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Citrus aurantium leaves extracts as a sustainable corrosion inhibitor of mild steel in sulfuric acid

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ABSTRACT

Corrosion inhibition of mild steel in 1 M H₂SO₄ was investigated in absence and presence of *Citrus aurantium* leaves extracts as a friendly inhibitor. The effect of temperature, time, and inhibitor concentration were studied using weight loss technique. The result obtained revealed that *Citrus aurantium* leaves extracts act as an inhibitor for mild steel in H₂SO₄ and reduces the corrosion rate. The inhibition efficiency was found to increase with increase in inhibitor concentration whereas the temperature shows otherwise. Higher inhibition efficiency was 89% at 40 °C and 10 ml/l inhibitor concentration. The adsorption of *Citrus aurantium* leaves extracts was found to follow Langmuir adsorption isotherm model. The values of the free energy of adsorption was around –20 kJ/mol, which is indicative of physical adsorption between charged molecules and a charged metal. Quantum chemical calculations were also used as a theoretical support to the experimental results. Finally the scanning electron microscope and Fourier transform infrared spectroscopy were evaluated to examine surface morphology and molecular structure of inhibitor respectively.

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1. Introduction

Steel and its alloys are widely used in industrial applications, and may be subjected to different acidic environments. Acids attack metal surface and lead to severe corrosion problems. Corrosion can be controlled by using inhibitors. Most of the well-known acid inhibitors used in industry are organic compounds having multiple bonds in their structure and contain mainly nitrogen, sulphur and oxygen atoms through which they adsorbed on the metal surface (Yaro et al., 2013a,b). Corrosion inhibitors generally control corrosion by forming various types of films in several ways: by adsorption, by the formation of bulky precipitates, and/or by the formation of a passive layer on the metal surface. Most of organic inhibitors retard corrosion by adsorption and forming a thin, invisible film with only a few molecules thick (Yaro et al., 2011, 2014; Lagrenee et al., 2001). Industrial synthesis of organic

inhibitors may cause a great destructive effect on the environment. The organic inhibitors separated from the organic extraction of plants and vegetable extracts, these extract are effective, economical and eco-friendly (Singh et al., 2010). The known hazardous effects of most synthetic corrosion inhibitors are the motivation for the use of some natural products. Most of the natural products are non-toxic, biodegradable and readily available in plenty. Several investigations have been reported using such naturally occurring substances as corrosion inhibitor for several metals in different media (Adardour et al., 2016; Chaieb et al., 2005; Chauhan and Gunasekaran, 2007; El-Etre et al., 2005). *Citrus aurantium* leaves (CAL) are very common, available and cheap plants in Diyala governorate/Iraq. In present work, the naturally corrosion inhibitor (CAL) was extracted and tested to control the corrosion of mild steel in 1 M H₂SO₄ at different operating condition.

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2. Experimental

2.1. Sample preparation

Mild steel samples were used in weight loss tests. The chemical compositions of these samples were as follows; C (0.09%), Mn (0.4%), Pb (0.004%), Cd (0.0%), Cr (0.01%), Ni (0.01%), Ca (0.0008%), Cu (0.01%) and the remainder is Fe. Rectangular sheet with a dimension of $3 \times 1 \times 0.1$ cm, were cut from a large one to have exposing surface area of about 7 cm^2 to the aggressive acid solution. The specimens were first annealed in vacuum at $600 \text{ }^\circ\text{C}$ for 1 h, cooled down to room temperature (Khadom, 2014). The samples cleaning procedure was carried out before tests (Khadom et al., 2015). The samples were abraded by emery paper of grade number, 200, 600 and 800, then washed with running tap water followed by distilled water and then dried with clean tissue, immersed in acetone and benzene, dried again, and finally kept in a desiccator over silica gel beads until use. The samples were weighted by 4-digits electronic balance, and the dimensions were measured by an electronic vernier. The metal samples were completely immersed in 200 cm^3 corrosion solution of $1 \text{ M H}_2\text{SO}_4$ contained in conical flask. They were exposed for a period of 3 h at the desired temperature, molarity and inhibitor concentration. Then the metal samples were cleaned, washed with running tap water followed by distilled water dried with clean tissue, immersed in acetone and benzene and dried again. Weight losses were determined in presence and absence of inhibitor at 30, 40, 50, and $60 \text{ }^\circ\text{C}$ and using 2, 4, 6, 8, and 10 ml/l inhibitor concentration. Each test was repeated twice and the average values were taken. Kinetics study was carried out at four different times (1, 2, 3 and 4 h), two temperatures (40 and $60 \text{ }^\circ\text{C}$) and with and without two inhibitor concentrations (0 and 6 ml/L).

2.2. Preparation of Citrus aurantium leaves extract

Citrus aurantium leaves (CAL), which is very common, available and cheap plants in Diyala governorate/Iraq were collected, shade dried, grind and convert to powder. The extract was prepared by refluxing 10 g of dry leaves powder in 100 ml of $1 \text{ M H}_2\text{SO}_4$ for 3 h and kept overnight. The product was then filtered and the volume of the filtrate was made up to 50 ml using the same acid and this was taken as stock solution and a portions with a volume of (2, 4, 6, 8 and 10 ml)/liter of $1 \text{ M H}_2\text{SO}_4$ was used as a corrosion solution.

2.3. Preparation of H_2SO_4 solution

The analytical grade 98% H_2SO_4 with molecular weight of 98.08 g/mole was used for preparing the acid electrolyte. The acid was exactly diluted with double distilled water to prepare $1 \text{ M H}_2\text{SO}_4$ solution. For each set of experiment freshly prepared $1 \text{ M H}_2\text{SO}_4$ solutions were used to avoid effect of any contamination.

2.4. Scanning electron microscope (SEM)

The scanning electron microscope (Model AIS2300C, made in Korea) was used to examine the morphology of mild steel surface in the absence and presence of *Citrus aurantium* leaves extracts where 3 h immersion period in $1 \text{ M H}_2\text{SO}_4$ at $30 \text{ }^\circ\text{C}$ was used.

2.5. Fourier transform infrared spectroscopy (FTIR)

Fourier transform infrared spectrometer type (FTIR-600) Biotech Engineering Management, UK was used to evaluate the molecular structure and active group of inhibitor of CAL.

3. Results and discussion

3.1. Weight loss measurements

Corrosion rates were determined in presence and absence of inhibitor using the following formula:

$$CR = \frac{\text{weight loss (g)}}{\text{area (m}^2\text{)} \times \text{time (day)}} \quad (1)$$

While inhibition efficiency was calculated using the equation below:

$$\%IE = \frac{CR_o - CR_i}{CR_o} \times 100 \quad (2)$$

where CR_o and CR_i are the corrosion rates in the absence and presence of various concentrations of inhibitor respectively. Corrosion rate and inhibitor efficiency were evaluated at different operating conditions. The results were presented in Table 1 through 24 test runs. It is clear that corrosion rate increased with temperature and decreased with inhibitor concentration.

3.2. Effect of temperature and thermodynamic parameters

Thermodynamic parameters of the corrosion reaction, namely activation energy E_{act} , change in entropy ΔS_{act} and change in enthalpy ΔH_{act} were calculated using Arrhenius equation (Eq. (3)) and transition state theory (Eq. (4)).

$$CR = A \exp\left(-\frac{E_a}{RT}\right) \quad (3)$$

Table 1 – Corrosion rate of mild steel in $1 \text{ M H}_2\text{SO}_4$ at different conditions.

Run	T, $^\circ\text{C}$	Ci ml/L	Corrosion rate (gmd)	%IE
1	30	0	1440	0
2		2	384	73.3
3		4	336	76.6
4		6	240	83.3
5		8	216	85
6		10	160	88.8
7	40	0	2640	0
8		2	720	72.7
9		4	528	80
10		6	408	84.5
11		8	312	88.1
12		10	288	89
13	50	0	4800	0
14		2	2000	58.3
15		4	1104	77
16		6	984	79.5
17		8	888	81.5
18		10	600	87.5
19	60	0	8640	0
20		2	4500	47.9
21		4	2640	69.4
22		6	2160	75
23		8	1920	77.7
24		10	1200	86.1

$$CR = \frac{RT}{Nh} \exp\left(\frac{\Delta S_{act}}{R}\right) \exp\left(-\frac{\Delta H_{act}}{RT}\right) \quad (4)$$

where A is frequency factor, T is the absolute temperature, R is the universal gas constant, N is Avogadro's number (6.022×10^{23} molecule mol^{-1}), and h is Planck's constant (6.626×10^{-34} J s). From Eq. (3) we can be plot $\ln CR$ against $1/T$ as shown in Fig. 1. Slope and intercept yield the values of A and E_a . While Eq. (4) can be plotted as $\ln(CR/T)$ against $1/T$ as with the results shown in Table 2. It can be seen from Table 2 that E_a is higher in the presence of inhibitors than in their absence and consequently the rate of corrosion decreases. The ΔH_{act} behaviour is similar to E_a which is higher in the presence of the inhibitors than in their absence. The increased value of the E_a in the presence of CAL is attributed to physical adsorption that happens during first step of adsorption processes. The positive values of ΔH_{act} reflect the endothermic behaviour of metal dissolution in acidic environment and the negative values of ΔS_{act} propose the formation of activated complex in the rate determining step which represent dissociation rather than association and thus suggesting that disorder increases on going from reactant to activated complex.

3.3. Effect of inhibitor concentration

It is well known that the first stage in inhibition of metals corrosion is the adsorption of organic inhibitor molecules at the metal/solution boundary. The surface coverage depends on inhibition efficiency and is defined as ($\theta = IE/100$) and concentration of CAL. The fraction of the surface covered by the adsorbed molecule increases with increased of inhibitor concentration. Two models were suggested to study the kinetics of adsorption of CAL on metal surface. Langmuir adsorption isotherm (Eq. (5)) and Freundlich adsorption isotherm (Eq. (6)).

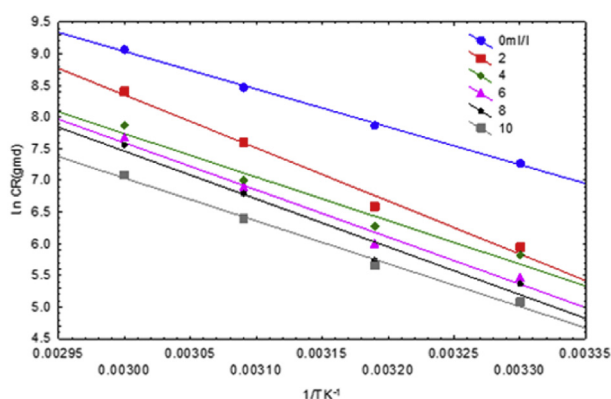


Fig. 1 – Arrhenius plots of mild steel in 1 M H_2SO_4 at different inhibitor concentration.

Table 2 – Activation parameters for corrosion of mild steel in inhabited 1 M H_2SO_4 .

C ml/L	A	E_a kJmol^{-1}	ΔH_{act} kJmol^{-1}	$-\Delta S_{act}$ kJmol^{-1}
0	4.955	49.583	46.976	0.150
2	3.385	69.580	66.982	0.204
4	2.012	57.069	54.479	0.162
6	9.516	61.778	59.145	0.174
8	1.173	62.725	60.077	0.176
10	7.179	56.159	53.504	0.153

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \quad (5)$$

$$\theta = K_{ads} C^n \quad (6)$$

where θ is the surface coverage, IE is the inhibitor efficiency, C is the inhibitor concentration, K_{ads} equilibrium adsorption constant, and n is constant. Equations (5) and (6) can be drawn as shown in Figs. 2 and 3. The Gibbs standard free energy of adsorption of the organic inhibitor can be estimated by means of Eq. (7) (see Fig. 4).

$$K_{ads} = \frac{1}{1000} \exp\left(-\frac{\Delta G_{ads}^0}{RT}\right) \quad (7)$$

The value of 1000 is the concentration of water in solution (ml/l). The kinetics parameters were listed in Table 3. As shown in Table 3, the higher correlation coefficients (R^2) were obtained via using Langmuir adsorption isotherm. Generally, a higher value of K_{ads} accompanying with higher trend to adsorb on mild steel surface, on the other hand, equilibrium constant of adsorption (K_{ads}) was noticed to decrease with increase in temperature, similar results was reported in the literature (Umoren et al., 2011). The values of free energy of adsorption, ΔG_{ads} , are negative which exposes the spontaneity of adsorption process and the stability of the adsorbed film on the metal surface. The obtained values of the adsorption free energy are around -18 kJ/mol that indicative of physical adsorption.

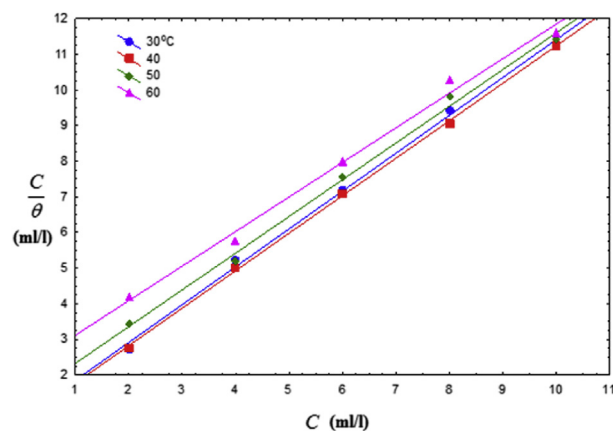


Fig. 2 – Langmuir adsorption isotherm of mild steel in 1 M H_2SO_4 at different conditions.

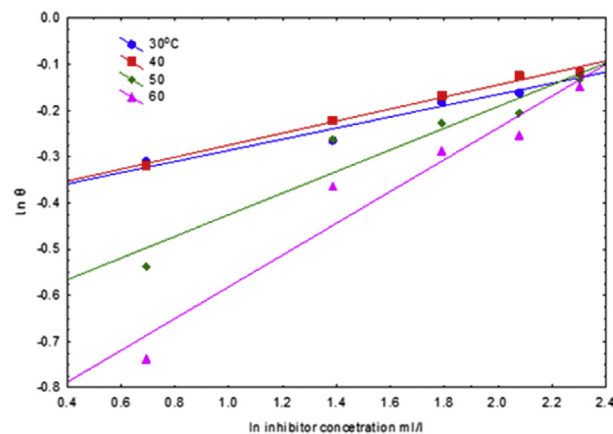


Fig. 3 – Freundlich adsorption isotherm of mild steel in 1 M H_2SO_4 at different conditions.

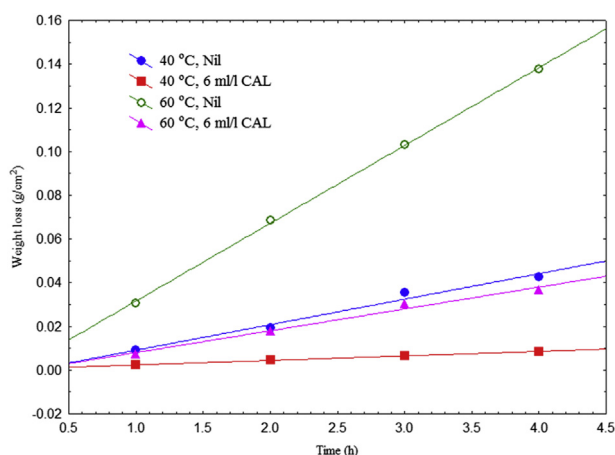


Fig. 4 – Zero order reaction kinetics of mild steel in 1 M H_2SO_4 .

Table 3 – Adsorption parameters for corrosion of mild steel in inhibited 1 M H_2SO_4 .

T, K	Langmuir adsorption isotherm			Freundlich adsorption isotherm		
	K_{ads} (l/ml)	ΔG kJ mol ⁻¹	R^2	K_{ads} (l/ml)	n	R^2
303	1.2693	-18.1	0.9976	0.665711	8.278	0.9551
313	1.3912	-18.8	0.9996	0.66711	7.686	0.9623
323	0.7705	-17.85	0.9961	0.516851	4.266	0.9128
333	0.4659	-17.1	0.9925	0.396373	2.906	0.9415

3.4. Reaction kinetics

The rate of reaction can be stated by following model (Khadom and Abdul-Hadi, 2014; Yaro et al., 2013b):

$$\frac{dW}{dt} = kW^n \quad (8)$$

where k is rate constant and n is order of reaction. Equation (8) can be integrated for different values of reaction order (n). Three reaction models were suggested. Zero, first, and second order models. Table 4 shows results of three order of reaction kinetic (zero, first, and second) at two temperature (40 and 60 °C) in presence and absence inhibitor concentration at different times (1, 2, 3, and 4 h). The integrated forms for zero, first and second order respectively are given below:

$$k = \frac{W_t - W_i}{t} \quad (9)$$

$$W_t = W_i \exp(kt) \quad (10)$$

$$k = \frac{1}{t} \left(\frac{1}{W_t} - \frac{1}{W_i} \right) \quad (11)$$

where W_t is mild steel consumption at any time, and W_i is the initial mild steel concentration. Equations (9) and (10) can be verified in order to determine the accurate order of reaction. As shown in Table 4, the values of correlation coefficients (R^2) were best fitted in case of equation (9) (i.e. the zero order reaction equation). The reaction rates can also be expressed in terms of half-life or half-life period $t_{1/2}$. The half-life period is defined as the time necessary for the concentration of a reactant to decrease to half of its initial value. Half-life indicates the stability of reactants, the longer half-life the greater the stability of reactants. For zero order reaction, half-life period can be defined as (Khadom and Abdul-Hadi, 2014):

$$t_{1/2} = \frac{W_i}{2k} \quad (12)$$

It was observed that values of $t_{1/2}$ decreases with increases of temperature and increases with inhibitor concentration, this mean that metal consume to its half original weight as temperature of acid increased. Furthermore, the presence of CAL raises the values of $t_{1/2}$.

3.5. FTIR studies

FTIR analyses have been made to obtain some understanding into the possible interactions between the adsorbed inhibitor and mild steel surface in acidic environment. The strength of the inhibition depends on the molecular structure of the inhibitor. Fig. 5 shows the FTIR spectrum of mild steel immersed in the inhibited solution containing CAL. Leaf extracts of CAL were investigated to evaluate the main functional group. It was observed that the peak for stretching vibrations of hydroxyl OH group located in the region 3200–3500 cm^{-1} , peak for group CO stretching vibrations located in region 1000–1250 cm^{-1} , and finally peak attributed to group C=C stretching was located at 1637 cm^{-1} , this is region in the range from 1585–1640 cm^{-1} . These ranges indicate that the most effective compounds of CAL is phenolic compounds.

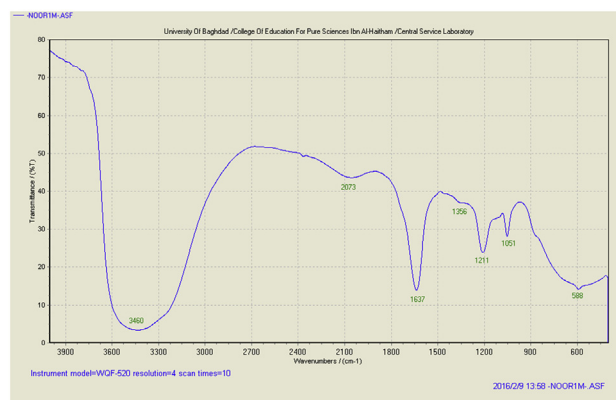


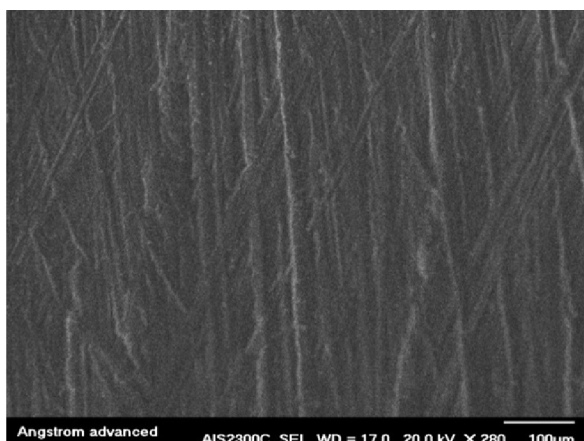
Fig. 5 – FTIR spectrum of mild steel exposed to corrosion in inhibited 1 M H_2SO_4 .

Table 4 – Reaction kinetics parameters for corrosion of mild steel in inhibited 1 M H_2SO_4 .

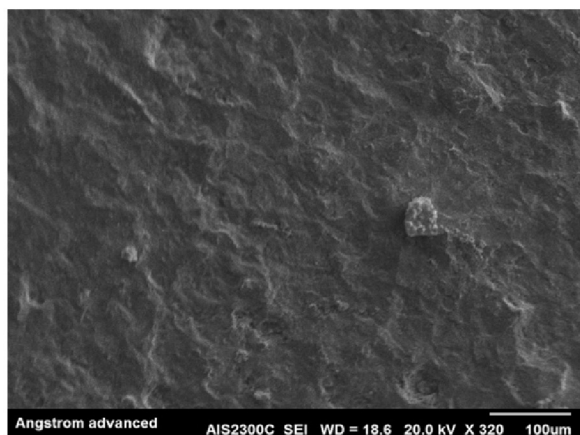
Conditions	Zero order			First order			Second order		
	k_o (g/m ² h)	$t_{1/2}$ (h)	R^2	k_1 (1/h)	$t_{1/2}$ (h)	R^2	k_2 (m ² h/g)	$t_{1/2}$ (h)	R^2
40, C = 0 ml/l	0.012	85.47	0.9922	0.0843	8.220	0.9517	0.0283	19.646	0.0503
40, C = 6 ml/l	0.002	476.19	0.9985	0.0134	51.716	0.1416	0.0145	30.487	0.1053
60, C = 0 ml/l	0.036	28.11	0.9993	0.1923	3.603	0.9401	0.066	10.799	0.0966
60, C = 0 ml/l	0.011	100.31	0.9932	0.0442	15.678	0.7503	0.0231	22.075	0.4522

3.6. Scanning electron microscope (SEM)

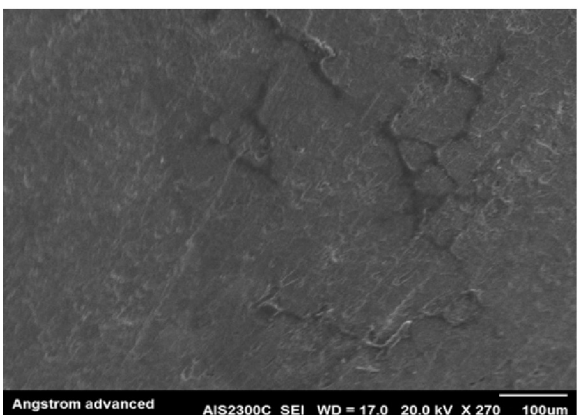
The scanning electron micrographs (SEM) were taken and detected in order to support the findings of present work. The polished specimens are immersed in the blank 1 M H₂SO₄ and in presence of CAL for 3 h were observed under a metallurgical microscope and photomicrographs are shown in Fig. 6A–C. Fig. 6A shows the polished mild steel surface before exposure to the corrosion solution, which is associated with polishing scratches. It is clear from Fig. 6B, that the surface of the mild steel was heavily corroded in 1 M H₂SO₄, whereas in the



A



B



C

Fig. 6 – SEM images of mild steel (A) before immersion in 1 M H₂SO₄ for 3 h (B) after immersion in 1 M H₂SO₄ for 3 h (C) after immersion in 1 M H₂SO₄ for 3 h and in the presence of CAL.

presence of inhibitor in 1 M H₂SO₄, the surface condition was comparatively better (Fig. 6C) depends on the concentration of the inhibitor solution suggesting that the presence of CAL protect the metal surface via formation of adsorbed layer on metal surface.

4. Conclusion

The acid extract of *Citrus aurantium* acts as good and efficient inhibitor for the corrosion of steel in sulphuric acid medium. Inhibition efficiency increases with inhibitor concentration and maximum inhibition efficiency for the extract was found to be 89% at the optimum concentration of 10 ml/l at 40 °C. The adsorption of different concentrations of the plant extract on the surface followed Langmuir adsorption isotherm. The negative value of the free energy of adsorption indicates that the adsorption of the CAL on the steel surface was a spontaneous process and be of physisorption one.

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