



## *Ziziphus mauritiana* leaves extracts as corrosion inhibitor for mild steel in H<sub>2</sub>SO<sub>4</sub> and HCl solutions

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### ABSTRACT

The inhibition performance of extracts of *Ziziphus mauritiana* on mild steel corrosion in 0.5 M H<sub>2</sub>SO<sub>4</sub> and 0.5 M HCl was investigated using gravimetric, electrochemical polarization, electrochemical impedance spectroscopy and scanning electron microscopic studies. The gravimetric results indicate that *Ziziphus mauritiana* leaves extract exhibits good inhibition efficiency in both the acids. Furthermore, the inhibition efficiency decreases with increase in temperature. Polarization measurements showed that the studied inhibitor is mixed type in both acids with significant reduction of cathodic and anodic current densities. Electrochemical impedance spectroscopy measurements revealed that the charge transfer resistance increases with increase in the concentration of *Ziziphus mauritiana* extracts. Various thermodynamic parameters such as activation energy, activation enthalpy and activation entropy are evaluated and discussed. Adsorption thermodynamic parameters are also computed, and SEM was used to analyze the surface adsorbed film.

### 1. Introduction

Mild steel is widely used as structural material in automobiles, pipes and chemical industries [1]. Mild steel undergoes severe corrosion in pickling processes. Hydrochloric and sulphuric acids are widely used for pickling and de-scaling of mild steel [2-4]. These issues can be resolved by introducing appropriate pickling inhibitor to the medium. Generally, organic compounds containing O, N, and S atoms are normally used as inhibitors to reduce the corrosion of mild steel in acid medium [5,6], but most of them are highly toxic to both human beings and environments [7]. These toxic effects have led to the use of natural products as anticorrosion agents which are eco-friendly and harmless. Further, the known hazardous effects of most synthetic corrosion inhibitors are the motivation for the use of some natural products. The plant extracts are viewed as an incredibly rich source of naturally synthesized chemical compounds that can be extracted by simple procedures with low cost, and are biodegradable in nature [8]. Recently, several natural compounds such as, *Azadirachta indica* [9], *Iseria coccinea* [10], *Prosopis cineraria* [11], *Hibiscus sabdariffa* extracts [12], *Clematis gouriana* [13], *Aloe vera* extracts [14], *Phyllanthus amarus* extracts [15], *Dacryodes edulis* [16], *Murraya koenigii* [17], *Foeniculum vulgare* [18], *Chlomolaena odorata* L. [19], *Radish and black cumin* [20], *Jasminum nudiflorum* [21] and *Bridelia retusa* leaves extract [22] have been reported as effective corrosion inhibitors for metals in acidic, alkaline and neutral solutions.

The *Ziziphus mauritiana* (ZM) is native plant from the province of Yunnan in Southern China to Afghanistan, India and Malaysia, and it is a good source of natural antioxidants, proteins and fats [23]. The major active constituents of *Ziziphus mauritiana* are found to be mucilage, flavonoids, alkaloids, tannins and fatty acids. The various parts of the plant are reported to have the following constituents. Seeds: Oleic acid,

linoleic acid, flavonoids, dammarane type tripterpene oligoglycosides A and C and acetyl jujuboside B [24-26]. Fresh fruit: Quercetin, citric acid in large quantities, malic acid and oxalic acid in small quantities [24] and triterpenoids [27]. Leaves: Protein, fibre, calcium, phosphorus, berberine, protopine alkaloids [25], vitamin E, carotenoid, rutin, saponins, flavonoids like ziziphin and jujubasaponins [28, 29]. However, *ziziphus mauritiana* leaves extract have never been used as the corrosion inhibitor. The aim of present work was to investigate the inhibition efficiency of *Ziziphus mauritiana* as corrosion inhibitor on mild steel in acid medium.

### 2. Experimental

#### 2.1. Preparation of specimens

Corrosion tests were performed on mild steel having the following composition (in wt%) 0.016 P, 0.322 Si, 0.01 Al, 0.062 Cr, 0.05 Mn, 0.09 C, 0.05 S and the remainder iron (Fe). Prior to gravimetric and electrochemical measurements, the surface of the specimens was washed under running tap water and then polished using SiC emery paper (grade 220-600), rinsed with distilled water, dried on a clean tissue paper, immersed in benzene for 5 s, dried and immersed in acetone for 5 s, and dried with clean tissue paper. Finally, the specimens were kept in desiccators until use. At the end of the test, the specimens were carefully washed with acetone and benzene, dried, and then weighed.

#### 2.2. Inhibitor preparation

Fresh *Ziziphus mauritiana* leaves were collected in and around Mysore city, India, cleaned with water and then dried in an oven at 60 °C and ground to powder.

**Table 1.** The corrosion rate (CR) and the inhibition efficiency (IE) obtained from weight loss measurements of mild steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> and 0.5 M HCl containing various concentrations of ZM leaves extracts at different temperatures.

| T (K) | C (ppm) | CR (mg/cm <sup>2</sup> .h)           | IE (%) | CR (mg/cm <sup>2</sup> .h) | IE (%) |
|-------|---------|--------------------------------------|--------|----------------------------|--------|
|       |         | 0.5 M H <sub>2</sub> SO <sub>4</sub> |        | 0.5 M HCl                  |        |
| 303   | Blank   | 1.99                                 | -      | 1.39                       | -      |
|       | 800     | 1.08                                 | 45.71  | 0.49                       | 64.63  |
|       | 1200    | 0.93                                 | 53.34  | 0.43                       | 69.44  |
|       | 1600    | 0.79                                 | 60.12  | 0.35                       | 74.61  |
|       | 2000    | 0.70                                 | 64.89  | 0.30                       | 78.41  |
|       | 2400    | 0.59                                 | 69.97  | 0.26                       | 81.20  |
|       | 2800    | 0.55                                 | 72.33  | 0.21                       | 84.86  |
| 313   | Blank   | 4.52                                 | -      | 1.90                       | -      |
|       | 800     | 2.67                                 | 40.82  | 0.81                       | 57.37  |
|       | 1200    | 2.30                                 | 49.05  | 0.73                       | 61.64  |
|       | 1600    | 2.01                                 | 55.51  | 0.61                       | 67.76  |
|       | 2000    | 1.76                                 | 60.98  | 0.54                       | 71.39  |
|       | 2400    | 1.63                                 | 63.86  | 0.43                       | 77.29  |
|       | 2800    | 1.41                                 | 68.77  | 0.37                       | 80.45  |
| 323   | Blank   | 7.71                                 | -      | 2.63                       | -      |
|       | 800     | 4.98                                 | 35.41  | 1.26                       | 52.09  |
|       | 1200    | 4.20                                 | 45.51  | 1.09                       | 58.45  |
|       | 1600    | 3.63                                 | 53.00  | 0.90                       | 65.68  |
|       | 2000    | 3.19                                 | 58.60  | 0.82                       | 68.84  |
|       | 2400    | 2.97                                 | 61.56  | 0.69                       | 73.59  |
|       | 2800    | 2.55                                 | 66.90  | 0.60                       | 77.14  |
| 333   | Blank   | 15.40                                | -      | 3.35                       | -      |
|       | 800     | 10.79                                | 29.92  | 1.79                       | 46.46  |
|       | 1200    | 9.52                                 | 38.19  | 1.58                       | 52.79  |
|       | 1600    | 8.35                                 | 45.82  | 1.36                       | 59.39  |
|       | 2000    | 7.55                                 | 50.99  | 1.24                       | 63.15  |
|       | 2400    | 6.54                                 | 57.52  | 1.09                       | 67.56  |
|       | 2800    | 6.20                                 | 59.73  | 0.92                       | 72.52  |

The 10 g of the powder sample was refluxed in 250 mL ethyl alcohol for 5 h. The refluxed solution was filtered and the filtrate was evaporated to 100 mL dark residue, and then degreased with petroleum ether and extracted with separating funnel. The solution was evaporated and the dark green solid residue obtained after complete drying was preserved in a desiccator. The residue so obtained was used in preparing different concentrations of the extracts in 0.5 M H<sub>2</sub>SO<sub>4</sub> and 0.5 M HCl solutions.

### 2.3. Weight loss measurements

Pre-weighed mild steel coupons with a dimension of 2 × 2 × 0.3 cm were immersed in 200 mL 0.5 M H<sub>2</sub>SO<sub>4</sub> and 0.5 M HCl with and without the addition of different concentrations of ZM extracts in an aerated condition. After 6 h of immersion, the specimens were taken out, washed, dried and weighed accurately. Experiments were carried out in triplicate. The average weight loss of the three parallel specimens was obtained. Relative weight losses of the coupons were used to calculate the percent inhibition efficiency (IE%). Then the tests were repeated with different concentrations of ZM at varying temperatures.

### 2.4. Electrochemical studies

Polarization and electrochemical impedance spectroscopy experiments were carried out using a CHI660D electrochemical workstation. A conventional three-electrode cell consisting of a saturated calomel reference electrode, a platinum auxiliary electrode and the working electrode with 1cm<sup>2</sup> exposed areas was used. The specimens were pre-treated similarly as done in the gravimetric measurements. The electrochemical tests were performed using various ZM extracts concentrations ranging from 0 to 2800 ppm at 30 °C using a thermostatically controlled water bath (Weiber, India) under aerated condition. Potentiodynamic polarization measurements were performed in the potential range from -900 to +500 mV with a scan rate of 0.4 mV/s. The AC impedance measurements were performed in the

frequency range of 10 to 0.05 MHz with signal amplitude of ± 10 mV.

### 2.5. Scanning electron microscopy

Samples for SEM experiments are mild steel sheets (1 × 1 × 0.3 cm). After 6 h of immersion, the surface features of the steel specimens exposed to 0.5 M H<sub>2</sub>SO<sub>4</sub> and 0.5 M HCl acid solutions as well as in inhibited acids were examined with the help of scanning electron microscope (Model JSM-5800).

## 3. Results and discussion

### 3.1. Gravimetric measurements

The corrosion rate (CR) and the values of inhibition efficiency (IE%) and degree of surface coverage (θ) obtained from gravimetric measurements of mild steel in the absence and in the presence of various concentrations of ZM extracts at different temperatures in 0.5 M H<sub>2</sub>SO<sub>4</sub> and 0.5 M HCl solutions after 6 h of immersion are shown in Table 1. The values of CR and IE (%) were calculated using the following equations:

$$CR = \frac{\Delta W}{S t} \quad (1)$$

$$IE(\%) = \frac{(CR)_a - (CR)_p}{(CR)_a} \times 100 \quad (2)$$

where, ΔW is the weight loss, S is the surface area of the specimen (cm<sup>2</sup>), t is immersion time (h), and CR is expressed in mg cm<sup>-2</sup> h<sup>-1</sup>. The data in Table 1 reveal that the addition of ZM extracts decreases markedly the corrosion rate of mild steel. The IE (%) increases as the concentration of added ZM extracts is increased at all temperatures, and when the concentration reached to 2800 ppm, IE (%) of ZM extracts reached a high values of 72.33 and 84.86 in 0.5 M H<sub>2</sub>SO<sub>4</sub> and 0.5 M HCl solutions, respectively at 30 °C, which represents excellent inhibitive ability of ZM extracts. This is due to the fact that, adsorption and the degree of surface coverage of the inhibitor on the mild steel increases with the inhibitor concentration,

thus the mild steel surface gets efficiently separated from the medium [30,20]. The results obtained from the weight loss measurements are in good agreement with those obtained from the electrochemical methods.

### 3.2. Potentiodynamic polarization

The anodic and cathodic polarization curves of mild steel electrode in 0.5 M HCl and 0.5 M H<sub>2</sub>SO<sub>4</sub> solutions in the absence and presence of various concentrations of ZM extracts at 30 °C are shown in Figures 1 and 2. The values of associated electrochemical parameters such as corrosion potential ( $E_{\text{corr}}$ ) and corrosion current density ( $I_{\text{corr}}$ ) were calculated from the intersection of anodic and cathodic Tafel slopes of the polarization curves. The IE (%) was calculated using the following equation:

$$\text{IE (\%)} = \frac{(I_{\text{corr}})_{\text{a}} - (I_{\text{corr}})_{\text{p}}}{(I_{\text{corr}})_{\text{a}}} \times 100 \quad (3)$$

Here,  $(I_{\text{corr}})_{\text{a}}$  and  $(I_{\text{corr}})_{\text{p}}$  are the corrosion current densities ( $\text{mA cm}^{-2}$ ) in the absence and presence of the inhibitor, respectively. It is clear from Figures 1 and 2 that the presence of ZM extracts decreases cathodic and anodic slopes with the increasing inhibitor concentration in both the acids but the effect is more in hydrochloric acid. This could be attributed to the adsorption of inhibitor over the corroded metal surface [31]. Since both anodic dissolution of iron and hydrogen evolution were suppressed, the ZM extracts behaves like a mixed inhibitor [32].

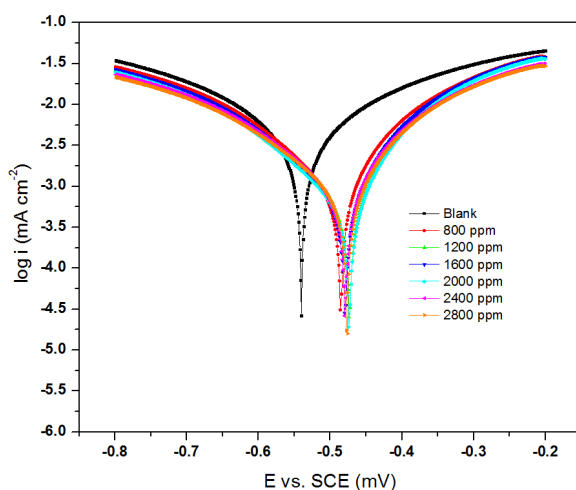


Figure 1. Polarization curves for mild steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> at various concentrations of ZM leaves extracts at 30 °C.

The results of polarization measurements are summarized in Table 2. It is evident that  $I_{\text{corr}}$  decreases significantly with increasing concentration of ZM extracts. The maximum IE (%) of 74.61 (0.5 M H<sub>2</sub>SO<sub>4</sub>) and 87.52 (0.5 M HCl) were observed at 2800 ppm of ZM extracts. This is because of increase in the blocked fraction of the metal surface by adsorption. Further, the concentration of ZM leaves extracts has less effect on the  $E_{\text{corr}}$  which indicates that ZM acts as a mixed type of inhibitor and its inhibitive property on mild steel is caused by geometric blocking effect [33].

### 3.3. Electrochemical impedance spectroscopy (EIS)

EIS is a powerful tool in studying corrosion mechanism and adsorption isotherm. Generally, the Nyquist plots are analysed in terms of equivalent circuit comprising of parallel capacitor and resistor, which include the solution resistance ( $R_s$ ) and

double layer capacitance ( $C_{\text{dl}}$ ). The corrosion behavior of mild steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> and 0.5 M HCl in the absence and presence of ZM extracts was investigated by impedance technique at 30 °C and results are represented by Nyquist plots as shown in Figures 3 and 4.

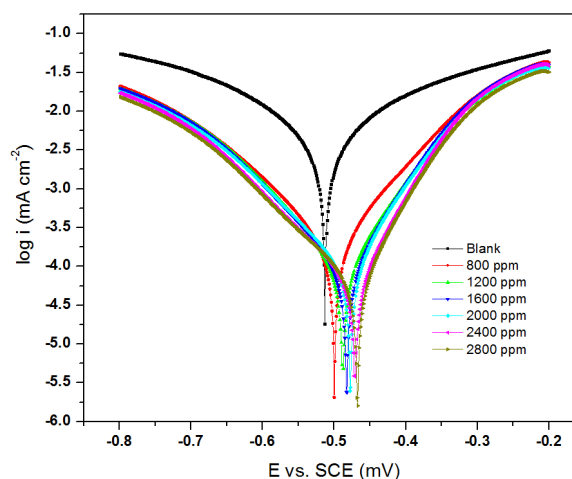


Figure 2. Polarization curves for mild steel in 0.5 M HCl at various concentrations of ZM leaves extracts at 30 °C.

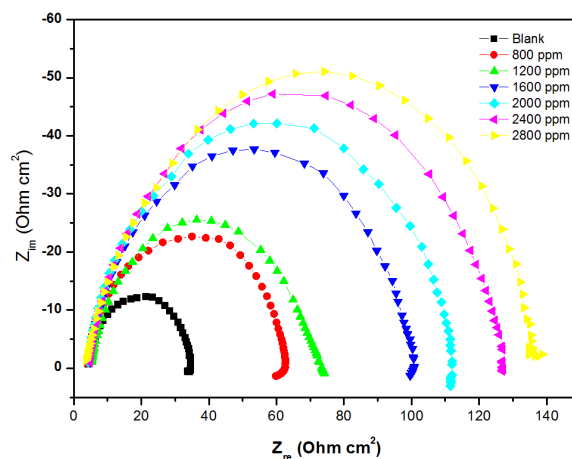


Figure 3. Nyquist plots of mild steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> in the absence and presence of various concentrations of ZM leaves extracts at 30 °C.

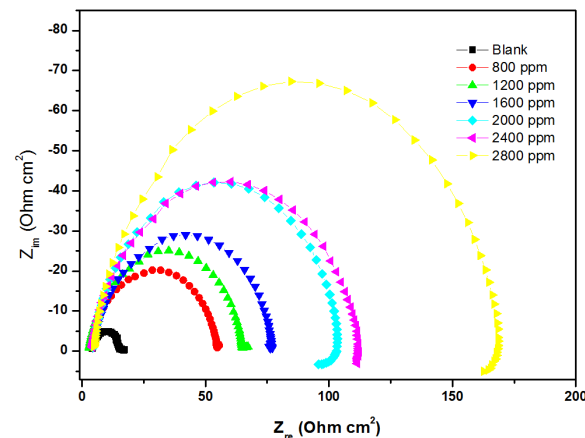


Figure 4. Nyquist plots of mild steel in 0.5 M HCl in the absence and presence of various concentrations of ZM leaves extracts at 30 °C.

**Table 2.**  $E_{corr}$ ,  $I_{corr}$ ,  $R_{ct}$  and IE (%) obtained from polarization and impedance measurements for mild steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> and 0.5 M HCl solutions containing various concentrations of ZM leaves extracts at 30 °C.

| Medium                               | C (ppm) | EIS                                   |        | Polarization    |                                  |        |
|--------------------------------------|---------|---------------------------------------|--------|-----------------|----------------------------------|--------|
|                                      |         | $R_{ct}$ ( $\Omega$ cm <sup>2</sup> ) | IE (%) | $E_{corr}$ (mV) | $I_{corr}$ (mA/cm <sup>2</sup> ) | IE (%) |
| 0.5 M H <sub>2</sub> SO <sub>4</sub> | 0       | 34.3                                  | -      | -538            | 3.954                            | -      |
|                                      | 800     | 59.2                                  | 42.06  | -491            | 2.221                            | 43.83  |
|                                      | 1200    | 78.1                                  | 56.10  | -489            | 1.723                            | 56.42  |
|                                      | 1600    | 99.5                                  | 65.54  | -487            | 1.396                            | 64.69  |
|                                      | 2000    | 112.2                                 | 69.44  | -485            | 1.231                            | 68.87  |
|                                      | 2400    | 124.5                                 | 72.45  | -483            | 1.053                            | 73.37  |
| 2800                                 | 137.6   | 75.07                                 | -482   | 1.004           | 74.61                            |        |
| 0.5 M HCl                            | 0       | 18.4                                  | -      | -513            | 4.840                            | -      |
|                                      | 800     | 57.3                                  | 67.91  | -498            | 1.515                            | 65.81  |
|                                      | 1200    | 66.9                                  | 72.48  | -489            | 1.302                            | 68.60  |
|                                      | 1600    | 78.1                                  | 76.43  | -480            | 1.126                            | 73.23  |
|                                      | 2000    | 100.6                                 | 81.70  | -478            | 0.886                            | 77.55  |
|                                      | 2400    | 121.5                                 | 84.85  | -474            | 0.769                            | 80.45  |
| 2800                                 | 163.3   | 88.73                                 | -472   | 0.613           | 87.52                            |        |

The IE (%) was calculated using the charge transfer resistance as follows:

$$IE(\%) = \frac{1/(R_{ct})_a - 1/(R_{ct})_p}{1/(R_{ct})_a} \times 100 \quad (4)$$

where,  $(R_{ct})_a$  and  $(R_{ct})_p$  are charge transfer resistances in the absence and presence of inhibitor, respectively.

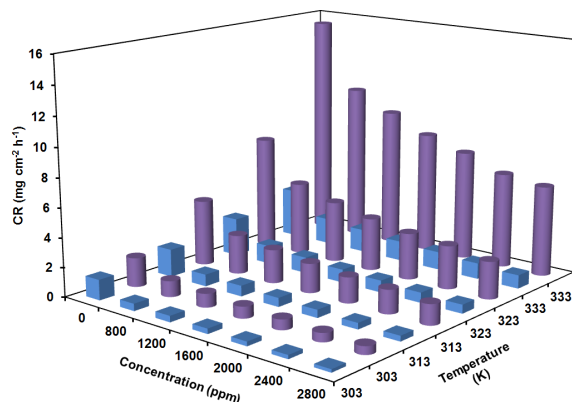
It is evident from the results that ZM leaves extracts inhibited the corrosion of mild steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> and 0.5 M HCl at all the concentrations used, and the IE (%) increased continuously with increasing concentration at 30 °C, and the maximum IE (%) of 75.07 and 88.73 were reached in 0.5 M H<sub>2</sub>SO<sub>4</sub> and 0.5 M HCl, respectively at 2800 ppm of ZM leaves extracts and further increase in concentration did not cause any noticeable change in IE (%). The results in Table 2 indicate that the  $R_{ct}$  significantly increases and  $C_{dl}$  tends to decrease. This decrease in  $C_{dl}$  may probably due to decrease in local dielectric constant and/or an increase in the thickness of a protective layer at electrode surface which enhances the corrosion resistance of the mild steel [34]. The increase in  $R_{ct}$  values is attributed to the formation of protective film at the metal-solution interface [35,36]. These observations suggest that ZM leaves extracts function by adsorption at the metal surface thereby causing decrease in  $C_{dl}$  values and increase in  $R_{ct}$  values. The decrease in  $C_{dl}$  can also be explained on the basis that the double layer between the charged metal surface and the solution is considered as an electrical capacitor. The adsorption of the inhibitor on the electrode surface reduces its electrical capacity because of the displacement of the water molecules and consequently decreases in the number of active sites necessary for the corrosion reaction [37]. The decrease in electrical capacity with increase in inhibitor concentration can be attributed to the formation of a protective layer on the electrode surface. The thickness of protective layer increases with increase in inhibitor concentration, because more inhibitor molecules get adsorbed on the electrode surface resulting in a noticeable decrease in  $C_{dl}$  [38].

### 3.4. Effect of temperature

In order to investigate the effect of temperature on the anticorrosion property of the inhibitor in 0.5 M H<sub>2</sub>SO<sub>4</sub> and 0.5 M HCl solutions, weight-loss measurements were studied in the temperature range of 30-60 °C in the absence and presence of different concentrations of inhibitor during 6 h of immersion. The CR gets increased with the rise in temperature in the uninhibited solution, but in the presence of inhibitor, CR gets highly reduced (Figure 5). Hence, inhibition efficiency decreases with the rise in temperature. It may be due to the fact that higher temperature accelerates hot-movement of the organic molecules and weakens the adsorption capacity of

inhibitor on the metal surface [39,40]. Thermodynamic parameters such as the activation energy  $E_a^*$ , the entropy of activation  $\Delta S^*$  and the enthalpy of activation  $\Delta H^*$  for the corrosion of mild steel in both the acids solution in the absence and presence of different concentrations ZM leaves extracts were calculated using the following Arrhenius-type equation:

$$CR = k \exp\left(-\frac{E_a^*}{RT}\right) \quad (5)$$



**Figure 5.** Variation of CR as a function of temperature and concentration of ZM leaves extracts.

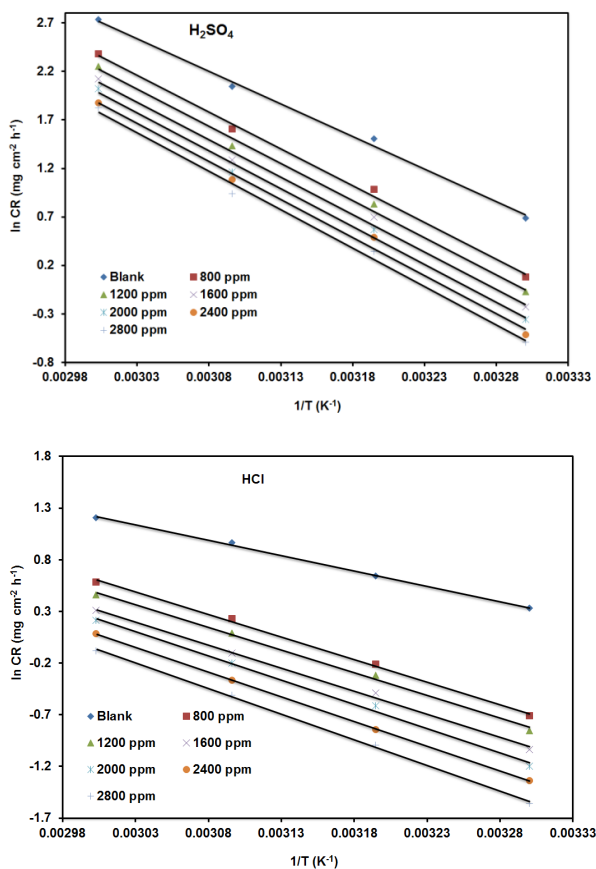
An alternative formulation of the Arrhenius equation is,

$$CR = \frac{RT}{Nh} \exp\left(\frac{\Delta S^*}{R}\right) \exp\left(-\frac{\Delta H^*}{RT}\right) \quad (6)$$

where,  $k$  is Arrhenius pre-exponential factor,  $h$  is Planck's constant,  $N$  is Avogadro's number,  $T$  is the absolute temperature and  $R$  is the universal gas constant. Using Eqn. (5), and from a plot of the  $\log CR$  versus  $1/T$  (Figure 6), the values of  $E_a^*$  and  $k$  at various concentrations of ZM leaves extracts were computed from slopes and intercepts, respectively. Further, using Eq. (6), plots of  $\log (CR/T)$  versus  $1/T$  gave straight lines (Figure 7) with a slope of  $(-\Delta H^*/2.303R)$  and an intercept of  $[\log (R/Nh) + \Delta S^*/2.303R]$  from which the values of  $\Delta H^*$  and  $\Delta S^*$  were calculated and are listed in Table 3. The lower or unchanged values of  $E_a^*$  in the inhibited systems compared to the blank suggest chemisorption mechanism [41], whereas higher values of  $E_a^*$  indicates a physical adsorption mechanism [42]. In the present study, the values of  $E_a^*$  in inhibited solution are increases when compared to uninhibited acid solutions (Table 3). This supports physisorption of ZM leaves extracts on mild steel surface.

**Table 3.** Activation parameters for mild steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> and 0.5 M HCl solutions in the absence and presence of different concentrations of ZM leaves extracts.

| Medium                               | Concentration (ppm) | <i>k</i>              | <i>E<sub>a</sub></i> (kJ/mol) | $\Delta H_a$ (kJ/mol) | $\Delta H_a = E_a - RT$ (kJ/mol) | $\Delta S_a$ (J/mol.K) |
|--------------------------------------|---------------------|-----------------------|-------------------------------|-----------------------|----------------------------------|------------------------|
| 0.5 M H <sub>2</sub> SO <sub>4</sub> | 0                   | 0.93×10 <sup>10</sup> | 56.01                         | 53.37                 | 53.16                            | -62.90                 |
|                                      | 800                 | 6.5×10 <sup>10</sup>  | 63.16                         | 60.53                 | 60.31                            | -44.39                 |
|                                      | 1200                | 7.2×10 <sup>10</sup>  | 63.63                         | 60.99                 | 60.77                            | -44.17                 |
|                                      | 1600                | 6.6×10 <sup>10</sup>  | 64.16                         | 61.52                 | 61.31                            | -43.67                 |
|                                      | 2000                | 10×10 <sup>10</sup>   | 64.86                         | 62.23                 | 62.01                            | -42.48                 |
|                                      | 2400                | 11×10 <sup>10</sup>   | 65.25                         | 62.61                 | 62.40                            | -42.19                 |
|                                      | 2800                | 13×10 <sup>10</sup>   | 65.90                         | 63.26                 | 63.04                            | -41.06                 |
| 0.5 M HCl                            | 0                   | 0.03×10 <sup>6</sup>  | 24.82                         | 22.18                 | 21.97                            | -169.06                |
|                                      | 800                 | 0.90×10 <sup>6</sup>  | 36.27                         | 33.63                 | 33.42                            | -140.56                |
|                                      | 1200                | 0.86×10 <sup>6</sup>  | 36.49                         | 33.85                 | 33.63                            | -140.17                |
|                                      | 1600                | 0.94×10 <sup>6</sup>  | 37.20                         | 34.56                 | 34.34                            | -139.39                |
|                                      | 2000                | 1.68×10 <sup>6</sup>  | 39.05                         | 36.41                 | 36.20                            | -134.55                |
|                                      | 2400                | 1.90×10 <sup>6</sup>  | 39.81                         | 37.17                 | 36.95                            | -133.54                |
|                                      | 2800                | 2.70×10 <sup>6</sup>  | 41.18                         | 38.54                 | 38.33                            | -130.63                |

**Figure 6.** Arrhenius plots of mild steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> and 0.5 M HCl in the absence and presence of different concentrations of ZM leaves extracts.

The positive sign of activation enthalpy ( $\Delta H^*$ ) reflects the endothermic nature of the steel dissolution process and that the dissolution of steel is difficult [43]. Negative values of ( $\Delta S^*$ ) imply that the activated complex in the rate determining step represents an association rather than a dissociation step, meaning that a decrease in disordering takes place on going from reactants to the activated complex [44,45].

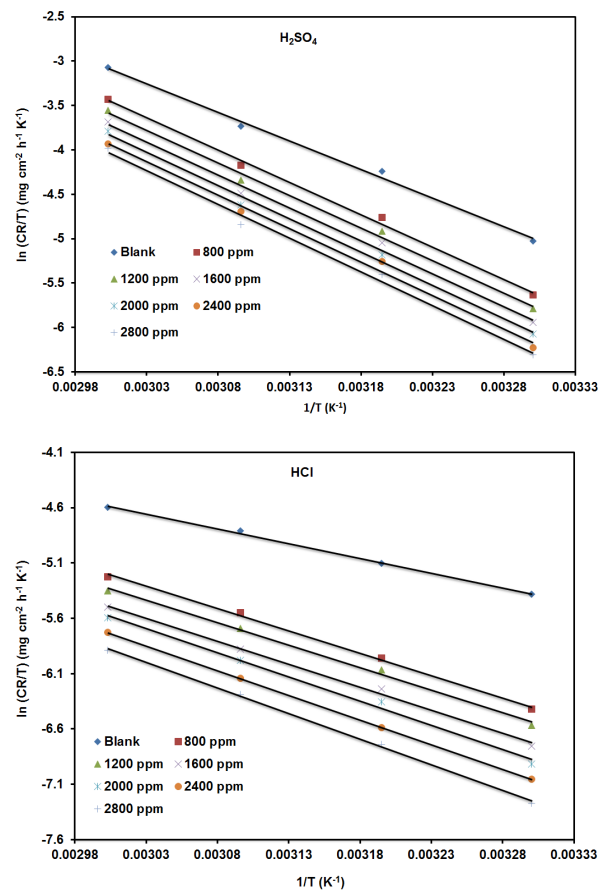
### 3.5. Adsorption isotherm

The degree of surface coverage ( $\theta$ ) as a function of the concentration of the inhibitor (C) was tested graphically by fitting it to various isotherms to find the best fit which describes this study. Langmuir adsorption isotherm was found to give the best description for ZM leaves extracts on mild steel.

According to this isotherm,  $\theta$  is related to the C and adsorption equilibrium constant  $K_{ads}$  as,

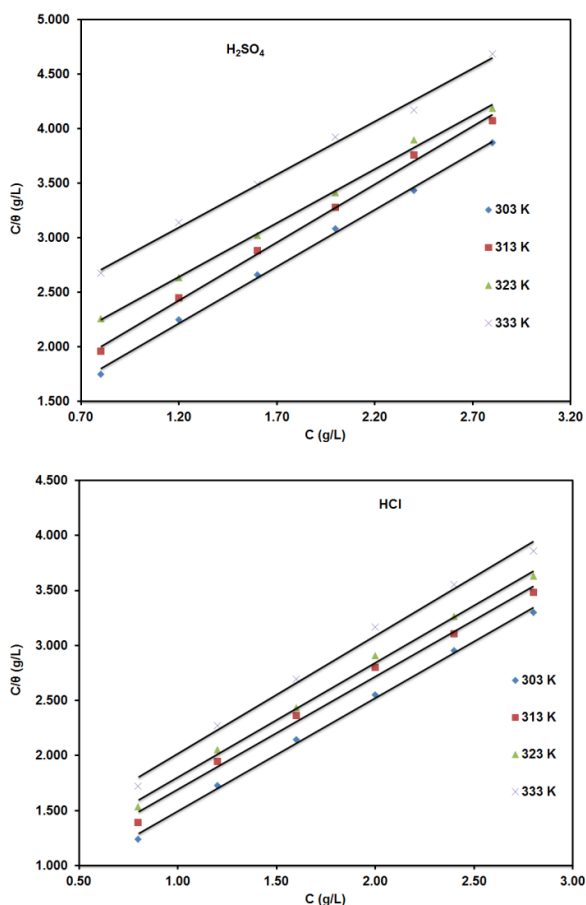
$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \quad (7)$$

The plot of  $C/\theta$  versus C gave a straight line (Figure 8) with a slope of around unity thereby confirming that the adsorption of ZM leaves extracts on mild steel surface in both the acids obeys the Langmuir adsorption isotherm.  $K_{ads}$  is related to the standard Gibbs' free energy of adsorption  $\Delta G_{ads}$  as per the equation 8.

**Figure 7.** Alternative Arrhenius plots of mild steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> and 0.5 M HCl in the absence and presence of different concentrations of ZM leaves extracts.

**Table 4.** Thermodynamic parameters for adsorption of *ZM* leaves extract on mild steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> and 0.5 M HCl solutions at different temperatures from Langmuir adsorption isotherm.

| Medium                               | Temperature (K) | R <sup>2</sup> | K <sub>ads</sub> (L/mol) | ΔG <sub>ads</sub> (kJ/mol) | ΔH <sub>ads</sub> (kJ/mol) | ΔS <sub>ads</sub> (J/mol.K) |
|--------------------------------------|-----------------|----------------|--------------------------|----------------------------|----------------------------|-----------------------------|
| 0.5 M H <sub>2</sub> SO <sub>4</sub> | 303             | 0.999          | 1.0341                   | -10.20                     | -19.59                     | -30.7                       |
|                                      | 313             | 0.997          | 0.8680                   | -10.08                     |                            |                             |
|                                      | 323             | 0.995          | 0.6849                   | -9.77                      |                            |                             |
|                                      | 333             | 0.992          | 0.5155                   | -9.29                      |                            |                             |
| 0.5 M HCl                            | 303             | 0.999          | 2.1739                   | -12.07                     | -20.52                     | -28.2                       |
|                                      | 313             | 0.997          | 1.4925                   | -11.49                     |                            |                             |
|                                      | 323             | 0.998          | 1.3157                   | -11.52                     |                            |                             |
|                                      | 333             | 0.996          | 1.0020                   | -11.12                     |                            |                             |

**Figure 8.** Langmuir adsorption isotherm of *ZM* leaves extracts on mild steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> and 0.5 M HCl at different temperatures.

$$K_{\text{ads}} = \frac{1}{55.5} \exp\left(\frac{-\Delta G_{\text{ads}}}{RT}\right) \quad (8)$$

where,  $R$  is the universal gas constant,  $T$  is the absolute temperature and 55.5 is the concentration of water in solution (mol/L). This isotherm assumes that the solid surface contains a fixed number of adsorption sites and each site holds one adsorbed species.

The negative values of  $\Delta G_{\text{ads}}$  suggest (Table 4) that the adsorption of inhibitor molecules onto steel surface is a spontaneous phenomenon. More negative values of  $\Delta G_{\text{ads}}$  suggest the strong interaction of the inhibitor molecules with the metal surface [46]. Generally, values of  $\Delta G_{\text{ads}}$  up to -20 kJ/mol are consistent with the electrostatic interaction between the charged molecules and the charged metal (physisorption) while those negative values higher than -40 kJ/mol involve sharing or transfer of electrons from the

inhibitor molecules to the metal surface to form a co-ordinate type of bond (chemisorption) [47]. In the present study the value of  $\Delta G_{\text{ads}}$  is about -20 kJ/mol which supports physisorption of *ZM* leaves extracts on mild steel [48]. The value of  $\Delta H_{\text{ads}}$  provides further information about the mechanism of corrosion inhibition. The negative value of  $\Delta H_{\text{ads}}$  indicates that adsorption process is exothermic. An exothermic adsorption process may be chemisorption or physisorption or mixture of both [49], whereas endothermic process is attributed to chemisorption [50]. In exothermic adsorption process, physisorption can be distinguished from the chemisorptions on the basis of values of  $\Delta H_{\text{ads}}$ . For physisorption process the magnitude of  $\Delta H_{\text{ads}}$  is around -40 kJ/mol or less negative while its value -100 kJ/mol or more negative for chemisorption [51]. In the present work, the value of  $\Delta H_{\text{ads}}$  indicates that the *ZM* extracts adsorb on the mild steel surface through physisorption.

### 3.6. Morphological Investigation

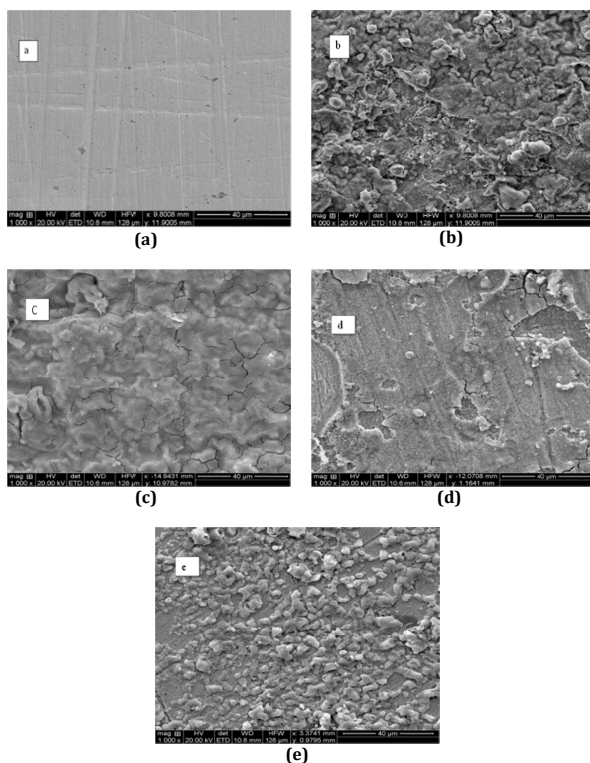
The protective layer that formed on the metal surface was characterized by SEM analysis. Morphologies of mild steel in the absence and presence of optimum concentration of *ZM* leaves extracts at 30 °C are shown in Figures 9a-e. It can be seen from Figure 9a that the mild steel samples before immersion seem smooth. Inspection of Figure 9b and 9c reveals that the mild steel surface after immersion in uninhibited 0.5 M sulphuric acid and 0.5 M hydrochloric acid solutions for 6 h shows an aggressive attack of the corroding medium on the steel surface. The corrosion products appeared very uneven and lepidoteral like morphology and the surface layer is rather rough. In contrast, in the presence of *ZM* leaves extracts there is an adsorbed film on the metal surface (Figure 9d and 9e).

### 4. Conclusion

The *ZM* leaves extracts effectively inhibited the corrosion of mild steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> and 0.5 M HCl solutions by forming protective layer, and it absorbs on the mild steel surface according to Langmuir adsorption isotherm. The inhibition efficiency increases with concentration. Electrochemical polarization study revealed that the *ZM* leaves extracts acts as mixed type of inhibitor by reducing both anodic and cathodic current densities. EIS results revealed that, as the inhibitor concentration increased the charge transfer resistance increased and the double layer capacity decreased. *ZM* leaves extracts was found to be a better corrosion inhibitor in 0.5 M HCl when compared to 0.5 M H<sub>2</sub>SO<sub>4</sub>. All the results obtained from EIS, polarization and weight loss are in good agreement with each other.

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**Figure 9.** SEM images of mild steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> and 0.5 M HCl solution after 6 h of immersion at 30 °C (a) Before immersion (polished) (b) After immersion in 0.5 M H<sub>2</sub>SO<sub>4</sub> without inhibitor (c) After immersion in 0.5 M HCl without inhibitor (d) with 2800 ppm ZM leaves extracts in 0.5 M H<sub>2</sub>SO<sub>4</sub> medium (e) with 2800 ppm ZM leaves extracts in 0.5 M HCl.

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