



## Studies on the Inhibitive Performance of *Cinnamomum zeylanicum* Extracts on the Corrosion of Mild Steel in Hydrochloric Acid and Sulphuric Acid Media

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### Abstract

The inhibitive performance of leaf extracts of *cinnamomum zeylanicum* (CZ) was tested as natural corrosion inhibitor for mild steel in 0.5 M HCl and 0.5 M H<sub>2</sub>SO<sub>4</sub>, respectively by using gravimetric and electrochemical techniques. The data obtained from both the methods are in good agreement with each other. Results indicate that leaf extracts of CZ is an efficient natural corrosion inhibitor in both the acid solutions. The inhibition efficiency was found to increase with increase in CZ extracts concentration in both the medium. Furthermore, the inhibition efficiency decreases with increase in temperature. Polarization measurements showed that the studied inhibitor acts as mixed inhibitor in both the acids with significant reduction of cathodic and anodic current densities. The adsorption characteristics of CZ extracts of on mild steel surface obeys Langmuir isotherm. Calculated values of free energy of adsorption and heat of adsorption indicate physical adsorption. The electrochemical impedance study further confirms the formation of an adsorbed film on the mild steel. Kinetic parameters were calculated and discussed, and SEM was used to analyze the surface adsorbed film.

**Keywords:** mild steel, polarization, adsorption, electrochemical impedance, SEM.

### 1. Introduction

Mild steel is commonly used in many industries because of cost-effective and easy fabrication, but it is prone to undergo corrosion in aggressive environmental conditions. Usually, sulphuric acid and hydrochloric acid are used in acid pickling, chemical cleaning to eliminate detrimental rust and scale in several industries. One of the significant methods of dealing with this problem is the usage of corrosion inhibitors in the aggressive media [1]. Number of synthetic compounds showed good anticorrosive activity, however many of them is highly harmful to environment [2]. Plant extracts contain mixtures of compounds having oxygen, sulphur and nitrogen have been employed as eco-friendly, cheap and renewable inhibitors [3-5]. A large number of research studies have been devoted to the inhibitive performance of natural corrosion inhibitors on the corrosion of metals in various aggressive solutions showing that these extracts could act as potential corrosion inhibitors. Extracts of *azadirachta indica* [6], *isertia coccinea* [7], *prosopis cineraria* [8], *hibiscus sabdariffa* extract [9], *clematis gouriana* [10], *phyllanthus amarus* extracts [11], *jasminum nudiflorum* [12], *acalypha indica* [13], henna [14], *carica papaya* extracts [15], *menthe pulegium* [16], *occimum viridis* extract [17], *Centella asiatica* [18] *Chamaerops humilis* [19], *Adhatoda vasica* [20], *Cyperus esculentus* L [21] and radish [22] have been used as corrosion inhibitors for mild steel in various media.

*Cinnamomum zeylanicum* is an evergreen tropical tree, belongs to the Lauraceae family. Cinnamon barks and leaves are extensively used as spice and flavouring agent in foods [23] and for several applications in medicine [24]. The major chemical constituent of cinnamon *zeylanicum* barks is trans-cinnamaldehyde, and it showed antimicrobial effects against animal and plant pathogens, food poisoning and spoilage bacteria and fungi [25]. The cinnamon leaves is rich in eugenol and buds contain large quantity of sesquiterpenes ( $\alpha$ -bergamotene and  $\alpha$ -copaene) [26]. It has been recognized that the oils and extracts from cinnamon possess a good antioxidant activity, which is mainly due to the presence of phenolic and polyphenolic substances [27]. In view of its phytochemical investigation, the present paper reporting for the first time the effect of CZ extracts on the corrosion behaviour of mild steel in HCl and H<sub>2</sub>SO<sub>4</sub> media using gravimetric, potentiodynamic polarization and electrochemical impedance measurements. Various thermodynamic parameters were computed from the

experimental data obtained from weight loss measurements at various temperatures. The energy of activation and pre-exponential factor at various concentrations of the CZ extracts were also calculated and their effects on the corrosion rate of mild steel were discussed. The surface morphology of the mild steel specimen has been analysed by SEM.

## 2. Materials and methods

### 2.1. Preparation of Plant extract

Dried Cinnamomum leaves were cleaned with water and then ground to powder. The 10 g of the powder sample was refluxed in 250 mL ethyl alcohol for 5 h. The refluxed solution was filtered and concentrated to 100 mL dark green 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. Various concentrations of the plant extracts were prepared by dissolving the known quantity of the resultant powder in 0.5 M HCl and 0.5 H<sub>2</sub>SO<sub>4</sub> solution.

### 2.2. Preparation of the Metal Specimen

Corrosion tests were carried out on mild steel having the following chemical 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. Before performing the gravimetric and electrochemical measurements, the surface of the specimens were polished under running tap water by using different grade SiC emery paper, cleaned 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 desiccator until use. At the end of the test, the specimens were carefully washed with acetone and benzene, dried, and then weighed.

### 2.3. Preparation of Aggressive Solutions

The aggressive solutions of 0.5 M HCl and 0.5 M H<sub>2</sub>SO<sub>4</sub> were prepared by dilution of analytical grade HCl and H<sub>2</sub>SO<sub>4</sub> with double distilled water. A series of concentrations of CZ extracts were (500 ppm-1750 ppm) used in both HCl and H<sub>2</sub>SO<sub>4</sub>, respectively.

### 2.4. Gravimetric Measurements

Pre-weighed mild steel coupons with a dimension of 2 × 2 × 0.3 cm were immersed in 200 ml 0.5 M HCl and 0.5 M H<sub>2</sub>SO<sub>4</sub> in the absence and presence of different concentrations of CZ extracts in an aerated condition. After 6 h of immersion, the specimens were removed, washed, dried and weighed accurately. Experiments were performed in triplicate. The average weight loss of the three parallel specimens was obtained. Average weight losses of the coupons were used to calculate the per cent inhibition efficiency (IE %). Then the tests were repeated with different concentrations of CZ at varying temperatures.

### 2.5. Electrochemical Measurements

Polarization and Electrochemical impedance spectroscopy (EIS) experiments were performed using a CHI660D electrochemical workstation. A conventional three-electrode cell with a saturated calomel reference electrode, a platinum auxiliary electrode and the working electrode with 1cm<sup>2</sup> exposed areas were used. The specimens were pre-treated similarly as done in the gravimetric measurements. The electrochemical tests were carried out at different concentrations of CZ extracts ranging from 0 to 1750 ppm at 30 °C using a thermostatically controlled water bath (Weiber, India) under aerated condition. Potentiodynamic polarization measurements were made in the potential range from -900 to +500 mV with a scan rate of 0.4 mV s<sup>-1</sup>. The AC impedance measurements were performed in the frequency range of 10 to 0.05 kHz with signal amplitude of ± 10 mA.

## 3. Results and discussion

### 3.1. Gravimetric measurements

Gravimetric measurements were carried out in the absence and presence of various concentrations of the CZ extracts at different temperature in 0.5 M HCl and 0.5 M H<sub>2</sub>SO<sub>4</sub> after 6 h of immersion and corresponding corrosion rate ( $C_R$ ), inhibition efficiency (IE%) and degree of surface coverage ( $\theta$ ) are tabulated in the Table 1. The values of  $C_R$  and IE (%) were calculated using the following equations:

$$C_R = \frac{W_a - W_f}{S t} \quad (1)$$

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

$$\theta = 1 - \frac{(C_R)_p}{(C_R)_a} \quad (3)$$

where  $W_a$  and  $W_p$  are the weight losses in the absence and presence of the inhibitor, respectively,  $S$  is the surface area of the specimen ( $\text{cm}^2$ ),  $t$  is immersion time (h), and  $C_R$  is expressed in  $\text{mg cm}^{-2} \text{h}^{-1}$ . Inspection of the data in Table 1 revealed that the addition of CZ decreases markedly the corrosion rate of mild steel. The inhibition efficiency increases with concentration of added CZ at all studied temperatures, and as the concentration reached to 1750 ppm, IE (%) of CZ extract gained a high value of 96.21 and 83.18 in 0.5 M HCl and 0.5 M  $\text{H}_2\text{SO}_4$ , respectively at 40 °C, which represents excellent inhibitive ability. This is due to the fact that, adsorption and the degree of surface coverage of inhibitor on the mild steel increases with the inhibitor concentration, consequently the mild steel surface is efficiently separated from the aggressive solution [28]. The results obtained from the gravimetric measurements are in good agreement with those obtained from the electrochemical methods.

**Table 1:** Corrosion parameters for mild steel in 0.5 M  $\text{H}_2\text{SO}_4$  and 0.5 M HCl containing various concentrations of CZ leave extracts at different temperatures

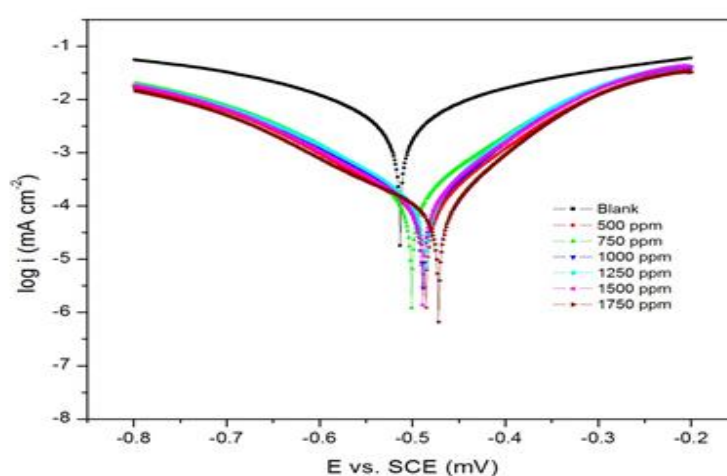
T (K)	C (ppm)	$C_R$ ( $\text{mg cm}^{-2} \text{h}^{-1}$ )	IE (%)	$C_R$ ( $\text{mg cm}^{-2} \text{h}^{-1}$ )	IE (%)
		0.5 M $\text{H}_2\text{SO}_4$		0.5 M HCl	
303	Blank	1.991	-	1.39	-
	500	0.913	54.14	0.211	84.86
	750	0.709	64.39	0.187	86.59
	1000	0.660	66.83	0.180	87.08
	1250	0.605	69.61	0.149	89.31
	1500	0.528	73.48	0.102	92.68
	1750	0.421	78.85	0.080	94.29
313	Blank	4.520	-	1.90	-
	500	2.124	52.99	0.351	81.50
	750	1.672	62.98	0.297	84.35
	1000	1.494	66.93	0.211	88.88
	1250	1.193	73.59	0.195	89.73
	1500	0.993	78.02	0.129	93.20
	1750	0.760	83.18	0.078	96.21
323	Blank	7.713	-	2.63	-
	500	4.332	43.84	0.681	74.09
	750	3.213	58.34	0.494	81.20
	1000	2.911	62.26	0.402	84.70
	1250	2.441	68.35	0.384	85.39
	1500	2.141	72.24	0.258	90.18
	1750	1.664	78.43	0.202	92.31
333	Blank	15.403	-	3.35	-
	500	10.123	34.28	1.304	61.09
	750	7.991	48.12	0.982	70.70
	1000	7.131	53.70	0.851	74.60
	1250	6.592	57.20	0.775	76.87
	1500	5.797	62.36	0.604	81.98
	1750	4.647	69.83	0.495	85.23

### 3.2. Potentiodynamic Polarization

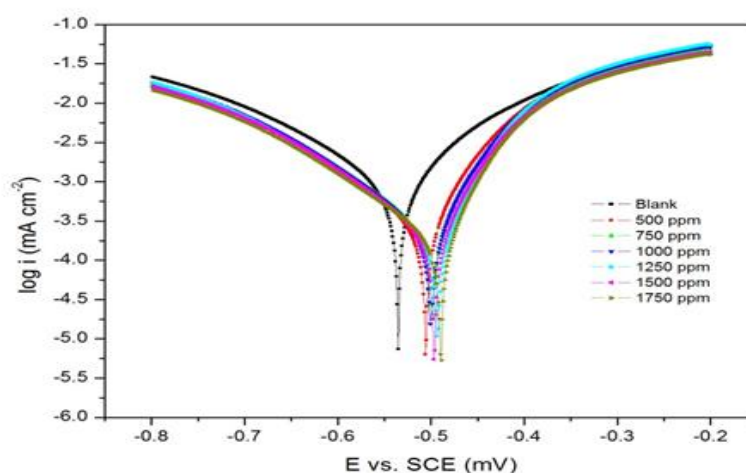
The anodic and cathodic polarization curves of mild steel electrode in 0.5 M HCl and 0.5 M H<sub>2</sub>SO<sub>4</sub> in the absence and presence of different concentrations of CZ extracts at 30 °C are revealed in Figs. 1 and 2. The values of associated electrochemical parameters such as corrosion potential ( $E_{corr}$ ) and corrosion current density ( $I_{corr}$ ) were calculated from the intersection of anodic and cathodic Tafel slopes of the polarization curves. The inhibition efficiency IE (%) can be calculated using the equation given below:

$$IE (\%) = \frac{(I_{corr})_a - (I_{corr})_p}{(I_{corr})_a} \times 100 \quad (4)$$

where  $(I_{corr})_a$  and  $(I_{corr})_p$  are the corrosion current density (mA cm<sup>-2</sup>) in the absence and the presence of the inhibitor, respectively. It is observed in Figs. 1 and 2 that the presence of CZ decreases both cathodic and anodic slopes with the increased inhibitor concentration. This may be ascribed to adsorption of inhibitor over the corroded metal surface [29]. Since both anodic and cathodic reactions were suppressed, the CZ extracts behaves as a mixed inhibitor [30].



**Figure 1:** Tafel plots for mild steel in 0.5 M HCl at different concentrations of CZ at 30 °C.



**Figure 2:** Tafel plots for mild steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> at different concentrations of CZ at 30 °C.

The results of the polarization measurements are tabulated in Table 2. It is apparent that  $I_{corr}$  decreases significantly with increasing concentration of CZ extracts, and the maximum IE (%) of 93.78 (0.5 M HCl) and 80.93 (0.5 M H<sub>2</sub>SO<sub>4</sub>) observed at 1750 ppm of CZ extracts. This is because of increase in the blocked portion of the metal surface by adsorption. Further, the concentration of CZ has less effect on the  $E_{corr}$  which shows that CZ acts as a mixed type of inhibitor. Ferreira and others [31-32] reported that, if the deviation in the  $E_{corr}$  is greater than 85 mV in the presence of inhibitor with respect to blank, the inhibitor could be recognized as cathodic or anodic type however the deviation in  $E_{corr}$  less than 85 mV, it could be recognized as mixed type of inhibitor. In

the present investigation, the maximum deviation range is less than 85 mV which reveals that CZ extracts acts as mixed type of inhibitor.

**Table 2:** Polarization and impedance parameters for mild steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> and 0.5 M HCl solutions containing different concentrations of CZ leaves extracts at 30 °C

C (ppm)	EIS		Polarization		
	$R_{ct}$ , $\Omega \text{ cm}^2$	IE (%)	$E_{corr}$ , mV	$I_{corr}$ , $\text{mA cm}^{-2}$	IE (%)
0.5 M H <sub>2</sub> SO <sub>4</sub>	34.3	-	-538	3.954	-
500	80.50	57.39	-508	1.623	58.95
750	98.78	65.28	-500	1.422	64.01
1000	119.54	71.31	-495	1.088	72.48
1250	129.55	73.52	-491	0.991	74.94
1500	147.87	76.80	-488	0.861	78.22
1750	185.62	81.52	-483	0.754	80.93
0.5 M HCl	18.40	-	-513	4.840	-
500	129.17	85.76	-496	0.672	86.11
750	144.73	87.29	-485	0.639	86.80
1000	169.30	89.13	-479	0.555	88.53
1250	199.39	90.77	-476	0.432	91.07
1500	334.21	94.49	-474	0.356	92.64
1750	433.91	95.76	-463	0.301	93.78

### 3.3 . Electrochemical impedance spectroscopy

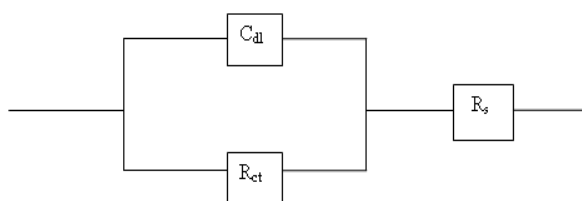
The outcome of the potentiodynamic polarization experiments were further confirmed by electrochemical impedance spectroscopy. Generally, the Nyquist plots are studied in terms of the equivalent circuit containing parallel capacitor and resistor, which includes the solution resistance ( $R_s$ ) and double layer capacitance ( $C_{dl}$ ) as shown in Fig. 3. The corrosion performance of mild steel in 0.5 M HCl and 0.5 M H<sub>2</sub>SO<sub>4</sub> in the absence and presence of CZ extracts was examined by the impedance technique at 30 °C and results are represented by Nyquist plots as revealed in Figs. 4 and 5.

The inhibition efficiency IE (%) was calculated by means of charge transfer resistance as given bellow.

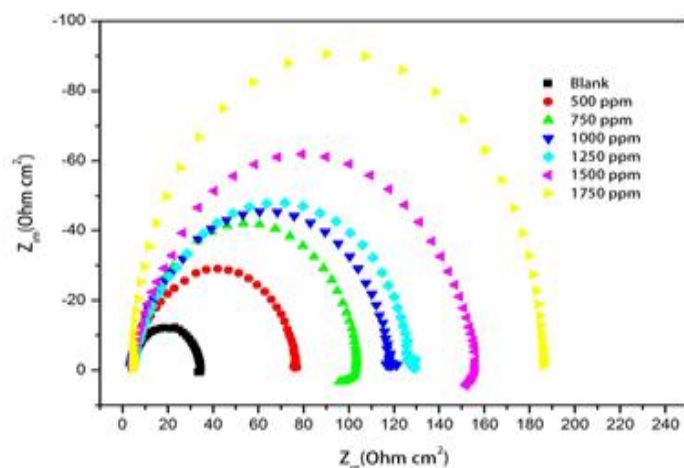
$$IE(\%) = \frac{(1/R_{ct})^a - (1/R_{ct})^p}{(1/R_{ct})^a} \times 100 \quad (5)$$

Where  $R_{ct(a)}$  and  $R_{ct(p)}$  are the charge transfer resistance in the absence and presence of inhibitor, respectively.

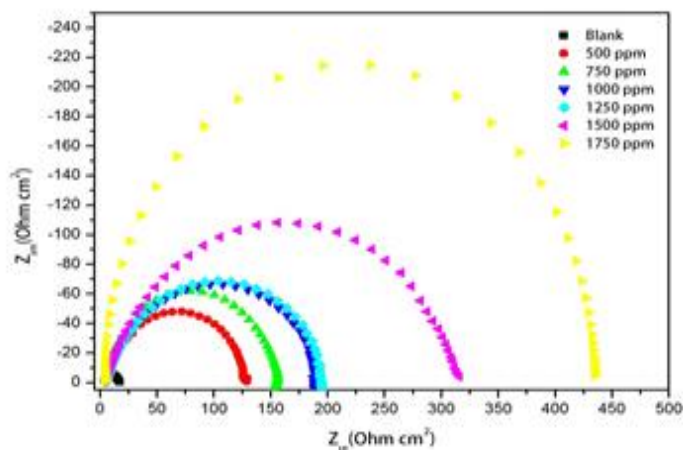
It is evident from the results that the CZ prevent the corrosion of mild steel in 0.5 M HCl and 0.5 M H<sub>2</sub>SO<sub>4</sub> solution at all studied concentrations, and the IE (%) was seem to rise continuously with increasing concentration at 30 °C, and the maximum IE (%) of 95.76 and 81.52 were observed at 1750 ppm. Inspection of the results in Table 2 indicates that the  $R_{ct}$  significantly increases and  $C_{dl}$  tend to decrease.



**Figure 3:** Equivalent circuit diagram.



**Figure 4:** 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 CZ leaves extracts at 30 °C.



**Figure 5:** Nyquist plots of mild steel in 0.5 M HCl in the absence and presence of various concentrations of CZ leaves extracts at 30 °C.

The decrease in  $C_{dl}$  may be because of a reduction 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 [33]. The increase in  $R_{ct}$  values is attributed to the development of a protective film on the metal-solution interface [34]. These observations indicate that CZ extracts function by adsorption at metal surface thus decreases  $C_{dl}$  values and increases in  $R_{ct}$  values. The reduction of  $C_{dl}$  values can also be explained in terms of double layer between the charged metal surface and the solution which acts as an electrical capacitor and adsorption of the inhibitor on the electrode surface which decreases its electrical capacity because they displace the water molecules and consequently reduction in the number of active sites needed for the corrosion reaction [35]. The reduction in double layer capacitance with increase in inhibitor concentration could be ascribed to the development of a protective film on the electrode surface.

### 3.4. Effect of temperature

In order to investigate the influence of temperature on the anticorrosion effectiveness of the inhibitor in 0.5 M HCl and 0.5 M H<sub>2</sub>SO<sub>4</sub>, gravimetric measurements were studied in the temperature range 30–60 °C in the absence and presence of different concentrations of inhibitor during 6 h of immersion. The resultant data are summarized in Table 1. It is confirmed that the increase of  $C_R$  is more prominent with increase in temperature for uninhibited solution and in the presence of inhibitor,  $C_R$  is significantly reduced. Hence, inhibition efficiency decreases with

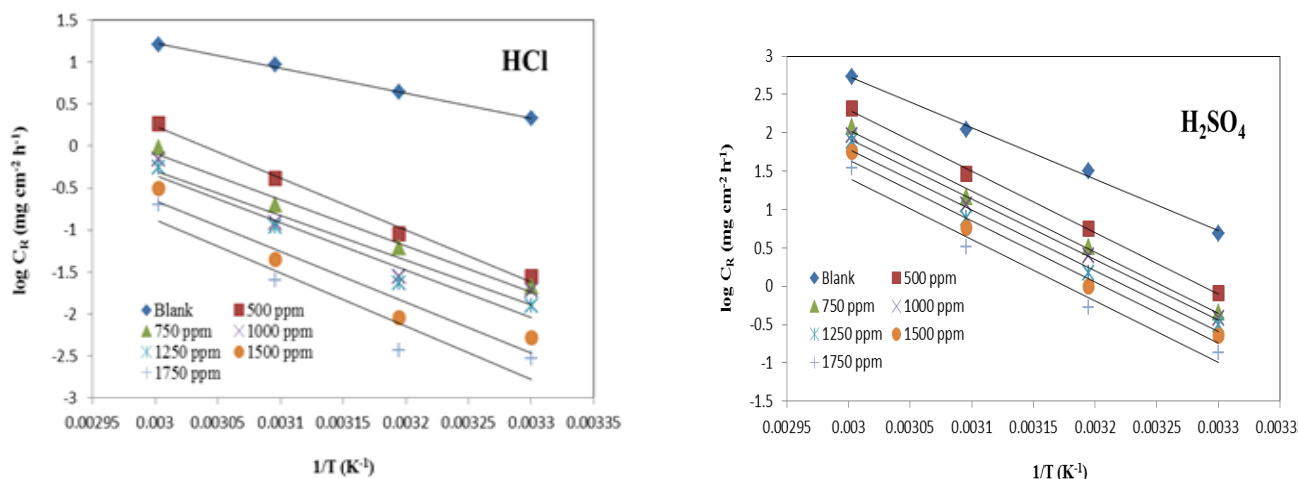
the rise of temperature in both the acids. It is probably due to fact that the higher temperature could accelerate hot-movement of the organic molecules and weaken the adsorption capacity of inhibitors on metal surface [36]. Thermodynamic parameters such as the energy of activation  $E_a^*$ , the entropy of activation  $\Delta S^*$  and the enthalpy of activation  $\Delta H^*$  for the corrosion of mild steel in 0.5 M HCl and H<sub>2</sub>SO<sub>4</sub> solutions in the absence and presence of various concentrations CZ extracts were calculated from the following Arrhenius-type equation:

$$C_R = A \exp\left(-\frac{E_a^*}{RT}\right) \quad (6)$$

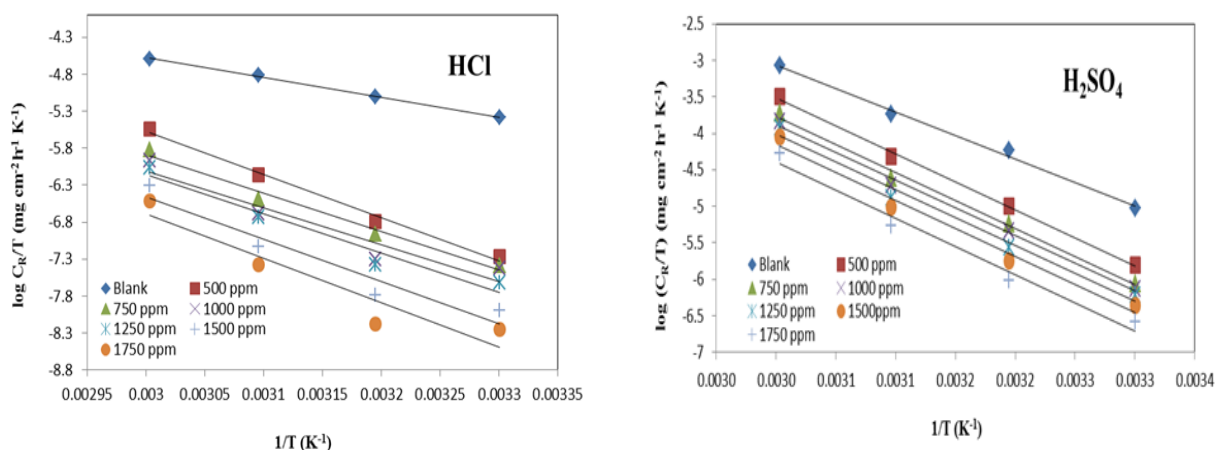
An alternative formulation of the Arrhenius equation is,

$$C_R = \frac{RT}{Nh} \exp\left(\frac{\Delta S^*}{R}\right) \exp\left(-\frac{\Delta H^*}{RT}\right) \quad (7)$$

where  $A$  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 Eq. (6), and from a plot of the log of  $C_R$  versus  $1/T$  (Fig. 6), the values of  $E_a^*$  and  $A$  at various concentrations of CZ extracts were calculated from slopes and intercepts, respectively. Further, using Eq. (7), plots of  $\log(C_R/T)$  versus  $1/T$  gave straight lines (Fig. 7) with a slope of  $(-\Delta H^*/2.303R)$  and an intercept of  $[\log(R/Nh) + \Delta S^*/2.303R]$  and corresponding values of  $\Delta H^*$  and  $\Delta S^*$  were calculated and are tabulated in Table 3.



**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 CZ leaves extracts



**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 various concentrations of CZ leaves extracts

According to Eq. (6), the influence of concentration on the apparent activation energy is shown in Fig. 6, and the values of  $E_a^*$  in the inhibited solutions are higher than those in the uninhibited acid solution (Table 3). The reduction of inhibition efficiencies with rise in temperature and the increase of  $E_a^*$  in the presence of the inhibitor indicates slow reaction and that the reaction is very sensitive to temperature [37]. This type of

inhibitors retard corrosion at normal temperatures, but inhibition is reduced at higher temperatures. The higher values of  $E_a^*$ , in inhibited solution when compared to that of uninhibited one is an indication of an electrostatic character of the inhibitor [38]. The positive sign of the activation enthalpy ( $\Delta H^*$ ) reveals the endothermic nature of the steel dissolution process and that the dissolution of steel is difficult [39].

**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 CZ leaves extracts

Concentration (ppm)	$k$	$E_a$ (kJ mol <sup>-1</sup> )	$\Delta H_a$ (kJ mol <sup>-1</sup> )	$\Delta H_a = E_a - RT$ (kJ mol <sup>-1</sup> )	$\Delta S_a$ (J mol <sup>-1</sup> K <sup>-1</sup> )
0.5 M H <sub>2</sub> SO <sub>4</sub>	$0.93 \times 10^{10}$	56.01	53.37	53.16	-62.90
500	$26 \times 10^{10}$	66.48	63.84	60.31	-35.25
750	$19 \times 10^{10}$	66.37	63.73	60.77	-37.75
1000	$12 \times 10^{10}$	65.40	62.76	61.31	-41.57
1250	$13 \times 10^{10}$	65.91	63.27	62.01	-41.15
1500	$14 \times 10^{10}$	66.51	63.87	62.40	-40.49
1750	$12 \times 10^{10}$	66.74	64.10	63.04	-41.82
0.5 M HCl	$0.03 \times 10^6$	24.82	22.18	21.97	-169.06
500	$0.90 \times 10^6$	51.29	48.65	33.42	-97.94
750	$0.86 \times 10^6$	45.86	43.22	33.63	-116.87
1000	$0.94 \times 10^6$	44.15	41.51	34.34	-123.78
1250	$1.68 \times 10^6$	46.92	44.28	36.20	-115.89
1500	$1.90 \times 10^6$	50.22	47.58	36.95	-108.50
1750	$2.70 \times 10^6$	52.54	49.90	38.33	-103.43

The activation entropy  $\Delta S^*$  increases more positively in the inhibited solution than in the uninhibited one. This reveals the formation of an ordered stable film of the inhibitor molecule on the steel surface [40], and the activated complex in the rate determining step represent an association rather than a dissociation step, meaning that an increase in disordering takes place on moving from reactants to the activated complex [41].

### 3.5. Adsorption isotherm

The interaction between the inhibitors and steel surface can be provided by the adsorption isotherm. During corrosion inhibition of mild steel, the nature of inhibitor on the corroding surface has been deduced in terms of adsorption behavior of inhibitors. Many attempts were made to find the best isotherm which describes this study. Langmuir adsorption isotherm was found to be the best description for CZ extracts on mild steel. According to this isotherm,  $\theta$  is related to the  $C$  and adsorption equilibrium constant  $K_{ads}$ , via:

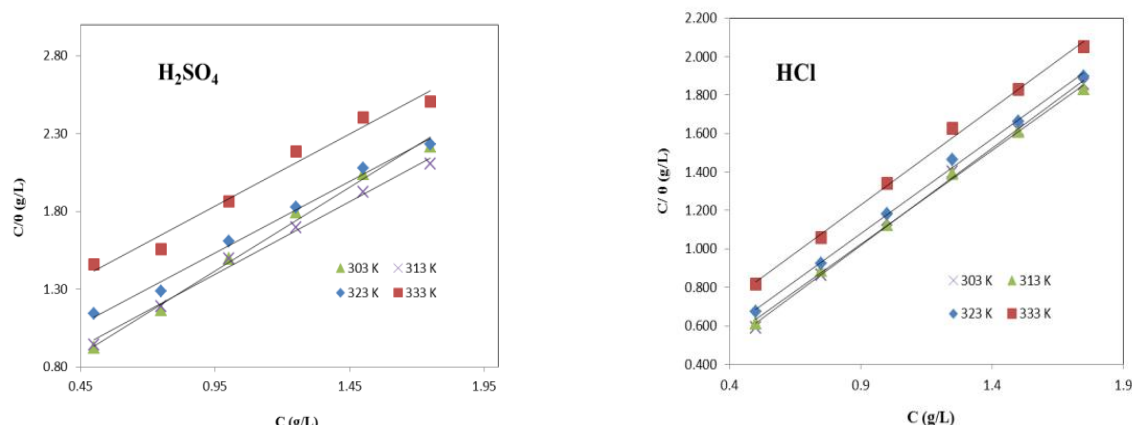
$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \quad (8)$$

The plot of  $C/\theta$  versus  $C$  gave a straight line (Fig. 8) with a slope of about unity confirming that the adsorption of CZ extracts on mild steel surface both HCl and H<sub>2</sub>SO<sub>4</sub> obeys the Langmuir adsorption isotherm.  $K_{ads}$  is connected to the standard Gibb's free energy of adsorption  $\Delta G_{ads}$ , according to the equation given below:

$$K_{ads} = \frac{1}{55.5} \exp\left(\frac{-\Delta G_{ads}}{RT}\right) \quad (9)$$

Where R is the universal gas constant, T is the absolute temperature and 55.5 is the concentration of water in solution (mol L<sup>-1</sup>). 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  $\Delta G_{ads}$  suggest that the adsorption of inhibitor onto steel surface is a spontaneous process [42]. More negative values of  $\Delta G_{ads}$  also indicate the strong interaction of the inhibitor molecules onto the metal surface [43].





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

The enthalpy and entropy of adsorption ( $\Delta H_{ads}$  and  $\Delta S_{ads}$ ) can be calculated using the equations (10) and (11).

$$\ln K_{ads} = \ln \left( \frac{1}{55.5} \right) - \frac{\Delta G_{ads}}{RT} \quad (10)$$

The values of  $\Delta H_{ads}$  and  $\Delta S_{ads}$  can also be calculated by using following equation:

$$\Delta G_{ads} = \Delta H_{ads} - T \Delta S_{ads} \quad (11)$$

Using Eq. (11), the plot of  $\Delta G_{ads}$  versus T gives a straight line with a slope of  $-\Delta S_{ads}$  and intercept of  $\Delta H_{ads}$ . The values obtained are correlated with those obtained from Eq. (11). The negative values of  $\Delta H_{ads}$  indicate that the adsorption process is an exothermic phenomenon [41]. The exothermic process is attributed to either physical or chemical adsorption or mixture of [44] whereas endothermic process corresponds to chemisorption [44-46]. The negative values of  $\Delta S_{ads}$  in both the acids implies that the activated complex in the rate determining step denotes an association rather than a dissociation step, meaning that a reduction in disordering takes place on going from reactants to the activated complex [47].

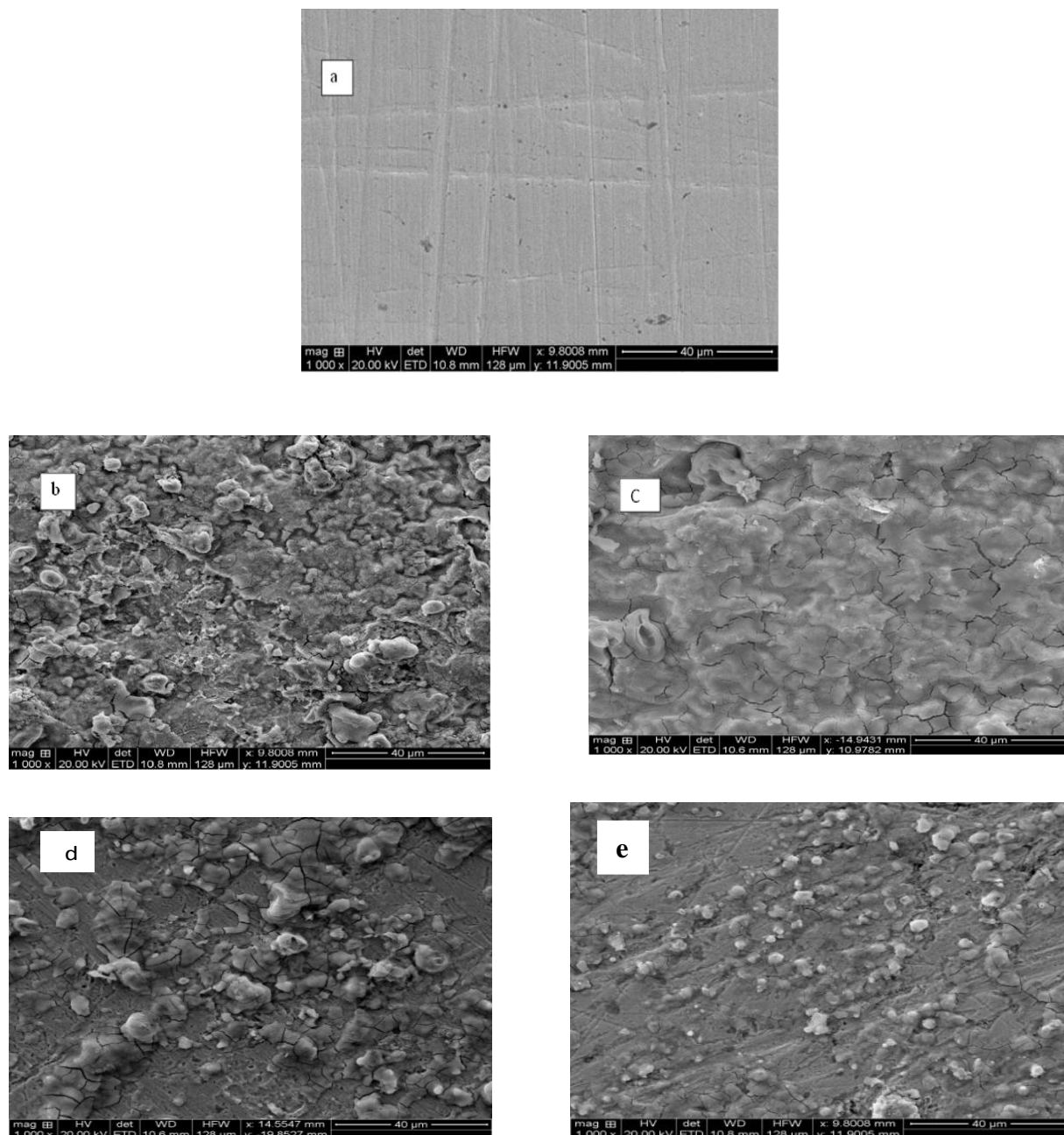
**Table 4:** Thermodynamic parameters for adsorption of CZ leaves extract on mild steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> and 0.5 M HCl solutions at different temperature

Temperature (K)	R <sup>2</sup>	K <sub>ads</sub> (L g <sup>-1</sup> )	ΔG <sub>ads</sub> (kJ g <sup>-1</sup> )	ΔH <sub>ads</sub> (kJ g <sup>-1</sup> )	ΔS <sub>ads</sub> (J g <sup>-1</sup> K <sup>-1</sup> )	ΔG=HΔ-TΔS (kJ g <sup>-1</sup> )
0.5M HCl						
303	0.992	2.519	-12.45	-24.45	-39.30	-12.54
313	0.994	1.984	-12.23			-12.15
323	0.991	1.515	-11.90			-11.76
333	0.975	1.047	-11.25			-11.36
0.5M H <sub>2</sub> SO <sub>4</sub>						
303	0.998	9.434	-15.77	-43.96	-90.20	-16.63
313	0.998	7.143	-15.57			-15.73
323	0.998	5.155	-15.19			-14.83
333	0.997	3.049	-14.21			-13.92

### 3.6. Morphological Investigation

Figures 9a – 9e show a SEM photographs recorded for mild steel samples exposed for 6 h in 0.5 M HCl and 0.5 M H<sub>2</sub>SO<sub>4</sub> in the absence and presence of 1750 ppm CZ extracts at 30 °C. It can be seen from Figure 9a that the mild steel samples before immersion appear smooth. Inspection of Figures 10b and 10c indicate that the mild steel surface after immersion in uninhibited 0.5 M sulphuric acid and 0.5 M hydrochloric acid solutions for 6 h

confirms an attack of the aggressive medium on the steel surface. But, in inhibited solution, the rate of corrosion is suppressed, as the electrode surface is nearly free from corrosion due to the adsorption of the inhibitor on the mild steel surface (Figures 9d and 9e)



**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 1750 ppm CZ leaves extracts in 0.5 M H<sub>2</sub>SO<sub>4</sub> medium (e) with 1750 ppm CZ leaves extracts in 0.5 M HCl

### Conclusions

The CZ leaves extracts effectively inhibit 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. The CZ leaves extracts on the mild steel surface follows Langmuir adsorption isotherm. The inhibition efficiency increases with concentration of the inhibitor. Electrochemical polarization study revealed that the CZ leaves extracts acts as mixed type of inhibitor by reducing both anodic and cathodic

current densities. EIS results indicate that, as the inhibitor concentration increased the charge transfer resistance increased and the double layer capacitance decreased. The results obtained from all the three methods are in good agreement with each other.

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