

Inhibition Effect of Reed Leaves Extract on Steel in Hydrochloric Acid and Sulphuric Acid Solutions

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The corrosion inhibition of mild steel in 1.0 M HCl and 0.5 M H₂SO₄ by the *reed* leaves extract (RLE) has been studied using weight loss methods and potentiodynamic polarization techniques. The results show that the inhibition efficiency increases with the increase of RLE concentration in both acids, and the higher inhibition efficiency is obtained in 0.5 M H₂SO₄ solutions. The effect of temperature, immersion time and acid concentration on the corrosion behavior of mild steel in 1M HCl and 0.5 M H₂SO₄ with addition of extract was also studied. The adsorption of RLE molecules on the steel surface obeys Langmuir adsorption isotherm in both acids, and occurs spontaneously. The activation energy as well as other thermodynamic parameters (E_a , ΔH , and ΔS) for the inhibition process was calculated. These thermodynamic parameters show strong interaction between inhibitor and mild steel surface.

Keywords: Mild steel, Corrosion, Weight loss, Polarization, Acidic solutions

1. INTRODUCTION

Use of inhibitors is one of the most practical methods for protection against corrosion especially in acid solutions to prevent unexpected metal dissolution and acid consumption [1]. A number of organic compounds have been reported as effective corrosion inhibitors [2-4]. But, most of them are highly toxic to both human being and environment. The known hazardous effects of most synthetic organic inhibitors and restrictive environmental regulations have now made researchers to focus on the need to develop cheap, non-toxic and environmentally benign natural products as corrosion inhibitors. These natural organic compounds are either synthesized or extracted from aromatic herbs, spices and medicinal plants.

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 the environment. As early as in 1930, plant extracts (dried stems, leaves and seeds) of *Chelidonium majus* and other plants were used as corrosion inhibitors for steel in H₂SO₄ pickling baths [1]. In 1972, El Hosary et al. [6] studied the extract of *Hibiscus subdariffa* as the corrosion inhibitor for Al and Zn in HCl and NaOH solutions. In 1980s, Saleh et al. [1] reported the inhibition effect of aqueous extracts of some plant leaves (*Opuntia*, *Aleo eru*) and fruit peels (orange, mango) on the corrosion of steel, aluminum, zinc and copper in acids and aluminum in NaOH solution. In 1990s, *Azadirachta* [8] and *Vernonia amygdalina* [9] leaves extracts were reported as good corrosion inhibitors for steel in HCl and H₂SO₄ solutions. Entering into the 21st century, along with people's increasing awareness of protecting the environment, a large number of researches about plant leaves extracts as effective corrosion inhibitors of iron or steel in acidic media have been reported, such as *henna* [10], *Nypa fruticans* Wurmb [11], *Azadirachta indica* [12], *Acalypha indica* [13], *Zenthoxylum alatum* [14], *Damsissa* [15], *Phyllanthus amarus* [16], *Murraya koenigii* [17], *Justicia gendarussa* [18], *Oxandra asbeckii* [19], *ginkgo* [20] and *Stevia rebaudiana* [21] etc. Through these studies, it is agreed that the inhibition performance of plant extract is normally ascribed to the presence in their composition of complex organic species such as tannins, alkaloids and nitrogen bases, carbohydrates, amino acids and proteins as well as hydrolysis products. These organic compounds contain polar functions with N, S, O atoms as well as conjugated double bonds or aromatic rings in their molecular structures, which are the major adsorption centers. However, confronting with the vast varieties of plant, the data regarding the use of plant leaves extract as the corrosion inhibitor are still poor. In the present work, *reed* leaves extract is chosen to be the corrosion inhibitor.

Reed, scientific named *phragmites australis*, belongs to family Phragmites and generally found in coastal region of China. *Reed* is found to contain alkaloids, lignans, naturally occurring phenolic dimmers, flavonoids and O-substituted aromatic amines. However, it has little been studied for the purpose of corrosion inhibition.

This study aims to gain some insight into the corrosion of mild steel in HCl and H₂SO₄ in the presence of *reed* leaves extract (RLE) as a corrosion inhibitor. The inhibition effect of this naturally occurring biological molecule on the corrosion of mild steel in 1M HCl and 0.5 H₂SO₄ was investigated by weight loss, potentiodynamic polarization. Additionally, thermodynamic data as well as the activation energy were obtained from Arrhenius plots.

2. EXPERIMENTAL

2.1 Preparation of plant extract

Dried *reed* (5g) plant leaves were soaked in deionized water (500ml) and refluxed for 5 h. The aqueous solution was filtered and concentrated to 100 ml. This concentrated solution was used to prepare solutions of different concentrations by dillution method. The *reed* plant extract was characterized by Fourier transform infrared (FTIR) spectroscopy. FTIR spectra was recorded in an

AVATAR-FTIR-360 spectrophotometer (Thermo Nicolet Company), which extended from 4000 to 400 cm^{-1} , using the KBr disk technique.

2.2 Weight loss method

Steel specimens of size 1 cm \times 2.5 cm \times 0.05 cm were used in weight loss experiments. Mild steel composed of (wt%) Fe 99.30%, C 0.076%, Si 0.026%, Mn 0.192%, P 0.012%, Cr 0.050% and Ni 0.050% were pre-treated prior to the experiment by grinding with emery paper (grade 600, 800, 1000 and 1200) then cleaned with double distilled water, degreased with acetone and dried. After weighting accurately using digital balance with sensitivity of ± 0.01 mg, the specimens were immersed in 250 ml test solutions. All the aggressive acid solutions were open to air. The measurements were performed at 298 K (except for temperature effect) for 6 h (except for immersion time effect) without and with various amounts of inhibitors. After the elapsed time, the specimen was taken out, washed, dried and weighted accurately. All the tests were conducted in aerated 1 M HCl. All the experiments were performed in triplicate and average values were recorded. The concentration of inhibitor for weight loss and electrochemical study were taken in mg L^{-1} . The inhibition efficiency η_w (%) and surface coverage θ was determined by using the following equation:

$$\theta = \frac{w_0 - w_i}{w_0}$$

$$\eta_w(\%) = \frac{w_0 - w_i}{w_0} \times 100$$

Where w_i and w_0 are the weight loss value in presence and absence of inhibitor, respectively.

The corrosion rate (C_R) of mild steel was calculated using the relation:

$$C_R = \frac{87.6w}{AtD}$$

Where w is the corrosion weight loss of mild steel (mg), A is the area of the coupon, t is the exposure time (h) and D is the density of mild steel (g ml^{-1}).

2.3 Electrochemical measurements

Electrochemical experiments were carried out in a conventional three-electrode cell with a platinum counter electrode (CE) and a saturated calomel electrode (SCE) coupled to a fine Luggin capillary as the reference electrode. To minimize the ohmic contribution, the tip of Luggin capillary was kept close to working electrode (WE). The WE was embedded in Teflon holder using epoxy resin with an exposed area of 0.785 cm^2 . Before measurement the electrode was prepared as described above (Section 2.2), and then immersed in test solution at open circuit potential (OCP) for 2 h to be sufficient

to attain the stable state. All electrochemical experiments were carried out using CHI660B electrochemical workstation. Each experiment was repeated at least three times to check the reproducibility and the good reproducible results were reported.

The potential of potentiodynamic polarization curves was started from cathodic potential of -250 mV to anodic potential of +250 mV vs. OCP at a sweep rate of 1 mV s⁻¹. Inhibition efficiency η_p (%) is defined as:

$$\eta_p (\%) = \frac{i_{corr}^0 - i_{corr}}{i_{corr}^0} \times 100$$

where i_{corr}^0 and i_{corr} are the corrosion current density values without and with inhibitor, respectively.

3. RESULTS AND DISCUSSION

3.1 Characterization of plant extract

FTIR spectrum of RLE is shown in Fig. 1. Original absorption at 3419 cm⁻¹ (associated hydroxyl) was overlapped by the strong stretching mode of N-H or O-H, and that at 2927 cm⁻¹ is related to C-H stretching vibration. The strong band at 1630 cm⁻¹ is assigned to C=C and C=O stretching vibration. Owing to the conjugation effect of flavonoids of RLE, the C=O peak shifts from about 1700 cm⁻¹ to lower wavenumber (approximately 1630 cm⁻¹), C=C and C=O stretching vibration bands are superposition [22]. The C-H bending bands in -CH₂ and -CH₃ are found to be at 1409 cm⁻¹. The absorption bands at 1272 cm⁻¹ could be assigned to the framework vibration of aromatic ring. Besides these, there are absorption bands at 1152 cm⁻¹, 1083 cm⁻¹ and 1027 cm⁻¹, which can be ascribed to the C-N or C-O stretching vibration.

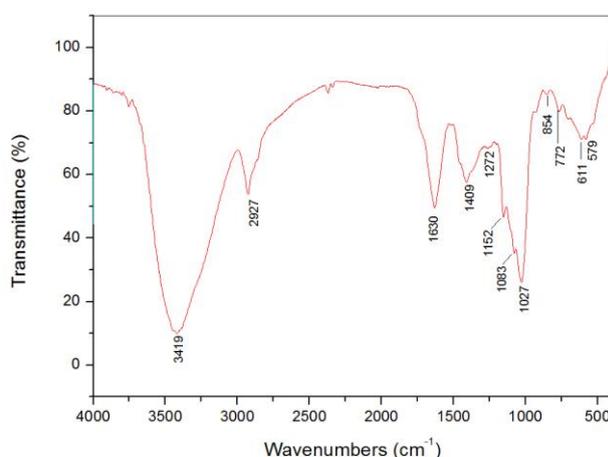


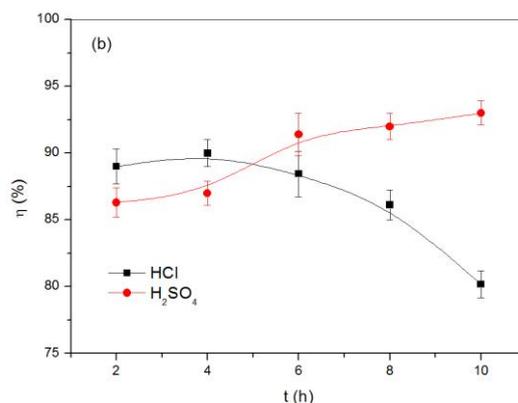
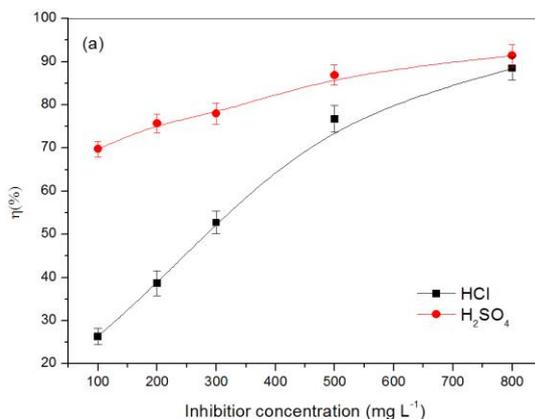
Figure 1. FTIR spectra of *Reed* leaves extract (RLE)

The absorption bands below 1000 cm^{-1} correspond to aliphatic and aromatic C-H group. These results indicate that RLE contains O and N atoms in functional group (O-H, N-H, C=C, C=O, C=N, C-N, C-O) and aromatic ring.

3.2 Weight loss studies

The weight loss method of monitoring corrosion rate and inhibition efficiency is useful because of its simple application and high reliability. For this study, the reproducibility of experimental data is determined by the value of standard deviation. At every inhibitor concentration, the standard deviation value for inhibition efficiency values is lower than 5%, which indicates that the reproducibility of results obtained for triplicate determination is very precise.

To study the effect of inhibitor concentration on the inhibition efficiency, weight loss experiments were carried out in both acid solutions at 298K for 6 h immersion period. Fig. 2a presents the effect of inhibitor concentration on inhibition efficiency in HCl and H₂SO₄. The extract showed maximum inhibition efficiency of 88.45% and 91.39% in HCl and H₂SO₄ at an optimum concentration of 800 mg L^{-1} . Further increase in extract concentration did not cause any significant change in the performance of the extract. The values of percentage inhibition efficiency (η_w , %) and corrosion rate (C_R) obtained from weight loss method at different concentrations of RLE at 298K are summarized in Table 1.



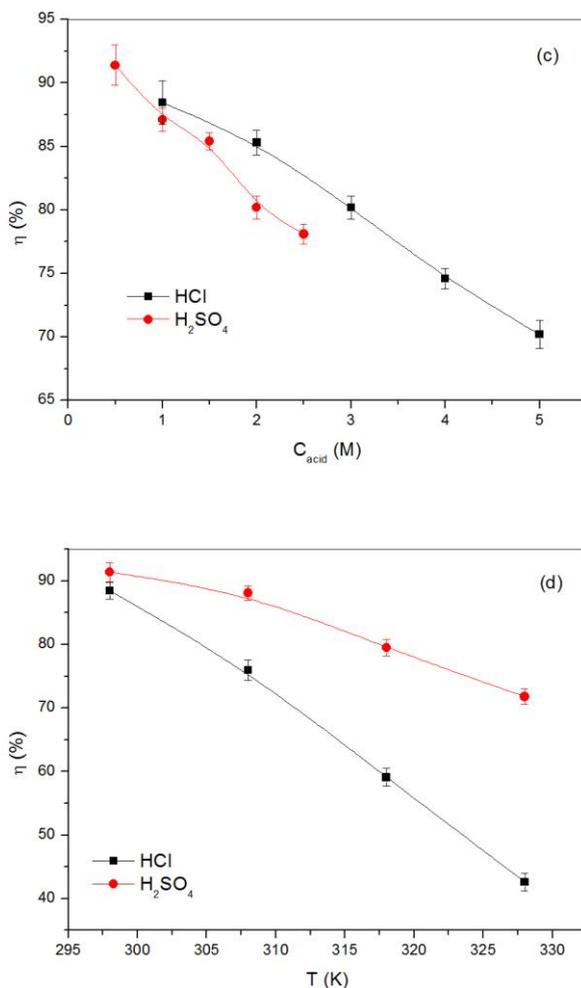


Figure 2. Variation of inhibition efficiency with (a) inhibitor concentration, (b) immersion period, (c) acid concentration and (d) temperature of solution.

The variation of inhibition efficiency with immersion time in HCl and H_2SO_4 is shown in Fig. 2b. It is found that inhibition efficiency increases with time in H_2SO_4 while it decreases in HCl. It is obvious that the weight loss varied linearly with immersion period in plain acid and inhibited acid, showing the absence of insoluble product on steel surface [23]. The relatively large divergence of the plot indicates the increase of (η_w , %) with time as shown in Fig. 2b.

Fig. 2c shows the effect of changing HCl (1.0-5.0 M) and H_2SO_4 (0.5-2.5 M) concentrations on the inhibition efficiency (η_w , %) of 800 mg L^{-1} RLE at 298 K. In both cases, increasing acid concentration resulted in decreasing η_w . The minimum η_w values are 70.2% and 78.1% in 5.0 M HCl and 2.5 M H_2SO_4 solutions, respectively. At same H^+ concentration solution, inhibition performance follows the order: $H_2SO_4 > HCl$.

Table 1. Corrosion parameters for mild steel in acid solutions without and with different concentrations of Reed leaves extract from weight loss measurements at 298 K for 6 h.

Acid solution	Inhibitor concentration (mg L ⁻¹)	Weight loss (mg cm ⁻²)	η (%)	C_R (mm year ⁻¹)
1 M HCl	Blank	21.01	-	77.63
	100	15.74	26.33	58.16
	200	13.28	38.63	49.07
	300	10.46	52.72	38.64
	500	5.66	76.71	20.91
	800	3.31	88.45	12.23
0.5 M H ₂ SO ₄	Blank	33.17	-	122.56
	100	10.04	69.72	37.09
	200	7.72	75.67	28.52
	300	7.31	77.96	27.01
	500	4.34	86.90	16.03
	800	2.85	91.39	10.53

To evaluate the adsorption of RLE and activation parameters of the corrosion process of steel in acidic media, weight loss measurements are investigated in the range of temperature 298–328 K, as shown in Fig. 2d, in the absence and presence of extract at optimum concentration during 6 h immersion time. At optimum concentration of inhibitor the η_w decreases with increasing temperature. This is due to increased rate of dissolution process of mild steel and partial desorption of the inhibitor from the metal surface [23].

The log of corrosion rate is a linear function with $1/T$ (Arrhenius equation) [24]:

$$C_R = k \exp\left(-\frac{E_a}{RT}\right)$$

Where k is the pre-exponential factor, R the general gas constant and E_a is the activation energy of the corrosion process. A plot of log of corrosion rate obtained by weight loss measurement vs. $1/T$ gave a straight line as shown in Fig. 3a with a slope of $-E_a/2.303R$. The values of activation energy are listed in Table 2.

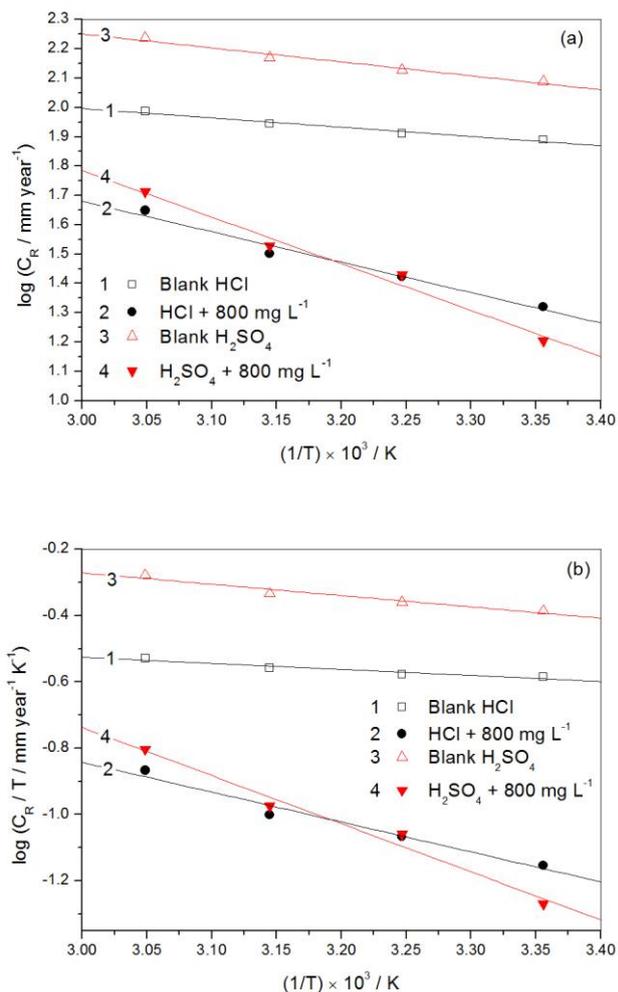


Figure 3. Arrhenius plot for (a) $\log C_R$ vs. $1/T$ and (b) $\log(C_R/T)$ vs. $1/T$.

The data shows that the thermodynamic activation functions (E_a) of the corrosion in mild steel in 1 M HCl and 0.5 M H₂SO₄ solution in the presence of extract are higher than those in the free acid solution indicating that extract exhibit low η_w at elevated temperatures.

An alternative formulation of Arrhenius equation is [25]:

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

Where h is the plank's constant, N is Avogadro's number, ΔS is the entropy of activation and ΔH is the enthalpy of activation. A plot of $\log(C_R/T)$ vs. $1/T$ (Fig. 3b) gave a straight line with the slope of $-\Delta H/2.303R$ and the intercept of $\log(R/Nh) + \Delta S/2.303R$, from which the values of ΔS and ΔH were calculated and given in Table 2. The positive signs of enthalpy (ΔH) reflect the endothermic nature of dissolution process. The shift towards positive value of entropy (ΔS) imply that the activated complex in the rate determining step represents dissociation rather than association, meaning that disordering increases on going from reactants to the activated complex [26].

Table 2. Activation parameters for the corrosion of mild steel in 1 M HCl and 0.5 M H₂SO₄ without and with 800 mg L⁻¹ extract.

Systems	E_a (kJ mol ⁻¹)	ΔH (kJ mol ⁻¹)	ΔS (J K ⁻¹ mol ⁻¹)
1 M HCl	6.07	3.47	-197.23
1 M HCl + 800 mg L ⁻¹ extract	19.87	17.28	-161.87
0.5 M H ₂ SO ₄	9.12	6.52	-183.19
0.5 M H ₂ SO ₄ + 800 mg L ⁻¹ extract	24.66	27.81	-128.27

3.3 Potentiodynamic polarization

Fig. 4a and 4b show potentiodynamic polarization curves for mild steel in 1.0 M HCl and 0.5 M H₂SO₄ solutions without and with various concentrations of RLE at 298 K (immersion time is 2 h), respectively. In 1.0 M HCl solution, the presence of RLE causes a remarkable decrease in the corrosion rate i.e., shifts the anodic curves to lower current densities. In other words, the anodic reactions of mild steel electrode are retarded by RLE in hydrochloric acid solution.

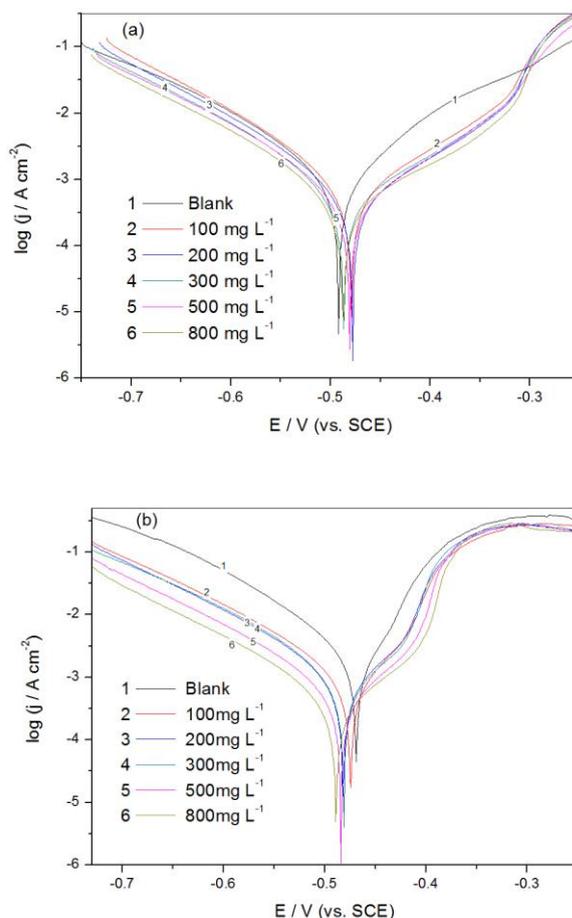


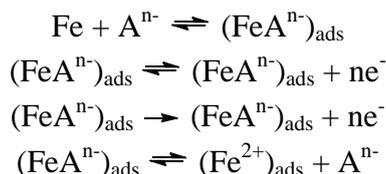
Figure 4. Potentiodynamic polarization curves for mild steel in (a) 1.0 M HCl and (b) 0.5 M H₂SO₄ without and with different concentrations of RLE at 298 K (immersion time is 2 h).

On the other hand, in 0.5 M H₂SO₄ solution, RLE prominently inhibits the cathodic reaction while has slight inhibitive effect on anodic reaction. The potentiodynamic polarization parameters including corrosion current densities (j_{corr}), corrosion potential (E_{corr}), cathodic Tafel slope (b_c), anodic Tafel slope (b_a), and inhibition efficiency (η_p) are presented in Table 3.

Table 3. Potentiodynamic polarization parameters for the corrosion of mild steel in acid solutions without and with different concentrations of Reed leaves extract.

Acid solution	Concentration (mg L ⁻¹)	E_{corr} (vs SCE/ V)	j_{corr} (mA cm ⁻²)	b_a (mV dec ⁻¹)	b_c (mV dec ⁻¹)	η_p (%)
1 M HCl	Blank	-0.492	0.98	96.53	107.05	-
	100	-0.479	0.77	108.47	101.50	21.39
	200	-0.478	0.61	109.02	102.17	37.70
	300	-0.487	0.50	112.84	104.64	48.91
	500	-0.481	0.26	102.32	105.25	72.96
	800	-0.487	0.11	129.63	108.05	88.12
0.5 M H ₂ SO ₄	Blank	-0.469	1.42	77.92	98.23	-
	100	-0.474	0.40	45.13	108.18	71.83
	200	-0.482	0.31	36.58	109.31	78.17
	300	-0.481	0.29	34.54	108.51	79.58
	500	-0.484	0.15	27.91	108.35	89.44
	800	-0.489	0.11	27.94	111.53	94.25

Inspection of Table 3 reveals that j_{corr} decreases considerably in the presence of RLE inhibitor in both acids, and decreases with increasing the inhibitor concentration. Correspondingly, η_p increases with the inhibitor concentration. η_p of 800 mg L⁻¹ RLE reaches up to a maximum of 88.12% in 1.0 M HCl; and 94.25% in 0.5 M H₂SO₄. In 1.0 M HCl solution, E_{corr} does not change obviously in the presence of RLE, which indicates RLE acts as a mixed-type inhibitor. According to Quraishi [27], the inhibition category belongs to geometric blocking effect. That is, the inhibition action is exhibited through the reduction of the reaction area on the surface of the corroding metal. On the other hand, in 0.5 M H₂SO₄ solution, E_{corr} shifts to negative, which indicates that RLE can be arranged as a cathodic inhibitor, and inhibitor molecules are more adsorbed on the cathodic sites resulting in an inhibition of the cathodic reactions. In the presence of RLE, the slight change of both b_c and b_a indicates that the corrosion mechanism of steel does not change. Some of the authors proposed the following mechanism for the corrosion of iron and steel in acid solution [17, 28]:



The cathodic hydrogen evolution

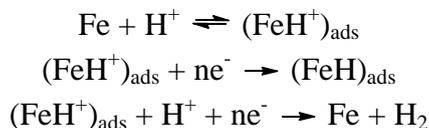


Table 3 also shows that at any inhibitor concentration, $j_{\text{corr}} (0.5 \text{ M H}_2\text{SO}_4) < j_{\text{corr}} (1.0 \text{ M HCl})$; while $\eta_p (1.0 \text{ M HCl}) < \eta_p (0.5 \text{ M H}_2\text{SO}_4)$. This is in good agreement with the results obtained from weight loss experiments.

3.4 Adsorption isotherm

The type of the adsorption isotherm can provide additional information about the properties of the tested compounds. For this purpose, the values of surface coverage (θ) corresponding to different concentrations of RLE have been used to determine the adsorption isotherm. The values of θ were calculated using the data obtained from the weight loss experiments as described above (Section 2.2). Attempts were made to fit experimental data to various isotherms including Frumkin, Langmuir, Temkin, Freundlich and Flory-Huggins isotherms. By far the results were well fitted by Langmuir [29] and Temkin [17] adsorption isotherms:

$$h\theta = \frac{KC_{\text{inh}}}{1 + KC_{\text{inh}}} \quad (\text{Langmuir isotherm})$$

$$\exp(-2a\theta) = KC_{\text{inh}} \quad (\text{Temkin isotherm})$$

where K is the equilibrium constant of the adsorption process. C_{inh} is the concentration of the inhibition, h is the correction factor, which characterize the interactions between the adsorbed molecules and the degree of uniformity of the adsorbent [30], and a is the molecular interaction parameter. The best fit was obtained with Langmuir isotherm (Fig. 5a). Fig. 5b gives the Temkin adsorption isotherm. The corresponding linear regression parameters from Fig. 5a are listed in Table 4. It is evident that both coefficient of determination (R^2) and slope are almost equal to 1, indicating the adsorption of RLE on mild steel surface obeys Langmuir adsorption isotherm in both acid solutions. h deviate from 1 in the hydrochloric acid, indicated that the interaction between the adsorption of inhibitor molecules. Also, Table 4 shows that K of 0.5 M H_2SO_4 is higher than that of 1.0 M HCl, which indicates that RLE exhibits a stronger tendency to adsorb on mild steel surface in sulfuric acid solution. This is good agreement with the results obtained from Section 3.1 and 3.2.

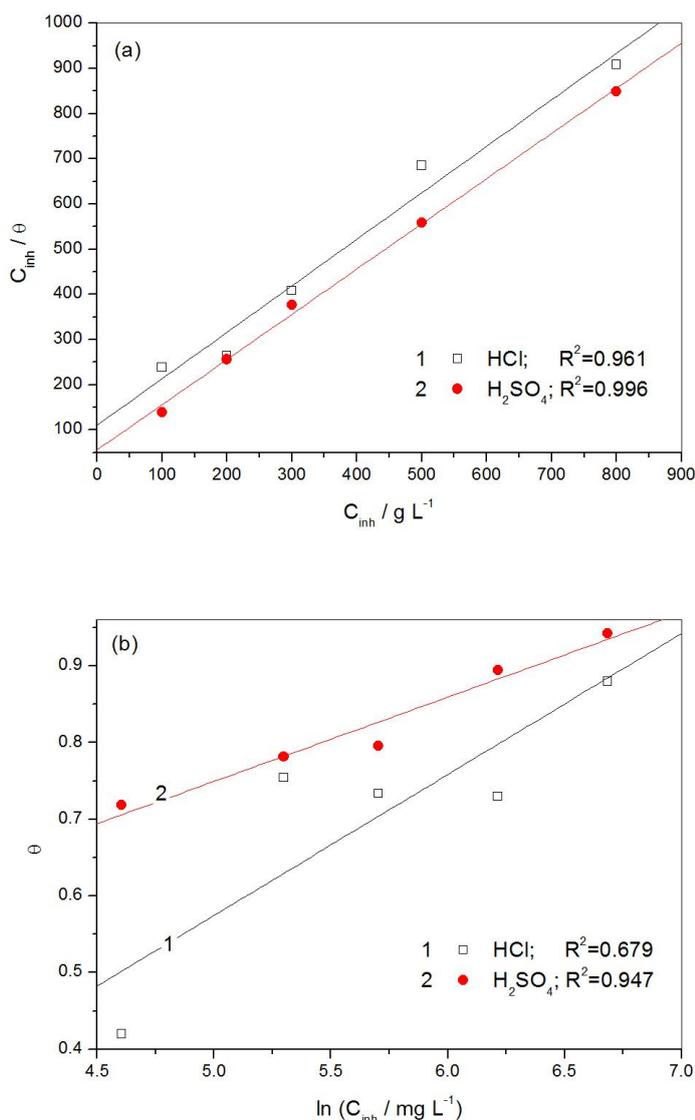


Figure 5. Adsorption isotherm plots for the adsorption of RLE in 1.0 M HCl and 0.5 M H_2SO_4 on the surface of mild steel at 298 K: (a) Langmuir’s isotherm and (b) Temkin’s isotherm.

Table 4. Parameters of the linear regression from the plots of $C_{inh}/\theta \sim C_{inh}$.

Acid solution	Coefficient determination (R^2)	of h	Intercept ($mg L^{-1}$)	$10^3 K (L mg^{-1})$
1 M HCl	0.961	1.029	110.292	9.329
0.5 M H_2SO_4	0.996	1.001	55.496	18.037

4. CONCLUSIONS

The inhibition effect of RLE on mild steel in hydrochloric acid and sulphuric acid solutions was examined by weight loss methods and potentiodynamic polarization. RLE acts as a good corrosion inhibitor in both 1.0 M HCl and 0.5 M H₂SO₄ solutions. Inhibition efficiency value increases with the increasing of inhibitor concentration, while the efficiency is slightly better in sulphuric acid than in hydrochloric acid. Polarization curves indicated that RLE acts as mixed type inhibitor in 1.0 M HCl but cathode type corrosion inhibitor in 0.5 M H₂SO₄ solutions. The inhibition is accomplished by adsorption of the extract components on the iron surface, and the adsorption is spontaneous and obeys the Langmuir isotherm.

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