

Corrosion Protection of mild steel by the aqueous extract of *LeucasAspera* Leaves in HCl medium

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Abstract:

Corrosion protection effect of aqueous extract of leaves of *Leucas Aspera* (ALA) on mild steel in 1M HCl medium has been investigated by weight loss and electrochemical techniques. The corrosion inhibition efficiency increases on increasing plant extract concentration up to 1.25 v/v. Inhibition efficiency of 87.22% was achieved with highest inhibitor (ALA) concentration (1.25 v/v) at room temperature. Adsorption of this plant extract on the mild steel surface obeys the Langmuir adsorption isotherm. Results obtained from the AC impedance reveal that the process of inhibition is through charge transfer reaction. Surface analysis (FE-SEM and EDXS, FT-IR) was also carried out to establish the corrosion inhibitive property of this plant extract in HCl solution. FE-SEM and FT-IR confirmed the adsorption of ALA on mild steel surface.

Keywords: Mild steel; Corrosion; Potentiodynamic polarization; electrochemical impedance spectroscopy; *Leucas Aspera*.

1 Introduction

The corrosion protection of mild steel is a significant concern among the corrosion scientists and material technologists as mild steel has remarkable economic and substantial applications. Hydrochloric acid is widely used for the removal of rust and scale in several industrial processes. The corrosion of steel and ferrous alloys in acidic environments and its inhibition constitute a complex problem. HCl is one of the most important pickling acids. Various types of synthetic organic compounds are widely used as corrosion inhibitors for the protection materials against deterioration from corrosion [1-9]. However, most of these compounds are not only expensive but also toxic to living beings. It is needless to point out the importance of cheap and safe inhibitors for corrosion of mild steel. Aiming to find cheap, environmentally benign non-toxic natural compound that could be used for acidization and acid pickling of metals in acid medium, numerous studies have been carried out with extracts from plant parts like seeds, fruits, leaves and flowers as corrosion inhibitors [10-21]. However, the constituents that provide inhibitive action, the mechanisms and the best condition for inhibition are still unclear.

Leucas Aspera (LA) belongs to the family Lamiaceae and generally found in wasteland and roadsides all over India. The plant is used for local use, primarily as a medicine. Phytochemical studies of this plant prove the presence of alkaloids, phytosterols, flavanoids, saponins, phenols and glycosides. The chloroform and ethanol soluble fractions of the above compounds are responsible for the antioxidant properties [22]. The leaves extract of this plant also shows the antibacterial and cytotoxic effects [23]. However, it has never been studied for the purpose of corrosion inhibition. Confirmation of ALA as corrosion inhibitor was done through weight loss, AC impedance spectroscopy and Potentiodynamic polarization spectroscopy. The protective film found on metal surface was characterized by analytical techniques like Fourier transform infrared spectroscopy (FT-IR), field emission scanning electron microscope (FESEM) and energy-dispersive X-ray spectrometer (EDXS)

2 Experimental

2.1 preparation of Specimen

The mild steel specimen of dimension 1 cm × 5 cm × 0.24 cm with an area of 12.99 cm² was used for the weight loss measurement. The specimens were polished successively using different grades (600, 800, 1000, and 1200) of emery sheets, degreased with acetone and conserved in a desiccator. Mild steel specimens having percentage composition of (wt. %) C 0.051%, Ni 0.004%, Mo 0.0076%, P 0.0099%, Si 0.423%, S 0.0033%, Cr 0.114%, Mn 1.159%, Cu 0.029% and 98.1992 % of Fe were used.

2.1.1 Preparation of the Extract

Fresh leaves of LA plant were collected and washed under running water, shade dried, and powdered. About 5 g of the powder was taken in a 500 ml round bottomed flask. To this, 100 ml of distilled water was added and refluxed for about 3 h at 60°C. After that, the solution was cooled overnight, filtered and used as the stock solution. Desired concentrations (0.25-1.25 v/v) were obtained by properly diluting the stock solution with distilled water.

2.2 Weight loss measurements

Weight loss of rectangular mild steel specimens of size 1-5-0.24 cm in triplicate were immersed in the test solutions for specified periods of immersion in the absence and presence of ALA was determined. The corrosion behaviour of MS in the presence of ALA was also studied at various temperatures (303, 313, 323 and 333K). The percentage of inhibition efficiency (%IE) was calculated using the following equation.

$$IE = (W_{(b)} - W_{(i)} / W_{(b)}) \times 100 \quad (1),$$

where $W_{(b)}$ and $W_{(i)}$ are the values of weight loss of the specimens without and with inhibitor respectively. The corrosion rate (CR) was calculated by the following equation:

$$CR \text{ (mpy)} = (K\Delta W) / \rho At \quad (2),$$

where, ΔW is the weight loss in grams, ρ is the density of coupon in g cm^{-3} , A is the area of the coupon in cm^2 and t is the exposure time in hours.

2.3 Electrochemical measurements

Potentiodynamic polarization (PDP) and electrochemical impedance spectroscopy (EIS) were performed using a CHI 608D model electrochemical analyzer. A three electrode cell assembly consisting of the mild steel coupon with an exposed area of 0.9785 cm^2 as the working electrode, a saturated calomel electrode as a reference electrode and a platinum mesh as auxiliary electrode was used. The polarization curves were recorded potentiodynamically between -0.250 and -0.750 V with the scan rate of 0.01 Vs^{-1} . The inhibition efficiency (%IE) from PDP data was calculated using the following equation.

$$(\% \text{IE}) = (I_{\text{corr}(b)} - I_{\text{corr}(i)}) / I_{\text{corr}(b)} \times 100 \quad (3),$$

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

Electrochemical impedance spectroscopy experiments were conducted in the frequency range $10 \text{ KHz} - 1 \text{ Hz}$ at open-circuit potential with an applied alternating current signal of 0.005 V peak-to-peak.

The percentage inhibition efficiency (%IE) was calculated from the following equation.

$$(\% \text{IE}) = (R_{\text{ct}(i)} - R_{\text{ct}(b)}) / R_{\text{ct}(i)} \times 100 \quad (4),$$

where $R_{\text{ct}(b)}$ is the charge transfer resistance in the absence of inhibitor and $R_{\text{ct}(i)}$ is the charge transfer resistance in the presence of inhibitor.

2.4 Surface analysis

In order to investigate the influence of the inhibitor on the corrosion phenomenon of mild steel, the scanning electron microscope (SEM) coupled with energy dispersive X-ray spectroscopy (EDXS), photographs of fresh, inhibited, and uninhibited MS samples were recorded using the microscope ZEISS sigma (5th version). Further, to confirm the nature of the chemical constituents adsorbed on the metal surface, the Fourier transform infra-red (FT-IR) spectra of the dried ALA extract and the material obtained by the scrapping of the metal surface after inhibition studies were recorded using BRUKER ALPHA II spectrometer.

3 Results and discussion

3.1 Weight loss measurements

The corrosion rate (CR) and inhibition efficiency (%IE) from weight loss studies of mild steel in 1 M HCl in the presence and absence of ALA at room temperature for various immersion times (1-7 h) at different concentrations are illustrated in Table 1. It is evident from these results that inhibition efficiency increases and

the corrosion rate decreases on addition of plant extracts with concentrations at all immersion times up to 5 h. This is due to the adsorbed layer of the inhibitor acts as a barrier between the steel surface and the acid solution, leading to a decreasing corrosion rate. It is found that %IE is 87.22 for the highest inhibitor concentration of 1.25v/v even at a longer immersion time of 5 h. The increase of %IE with increasing the inhibitor concentration indicates more inhibitor molecules are adsorbed on the steel surface in 1M HCl medium by blocking more corrosion active sites. Fig.1 shows the variation of inhibition efficiency of ALA with its concentration in 1M HCl. At an immersion period of 7 h, there was a decrease in inhibition efficiency ie.74.55 %. The decrease of %IE with increasing the immersion time indicates the inhibitor molecules are desorbed from the surface of MS on long standing.

3.2 Temperature studies and thermodynamic parameters

To study the effect of temperature on the corrosion inhibition properties, mild steel specimens were exposed to 1 M HCl containing various concentration of ALA for 1h immersion time at the temperature range 303-333 K. The effect of temperature on the rate of corrosion is shown in Fig. 2 and the data calculated corrosion rate and inhibition efficiencies are shown in Table 2. As the temperature increases, the corrosion rate increases and the inhibition efficiency decreases at all concentrations. The maximum inhibition efficiency (%IE) of 85.94 is obtained at 303 K followed by 56.37 % at 333 K. The slope of the curve gradually decreases on increasing ALA concentration, which seems to point out simple adsorption behaviour. This shows that ALA prevents iron dissolution in aggressive acids through physical adsorption [24].

The log of corrosion rate and the temperature is given by the Arrhenius equation

$$\text{Log CR} = \log A - (E_a / 2.303 RT) \quad (5),$$

where CR is the corrosion rate, E_a is the apparent activation energy, R is the molar gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), T is the temperature in K and A is the frequency factor. The E_a values can be determined from the slopes of Arrhenius plots ($\log \text{CR}$ vs. $1/T$) (Fig. 3).

$$E_a / (2.303 RT) = \text{slope} \quad (6),$$

The activation energy (E_a) values are given in Table 3. The E_a values are higher for an inhibited solution than that for the uninhibited one, indicating a strong inhibitive action of ALA by increasing the energy barrier for the corrosion process. This is an indication of spontaneous adsorption of the inhibitor molecules on the MS surface and is attributed to physisorption [25].

3.3 Adsorption isotherm

The values of the free energy of adsorption $(\Delta G)_{\text{ads}}$ were obtained from equation (7) and are also tabulated in Table.3.

$$\text{Log C} = [\ln \theta / (1 - \theta)] - \log B \quad (7),$$

where $\log B = -1.74[-(\Delta G)_{\text{ads}}/2.303RT]$, C is the concentration of the inhibitor, θ is the surface coverage. The negative values of free energy of adsorption ensure the spontaneity of the adsorption process and stability of the adsorbed layer on the metal surface [26]. It is described in the literature that a value of ΔG_{ads} upto -20 kJ mol^{-1} or less negative implies that the adsorption is due to electrostatic interaction between charged molecules and a charged metal and the process indicates physical adsorption, while those more negative than -40 kJ mol^{-1} involves charge sharing or transfer from the inhibitor molecules to the metal surface to form a co-ordinate type of bond that indicates chemical adsorption [27]. Analysis of results presented in Table 3 shows that the values of ΔG_{ads} are less negative than -20 kJ mol^{-1} , proposing that the inhibition to be through physisorption. The negative values of ΔG_{ads} reflect the spontaneous adsorption of the inhibitor molecules on the metal surface [28, 29].

From the basic thermodynamic reaction [30],

$$\Delta G_{\text{ads}} = \Delta H_{\text{ads}} - T \Delta S_{\text{ads}} \quad (8)$$

In order to have a better understanding of the adsorption process, the enthalpy of adsorption (ΔH_{ads}) and entropy of adsorption (ΔS_{ads}) were obtained from the ΔG_{ads} vs T plot. The intercept of the plot gives the values of ΔH_{ads} and the slope gives the value of ΔS_{ads} .

From Table 3, it is also clear that the ΔH_{ads} values are negative and ΔS_{ads} values in the presence of inhibitor are positive. The negative value of ΔH_{ads} indicates that the adsorption of inhibitor molecules on the metal surface is an exothermic process. The positive value of ΔS_{ads} implies that the formation of the activated complex is the rate determining step representing association rather than dissociation, indicating that a decrease in disorder on going on from reactants to the activated complex [31].

The interaction between metal surface and inhibitor molecule can be explained by studying adsorption isotherm. Most commonly used isotherms are Freundlich, Langmuir and Frumkin. The values of surface coverage (θ) at different concentrations (C) of ALA in HCl medium in the temperature range (303-333 K) have been used to construct a suitable isotherm. Attempts were made to fit the experimental data to Langmuir, Freundlich, Tempkin, Frumkin, El-awady and Flory-Huggins isotherms. The plot of $\log C/\theta$ against concentration yielded a straight line. It has been found that the experimental data fit well with Langmuir adsorption isotherm (Fig. 4) with correlation coefficient nearing almost unity.

3.4 Potentiodynamic polarization

The effect of plant extract concentration on the anodic and cathodic polarization behaviour of mild steel in 1 M HCl solution has been studied by polarization measurements and the recorded Tafel plots of the corrosion inhibition studies on mild steel with different concentrations of ALA are shown in Fig.5a. Tafel slopes were calculated by the linear extrapolation of the cathodic and anodic branch of the polarization curves.

The electrochemical parameters like corrosion potential (E_{corr}), corrosion current density (I_{corr}), anodic slope (b_a), and cathodic slope (b_c) were obtained from Tafel plots and %IE are tabulated in Table 5. Corrosion current was calculated from the slope of the polarization curve (b_a and b_c) and linear polarization resistance R_p using the Stern-Geary equation.

$$I_{\text{corr}} = [b_a b_c / 2.303(b_a + b_c)] \times (1/R_p) \quad (9),$$

The polarization data in Table 5 shows that the addition of the inhibitor alters both b_a and b_c values, suggesting that the inhibitor reduces both anodic dissolutions of the metal and retard hydrogen evolution reaction. This indicates the mixed nature of the inhibitor. The I_{corr} values decrease while increasing the concentration of inhibitors represents the higher surface coverage [32-34].

3.5 Electrochemical impedance spectroscopy (EIS)

The kinetics of mild steel corrosion in 1 M HCl solution in the absence and presence of different concentrations of ALA was investigated using electrochemical impedance spectroscopy (EIS). The Nyquist plots for MS in 1M HCl without and with various concentrations of ALA are shown in Fig. 5b. The depressed semicircles of the Nyquist plots are probably due to heterogeneity of the metal sample, which might be due to the increase in surface roughness, dislocations, distribution of the active sites or the adsorption of the inhibitor molecules [35]. The diameter of the semicircle increases as the inhibitor concentration increases. This is an indication of the fact that the adsorption of the inhibitor molecules on the mild steel surface leads to the formation of a surface protective film, which reduces the corrosion active sites on the metal surface, enhancing its corrosion resistance [36].

The Randles equivalent circuit used for impedance studies is given as inset in Fig. 5b, where R_s is a solution resistance, C_{dl} is the double layer capacitance and R_{ct} is the charge transfer resistance. The electrochemical parameters of R_{ct} , C_{dl} and %IE in the presence and absence of ALA in 1 M HCl are listed in Table 5. It is clear from Table 5 that the C_{dl} values tend to decrease and R_{ct} values increase with increasing inhibitor concentration. The decrease in C_{dl} values can be attributed to a decrease in local dielectric constant and/or an increase in the thickness of the electrical double layer, suggesting that ALA extract act by adsorption at the mild steel/solution interface [37]. The adsorption can occur directly on the basis of donor-acceptor interactions between the lone pair of electrons/ π electrons in ALA and the vacant d orbital of iron atoms [38]. The increasing values of R_{ct} in the presence of ALA is due to the fact that the added inhibitor molecules displace the water molecules at the interface of the double layer leading to the transfer of charge from solution to the metal surface.

3.6 Surface analysis

3.6.1 SEM analysis

Fig. 6 (a) depicts the SEM images of polished mild steel (b) mild steel sample after 5 h of immersion in 1 M HCl and (c) mild steel sample exposed for 5 h in 1 M HCl with 1.25 v/v of ALA respectively. It can be clearly observed that the mild steel surface was strongly damaged with areas of uniform corrosion, where the

metal is attacked more or less evenly over the entire surface. Examination on the surface morphology of treated mild steel in 1.25 v/v extract reveals that the metal surface is in better conditions by having smooth surfaces compared to the untreated mild steel.

3.6.2 EDXS analysis

The EDXS analysis of the mild steel surface was done at different spots of the surface. Since the corrosive media is 1 M HCl and the extract consist mainly of carbon (C) and oxygen (O) atoms, the variation of C, chloride (Cl) and O weight percentage on the surface can be used quantitatively to explain the adsorption of extract. The results are given in Table 6 and the corresponding EDXS image of the uninhibited and inhibited MS samples is in Figs. 7(a) and 7(b) respectively. Fig. 7(a) shows the presence of the elements namely Fe, Cl, C and O. The iron peak (80.28%) and small peaks of Cl (1.38%), C (1.48%), O (16.86%) were detected. Figure 7(b) is also found to contain the elements Fe, Cl, C, O, Mn and Si. The percentages of these elements were: Fe - 65.51%, Cl -0.30%, C- 5.85%, O -27.60 %, Mn -0.35 % and Si- 0.39%. From the above data, it is clear that the percentage of iron in the inhibited sample has been decreased to 14.77%, indicating that the inhibitor molecules adsorbed on the MS surface. Thus, it can be concluded that there is a good protective film adsorbed on the mild steel surface which is responsible for the corrosion inhibitive effect.

3.6.3 FT-IR analysis

The FT-IR spectra of the crude ALA and that of the scrapped products from the surface of specimen after immersion in 1 M HCl containing 1.25 v/v of ALA for 5 h shown in Fig.8(a) and 8(b) respectively provide information concerning the nature of the interaction between the metal surface and the inhibitor molecules. The broad band at 3612 cm^{-1} in Fig. 8 (a) is due to O-H stretching of carboxylic acid. The band at 2902 cm^{-1} is due to C-H stretching, while the one at 1547 cm^{-1} is due to C=O stretching of carboxylic acid. The broad band at 3612 cm^{-1} and 1547 cm^{-1} in the spectrum of ALA shifted to 3394 cm^{-1} and 1560 cm^{-1} in the spectrum of the scrapped material. The results obtained show that the corrosion inhibition takes place through an adsorption process.

4. Conclusion

- 1) The aqueous extract of *Leucas Aspera* leaves shows promising inhibitive properties against corrosion of MS in 1M HCl medium.
- 2) Increasing the concentration of inhibitor increases the inhibition efficiency. The inhibition efficiency of ALA decreases with increase in temperature, which suggests that the adsorption process follows the physical adsorption mechanism.
- 3) The calculated values of activation energies are found to be higher for the inhibited system than that for the uninhibited system. It clearly explains the physisorption of the inhibitor molecules on the metal surface.

- 4) The adsorption of the extract followed a Langmuir isotherm.
- 5) Polarization studies reveal that ALA acts as a mixed type inhibitor. The obtained inhibition efficiency values from weight loss and electrochemical studies are in good agreement.
- 6) The adsorption of the inhibitor molecules on the MS surface is confirmed by the results of FT-IR and EDXS studies.

References

- [1] Bahrami.M.J,Hosseini.S.M.A,Pilvar.P,Experimental and theoretical investigation of organic compounds as inhibitors for mild steel corrosion in sulphuric acid medium. *CorrosSci*,2010,52,2793–2803.
- [2] Zhang.Q.B, Hua.Y.X, Corrosion inhibition of mild steel by alkylimidazolium ionic liquids in hydrochloric acid. *ElectrochimActa*,2009,54,1881–1887.
- [3] Abdalla.M, Guar gum as corrosion inhibitor for carbon steel in sulphuric acid solutions. *PortElectrochimActa*,2004, 22,161–175.
- [4] Zhang.D.Q, Cai.Q.R, Gao.L.X, Lee.K.Y, Effect of serine, threonine and glutamic acid on the corrosion of copper in aerated hydrochloric acid. *CorrosSci*2008,50,3615-3621.
- [5] Ozcan.M,Solmaz.R,Kardas.G,Dehri.I,Adsorption properties of barbiturates as green corrosion inhibitors of mild steel in phosphoric acid. *Colloids and Surf*,2008,A 325:57–63.
- [6] Talati.J.D,Gandhi.D.K,Triphenylmethane dyes as corrosion inhibitors for aluminium–copper alloy in HCl acid. *Mater Corros*,2004,33(3),155–163.
- [7] Prabhu.R.A,Venkatesha.T.V,Shanbhag.A.V, Carmine and fast green as corrosion inhibitors for mild steel in hydrochloric acid solution. *J Iran Chem Soc*,2009,6(2),353–363.
- [8] Baeza.H,Guzman.M,Ortega.P,Vera.L, Corrosion inhibition of copper in 0.5 M hydrochloric acid by 1,3,4-thiadiazole-2,5-dithiol. *J ChilChem Soc*,2003,48(3), 23–30.
- [9] Ebenso.E.E,Oguzie.E.E, Corrosion inhibition of mild steel in acidic media by some organic dyes. *Mater Lett*,2005,59,2163–2165.
- [10] El-Etre.A.Y,Khillah extract as inhibitor for acid corrosion of SX 316 steel. *Appl Surf Sci*, 2006,252,8521–8525.
- [11] Oguzie.E.E, Evaluation of the inhibitive effect of some plant extracts on the acid corrosion of Mild Steel. *CorrosSci*,2008,50,2993–2998.

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- [12] Okafor.P.C,Ikpi.M.E,Uwah.I.E,Ebenso.E.E,Ekpe.U.J,Umoren.S.A,Inhibitory action of *Phyllanthusamarus* extracts on the corrosion of mild steel in acidic media. *CorrosSci*,2008,50,2310–2317.
- [13] Perumal. S, Muthumanickam. S, Elangovan. A, Karthik.R, and Mothilal. K, Bauhinia tomentosa Leaves Extract as Green Corrosion Inhibitor for Mild Steel in 1 M HCl Medium, *Journal of Bio and Tribo-Corrosion*, 2017, 3(2), 13.

- [14] Chauhan.L.R,Gunasekaran.G, Corrosion inhibition of mild steel by plant extract in dilute HCl medium. *Corros Sci*,2007,49,1143–1161.
- [15] Da Rocha.J.C, Da Cunha Ponciano Gomes.J.A, D'Elia.E, Corrosion inhibition of carbon steel in hydrochloric solution by fruit peel aqueous extracts. *Corros Sci*,2010,52,2341–2348.
- [16] Lebrini.M, Bentiss.F, Vezin.H, Lagrenee.M, The inhibition of mild steel corrosion in acidic solutions by 2,5-bis(4-pyridyl)-1,3,4-thiadiazole: structure–activity correlation. *Corros Sci*,2006,48,1279–1291.
- [17] El-Etre.A.Y, Inhibition of acid corrosion of carbon steel using an aqueous extract of olive leaves. *J Colloid Interface Sci*,2007,314,578–583.
- [18] Satapathy.A.K, Gunasekaran.G, Sahoo.S.C, Amit.K, Rodrigues.P.V, Corrosion inhibition by *Justiciagendarussa* plant extract in hydrochloric acid solution. *Corros Sci*,2009,51,2848–2856.
- [19] Quraishi.M.A, Singh.A, Singh.V.K, Yadav.D.K, Singh.A.K, Green approach to corrosion inhibition of mild steel in hydrochloric acid and sulphuric acid solutions by the extract of *Murrayakoenigii* leaves. *Mater Chem Phys*, 2010,122(2010),114–122.
- [20] Rajendran.S, Jeyasundari.J, Usha.P, Selvi.J.A, Narayanasamy.B, Regis.A.P.P, Rengan.P, Corrosion behaviour of aluminium in the presence of an aqueous extract of *Hibiscus rosasinensis*. *Port Electrochim Acta*,2009,27(2),153–164.
- [21] Krishnaveni. K, and Ravichandran. J, A Study on the Inhibition of Copper Corrosion in Sulphuric Acid by Aqueous Extract Leaves of *Morinda Tinctoria*, *Journal of Failure Analysis and Prevention*, 2015, 15(5), 711-721.
- [22] Latha. B, Rumaisa. Y, Soumya. C. K, Shafeena Shahul, and Sandhiya. N, *Journal of chemical and Pharmaceutical Research*, 2013,5(4), 222-228.
- [23] Rahman. M. A, Islam. M. S, Antioxidant, antibacterial and cytotoxic effects of the phytochemicals of whole *Leucas Aspera* extract. *Asian Pacific journal of tropical biomedicine*, 2013, 3(4), 273.
- [24] Gunasekaran. G, Chauhan. L.R, Eco-friendly inhibitor for corrosion inhibition of mild steel in phosphoric acid medium. *Electrochimica Acta*,2004, 49(25),4387-4395.
- [25] Krishnaveni. K, Ravichandran. J, Selvaraj. A, Effect of *Morinda tinctoria* leaves extract on the corrosion inhibition of mild steel in acid medium, *Acta Metallurgica Sinica (English Letters)*, 2013, 26(3), 321-7.
- [26] Bentiss. F, Lebrini. M, Lagrenee. M, Thermodynamic characterization of metal dissolution and inhibitor adsorption processes in mild steel/2,5-bis(*n*-thienyl)-1,3,4-thiadiazoles/hydrochloric acid system, *Corros. Sci*,2005, 47(12),2915.
- [27] Brinic.S.Z, Grubac.R, Babic. M, Metikos-Hukovic, In 8th European symposium on corrosion inhibitors, Ferrara, Italy, vol.1 (1995) 197.

- [28] Kathiravan. S, Ragul. R, Raja. G and Ravichandran. J, Theoretical and Experimental Studies About the Inhibitive Action of *Ruelliatuberosa* L on Mild Steel in HCl Medium, *Journal of Bio-and Tribo-Corrosion*, 2018, 4(3), 46.
- [29] Kavitha. N, Kathiravan. S, Jyothi. S, Muruges. A and Ravichandran. J, Adsorption and Inhibitive properties of Methanol extract of *Leucas Aspera* leaves for the corrosion of Mild Steel in HCl medium, *Journal of Bio and Tribo Corrosion*, 2019,5(2), 51.
- [30] Roy. P, Maji. T, Dey. S and Sukul.D, Adsorptionbehaviour of gluten hydrolysate on mild steel in 1 M HCl and its role as a green corrosion inhibitor, *RSC Advances*. 2015, 5(75), 61170-61178.
- [31] Manimegalai, S, and Manjula. P, Thermodynamic and Adsorption studies for Corrosion Inhibition of Mild steel in Aqueous Media by *Sargasamswartzii* (Brown algae), *Journal of Material and Environmental Science*, 2015, 6(6), 1629-1.
- [32] Khaled. KF, The inhibition of benzimidazole derivatives on corrosion of iron in 1M HCl solutions. *ElectrochimActa* , 2003, 48(17), 2493-2503.
- [33] McCafferty. E, Hackerman. N, Double layer capacitance of iron and corrosion inhibition with polymethylenediamines. *J Electrochemical Soc*, 1972, 119(2), 146-154.
- [34] Raja. PB, Sethuraman. MG, Natural products as a corrosion inhibitor for metals in corrosive media – a review. *MaterLett*, 2008, 62(1), 112-116.
- [35] Shukla. S. K, Quraishi. M. A, Ebenso. E. E, Adsorption and corrosion inhibition properties of cefadroxil on mild steel in hydrochloric acid, *International Journal of Electrochemical Science*, 2011, 6, 2912-31.
- [36] Jyothi. S and Ravichandran. J, Inhibitive action of the acid extract of *Luffaaegyptica* leaves on the corrosion of mild steel in acidic medium, *Journal of Adhesion Science and Technology*, 2015, 29(3), 207-231.
- [37] Elayyachy .M, El Idrissi .A, Hammouti .B, *Corros. Sci*, 48 (2006), 2470.
- [38] Saker. S, Aliouane. N, Hammache. H, Chafaa. S and Bouet.G, Tetraphosphoric acid on eco-friendly corrosion inhibitor on carbon steel in 3N NaCl aqueous solutions, *Ionics*, 2015, 21(7), 2079-2090.

Table captions

Table 1 Effect of the concentration of ALA on the corrosion of MS in 1 M HCl from weight loss method.

Table 2 Effect of temperature on the corrosion of MS in 1 M HCl with ALA

Table 3 Value of activation energy and thermodynamic parameters for the corrosion of MS with and without different concentrations of ALA

Table 4 Electrochemical parameters for the corrosion of MS 1 M HCl at different the concentrations of the inhibitor

Table 5 EDXS analysis results of fresh MS on 1M HCl in the absence and presence of ALA



Table 1. Effect of the concentration of ALA on the corrosion of MS in 1 M HCl from weight loss method.

Conc. of ALA (v/v)	1 h		3 h		5 h		7 h	
	CR (mpy)	(%)IE	CR (mpy)	(%)IE	CR (mpy)	(%)IE	CR (mpy)	(%)IE
Blank	215.87	-	202.83		197.04		128.17	
0.25	70.83	67.19	62.22	69.32	55.21	71.98	57.34	55.26
0.50	60.71	71.88	56.55	72.11	51.62	73.8	40.47	68.42
0.75	50.59	76.56	47.56	76.55	46.01	76.64	38.72	69.79
1.00	40.47	81.25	33.71	83.38	28.83	85.36	36.29	71.68
1.25	30.35	85.94	26.62	86.87	25.17	87.22	32.21	74.55

Table 2. Effect of temperature on the corrosion of MS in 1 M HCl with ALA

Conc. of ALA (v/v)	303 K		313 K		323 K		333 K	
	CR (mpy)	(%)IE	CR (mpy)	(%)IE	CR (mpy)	(%)IE	CR (mpy)	(%)IE
Blank	215.87	-	984.91	-	2425.17	-	2873.78	-
0.25	70.83	67.19	327.17	66.78	1720.22	29.06	2069.02	28
0.50	60.71	71.88	296.82	69.86	1221.02	49.65	1856.52	35.39
0.75	50.59	76.56	246.22	75.0	1173.79	51.59	1504.35	47.65
1.00	40.47	81.25	205.75	79.1	1116.45	53.96	1480.74	48.47
1.25	30.35	85.94	161.9	83.56	998.4	58.83	1253.75	56.37

Table 3. Value of activation energy and thermodynamic parameters for the corrosion of MS with and without different concentrations of ALA

S.No.	Conc. of ALA (v/v)	E _a (kJ mol ⁻¹)	-ΔG _{ads} (kJ mol ⁻¹)				-ΔH _{ads} (kJ mol ⁻¹)	ΔS _{ads} (kJ mol ⁻¹ K ⁻¹)
			303 K	313 K	323 K	333 K		
1	Blank	73.15	-	-	-	-	-	
2	0.25	99.51	16.46	14.99	13.53	12.06	60.85	0.1465
3	0.50	98.51	15.25	14.06	12.87	11.69	51.28	0.1189
4	0.75	99.13	14.65	13.62	12.59	11.57	45.86	0.1030
5	1.00	105.44	14.67	13.40	12.12	10.85	53.34	0.1276
6	1.25	109.62	14.91	13.59	12.28	10.96	54.86	0.1318

Table 4. Electrochemical parameters for the corrosion of MS 1 M HCl at different the concentrations of the inhibitor

Conc. of ALA (v/v)	PDP					EIS		
	b_a $mV dec^{-1}$	b_c $mV dec^{-1}$	$(-E_{corr})$ $mV sec^{-1}$	I_{corr} * 10^4	% IE	R_{ct}	C_{dl} * 10^{-5}	IE
Blank	242.54	124.51	438.3	1.477	-	107.8	18.32	-
0.25	95.95	122.89	454.9	1.425	3.52	121.8	18.66	10.67
0.50	98.17	124.25	465.6	1.461	10.83	123.9	18.10	12.99
0.75	166.38	127.35	469.9	1.315	10.96	128.2	17.36	15.91
1.00	177.52	114.90	478.4	1.279	13.40	130.8	16.67	17.58
1.25	181.88	119.56	479.8	1.204	18.48	138.6	16.40	22.2

Table 5. EDXS analysis results of fresh MS on 1M HCl in the absence and presence of ALA

HCl medium	Composition (%)					
	Fe	Cl	C	O	Mn	Si
MS in 1M HCl	80.28	1.38	1.48	16.86	-	-
MS in 1M HCl+ALA	65.51	0.30	5.85	27.60	0.35	0.39

Figure Captions

Fig.1.Effect of concentration of ALA on the corrosion of MS in 1 M HCl from weight loss method

Fig.2. Effect of temperature on the corrosion of MS in 1 M HCl with ALA

Fig. 3.Arrhenius plots for the corrosion of MS in 1 M HCl with ALA

Fig.4. Langmuir adsorption isotherm for the corrosion of MS in 1 M HCl

Fig.5 (a) Tafel plots for the corrosion of MS in 1 M HCl with various concentrations of ALA

Fig.5 (b) Nyquist plots for the corrosion of MS in 1 M HCl with various concentrations of ALA

Fig.6 (a) Polished MS sample, **Fig.6 (b)** MS sample exposed for 5 h in 1 M HCl and **Fig.6 (c)**

MS sample exposed for 5 h in 1 M HCl with 0.25 v/v of ALA

Fig.7 (a) The EDXS image of the MS sample in 1M HCl

Fig.7 (b) The EDXS image of the MS sample in 1M HCl with 0.25v/v of ALA

Fig.8 (a) FTIR spectra of crude ALA and (b) The scrapped material from MS surface after immersion in 1M HCl containing 0.25 v/v of ALA.



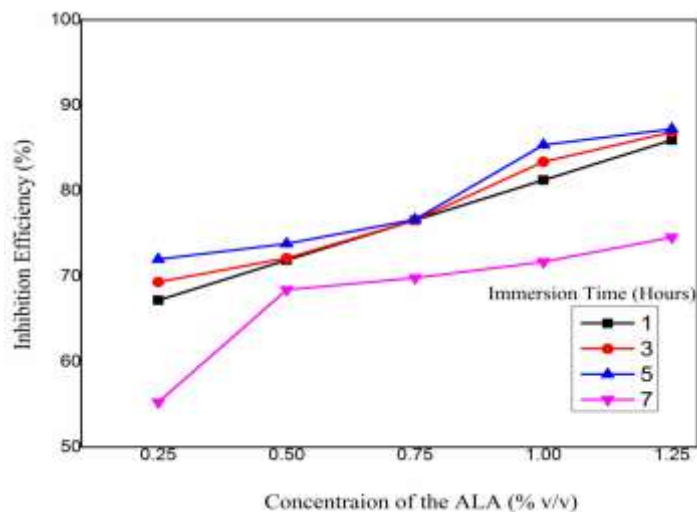


Fig.1. Effect of concentration of ALA on the corrosion of MS in 1 M HCl from weight loss method

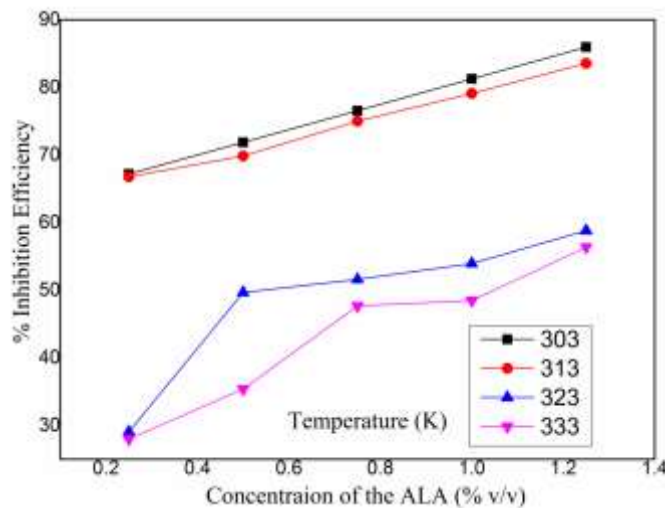


Fig.2. Effect of temperature on the corrosion of MS in 1 M HCl with ALA

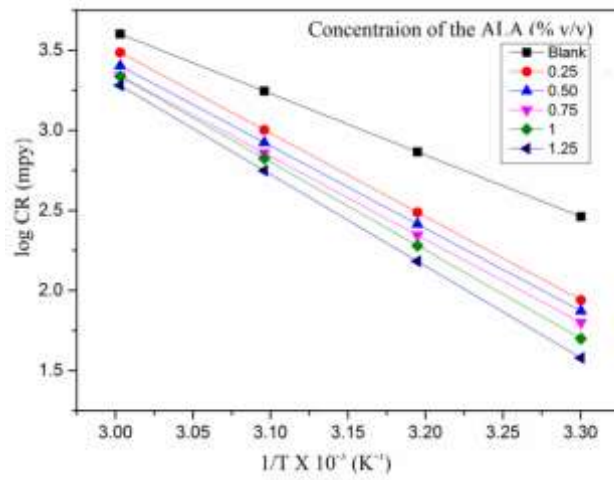


Fig. 3. Arrhenius plots for the corrosion of MS in 1 M HCl with ALA

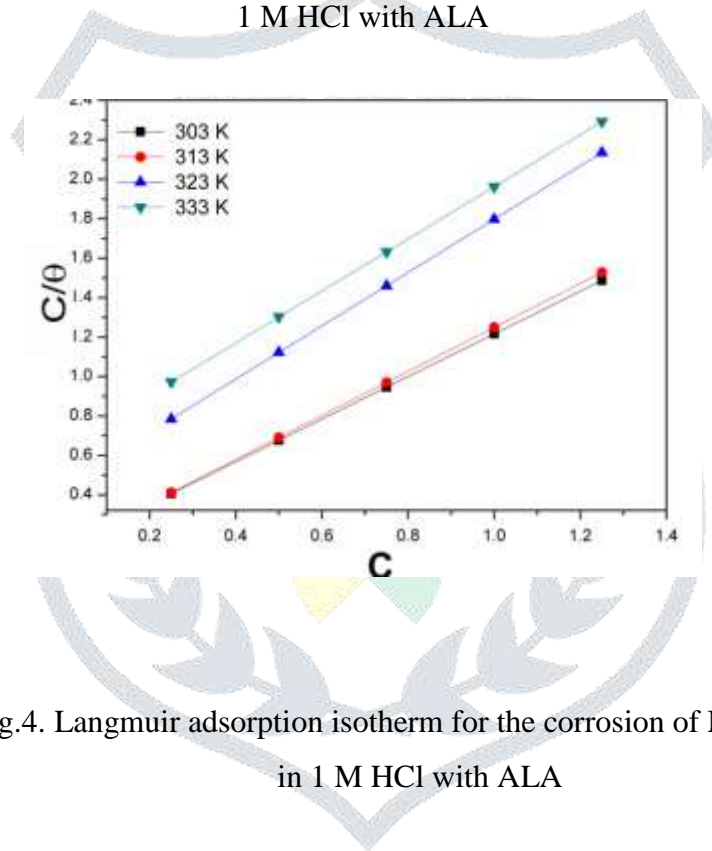


Fig.4. Langmuir adsorption isotherm for the corrosion of MS in 1 M HCl with ALA

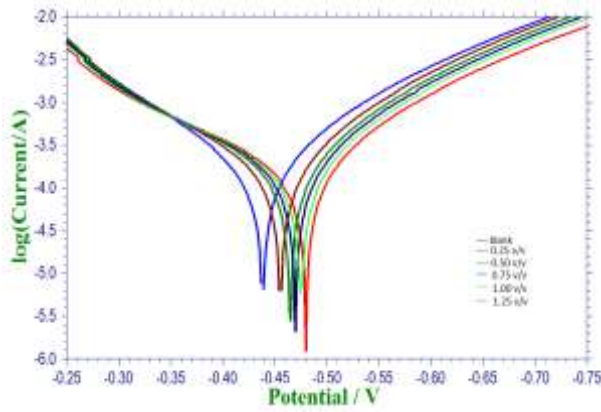


Fig.5 (a) Tafel plots for the corrosion of MS in 1 M HCl with various concentrations of ALA

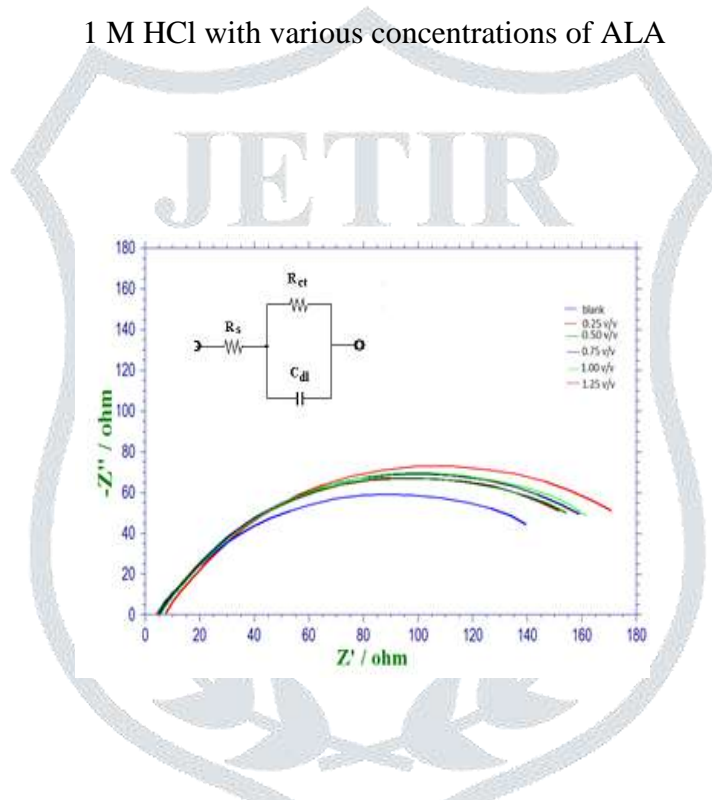


Fig.5 (b) Nyquist plots for the corrosion of MS in 1 M HCl with various concentrations of ALA

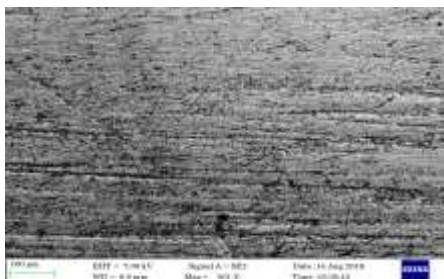


Fig.6 (a) Polished MS sample



Fig.6 (b) MS sample exposed for 5 h in 1 M HCl

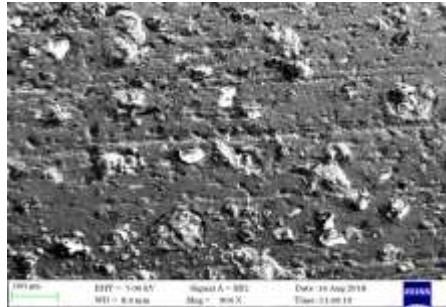


Fig.6 (c) MS sample exposed for 5 h in 1 M HCl with 0.25 v/v of ALA

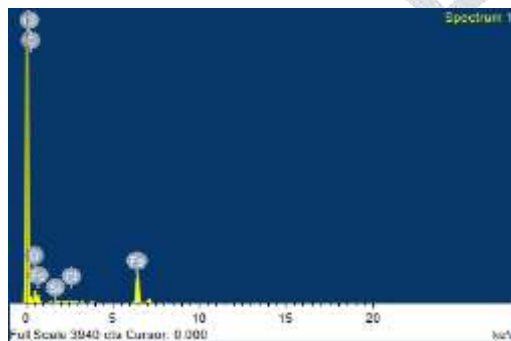


Fig.7 (a) The EDXS image of the MS sample in 1M HCl

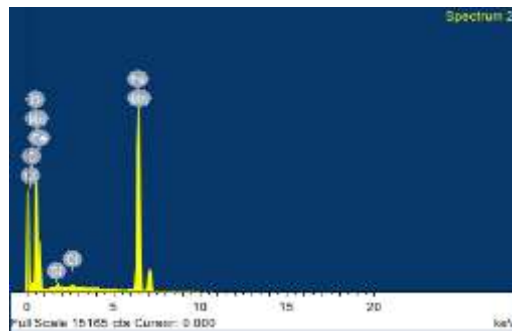


Fig.7 (b) The EDXS image of the MS sample in 1M HCl

with 0.25v/v of ALA

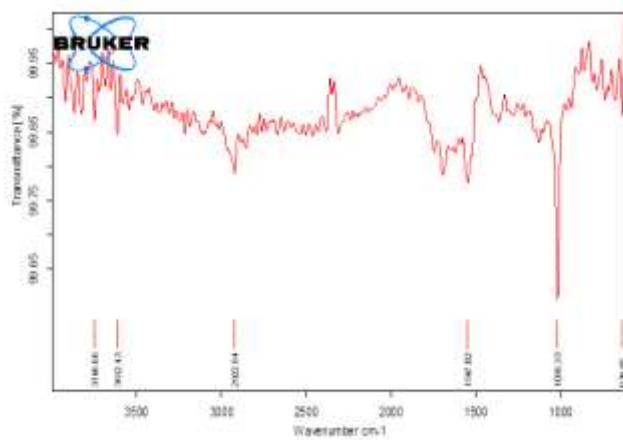


Fig.8 (a)

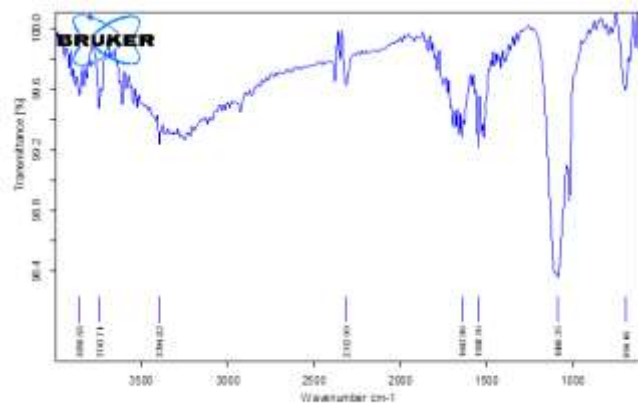


Fig.8 (b)

Fig.8. FTIR spectra of samples (a) crude ALA and (b) the scrapped material from MS surface after immersion in 1M HCl containing 0.25 v/v of ALA.