, \quad (3)$$

where W_0 and W are the values of weight loss without and with inhibitor, respectively. ΔW is the weight loss in g, ρ is the density of coupon in g/cm^3 , A is the area of coupon in cm^2 and t is the exposure period in h.

2.3 Colorimetric Measurement

MS when placed in contact with aggressive medium, iron gets dissolved and goes into the solution. The amount of iron present in both uninhibited and inhibited experimental solutions due to immersion of MS for specified periods of time was determined colorimetrically using Spectronic 20 spectrophotometer. The principle behind colorimetric method is to find a chemical agent or agents that react

specifically with iron, so that a coloured solution results. The intensity of the colour depends quantitatively on the amount of iron in the sample. The chemical agents such potassium thiocyanate (KSCN) combine with iron to produce a distinctive red colour. This red colour intensifies as the iron concentration increases. The colorimetric procedure involves making up a series of standard iron solutions and treating them with potassium thiocyanate. The inhibited and uninhibited solutions were also treated with KSCN and the colour was compared with that of the standard solutions. This is done by using colorimeter. The colorimeter does this by measuring the absorbance of a specific wavelength of light as it passes through the coloured sample. Each of the standard iron solution absorbs the different amounts of light. The more the iron in the solution, the greater is the absorption. A standard graph was plotted between concentration of standard iron solution and absorbance. The procedure gives a straight line, called a calibration curve. From the calibration curve, the amount of the iron present in the sample was found by noting the concentration corresponding to the absorbance of the unknown solutions (uninhibited and inhibited). The IE was calculated using Eq. (4).

$$(\text{IE}) = ((W_0 - W) / W_0) \times 100, \quad (4)$$

where W_0 and W are the values of weight of the iron without and with inhibitor, respectively.

2.4 Electrochemical Measurements

The specimen with 7-cm long stem connected with clips for electrical conductance and mounted into cell to offer only one active flat surface having 0.9785 cm^2 surface area was exposed to the corrosive environment. Before each experiment, the electrode surface was cleaned with a sequence of emery papers of different grades (320, 500 and 800), washed with distilled water and degreased with acetone. Electrochemical studies, including potentiodynamic polarisation (PDP) and electrochemical impedance spectroscopy (EIS), were performed using CHI 604A model electrochemical analyser of CH instruments connected to a personal computer. A three-electrode cell assembly consisting of a MS coupon of the mentioned dimension was used as working electrode (WE). A saturated calomel electrode (SCE) and a large-area platinum wire mesh were used as reference and auxiliary electrodes, respectively. All the experiments were performed in 100 mL of electrolytes under non-stirred and naturally aerated conditions. During the experiment, the test solution was maintained at room temperature. Before each experiment, the electrode was permitted to corrode freely for about 15 min at its open-circuit potential (OCP). The polarisation curves were obtained potentiodynamically

between -0.250 and -0.750 V with the scan rate of 0.001 V/s. The electrochemical impedance spectroscopy experiments were conducted in the frequency range of 100 kHz– 10 Hz at open-circuit potential by applying alternating current signal of 0.005 V peak-to-peak. The inhibition efficiency values were obtained from PDP experiment, using the following equation,

$$(IE) = ((I_{\text{corr}(b)} - I_{\text{corr}(i)}) / I_{\text{corr}(b)}) \times 100, \quad (5)$$

where $I_{\text{corr}(b)}$ is the corrosion current density in the absence of inhibitor. $I_{\text{corr}(i)}$ is the corrosion current density in the presence of inhibitor obtained from Tafel plots.

The inhibition efficiency (IE) from EIS data was calculated by using the following equation:

$$(IE) = ((R_{\text{ct}} - R_{\text{ct}(b)}) / R_{\text{ct}}) \times 100, \quad (6)$$

where $R_{\text{ct}(b)}$ is the charge transfer resistance in the absence of inhibitor and R_{ct} is the charge transfer resistance in the presence of inhibitor obtained from the electrochemical impedance diagram.

2.5 FTIR Spectral Analysis

Fourier transform infrared (FTIR) spectra were recorded in Instant nam-SHIMADZU model-IRAFFINITY-1, using the KBr disc technique. The pure solid ALA was mixed with KBr and made into a disc. The MS specimen after immersion experiment in the presence of ALA was cleaned with distilled water and then dried. Then, the thin adsorption layer formed on the steel surface was scrapped. The scrapped material was mixed with a small amount of KBr powder in an agate mortar and made into a KBr disc.

2.6 Surface Analysis

The specimens used for surface morphology examination were immersed in 0.5 mol/L H_2SO_4 in the absence and presence of ALA at 27°C for 7 h. The analysis was performed using Zeta-200 optical profiler. The Zeta-200 generates 2D and 3D images of a surface by acquiring a stack of images at various heights, typically a few nanometres apart. This non-contact 3D imaging system incorporates a ZDotTM-based vertical scanning mechanism as well as a wide area interferometer and spectroscopic reflectometer.

3 Results and Discussion

3.1 Weight Loss and Colorimetric Measurements

The weight loss method of monitoring corrosion rates (CR) and inhibition efficiency (IE) is useful because of its simple

application and high reliability [11]. Table 1 shows the IE and CR for ALA in 0.5 mol/L H_2SO_4 at room temperature [$(28 \pm 1)^\circ\text{C}$]. From the table, it is evident that the addition of ALA strongly suppressed the corrosion rate and this leads to an increase in the IE. The increase in IE with the inhibitor concentration indicates that the inhibitor molecules get adsorbed on the metal surface and it prevents from further corrosion. However, addition of the inhibitor (ALA) beyond certain concentration namely, 0.28 vol%, the IE decreases indicating desorption of the inhibitor molecule. For the present study, the reproducibility of the experimental data was determined by the value of standard deviation. At every inhibitor concentration, the standard deviation value for either corrosion rate or IE values is lower than 5% , indicating the reproducibility of results obtained.

In colorimetric analysis, the amount of iron present in inhibited and uninhibited test solutions was quantified using a colorimeter. Colorimetric experiments were carried after immersion experiments on all the test solutions used in gravimetric studies. Table 2 shows the results of the colorimetric analysis obtained by varying concentrations of ALA in 0.5 mol/L H_2SO_4 . It is clear from the table that the concentration of iron present in the inhibited solutions is less than that in uninhibited solution. The absorbance of the uninhibited solution is more when compared to that of the inhibited solutions. As we increase the concentration of the ALA, the absorbance values decrease up to optimum concentration after that the absorbance values increase. The corresponding IE values obtained from these data also increase up to the optimum concentrations of ALA. The results are in consistent with that observed from mass loss measurements.

The immersion time is another important parameter which ascertains the inhibitive effect of the inhibitor on standing. In the present study, the effect of immersion time (1 – 9 h) on corrosion inhibition of ALA in 0.5 mol/L H_2SO_4 at room temperature was investigated using weight loss and colorimetric methods. It is apparent from Tables 1 and 2 that the IE increases gradually with increasing immersion time and attains an optimum values around 94% at 7 h for 0.28 vol% of ALA. The inhibition efficiency increases from 1 to 7 h and beyond 7 h it starts declining. The increase in IE with increasing immersion time is due to the increase in the surface coverage with time. However, the decrease in inhibition efficiency at higher immersion period might be due to the biodegradation of ALA on standing.

The effect of sulphuric acid concentration (0.5 – 2 mol/L) on MS corrosion was also studied. Figure 1 shows the effect of changing sulphuric acid concentration at room temperature on the IE of ALA. At all dosages of inhibitor, increasing acid concentration resulted in decreasing IE, and

Table 1 Weight loss data for the corrosion inhibition of MS in 0.5 mol/L H₂SO₄ at various concentrations of ALA at room temperature

ALA conc. (vol%)	1 h		3 h		5 h		7 h		9 h	
	CR (mpy)	IE	CR (mpy)	IE	CR (mpy)	IE	CR (mpy)	IE	CR (mpy)	IE
0	191.91	–	1,083.34	–	1,026.16	–	907.25	–	1,123.85	–
0.04	145.00	23.60	400.92	62.99	308.79	69.99	269.31	70.25	612.08	45.54
0.08	132.21	30.34	328.41	69.55	284.05	72.49	234.58	74.14	534.16	52.47
0.12	110.88	41.57	305.67	71.78	264.43	74.23	198.63	77.97	501.47	55.38
0.16	102.35	46.07	272.97	74.80	214.10	79.14	155.37	82.87	475.95	57.65
0.20	93.82	50.56	250.22	76.90	166.34	83.79	106.63	88.31	452.18	59.77
0.24	85.29	51.46	197.62	81.76	134.77	86.87	74.33	91.81	444.74	60.43
0.28	68.24	64.04	176.29	83.86	95.54	90.69	51.79	94.29	435.78	61.22
0.32	82.89	56.81	189.03	82.55	128.65	87.46	104.57	88.47	487.82	56.59
0.36	89.52	53.35	214.87	80.17	178.85	82.57	152.12	83.23	542.99	51.69

the minimum IE of 12.35% is obtained in 2 mol/L H₂SO₄ with 0.04 vol% of ALA. The decrease in IE values with the increase in acid concentration is due to the aggressiveness of the acid.

Halides have been reported to inhibit the corrosion of some metals in strong acids, and this effect depends on the ionic size and charge, the electrostatic field set up by the negative charge of the anion on adsorption sites and the nature and concentration of the halide ion. It has also been reported that the inhibitive effect increases in the order $\text{Cl}^- < \text{Br}^- < \text{I}^-$, which seems to indicate that the radii of halide ions may have an important role to play. For example, the iodide ion (radius: 0.135 nm) is more pre-disposed to adsorption than is the bromide ion (radius: 114 pm) or the chloride ion (radius: 90 pm). The IE is observed to be greater in the inhibiting solutions containing extract-halide ions combination than that of the extract alone. The results are given in Table 3 and they clearly show that the inhibition efficiency of the ALA has enhanced considerably on the addition of halide ions and could be ascribed to synergistic effect. The anodic dissolution of the steel in aqueous solution is known to be significantly facilitated by hydroxyl ions that form intermediate catalytic complexes on the metal surface [12]. Halide ions, at some concentrations, may replace hydroxyl ions adsorbed on the surface of the metal, thus leading to a reduction in the catalytic effect of the hydroxyl ions. The results reveal that the synergistic effect due to the addition of halide ions follows the order of $\text{I}^- > \text{Br}^- > \text{Cl}^-$. The greater influence of the iodide ion is often attributed to its large ionic radius, high hydrophobicity and low electronegativity compared to the other halide ions [13]. The results obtained from colorimetric estimation for varying acid concentration and synergistic influences due to halide ions are comparable with that of mass loss experiment.

3.2 Electrochemical Measurements

3.2.1 PDP Measurements

The kinetics of the anodic and cathodic reactions occurring on MS in 0.5 mol/L H₂SO₄ solutions with different concentrations of ALA was studied through the polarisation measurements. Table 4 represents the corrosion parameters of the metal in 0.5 mol/L H₂SO₄ solution with ALA at room temperature including corrosion current density (I_{corr}), corrosion potential (E_{corr}) and IE. Tafel slopes were calculated by linear extrapolation of cathodic and anodic branch of the polarisation curves. Corrosion current (I_{corr}) was calculated using Stern-Geary equation which is given below [14]:

$$I_{\text{corr}} = b_a b_c / [2.303(b_a + b_c)] \times 1/R_p, \quad (7)$$

where R_p is linear polarisation resistance, b_a and b_c were anodic and cathodic Tafel slopes.

In acidic solutions, the anodic reaction of corrosion is the passage of the metal ions from the metal surface into the solution, and the cathodic reaction is the discharge of hydrogen ions to produce hydrogen gas or to reduce oxygen. The inhibitor may affect either the anodic or the cathodic reaction, or both. Figure 2 shows the anodic and cathodic polarisation curves of MS in 0.5 mol/L H₂SO₄ solution, without and with (0.04–0.36) vol% of ALA. Inspection of Fig. 2 shows that the addition of ALA has an inhibitive effect in the both anodic and cathodic parts of the polarisation curves and shifts both the anodic and cathodic curves to lower current densities. It can be seen from these polarisation results in Table 4 that the corrosion current density decreases noticeably with the increase in inhibitor concentration. This indicates the dissolution of the metal is reduced and that of the hydrogen evolution reaction is

diminished by the blocking effect of ALA [15]. It is clear that the corrosion potential of MS is shifted in the negative direction compared to that of blank indicating that the extract predominantly controls the cathodic reaction. The changes of E_{corr} values in the presence and absence of ALA are less than 85 mV [16–18], which indicate that ALA acts as a mixed type inhibitor for the corrosion of MS in 0.5 mol/L H_2SO_4 . These results reveal that ALA behaves as a mixed inhibitor but predominantly controls the cathodic reaction. The IE increases with the concentration of ALA. However, addition of the inhibitor beyond certain concentration namely, 0.28 vol%, the IE decreases indicating desorption of the inhibitor molecule.

PDP experiments were carried out by varying the strength of acid with and without the optimum concentration of ALA. Table 5 shows the effect of the concentration of the acid on the inhibition efficiency with ALA. Increasing acid concentration from 0.5–2 mol/L resulted in decreasing IE. This is due to the aggressiveness of the acid.

3.2.2 EIS Measurements

In order to obtain information about the kinetics of MS corrosion in the presence of ALA, impedance measurements were carried out at open circuit in 0.5 mol/L H_2SO_4 with and without ALA. Figures 3 and 4 show the corresponding Nyquist and Bode's plots, respectively. The impedance response of MS in acid solution has significantly changed after the addition of ALA, and the impedance of the inhibited system increased with inhibitor concentration. Furthermore, the highest inhibitor concentration of ALA (0.28 vol%) gives rise to much larger semicircle diameter than other lower concentrations of ALA. The impedance data were generated by the equivalent circuit model shown in Fig. 3. The circuit allows to identify both solution resistance (R_s), charge transfer resistance (R_{ct}) and the double-layer capacitance (C_{dl}). Table 6 summarizes the impedance data obtained from EIS experiments carried out both in the absence and presence of ALA. The higher R_{ct} values were obtained in the presence of the ALA due to the reduction of dielectric constant of aqueous solutions. The EIS results clearly indicate that ALA decreases C_{dl} and increases R_{ct} as consequence a larger diameter of the semicircle is observed in Nyquist plots. The magnitude of C_{dl} decreases with increasing inhibitor concentration. The decrease in C_{dl} could be in relation to the adsorption of inhibitor molecules at solution-metal interface [19]. According to the parallel-plate model for the electrical double layer:

$$C_{\text{dl}} = \varepsilon/4\pi d, \quad (8)$$

where C_{dl} is the capacitance per unit area of the condenser plates, d is the distance between the plates i.e. thickness of

the electric double layer and ε is the dielectric constant of material between the plates [20, 21]. The decrease of C_{dl} could be due to an increase in the thickness of the electrical double layer and/or to a local dielectric constant decrease. The increase in the thickness of the double layer is caused by the substitution of water molecules by adsorbed ALA.

It is clear from Fig. 4 that the impedance spectra exhibit one single capacitive loop, which indicates the formation of charge transfer complexes at the electrode/solution interface [22, 23] and the transfer process controls corrosion reaction. The similar behaviour of the different capacitive loops indicates that the presence of inhibitor does not change the mechanism of MS dissolution mechanism [24]. The increase of absolute impedance at low frequencies in Bode plot confirms the higher protection with increasing the concentration of the inhibitor, which is related to adsorption of ALA on the MS surface [25].

The important role in assessing the stability of inhibitive behaviour of inhibitor is strength of the acid. So, it is necessary to evaluate the inhibition efficiency of the inhibitor for higher strength of an acid. In the present study, the effect of the concentration of acid (0.5–2 mol/L) on corrosion inhibition of MS in the absence and presence of ALA was also studied by using EIS techniques at room temperature. The impedance data for the corrosion of MS with varying concentrations of acid in the presence and absence of ALA are shown in Table 7. From the data, it is clear that the inhibition efficiency decreases with the concentration of acid. The results obtained are in good agreement with those obtained from PDP measurement.

3.3 Effect of Temperature

The temperature is an important parameter in the studies on metal dissolution [26]. The corrosion rate in acid solution, for example, increases exponentially with temperature because the hydrogen evolution over potential decreases [27]. To assess the effect of the temperature on corrosion and corrosion inhibitive process, weight loss experiments were performed in the temperature range of 303–333 K in uninhibited acid and in inhibited solutions containing different concentrations of ALA. The results obtained from the mass loss experiment indicate that corrosion rates increase with rise of the temperature both in uninhibited and inhibited solutions. Similarly in colorimetric measurements, the values of absorbance increase with increase in the temperature with and without the ALA. More so, inhibition efficiency of the extract decreases with the increase in temperature. The results of weight loss measurements are tabulated in Table 8. The dependence of the corrosion rate on the temperature can be regarded as an Arrhenius-type process, the rate of which is given by

Table 2 Colorimetric data for the corrosion inhibition of MS in 0.5 mol/L H₂SO₄ at various concentrations of ALA at room temperature

ALA conc. (vol%)	1 h			3 h			5 h			7 h			9 h		
	Absorbance	Weight of iron (10 ⁻³ g)	IE (%)	Absorbance	Weight of iron (10 ⁻³ g)	IE (%)	Absorbance	Weight of iron (10 ⁻³ g)	IE (%)	Absorbance	Weight of iron (10 ⁻³ g)	IE (%)	Absorbance	Weight of iron (10 ⁻³ g)	IE (%)
0	0.19	5.51	–	0.52	13.68	–	0.62	16.16	–	0.76	19.59	–	0.77	19.8	–
0.04	0.09	3.03	45.0	0.155	4.64	66.1	0.16	4.72	70.8	0.16	4.72	75.9	0.45	12.01	39.34
0.08	0.06	2.32	57.9	0.135	4.14	69.7	0.14	4.24	73.8	0.14	4.24	78.4	0.39	10.52	46.87
0.12	0.055	2.20	60.1	0.12	3.75	72.6	0.11	3.54	78.1	0.12	3.75	80.9	0.31	8.48	57.17
0.16	0.050	2.02	63.4	0.10	3.23	76.4	0.09	3.03	81.3	0.08	2.74	86.0	0.25	7.02	64.55
0.20	0.045	1.82	67.0	0.07	2.43	82.2	0.07	2.43	85.0	0.06	2.32	88.2	0.21	5.71	71.16
0.24	0.040	1.62	70.6	0.06	2.32	83.0	0.05	2.02	87.5	0.04	1.62	91.7	0.19	5.51	72.17
0.28	0.035	1.41	74.4	0.045	1.82	86.7	0.035	1.41	91.3	0.025	1.01	94.8	0.17	4.91	75.20
0.32	0.052	2.28	62.8	0.11	4.28	63.8	0.10	4.56	75.8	0.09	4.61	75.9	0.29	7.92	60.00
0.36	0.080	2.85	49.3	0.14	4.54	50.3	0.165	4.65	51.8	0.015	4.70	56.2	0.415	11.11	43.89

$$\lg CR = \lg A - [E_a / (2.303RT)], \quad (9)$$

where E_a is the apparent activation energy, R is the molar gas constant (8.314 J/(mol K)), T is the temperature in K and A is the frequency factor.

The Arrhenius plots for MS corrosion in free acid solution and inhibited solution containing ALA are shown in Fig. 5. From the slopes of the linear plots, the activation energy (E_a) values were obtained and are listed in Table 9.

$$E_a / (2.303R) = \text{slope}. \quad (10)$$

The temperature dependence of the inhibiting effect and the comparison of the values of the apparent activation energy of the corrosion process in the absence and presence of inhibitors can provide further evidence [28] concerning the mechanism of the inhibiting action. The higher E_a values in the presence of inhibitor compared to the blank solution indicate that the inhibitor is effective at low temperatures and efficiency gets diminished at higher temperatures. Table 9 shows that the activation energy, E_a values are higher for inhibited solution than the uninhibited one, indicating a strong inhibitive action of the additives by increasing energy barrier for the corrosion process. The energy of activation values observed is in order of 46–55 kJ/mol in the presence of ALA. Since the E_a values are less than 80 kJ/mol, physical adsorption or physisorption of the inhibitor molecules on the surface of the MS is advocated [8, 29]. The thermodynamic adsorption parameters, ΔG_{ads} are obtained from the Eq. (11) and are given in Table 9.

$$\lg C = [\lg \theta / (1 - \theta)] - \lg B, \quad (11)$$

where $\lg B = -1.74 - [-\Delta G_{\text{ads}} / (2.303RT)]$, C is the concentration of the inhibitor, θ is the surface coverage and ΔG_{ads} is the free energy of adsorption (kJ/mol).

Results obtained indicate that the values of ΔG_{ads} are negative in all the cases indicating that acid extract of LA leaves is strongly adsorbed on the metal surface. The negative values of ΔG_{ads} indicate spontaneous adsorption of the inhibitor molecules on the MS surface [30]. With regard to the free energies of adsorption values, it is generally accepted that values of ΔG_{ads} around –20 kJ/mol or lower are consistent with the electrostatic interaction between charged molecules and charged metal surface (physisorption) and those around –40 kJ/mol or higher involve charge sharing or transfer of electrons from organic molecules to the metal surface to form a coordinate type of metal bond (chemisorption) [31]. In the present investigation, the values of ΔG_{ads} obtained for the corrosion inhibition process of MS in 0.5 mol/L H₂SO₄ for different concentrations of the extract at all temperatures studied are less than –20 kJ/mol. Hence the corrosion inhibition of MS with ALA is considered to follow physical adsorption in the temperature range of 303–333 K.

Fig. 1 Effect of acid strength on the corrosion of MS in 0.5 mol/L H_2SO_4 with ALA

Table 3 Effect of halide ions on the corrosion inhibition of MS in 0.5 mol/L H_2SO_4 with ALA at room temperature

ALA conc. (vol%)/0.001 (vol%) halide ion	IE
0.04	23.60
0.04 + KCl	34.09
0.04 + KBr	54.55
0.04 + KI	70.45
0.16	46.07
0.16 + KCl	56.82
0.16 + KBr	70.45
0.16 + KI	79.55
0.28	64.04
0.28 + KCl	75.00
0.28 + KBr	84.09
0.28 + KI	90.91

The values of enthalpy of adsorption ΔH_{ads} and entropy of adsorption ΔS_{ads} are found out from the basic thermodynamic equation.

$$\Delta G_{\text{ads}} = \Delta H_{\text{ads}} - T\Delta S_{\text{ads}} \quad (12)$$

The ΔH_{ads} and ΔS_{ads} values for the dissolution of mild steel in the presence and absence of ALA in 0.5 mol/L H_2SO_4 obtained from linear square fit of ΔG_{ads} versus T and are presented in Table 9. The higher values for ΔH_{ads} in the presence of the ALA are indicative of the higher protection efficiency observed for the system [32]. Generally, negative values of ΔH_{ads} were obtained indicating an exothermic adsorption process. The exothermic adsorption process signifies either physical or chemical adsorption, while endothermic adsorption process is attributable to chemisorption. In an exothermic process, physical adsorption is distinguished from chemisorption by considering the

Table 4 Polarisation data for the corrosion inhibition of MS in 0.5 mol/L H_2SO_4 at various concentrations of ALA at room temperature

ALA conc. (vol%)	I_{corr} (10^{-3} A/cm ²)	b_a (mV/dec)	b_c (mV/dec)	$-E_{\text{corr}}$ (mV)	IE
0	1.0380	114.90	163.00	479.50	–
0.04	0.3833	105.24	143.47	488.70	63.07
0.08	0.3624	106.62	147.10	493.10	65.09
0.12	0.2078	103.09	127.49	499.80	79.98
0.16	0.1301	103.02	127.94	512.70	87.47
0.20	0.0980	99.93	121.20	513.90	90.56
0.24	0.0892	87.05	118.62	515.20	91.40
0.28	0.0743	72.31	111.51	512.10	92.84
0.32	0.4192	109.32	143.90	513.90	59.61
0.36	0.7250	113.84	163.73	505.90	30.15

Fig. 2 Tafel plots for the corrosion of MS in 0.5 mol/L H_2SO_4 at various concentrations of ALA at room temperature

absolute value of enthalpy of adsorption. Typically, enthalpy of physical adsorption process is lower than 80 kJ/mol, while the enthalpy of chemisorption process approaches 100 kJ/mol [33]. Therefore, the obtained values of ΔH_{ads} suggest physical adsorption of the components of the plant extracts on the surface of the metal. The ΔS_{ads} values in the presence of ALA are negative. This implies that the activation complex in the rate-determining step represents association rather than dissociation, meaning that a decrease in disordering takes place on going from reactants to the activated complex [34].

3.4 Adsorption Isotherm

Information on the interaction between the inhibitor molecules and the metal surface can be provided by adsorption isotherm. Therefore, the degree of surface coverage calculated from weight loss measurements corresponding to different concentrations of ALA in the temperature range of 303–333 K was used to find suitable adsorption isotherm.

Table 5 Polarisation data for the corrosion of MS at various concentrations of H₂SO₄ with and without 0.28 vol% ALA at room temperature

Test solution	I_{corr} (10 ⁻³ A/cm ²)	b_a (mV/ dec)	b_c (mV/ dec)	$-E_{\text{corr}}$ (mV)	IE
Blank 0.5 mol/L	1.0380	114.90	163.00	479.50	–
With inhibitor	0.0743	72.31	111.51	512.10	92.84
Blank 1 mol/L	8.7250	185.25	227.43	480.70	–
With inhibitor	0.3523	64.78	149.39	483.80	91.94
Blank 1.5 mol/L	11.5000	186.60	227.17	472.10	–
With inhibitor	0.9448	68.86	151.95	476.50	91.78
Blank 2 mol/L	12.4100	185.36	240.33	459.90	–
With inhibitor	0.9794	69.82	148.46	464.10	90.60

Fig. 3 Nyquist plots for the corrosion of MS in 0.5 mol/L H₂SO₄ at various concentrations of ALA at room temperature

Attempts were made to fit the experimental data to various isotherms including Frumkin, Langmuir, Temkin and Freundlich. The Langmuir's adsorption isotherm (Fig. 6) with correlation coefficients nearing unity was found to be the best description of the adsorption behaviour of ALA on MS. The Langmuir's isotherm can be written as the Eq. (13).

$$C/\theta = 1/K_{\text{ads}} + C, \quad (13)$$

where K_{ads} is the equilibrium constant of the inhibitor adsorption process, C is the inhibitor concentration and θ is the surface coverage. Further the kinetic thermodynamic model of El-awady was applied to explain the inhibiting nature of the inhibitor.

The model of El-awady is represented by the Eq. (14)

$$\lg[\theta/(1 - \theta)] = \lg K' + y \lg C, \quad (14)$$

where C is the concentration of the adsorbate, θ is the coverage degree and $1/y$ is the number of inhibitor molecules occupying one active site. The binding constant K is given by

$$K = K'^{(1/y)}. \quad (15)$$

The data obtained are given in Table 10. The efficiency of a given inhibitor is a function of both the magnitude of its binding constant K and the number of active sites ($1/y$) it is capable of blocking, with the former being the most important [34]. Large values of K mean better and strong interaction, whereas small values of K indicate a weaker interaction between the inhibitor molecules and the metal. Inspection of Table 10 shows that K values decrease with the increase in the temperature. This is interpreted to mean that weaker surface interaction results at higher temperatures. The values of $1/y$ obtained are more than 1 in the temperature range of 303–313 K. However, at higher temperatures, the values of $1/y$ are around 1 indicating that at higher temperature, the number of active sites occupied by the inhibitor molecule decrease leading to the lower inhibition efficiencies [34].

3.5 FTIR Analysis

FTIR is a powerful tool that is always used to identify the nature of functional groups present in an organic molecule that is involved in the process of adsorption on the metal surface and it is also used to ascertain the nature of bonding. The FTIR spectra of the crude ALA and that of the scrapped products from the surface of MS after immersion in 0.5 mol/L H₂SO₄ containing 0.28 vol% of ALA for 7 h (Fig. 7a, b) provided information concerning the nature of the bonds between the metal surface and the inhibitor molecules. Comparison of the above figures clearly indicates that the characteristic frequencies corresponding to the various functional groups are shifted indicating the adsorption of the inhibitor molecule on the MS surface. Figure 7a shows the FTIR spectrum of the ALA. The very strong broad band at 3,379/cm is attributed to N–H or O–H stretching. The absorption band at 1,639/cm corresponds to the C=O stretching vibration. The band at 1,458/cm is assigned to C=C stretching vibrations [35, 36]. The band around 1,107/cm is the C–O–C asymmetric stretching vibration. The band at 1,059/cm indicates the stretching vibration of C–N. Hence, it can be inferred that ALA contains oxygen and nitrogen atoms in functional groups (O–H, N–H, C=O, C–N and C–O) and C=C in alkenes and aromatic rings, which meets the general structural consideration of the corrosion inhibitors. Figure 7b illustrates the FTIR spectrum of the scrapped material. Comparison of Fig. 7a with Fig. 7b shows that the band at 3,379/cm is shifted to 3,387/cm. The C=O group frequency has also decreased from 1,639 to 1,627/cm. The absorption band at 1,458/cm is shifted to 1,442/cm. Moreover, the bands around 3,780/cm in Fig. 7b are not present in pure extract, and are attributed to the complex between Fe²⁺

Fig. 4 Bode's plots for the corrosion of MS in 0.5 mol/L H_2SO_4 at various concentrations of ALA at room temperature

Table 6 Impedance data for the corrosion inhibition of MS in 0.5 mol/L H_2SO_4 at various concentrations of ALA at room temperature

ALA conc. (vol%)	R_{ct} ($\Omega \text{ cm}^2$)	IE	C_{dl} (F/cm 2)	θ
0	16.15	–	4.1130	–
0.04	78.40	79.40	0.3207	0.7940
0.08	140.60	88.51	0.3008	0.8851
0.12	158.70	89.82	0.2662	0.8982
0.16	180.00	91.03	0.2942	0.9103
0.20	209.40	92.29	0.2527	0.9229
0.24	229.20	92.95	0.2365	0.9295
0.28	261.30	93.82	0.2242	0.9382
0.32	115.10	85.96	0.2541	0.8596
0.36	37.79	57.26	0.7873	0.5726

Table 7 Impedance data for the corrosion of MS at various concentrations of H_2SO_4 with and without 0.28 vol% ALA at room temperature

Test solution	R_{ct} ($\Omega \text{ cm}^2$)	IE	C_{dl} (F/cm 2)	θ
Blank 0.5 mol/L	16.15	–	4.1130	–
With Inhibitor	261.30	93.82	0.3207	0.9382
Blank 1 mol/L	4.64	–	6.7350	–
With Inhibitor	48.44	90.43	0.5767	0.9043
Blank 1.5 mol/L	3.70	–	7.8510	–
With Inhibitor	32.11	88.49	3.0840	0.8849
Blank 2 mol/L	2.22	–	9.7370	–
With Inhibitor	12.56	82.29	3.2400	0.8229

and ALA [37]. Further, the prominent bands at 432 and 609/cm are characteristic of iron oxide which is absent in the pure ALA. The shift in vibrational frequencies noted on comparison of the two spectra clearly indicates the interaction of the lone pair of electrons of hetero atom and the

π -electrons of $\text{C}=\text{C}$, $\text{C}=\text{O}$ with the metal leading to the formation of a protective layer of ALA on the metal surface.

3.6 Surface Analysis

The optical profiler provides a powerful means of characterizing the microstructure. The two-dimensional and three-dimensional optical profiler images of MS surface in the presence and absence of ALA in 0.5 mol/L H_2SO_4 are shown in Figs. 8 and 9, respectively. Figures 8a and 9a show the topography of MS surface in the absence of inhibitor and Figs. 8b, 9b are that of MS in the presence on ALA. Figures 8a and 9a show a wafer with good surface roughness, while the rest of the figures show a wafer with poor surface roughness. The surface morphology reveals the formation of adsorbed layer onto the surface of iron in the acidic condition. Surface morphology of iron shows cracks or depth on the MS surface which is due to the attack of acid on it and is shown in Fig. 8a. Figure 8b shows that after the addition of optimum concentration of ALA, the cracks on the surface of the metal are covered uniformly. Further, the iron surfaces with the inhibitor are found to be smoother and have smooth globular structure. It could also be observed that the metal surface is decorated with the inhibitor molecules forming a film which is compact and even covering the entire surface. Moreover, the average roughness on iron sample was reduced from 735.4 nm for MS without inhibitor to 136.9 nm for MS with optimum concentration of ALA.

4 Conclusions

Acid extract of LA acts as a good inhibitor for the corrosion of MS in 0.5 mol/L H_2SO_4 . Inhibition efficiency increases with the inhibitor concentration and time of

Table 8 Effect of temperature on corrosion of MS at various concentrations of ALA in 0.5 mol/L H₂SO₄

ALA conc. (vol%)	303 K		313 K		323 K		333 K	
	CR (mpy)	IE	CR (mpy)	IE	CR (mpy)	IE	CR (mpy)	IE
0	1,650.44	—	2,375.44	—	3,953.38	—	8,968.66	—
0.04	1,113.09	32.56	1,799.70	24.24	3,411.76	13.70	8,081.61	9.89
0.08	1,019.26	38.24	1,595.00	32.85	3,096.17	21.68	7,203.08	19.69
0.12	946.76	42.63	1,492.65	37.16	2,789.11	29.44	6,674.26	25.58
0.16	840.15	49.10	1,343.38	43.45	2,439.41	38.30	6,047.34	32.57
0.20	737.79	55.97	1,232.50	48.11	2,068.38	47.68	5,352.20	40.32
0.24	665.29	59.69	968.09	59.24	1,714.41	56.63	4,375.58	51.21
0.28	524.56	68.22	844.41	64.45	1,492.65	62.24	3,625.00	59.58

Fig. 5 Arrhenius plots for the corrosion of MS in 0.5 mol/L H₂SO₄ with ALA**Table 9** Values of E_a , ΔG_{ads} , ΔH_{ads} and ΔS_{ads} for corrosion of MS in 0.5 mol/L H₂SO₄ with ALA

ALA conc. (vol%)	E_a (kJ/mol)	$-\Delta G_{\text{ads}}$ (kJ/mol)				$-\Delta H_{\text{ads}}$ (kJ/mol)	$-\Delta S_{\text{ads}}$ (kJ/mol K)
		303 K	313 K	323 K	333 K		
0	46.61	—	—	—	—	—	—
0.04	51.88	16.37	15.84	14.46	13.89	43.46	0.0890
0.08	53.19	15.25	15.14	14.10	14.20	28.21	0.0426
0.12	53.96	14.69	14.58	14.11	14.01	22.44	0.0254
0.16	54.15	14.62	14.51	14.40	14.15	19.31	0.0154
0.20	54.42	14.75	14.42	14.83	14.46	15.86	0.0039
0.24	54.54	14.68	15.12	15.31	15.18	10.08	0.0157
0.28	55.03	15.23	15.29	15.52	15.69	10.13	0.0167

immersion and decrease with temperature. The performance of the inhibitor improves with the addition of halide ions. Inhibition efficiency decreases gradually with acid concentration (0.5–2 mol/L H₂SO₄). Polarisation studies

Fig. 6 Langmuir isotherm for the corrosion of MS in 0.5 mol/L H₂SO₄ with ALA**Table 10** Adsorption parameters for MS corrosion in 0.5 mol/L H₂SO₄ containing ALA

Temperature (K)	Adsorption parameter	
	k	$1/\gamma$
303	7.19	1.38
313	5.52	1.17
323	4.73	0.82
333	4.10	0.78

reveal that ALA behaves as a mixed inhibitor but predominantly controls cathodic reaction. The adsorption of ALA on MS surface obeys Langmuir adsorption isotherm and follows the kinetic model of El-Awady. The adsorption process is mainly controlled by physisorption and is exothermic in nature accompanied by an increase in entropy. The inhibition efficiency values obtained from weight loss, colorimetric and electrochemical experiments are in good agreement. The addition of ALA to H₂SO₄ results in the

Fig. 7 FTIR spectra of ALA **a** and the scrapped material **b**

Fig. 8 Two-dimensional optical profiler images of MS in the absence of ALA **a** and MS in the presence of ALA **b**

Fig. 9 Three-dimensional optical profiler images of MS in the absence of ALA **a** and MS in the presence of ALA **b**

formation of a film on the MS surface, protecting steel from corrosion.

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References

- [1] A. Ostovari, S.M. Hoseinie, M. Peikari, S.R. Shadizadeh, S.J. Hashemi, *Corros. Sci.* **51**, 1935 (2009)
- [2] P.B. Raja, M.G. Sethuraman, *Mater. Lett.* **62**, 113 (2008)
- [3] U.J. Ekpe, E.E. Ebenso, U.J. Ibok, *J. West Afr. Assoc.* **37**, 13 (1994)

- [4] C.A. Loto, Niger. Corros. J. **19**, 20 (1998)
- [5] H. Al-Sehaibani, Mater. Wissen. Werkst. Technol. **31**, 1060 (2000)
- [6] A. Chetouani, B. Hammouti, Bull. Electrochem. **19**, 23 (2001)
- [7] U.F. Ekanem, S.A. Umoren, I.I. Udousoro, A.P. Udoh, J. Mater. Sci. **45**, 558 (2010)
- [8] K.O. Orubite, N.C. Oforka, Mater. Lett. **58**, 1768 (2004)
- [9] K. Krishnaveni, J. Ravichandran, A. Selvaraj, Acta Metall. Sin. (Engl. Lett.) **26**, 321 (2013)
- [10] P. Tiwari, B. Kumar, M. Kaur, G. Kaur, H. Kaur, Int. Pharm. Sci. **1**, 98 (2011)
- [11] I.B. Obot, N.O. Obi-Egbedi, Corros. Sci. **52**, 198 (2010)
- [12] J.O.M. Bockris, D. Drazic, R. Despic, Electrochim. Acta **4**, 325 (1961)
- [13] C. Jeyaprabha, S. Sathiyarayanan, S. Muralidharan, G. Venkatachari, J. Braz. Chem. Soc. **17**, 61 (2006)
- [14] G. Moretti, F. Guidi, G. Grion, Corros. Sci. **46**, 387 (2004)
- [15] H. Keles, Mater. Chem. Phys. **130**, 1317 (2011)
- [16] A.K. Satapathy, G. Gunasekaran, S.C. Sahoo, K. Amit, P.V. Rodrigues, Corros. Sci. **51**, 2848 (2009)
- [17] E.S. Ferreira, F.C. Giacomelli, A. Spinelli, Mater. Chem. Phys. **83**, 129 (2004)
- [18] S. Issaadi, T. Douadi, A. Zouaoui, S. Chafaa, M.A. Khan, G. Bouet, Corros. Sci. **53**, 1484 (2011)
- [19] I.L. Rozendeld, *Corrosion Inhibitors* (McGraw-Hill, New York, 1981)
- [20] J.O.M. Bockris, A.K.N. Reddy, *Modern Electrochemistry, Third Printing*, vol. 2 (Plenum Press, New York, 1972)
- [21] G. Schmitt, in *Proceedings 6th European Symposium on Corrosion Inhibitors* (Ferrara, Italy, 1985)
- [22] T. Poornima, N. Jagannath, N. Shetty, Corros. Sci. **53**, 3688 (2011)
- [23] J.M. Benabdellah, R. Touzani, A. Dafali, B. Hammouti, S. El Kadiri, Mater. Lett. **61**, 1197 (2007)
- [24] L. Larabi, Y. Harek, M. Traisnel, A. Mansri, J. Appl. Electrochem. **34**, 833 (2004)
- [25] M. Mahdavian, S. Ashhari, Electrochim. Acta **55**, 1720 (2010)
- [26] F.S. de Souza, A. Spinelli, Corros. Sci. **51**, 642 (2009)
- [27] A. Popova, E. Sokolova, M. Christov, Corros. Sci. **4**, 33 (2003)
- [28] T. Szauer, A. Brandt, Electrochim. Acta **26**, 1257 (1981)
- [29] D.S. Sheatty, P. Shetty, H.V.S. Nayak, J. Chil. Chem. Soc. **51**, 849 (2006)
- [30] C. Kustu, K.C. Emregül, O. Atakol, Corros. Sci. **49**, 2800 (2007)
- [31] E.A. Noor, A.H. Al-Moubaraki, Mater. Chem. Phys. **110**, 145 (2008)
- [32] A.A. El-Awady, B.A. Abd-El-Nabey, S.G. Aziz, J. Electrochem. Soc. **139**, 2149 (1992)
- [33] S. Martinez, I. Stern, Appl. Surf. Sci. **199**, 83 (2002)
- [34] S.S. Abd El Rehim, M.A.M. Ibrahim, K.F. Khaled, Mater. Chem. Phys. **70**, 268 (2001)
- [35] P.A. Tarantilis, V.E. Troianou, C.S. Pappas, Y.S. Kotseridis, M.G. Polissiou, Food Chem. **111**, 192 (2008)
- [36] A.P. Srikanth, T.G. Sunitha, V. Raman, S. Nanjundan, N. Rajendran, Mater. Chem. Phys. **103**, 241 (2007)
- [37] J.G. Wu, *Techniques and Applications of Infrared Fourier Transform Spectroscopy* (Science and Technology Information Press, Beijing, 1994)