

Ziziphus Leaves Extract as Friendly Inhibitor for Galvanic Corrosion of Steel-Copper Couple in Petroleum Waste Water

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Abstract: The inhibition of steel-copper couple galvanic corrosion in petroleum waste water solution by Zizyphus leaves extract was studied at different temperature and different cathode to anode area ratio using weight loss technique. Inhibition efficiency increases with increase in inhibitor concentration but decrease with rise in temperature. Maximum inhibitor efficiency was around 90%. The adsorption behavior of Zizyphus leaves extract obeyed the Langmuir adsorption isotherm while the effect of temperature was according to Arrhenius Model.

Key words: Galvanic corrosion, green inhibitor, kinetic parameters, regression, Langmuir, efficiency

INTRODUCTION

Petroleum industry is a very important and widely spread specially in oil producing countries. Petroleum passes through several industrial and chemical processes during transportation, treatments and refinery. Presence of salts in petroleum and produced waste water may leads to damage and failure in industrial equipment, pipelines, storage tanks, pumps, heat exchangers, etc. In addition to metallic equipment damage, corrosion by industrial wastewater leads to water pollution by the dissolved metal ions (Salvato, 1982) which themselves also may be toxic. Petroleum salts removal is a necessary step to reduce the quantity of salts that dissolved in produced water. The rate of corrosion depends on the kind and concentration of contaminants present in the wastewater. Corrosion can be classified as uniform attack, pitting, erosion, galvanic, etc. Galvanic corrosion takes place when more and less noble materials are engaged together; the more noble material offers an extra area for the cathodic reaction. Therefore, the total rate of the cathodic reaction is increased and this is balanced with an increased anodic reaction, i.e., increased dissolution of the less noble material (Bardal, 2004; AlHaza'a *et al.*, 2015; Qafsaoui *et al.*, 2015). To prevent from aqueous solutions attack, the use of organic inhibitors is one of the most practical ways and cost-effective choices for protect metals against corrosion. Organic inhibitors are usually adsorbed on the metal surface by formation of a coordinate covalent bond (chemical adsorption) or the electrostatic interaction between the metals and inhibitor (physical adsorption) (Avci, 2008). This adsorption yields a uniform film which isolates the metal surface from the

solution attack and consequently reduces the corrosion rate (Meresht *et al.*, 2012). The increasing ecological awareness and firm environmental rules as well as the expected drive toward sustainable and environmentally friendly processes, drew attention towards the development of nontoxic alternatives to corrosion inhibitors. Presently, research in corrosion is focused on the development of green corrosion inhibitors with good inhibition efficiency, renewable, biodegradable, cheap, non-toxic and a low risk of environmental pollution (Lecante *et al.*, 2011). Most of natural corrosion inhibitors are organic components. These organic corrosion inhibitors have been widely applied in solving corrosion problems because of their availability and ease of application. Organic corrosion inhibitors are typically consisted of hetero-atoms such as nitrogen, sulfur and oxygen. The heteroatom is used for adsorption on the surface of the metal (Oguzie, 2007; Obot *et al.*, 2012). Research results have shown that compounds containing the following functional groups, -NH₂, -N=N, C=N, -S-CH₃, C=S, N-H, -CO, -CNS, CHO inhibit the corrosion of metals (Morad and El-Dean, 2006). The aim of this study was to investigate the inhibitive action, adsorption kinetics, mathematical and statistical modeling of Zizyphus leaves extract as a low cost, natural and non-toxic corrosion inhibitor for galvanic corrosion of steel-copper couple in desalination units of petroleum refinery equipment at different temperatures.

MATERIALS AND METHODS

The galvanic corrosion rate of steel-copper couple in absence and presence of inhibitor concentration of 0, 120,

Table 1: Composition of working electrode

Elements	Values
Steel alloy (%)	
C	0.25
Mn	0.3
P	0.03
S	0.03
Si	0.1
Cr	0.4
Mo	0.2
Fe	Rest
Copper alloy (%)	
Cu	71
Pb	0.0007
Fe	0.0006
Sb	0.001
Sn	0.01
Zn	Rest

240, 360 and 480 ppm, area ratio of cathode to anode (Ac/Aa) 0.5:1, 1:1, 2:1), at different temperature (30, 35 and 40°C) using weight loss methods was evaluated in 1% (wt.) $MgCl_2$ and pH 6. The working electrode were 2 coupons from carbon steel type (ASTM A 106/A) and copper type (ASTM B-111-443). Big coupon with dimensions of 4×3×0.3 cm and small coupon of 2×3×0.3 cm. Table 1-3 show chemical compositions (%wt.) of working electrodes.

Fresh Zizyphus leaves were washed under running water, sliced into small pieces before drying in a hot air oven at 50°C for about 6 h, dry slice was collected and ground into fine powder using a high-speed blender. The dry, Curcuma longa was packed in a plastic bag, sealed and kept until used. The slice (25 g) was blended in distilled water (250 mL) in a reflux heater with conical flax (500 mL) for 3 h at 70°C. The conical flax was supplied with mixer to avoid powder sedimentation and uniform temperature distribution. The solution is then cooled followed by filtration to extract the inhibitor solution without any solid particles.

Weight loss technique is the widely used method for measuring the corrosion rate and inhibitor efficiency. Mild steel and copper specimens were cleaned using emery paper of grade number 220, 320, 400 and 600, then washed with running tap water followed by distilled water then dried with clean tissue, degreased with benzene, dried, degreased with acetone, dried and finally left in desiccator over silica gel. Weighing the specimen was carried out using 4 decimals digital balance and its dimensions were measured with vernier to the 2nd decimal of millimeter. A specimen of known surface area and mass is exposed to the test corrosive solution as a couple for a 12 h. The loss of a metal as a result of corrosion is then determined from the loss of masses after removal the corrosion products or other deposits from the metal. Mass loss values are usually recorded together with the exposed surface area of the specimen and the period of the test. Data are expressed as mass loss per unit time per unit area, e.g., g/m²day (gday). Couple samples were completely immersed in 250 cm³ corrosive solution at a desired

Table 2: Corrosion parameters for mild steel in 1% $MgCl_2$, pH = 6, area ratio Ac/Aa = 0.5:1 containing various concentrations of extract at different conditions

Run	Temp. (°C)	C (ppm)	CR (gday)	IE (%)
1	30	Blank	5.416	0.0
2		120	1.299	76.1
3		240	1.137	79.8
4		360	0.812	85.5
5	35	480	0.649	88.4
6		Blank	6.121	0.0
7		120	1.958	68.3
8		240	1.713	72.2
9	40	360	1.285	79.7
10		480	1.162	81.8
11		Blank	6.732	0.0
12		120	2.558	62.6
13	45	240	2.221	67.2
14		360	1.885	72.7
15		480	1.615	76.5
16		Blank	8.078	0.0
17		120	3.473	57.4
18		240	3.151	61.3
19		360	2.746	66.6
20		480	2.342	71.7

Table 3: Corrosion parameters for mild steel in 1% $MgCl_2$, pH = 6, area ratio Ac/Aa = 1:1 containing various concentrations of extract at the influence of temperature

Run	Temp. (°C)	C (ppm)	CR (gday)	IE (%)
1	30	Blank	8.110	0.0
2		120	1.689	79.0
3		240	1.478	81.7
4		360	1.056	86.9
5	35	480	0.845	89.6
6		Blank	8.610	0.0
7		120	2.448	71.6
8		240	2.142	75.2
9	40	360	1.606	81.3
10		480	1.454	83.2
11		Blank	9.700	0.0
12		120	3.581	63.0
13	45	240	3.110	67.9
14		360	2.639	72.8
15		480	2.262	76.7
16		Blank	12.500	0.0
17		120	5.211	58.3
18		240	4.726	62.2
19		360	4.121	67.1
20		480	3.514	71.9

temperature, area ratio and inhibitor concentration. Weight losses were determined in absence and presence of inhibitors.

RESULTS AND DISCUSSION

Corrosion rate studies: Table 4 collected the results of 60 test runs of couple corrosion in 1% $MgCl_2$ solution as a function of temperature in the absence and presence of Zizyphus leaves extract as a corrosion inhibitor. The value of corrosion rate was determined using the following Eq. 1:

$$CR = \frac{\text{Weight loss (g)}}{\text{Area (m}^2\text{)} \times \text{Time (day)}} \quad (1)$$

Table 4: Corrosion parameters for mild steel in 1% MgCl₂, pH = 6, area ratio Ac/Aa = 2:1 containing various concentrations of extract at the influence of temperature

Run	Temp. (°C)	C (ppm)	CR (g/day)	IE (%)
1	30	Blank	10.881	0.0
2		120	2.534	76.7
3		240	2.217	79.6
4		360	1.584	85.4
5		480	1.267	88.4
6	35	Blank	13.452	0.0
7		120	4.173	68.9
8		240	3.652	72.8
9		360	2.739	79.6
10		480	2.478	81.5
11	40	Blank	15.637	0.0
12		120	5.730	63.3
13		240	4.976	68.2
14		360	4.222	72.9
15		480	3.619	76.8
16	45	Blank	21.892	0.0
17		120	9.222	57.8
18		240	8.365	61.7
19		360	7.292	66.6
20		480	6.221	71.5

The percentage inhibition efficiency was calculated using the following Eq. 2:

$$IE (\%) = \frac{CR_{uninhibit} - CR_{inhibit}}{CR_{uninhibit}} \times 100 \quad (2)$$

where, $CR_{uninhibit}$ and $CR_{inhibit}$ the corrosion rates in absence and presence of inhibitor, respectively. In absence and presence of a certain concentration of inhibitor, the corrosion rate of steel increases with rise in temperature. Values of inhibitor efficiency increase with increasing inhibitor concentration. It is also clear that at certain experimental temperature, corrosion rate of couple decreases with an increase in concentration of inhibitor.

Effect of inhibitor concentration and adsorption studies:

The important step in the action of inhibitors in aqueous solution is usually approved to be adsorption on the metal surface. This involves the assumption that the corrosion reactions are banned from happening over the area (or active sites) of the metal surface covered by adsorbed inhibitor molecules whereas these corrosion reaction occurred normally on the inhibitor-free area (Khadom *et al.*, 2015). Therefore, the fraction of surface covered with inhibitor species ($\theta = IE\%/100$) can surveyed as a function of inhibitor concentration and solution temperature. The surface coverage (θ) data are very valuable while discussing the adsorption characteristics when the fraction of surface covered is determined as a function of the concentration at constant temperature, adsorption isotherm could be assessed at equilibrium condition. Different adsorption isotherms were tested. Langmuir, Freundlich, Frumkin and Temkin

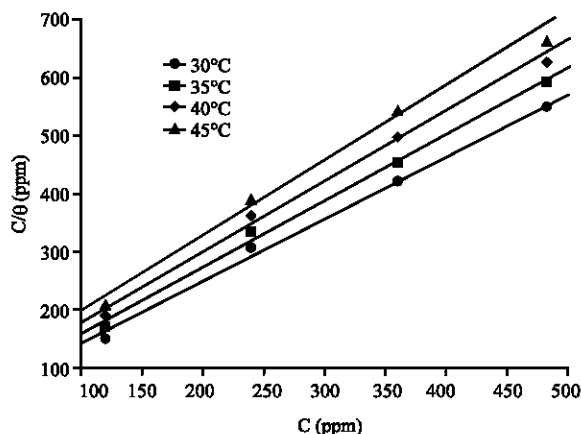


Fig. 1: Langmuir adsorption isotherm at Ac/Aa = 0.5:1

adsorption isotherms were evaluated. The best fitting was obtained by Langmuir, adsorption isotherm. Figure 1 shows the linear plots for C/θ versus C , suggestion that the adsorption follows the Langmuir isotherm (Hassan *et al.*, 2016):

$$\frac{C}{\theta} = \frac{1}{K} + C \quad (3)$$

Where:

C = The inhibitor concentration

K = Adsorptive equilibrium constant

Signifying the degree of adsorption (i.e., the higher the value of K indicates that the inhibitor is strongly adsorbed on the metal surface). The standard adsorption free energy (ΔG°_{ads}) was calculated using the following equation (Noor, 2009):

$$K = \frac{1}{55.5} \exp \left(-\frac{\Delta G^{\circ}_{ads}}{RT} \right) \quad (4)$$

Where:

55.5 = The concentration of water in solution expressed in molar

R = Gas constant

T = Absolute temperature

The average value of standard adsorption free energy (ΔG°_{ads}) was -25.61 kJ/mol. The negative value of ΔG°_{ads} ensure the spontaneity of the adsorption process and stability of the adsorbed layer on the metal surface. Normally, value of ΔG°_{ads} up to -20 kJ/mol is consistent with electrostatic interaction between the charged molecules and the charged metal (physisorption) while those around -40 kJ/mol or higher are associated with chemisorptions as a result of sharing or transfer of electrons from the molecules to the metal surface to form

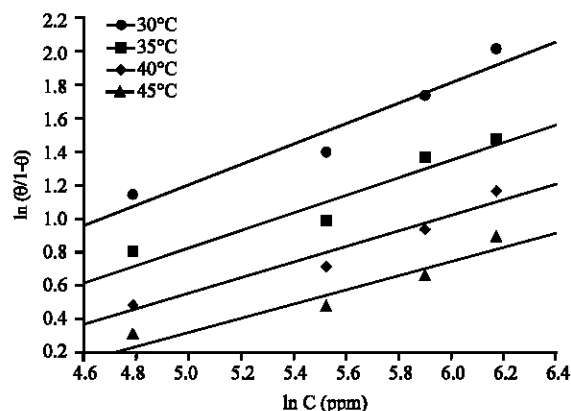


Fig. 2: Kinetic thermodynamic model at Ac/Aa = 0.5:1

a coordinate type of bond (Khadom and Yaro, 2011). While other researchers suggested that the range of $\Delta G^{\circ}_{\text{ads}}$ of physical and chemical adsorption processes for inhibitor in aqueous media lies between -20 to 40 kJ/mol (Khadom *et al.*, 2010). Therefore, for present research the values of $\Delta G^{\circ}_{\text{ads}}$ has been considered within the range of physical-chemical adsorption. Recent researches have looked into the action of an adsorptive inhibitor from a purely mechanistic kinetic point of view (Khadom, 2015). This relation can be expressed as:

$$\frac{\theta}{1-\theta} = K' C^y \quad (5)$$

or this equation can be writing in linear form as:

$$\ln\left(\frac{\theta}{1-\theta}\right) = \ln K' + y \ln C \quad (6)$$

Where:

$K' = A$ constant

y = The number of inhibitor molecules occupying one active site

A plot of $(\theta/(1-\theta))$ vs. $\ln C$ (Fig. 2) gives a straight line of slope y and intercept of $\ln K'$. Equilibrium constant corresponding to adsorption isotherm is given by $K = K'^{1/y}$. Values of $y > 1$ implies the formation of multilayer of inhibitor on the surface of metal. Values of $y < 1$ mean a given inhibitor molecules will occupy more than one active site.

As shown in Table 5, the kinetic-thermodynamic model data were in a good agreement with that obtained by Langmuir adsorption isotherm model. The values of y were lower than unity indicating the formation of monolayer on the metal surface and the values of K were comparable.

Effect of temperature and activation studies: Thermodynamic parameters of the corrosion reaction,

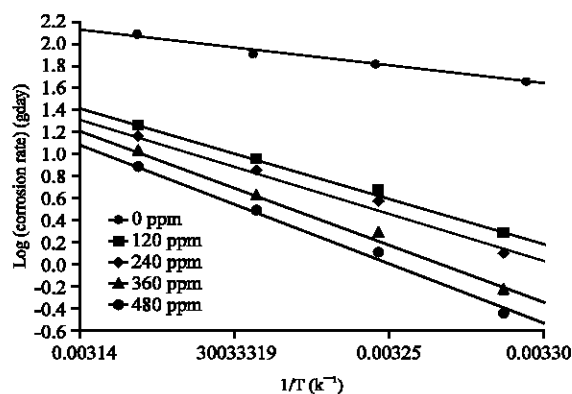


Fig. 3: Arrhenius plot for mild steel coupled with copper in 1% MgCl_2 at different concentration of extract and area ratio 0.5:1

Table 5: Absorption isotherms parameters

Area ratio		Langmuir isotherm		Kinetics thermodynamic		$\Delta G^{\circ}_{\text{ads}}$ from (kJ/mol)
		n	K	y	K	
0.5: 1	30	1.70	0.027	0.61	0.0490	-25.71
	35	1.40	0.021	0.52	0.0320	-25.48
	40	1.21	0.017	0.47	0.0220	-25.34
	45	1.29	0.014	0.43	0.0150	-25.23
	Average	1.18	0.029	0.51	0.0190	-25.44
1:1	30	1.06	0.032	0.59	0.0710	-26.13
	35	1.12	0.026	0.50	0.0470	-26.02
	40	1.21	0.019	0.46	0.0240	-25.64
	45	1.28	0.015	0.42	0.0165	-25.42
	Average	1.17	0.023	0.49	0.0390	-25.81
2:1	30	1.07	0.028	0.60	0.0520	-25.79
	35	1.14	0.022	0.52	0.0360	-25.60
	40	1.20	0.019	0.46	0.0250	-25.62
	45	1.28	0.015	0.42	0.0160	-25.43
	Average	1.17	0.021	0.50	0.0320	-25.61

such as activation energy E_{act} can be calculated using Arrhenius equation. From the corrosion rate data at different temperatures in absence and presence of Zizyphus leaves extract as a corrosion inhibitor, Arrhenius plots were shown in Fig. 3 for a temperature range of (30-45°C). Activation energies were calculated from the Arrhenius plots which represent the relationship between log (CR) and the reciprocal absolute temperature (Khadom and Abdul-Hadi, 2014):

$$\log CR = \log A - \frac{E_a}{2.303RT} \quad (7)$$

Where:

A = Frequency factor

T = The absolute temperature

R = The universal gas constant

The values of activation energy were listed in Table 6. It is also observed that the activation energy E_a

Table 6: Activation energy of dissolution reaction of mild steel in 1% MgCl₂, containing various concentrations of extract

Ac/Aa	C (ppm)	E _a (kJ/mol)
0.5:1	Blank	20.71
	120	51.57
	240	53.15
	360	64.72
	480	66.99
1:1	Blank	22.59
	120	60.21
	240	61.81
	360	73.37
	480	75.65
2:1	Blank	35.96
	120	67.17
	240	68.76
	360	80.32
	480	82.60

for uninhibited acid were lower than in inhibited acid. The results showed positive sign for both E_{act} reflecting the endothermic nature of the corrosion process. The values of E_a increases in the presence of the inhibitor. Some researcher (Ashassi-Sorkhabi *et al.*, 2006) attributed this result to the fact that the inhibitor species is physically adsorbed on metal surface.

CONCLUSION

Ziziypus leaves extract is effective inhibitor of galvanic corrosion of steel-copper couple in petroleum waste water solution with maximum inhibitor efficiency 89.6% at 30°C, 1:1 area ratio and higher level of inhibitor concentration. The adsorption model of Ziziypus leaves extract obeyed the Langmuir adsorption isotherm. The negative sign of VG_{ads}⁰ indicate that the adsorption process is a spontaneous and exothermic. The values of E_a of the corrosion process in the corrosive medium in the presence of Ziziypus leaves extract are higher than those in the uninhibited medium. This indicates the increase in the energy barrier for the corrosion reaction with the increasing concentrations of the inhibitor.

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