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Thermodynamics and Kinetics of Inhibition of Aluminum in Hydrochloric Acid by Date Palm Leaf Extract

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KEYWORDS: Green inhibitor, corrosion rate, inhibition thermodynamics, inhibition kinetics, aluminum, hydrochloric acid, date palm leaf extract, *Phoenix dactylifera*

ABSTRACT: The corrosion behavior of commercial aluminum in HCl was investigated by gravimetric method in absence and presence of date palm leaf extract (DPLE) as inhibitor. Corrosion rates in absence of extract ranged from 2.4-8.0 mg/cm^2/h in the temperature range 20-50ºC but decreased down to 0.30-2.6 mg/cm^2/h in presence of the inhibitor. Hot-water extract of date palm leaves has shown inhibition efficiency (IE) of 40- 88%at the tested conditions. IE was found to increase with increasing inhibitor concentration from 0.2 to 0.6 g/L and decrease as temperature increased. Data showed that Langmuir adsorption isotherm represents surface coverage versus extract concentration data indicating that inhibition is due to monolayer adsorption of extract components on aluminum surface. Low activation energy and enthalpy values support physical adsorption mechanism. SEM-EDS microanalysis of aluminum surface supported the inhibitive effect of the extract at the metal surface.© JASEM

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Introduction. Aluminum and its alloys are important materials which are used in many engineering applications such as construction, vehicles, chemical reactors, pipes and batteries. Aluminum forms a protective layer of oxide on its surface but this oxide dissolves and makes the metal susceptible to corrosion in acid, salty and alkaline media (El-Maghraby, 2009; Ating et al, 2010). The use of corrosion inhibitors is necessary in such cases like exposure of Al alloy to acid or salt solution. Synthetic chemical inhibitors, commonly chromates, are toxic to life in the environment upon disposal or leaks and they may be also a health and safety hazard in their handling (Kesavan et al, 2012; El-Etre, 2003) . The search of green corrosion inhibitors has been active in the last two decades and many plant extracts were investigated in connection with different metals and corrosive environments (Kesavan et al, 2012; Amitha Rani and Basu , 2011; Sangeetha, 2013). In particular, several plant extracts have been reported as potential green inhibitors for aluminum in acid and salt media (Ating et al, 2010; Oguzie , 2007;Umoren , 2008; Alinnor and Ejikeme, 2012; Ali and Foaud, 2012). Date palm (*Phoenix dactylifera*) is an important food crop around the world. Counties of the Middle East and North Africa possess 70% of the 120 million world's date palm trees and responsible for 67% of the global date production .The annual world production of dates is around 7.4 million tons and it has increased from approximately 2 million tons in 1962 to almost 7million tons in 2005 (Juhany , 2010; FAO, 2006). Palm trees are also planted for landscape. The plant leaves can be easily obtained at no cost being waste material from regular tree trimmings.

The corrosion inhibition effects of extracts from products or parts of the date palm tree have been reported by several researchers. Gerengi (2012) reported that date palm fruit juice has anticorrosive properties for 7075 type aluminum alloy in 3.5% NaCl solution. The inhibition efficiency increased with increase of fruit juice concentration. The adsorption of extract on the metal surface was found to be physisorption in mechanism. Al-Turkstani et.al.(2013) evaluated the *Phoenix dactylifera* seeds aqueous extract as inhibitor for mild steel in a 0.25M to 2.5M H_2SO_4. They found that inhibition efficiency increased with increasing extract concentration and immersion time but decreased with increasing acid concentration and temperature. The adsorption of the phytochemical constituents on to the surface of mild

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steel was represented by Langmuir isotherm. Umoren et.al.(2013) studied the corrosion inhibition effect of date palm seed extracts for mild steel in 1 M HCl and 0.5 M H_2SO_4 solutions. They found that inhibition efficiency increased with increase of extract concentration and decreased with increase in temperature. Adsorption of the extract onto a mild steel surface followed the Langmuir adsorption isotherm and the mechanism of physical adsorption. The immersion time was also found to influence the corrosion inhibition effect in both acidic media. Sultan et.al (2014) studied the effects of aqueous extract of *Phoenix Dactylifera* Gummara (apical meristem or the pith of the palm tree) on the corrosion inhibition of mild steel in 1M HCl solution by weight loss measurements at temperatures of 30-60°C. They found that inhibition efficiency increases with increasing of inhibitor concentration and decreases with increasing of temperature, reaching 93.8% at 30°C. The values of activation energy, enthalpy and entropy of adsorption were found to increase with extract concentration. Adsorption of extract components on metal surface was shown to occur spontaneously and the data follow Langmuir isotherm model.

More relevant to this work are the studies of Rehan (2003) and Shalabi et al (2014) who prepared the extracts from date palm leaves and tested their performance as corrosion inhibitors. Rehan (2003) has found that water-soluble extracts of date palm leaves were highly effective in reducing corrosion rate of aluminum in sodium hydroxide solutions as well as steel in acid chloride solutions. The inhibition efficiency (IE), increased with increasing extract concentration. The IE values for corrosion inhibition in 0.2 M HCl were 78.7 for steel and 32.6% for aluminum. In 0.2 M KOH, the IE value for aluminum inhibition was 70.6%, all at 25ºC. Activation energy (E_a) values in presence of extract were higher than in the absence of extract. E_a values ranged from 9.8-13.5 kcal/mol for steel in HCl solution but no data were reported on E_a for aluminum corrosion inhibition. Thermodynamics and kinetics for aluminum inhibition are not reported and still needed.

Shalabi et al (2014) studied the inhibitive properties of alcoholic extract of palm date leaves and find that physical adsorption of phytochemical compounds resulted in 62-89% inhibition efficiency of Al corrosion in 0.5M HCl using 200-1000ppm dose of the extract at 20°C.

While other studies on palm date extracts reported in the literature reviewed above used chemical solvents (e.g. ethanol), this work is suggesting a DPLE produced by extraction with hot water thus completely eliminates chemical usage both as inhibitors or extraction solvents.

In this work, a green inhibitor produced by extraction of date palm leaves using hot water as solvent is suggested. The performance of this extract is evaluated by studying the inhibition of aluminum corrosion in hydrochloric acid considering both thermodynamic and kinetic parameters. The effects of process variables, namely, contact time, extract concentration and solution temperature were considered in evaluating the inhibition performance of DPLE.

MATERIALS AND METHODS

*Materials***.** Pure commercial aluminum is used as substrate. The chemical composition of the metal is given in Table 1.The corrosive medium is 1.0M hydrochloric acid (HCl). This is prepared by diluting the stock acid solution of 35-38% HCl (average of 36.5% with density of 1.18 g/L) in distilled deionized water. This solution is used for all experiments. Date palm leaves were cut into small pieces to increase surface area, washed thoroughly and repeatedly with tap water and distilled water, dried and stored for extraction.

Extraction. Clean, dry date palm leaves were contacted with hot water at 80ºC in a solid-to-liquid ratio of 1:50 for 3 hours in 2000mL thermal-glass beaker under adequate shaking conditions. The extract was then filtered by vacuum filtration apparatus through 0.45µm pore size membrane and the filtrate stored for corrosion inhibition experiments. This will be referred to later as DPLE.

Preparation of inhibitor solution. A 4.0 g/L solution of DPLE (4000 ppm) is used as stock extract solution. A volume of 25, 50 or 75 mL of this stock was added to a calculated volume of HCl and diluted with distilled deionized water to 500 mL in the corrosion cell to produce 0.20, 0.40 or 0.60 g/L concentration of DPLE in 1.0M HCl. Blank solution contains 1.0M HClin 500mL inhibitor-free solution.

Apparatus. A round-bottom borosilicate glass vessel (1000mL) is supported by Teflon and metal stand and covered by Teflon plate. Appropriate openings were made for rotating motor-driven Teflon shaft and thermometer. The shaft supports aluminum coupon sleeves having 1.0 cm diameter and 1.0 cm height with surface area of 3.14 cm^2 exposed to corrosive medium. The corrosion cell is immersed in a shaking bath for temperature control.

Corrosion Rate Measurement. The weight of aluminum specimen was taken before and after immersion in the corrosive solution to 4-digit accuracy using analytical balance (Sartorius, Germany). The solution is heated to the desired temperature of 20, 35 or 50ºC in a water bath (Thermo Scientific, USA). After a given immersion time (2, 4, 6 or 8 h), the specimen was retrieved from corrosion cell, immersed for 3-5 seconds in 1.0M NaOH solution to neutralize excess acid on metal surface, rinsed by distilled water and dried in oven at 100ºC for 15 minutes before final weight is taken. The weight difference is taken as metal loss due to corrosion. The corrosion rate (CR, $mg/cm^2/h$) is calculated by dividing the weight loss (W, mg) obtained from experiments by the metal surface area in contact with solution (A, cm^2) and the immersion time (Δt, h) as expressed in the equation:

$$CR = W/A.\ \Delta t \qquad (1)$$

The percentage inhibition efficiency, IE, is determined as follows (Oguzie, 2007):

$$IE = [(CR_b – CR_i) / CR_b] \times 100 \qquad (2)$$

where CR_b and $CR_i$are corrosion rates for blank (uninhibited) and inhibited solutions, respectively.

*Surface Microanalysis.*SEM and EDS analyses were conducted using Scanning Electron Microscope/ Energy Dispersive X-Ray Spectrometer (SEM/EDS) Model JEOL 5800LV- Tungsten filament, automated stage with x, y, z, tilt and rotational movement, Energy dispersive x-ray spectroscopy (EDS) coupled with SEM is used to determine chemical composition of micro-features.

RESULTS AND DISCUSSION

In this section, the results obtained from the experiments are discussed in the light of theory of corrosion and corrosion inhibition kinetics and thermodynamics as well as surface characterization analysis.

Effect of Process Variables on Corrosion Process. Three variables are considered for their effect on the corrosion of aluminum in 1.0M HCl, namely, contact time between metal and corrosive medium, DPLE (extract) concentration and solution temperature. The effects of contact time and extract concentration at constant temperature on weight loss are illustrated in Figs. 1-3. At constant temperature in the studied range of 20-50°C, these Figures show that as time increased, the weight loss increased for all solutions tested including blank, which conforms to chemical reaction theory. Also, as the extract concentration increased (at fixed time and temperature), the weight loss of metal generally decreased due to the inhibition effect of the extract components which cover more of the metal surface as the extract concentration increased. This result is in agreement of that of Gerengi (2012) who investigated the inhibition of aluminum in NaCl solution by date palm fruit juice.

In Fig.1, the aluminum weight loss was much lower in presence of extract compared to that in blank acid solution indicating a strong inhibition effect at the lower temperature of 20°C.There was essentially no effect of extract concentration beyond 0.2 g/L on weight loss at this temperature. This can be explained by the fact that the surface coverage by extract molecules is sufficient to oppose and resist the metal dissolution process. This is not the case, however, at the highest investigated temperature of 50°C (Fig. 3) where the extract is less effective as inhibitor, which can be explained considering the inhibition mechanism which has be shown to be based on adsorption of inhibitor species on metal surface and subsequent attachment. As temperature increases, surface coverage of adsorbate becomes less due to losses in favor of desorption. Also, the metal dissolution (corrosion) rate is higher at higher temperatures as predicted by Arrhenius equation of chemical kinetics. In Fig. 2, whose data were obtained at the intermediate temperature of 35°C, the observed behavior of aluminum in blank acid and extract-inhibited solutions lies intermediate between those at 20 and 50°C.

The effect of temperature on weight loss is also depicted in Fig. 4 for a more quantitative comparison. After 8 hours of contact with corrosive solutions (0.0-0.6 g extract/L), the weight loss increased by 3-4 times when solution temperature increased from 20 to 35°C and by 9-10 times from 20 to 50°C. This Figure shows that the weight loss of aluminum in blank and inhibited acid solutions increases non-linearly with increasing temperature. The influence of temperature on weight (and consequently on corrosion rates) was more profound in inhibited solutions compared to that blank acid solution.

The above argument explains the observation that the inhibition efficiency (IE) of the extract decreases with increasing temperature as shown in Table 2. In this table, calculations of corrosion rate (CR) and percent inhibition efficiency (IE) are presented for various conditions using Eq.1 and Eq. 2. IE ranged between 40-88% depending on both temperature and extract concentration. This trend of temperature effect on the performance plant extracts as inhibitors of aluminum corrosion in acids was reported by several researchers who investigated extracts of *opuntia* (El-Etre, 2003), Gum Arabic (Umoren , 2008), *Ocimumgratissimum* (Alinnor and Ejikeme, 2012), black mulberry (Ali and Foaud, 2012) and *Treculia Africana* leaves (Ejikeme et al, 2012)and alcoholic-extract of *Phoenix dactylifera* (Shalabi et al, 2014) where corrosion inhibition became less effective at higher temperatures.

Adsorption in Corrosion Inhibition Process. Many previously published studies have demonstrated that corrosion inhibition works when active ingredients in the extract are adsorbed on metal surface by physical or chemical means. According to Trabanelli (1987), physisorption is weak indirect interaction due to electrostatic attraction between inhibiting organic ions or dipoles and the electrically charged surface of the metal. Chemical adsorption involves charge sharing or charge transfer from adsorbate to the metal surface atoms in order to form a coordinate type bond. Chemical adsorption is distinguished by relatively high free energy compared to physisorption.

The construction of adsorption isotherms for corrosion inhibitor can help understanding the nature of the metal-inhibitor interactions. The experimental data would fit one of the common adsorption isotherms such as Langmuir's model. This model can be expressed in the linear form as follows:

$C/\Theta = (1/K) + C$ (3) where Θ = surface coverage (fraction, dimensionless), C = adsorbate concentration and K = equilibrium constant. Since the percentage inhibition efficiency depends essentially on surface coverage, the latter was calculated by the following equation:

$\Theta = IE/100$ (4)

To elucidate the inhibition mechanism, the ratio C/Θ was plotted against "C" for 20, 35 and 50°C as shown in Fig. 5. The straight lines with high correlation coefficients (0.998-1.000, Table 3) indicate that DPLE components are attached to aluminum surface through adsorption process. The slope of the line is unity as suggested by Langmuir equation above and K is obtained from the line intercept. The quantification of thermodynamic properties of corrosion in blank and inhibited solutions helps to understand and ensure the effect of inhibitor on the surface of metal substrate. The equilibrium constant for adsorption, K, is related to the standard Gibbs (free) energy change of the process by the following equation (Umoren , 2008;Gerengi, 2012):

$$K = (1/C_w) \text{ Exp } (-\Delta G°/RT) \quad (5)$$

where C_w is the molar concentration of water (55.5 mol/L). $\Delta G°$ can characterize the interaction of adsorbed molecules and metal surface. These quantities were determined at the intermediate temperature of 35°C and presented in Table 3.The small values of $\Delta G°$ (around -20 kJ/mol or less negative) are normally accepted to support physisorption exhibited through electrostatic attraction between inhibitor and the charged metal surface; while $\Delta G°$ values around -40 kJ/mol or more negative are indication of chemisorption which mechanistically occurs through charge sharing or transferring from inhibitive species to the metal surface to form a coordinate bond (Wang, 2001; Bentiss et al, 2005;Yurt et al, 2006; Umoren et al, 2008).According to Sharma et al (2013), the decrease in inhibition efficiency with rise in temperature is ascribed to physical adsorption mechanism. Their experimental data fit into Langmuir adsorption isotherm. The negative sign of $\Delta G°$ indicates a spontaneous adsorption process which is the case in other green inhibitors systems as reported by El-Etre (2003), Umoren et al (2008) and Alinnor and Ejikeme (2012).

The chemical nature of extract components responsible for the corrosion inhibition has been reported in recent publications. The leaves are rich in phytochemicals like phenolics, carotenoids, and flavonoids (Baliga et al, 2011).These compounds present conjugated aromatic structures, long aliphatic chains containing nitrogen, sulfur and oxygen hetero atoms with multiple bonds and free electron pairs that are available to form bonds with the metal surface. The net effect of adsorption of such extract components is the protection of the metal surfaces from the attack of the aggressive ions of the acid medium. However, owing to the complex chemical composition of the extract, it would be difficult to assign the inhibitive effect to a particular phytochemical constituent (Ejikeme et al, 2012).

Corrosion and Corrosion Inhibition Kinetics. The dissolution reactions of aluminum in acid have been investigated by Nguyen and Foley (1982):

$$Al_{(s)} + H_2O \leftrightarrow AlOH_{ads} + H^+ + e^- \quad (6)$$

$$AlOH_{ads} + 5H_2O + H^+ \leftrightarrow Al^{3+} + 6H_2O + 2e^- \quad (7)$$

$$Al^{3+} + H_2O \leftrightarrow [AlOH]^{2+} + H^+ \quad (8)$$

$$[AlOH]^{2+} + X^- \leftrightarrow [AlOHX]^+ \quad (9)$$

In HCl solution, the latter reaction corresponds to:

$$[AlOH]^{2+} + Cl^- \leftrightarrow [AlOHCl]^+ \quad (10)$$

The above complexation reaction is the controlling step in the metal dissolution and it represents the main corrosion reaction. The complex ion $[AlOHCl]^+$ is the main soluble corroded metal form. In the presence of plant extract, the soluble organic molecules (ORG) adsorb on the metal surface as replacement of water molecules thus preventing metal dissolution. The adsorption process can be represented by the following equation (Sahin, 2002):

$ORG_{sol} + H_2O_{ads} \leftrightarrow ORG_{ads} + H_2O_{sol}$ (11)

where the subscripts *sol* and *ads* refer to solution and adsorbate layer phases, respectively. The above equation is the basis for determining the equilibrium constant of adsorption (K).

To understand the effect of inhibitor on corrosion rates at different temperatures, the linearized Arrhenius equation of chemical kinetics was considered:

($\log CR = \log A - E_a/R.T$ 12)

where "A" is the frequency factor, E_a is the apparent activation energy for corrosion reaction (kJ/mol) and R is the universal gas constant (kJ/mol/K). A plot of "log CR" versus the reciprocal of absolute temperature (1/T) produced straight lines as shown in Fig. 6 for blank and inhibited solutions. The values of E_a and the derived thermodynamic functions were obtained from the slopes of these lines and given in Table 4. The correlation coefficients of these lines (also given in Table 4), ranged from 0.952 to 0.995 indicating a very good fit of experimental data. The apparent activation energy for the corrosion reaction has increased from 13.18 kJ/mol in blank acid to an average of 24.75 kJ/mol with addition of DPLE which indicates that the corrosion process is inhibited via increasing the activation energy required for the aluminum dissolution reaction.

The increase in activation energy is achieved presumably via formation of a thin coat or film on the metal surface that has become a barrier to both energy and mass transfer. However, increasing the solution temperature weakens the inhibition effect by enhancing the counter process of desorption. That is why the inhibition efficiency (IE) values decreased with temperature increase as shown in Table 2.This result is in agreement with other published studies on similar systems involving green inhibitors (El-Etre, 2003;Ali and Foaud , 2012;Umoren et al, 2008;Obot et al, 2009;Eddy et al, 2009).

The thermodynamic functions of ΔH° and ΔS° for corrosion in blank and inhibited solutions were obtained from the following equations and the values are presented in Table 4:

$\Delta H° = E_a - R.T$ (13)

$\Delta G° = \Delta H° - T.\Delta S°$ (14)

The small values of ΔH°in presence of inhibitor (around +22 kJ/mol) are typical of a physisorption process. ΔS values were around +120 J/mol/K and the sign indicates increase in system disorder in the transition state due to interfacial processes as well as mass transfer in bulk solution and at the metallic surface. Shalabi et al (2014) who used alcoholic-extract of date palm leaves have reported almost similar values of ΔH° (14.6 and 19.9 kJ/mol for blank and inhibited solutions, respectively) reported with a proposed physisorption mechanism. However, higher values of activation energy, E_a of 36.1 and 48.4 kJ/mol for blank and inhibited solutions, respectively were reported probably due to the high dose (1000ppm) of extract added in addition to different HCl solution concentration.

Surface Microanalysis. The surface morphology was studied by means of scanning electron microscopy (SEM) with associated elemental analysis by energy dispersive spectrometry (EDS). The surface of aluminum coupon is morphologically characterized by SEM and the images obtained are shown in Fig. 7. In comparison with image (a) which shows the crystalline structure of untreated Al coupon, image (b) illustrates clearly the surface washout, pitting and severe damage of aluminum alloy due to corrosive medium effect. In image (c), the coupon surface looks much less distorted by acid attack and there is a deposit or adsorbate attached to the surface. This confirms the experimental results of lower corrosion rates in presence of date palm leaf extract.

In addition, Fig. 8 shows EDS elemental analysis spectra for the same aluminum coupon at different conditions of (a) no-acid contact, (b) corroding in acid and (c) inhibited by the extract. Chlorine peaks in different surface locations are shown in spectrum (b) indicating the attack of Cl^- ions in HCl at aluminum surface causing pitting corrosion in addition to surface washout. Such peaks were not observed in spectrum (c) where the surface was covered by extract components; thus confirming the inhibitive effect of DPLE as corrosion inhibitor.

Conclusions: Hot-water extract of date palm leaves was shown to be an effective green inhibitor for corrosion of aluminum in 1.0M hydrochloric acid. The inhibition efficiency increased with increase in extract concentration, but decreased with increase in temperature. The inhibitive action is suggested to be realized through adsorption of extract phytochemical compounds onto aluminum surface as demonstrated by fitting to Langmuir adsorption isotherm. Thermodynamic data obtained support physisorption and spontaneous inhibition process. The presence of the extract increases the activation energy of the corrosion reaction. Activation energy, enthalpy and entropy were relatively small and thus independent of extract concentration.

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Table 1: Elemental composition of Al alloy used as substrate

Component	Al	Mg	Si	Fe	Ti	Mn	Zn	Cu	Cr	Pb
Weight percent	98.8	0.511	0.459	0.190	0.010	0.0094	0.0084	0.0059	0.0022	0.0008

Table 2: Calculated values of Corrosion Rate and Inhibition Efficiency of date palm leaf extract for aluminum in acid at different temperatures for 8 hours contact

No.	Medium \ Temperature	Corrosion Rate ($mg/cm^2/h$)			Inhibition Efficiency (IE %)		
		293 K	308 K	323 K	293 K	308 K	323 K
1	1.0M HCl (blank)	2.46	5.11	7.97	---	---	---
2	1.0M HCl + 0.20 g extract/L	0.51	2.20	4.66	79.3	56.9	40.2
3	1.0M HCl + 0.40 g extract/L	0.40	1.57	3.33	83.7	69.3	57.3
4	1.0M HCl + 0.60 g extract/L	0.30	1.02	2.63	87.8	80.0	66.2

Table 3: Parameters obtained from linear regression analysis of Langmuir adsorption isotherms

Temperature (K)	Slope	K	ΔG° (kJ/mol)	St. Dev. of Error	R^2
293	1.078	0.040	-17.63	0.0082	0.999
308	0.996	0.161	-14.96	0.0216	0.998
323	1.022	0.292	-14.09	0.0031	1.000

Table 4: Activation energy and thermodynamic functions from Arrhenius plots of corrosion rates

System	E_a (kJ/mol)	St. Dev. of Error	R^2	ΔH° @308K (kJ/mol)	ΔS° @ 308K (J/mol.K)
Blank	13.18	0.0449	0.984	10.62	83.05
0.20 g extract/L	25.24	0.1074	0.976	22.78	122.53
0.40 g extract/L	24.28	0.0924	0.981	21.72	119.09
0.60 g extract /L	24.74	0.0307	0.998	22.18	120.58

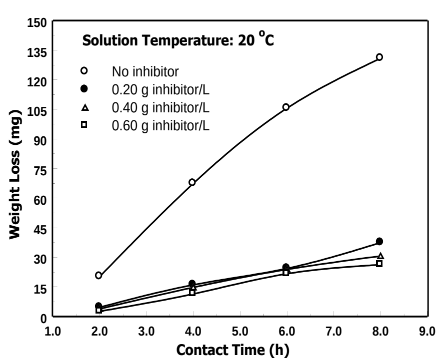

Fig. 1: Weight loss versus contact time for blank acid and solutions inhibited by date palm leaf extract at 20ºC.

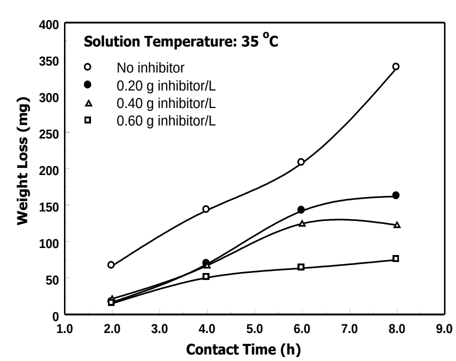

Fig. 2: Weight loss versus contact time for blank acid and solutions inhibited by date palm leaf extract at 35ºC.

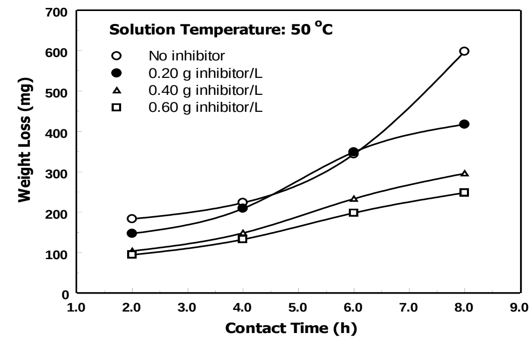

Fig.3: Weight loss versus contact time for blank acid and solutions inhibited by date palm leaf extract at 50ºC.

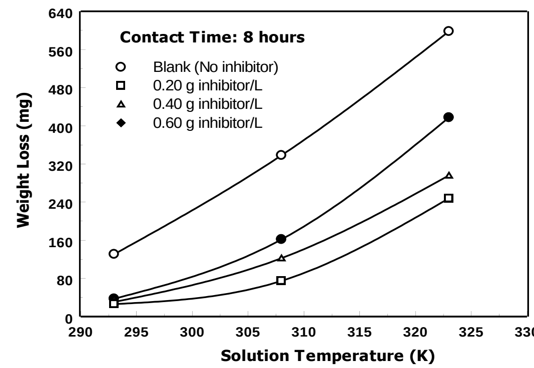

Fig. 4: Effect of solution temperature on Al weight loss in blank acid and solutions inhibited by date palm leaf extract

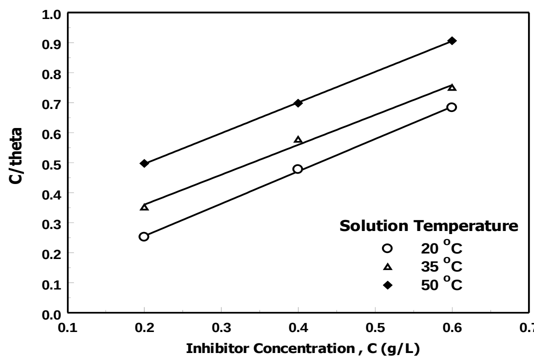

Fig. 5: Langmuir adsorption isotherms for inhibition of Al corrosion in 1.0M HCl by date palm leaf extract at different temperatures.

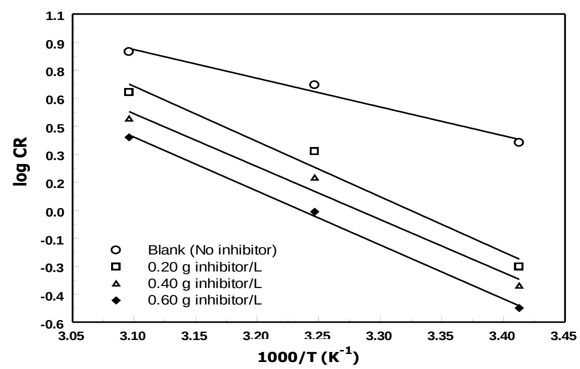

Fig. 6: Arrhenius plots for aluminium corrosion in 1.0M blank and inhibited HCl solutions by date palm leaf extract

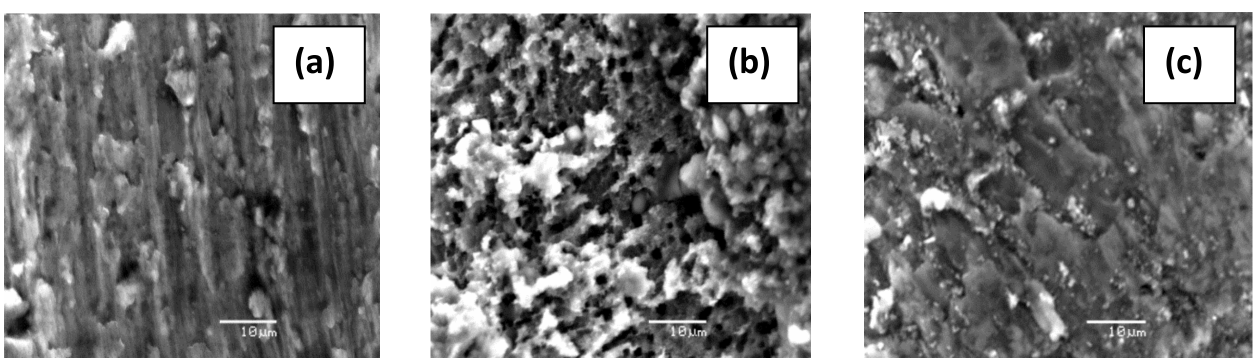

Fig. 7: Digital microscopic photographs of aluminum alloy at X2000: (a) not exposed to corrosive medium, (b) immersed in blank 1.0 M HCl, and (c) immersed in 1.0M HCl inhibited with date palm leaf extract (0.40 g/L) at 35ºC.

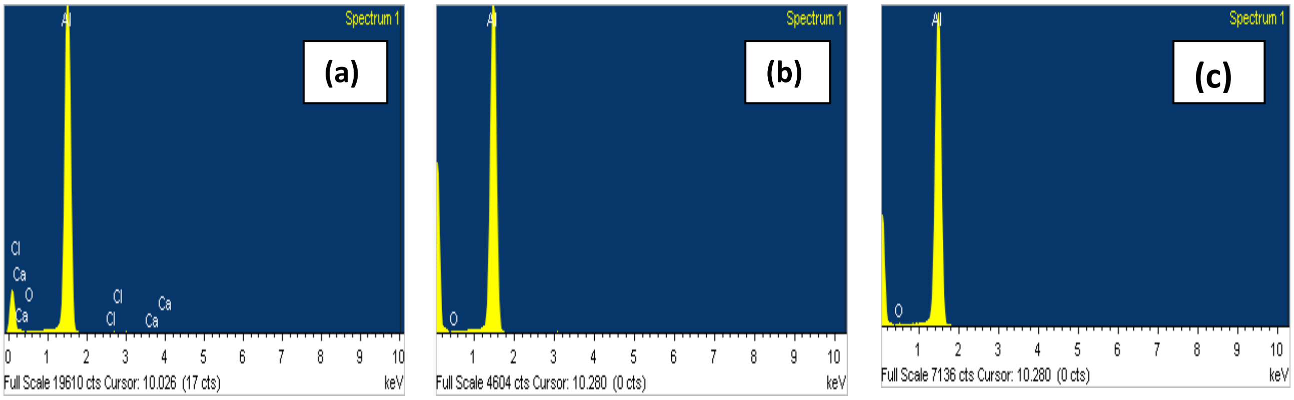

Fig. 8: EDS elemental analysis spectra for aluminum alloy: (a) not exposed to corrosive medium, (b) immersed in blank 1.0M HCl and (c) immersed in 1.0M HCl inhibited with date palm leaf extract (0.40 g/L) at 35ºC.

REFERENCES

Ali, A I; Foaud, N (2012). Inhibition of aluminum corrosion in hydrochloric acid solution using black mulberry extract. J Mater Environ Sci 3(5): 917-924.

Alinnor, I J; Ejikeme, P M (2012). Corrosion inhibition of aluminum in acidic medium by different extracts of *Ocimum gratissimum*. Amer Chem Sci J 2(4): 122-135.

Al-Turkustani, A M , Al-Sawat, R M; Al-Hassani, R H; Al-Ghamdi, N S; Al-Harbi, E M; Al-Gamdi, M A; Al-Solmi, S A (2013). Corrosion behaviour of mild steel in acidic solution using the aqueous seed extract of *Phoenix dactylifera L* (Date seeds). J Chemica Acta 2:53-61.

Amitha Rani, B E; Basu, B B (2012). Green inhibitors for corrosion protection of metals and alloys: An overview. Inter J Corrosion, Article ID 380217, pp. 1-15.

Ating, E I; Umoren, S A; Udousoro, I I; Ebenso, E E; Udoh, A P (2010). Leaves extract of Ananas sativum as green inhibitor for aluminum in hydrochloric acid solutions. Green Chem Letters & Reviews 3(2): 61-68.

Baliga, M S; Baliga; B R, Kandathil, S M (2011). A review of the chemistry and pharmacology of the date fruits (*Phoenix dactylifera L.*) Food Res Inter 44:1812-1822.

Bentiss, F; Lebrini, M; Lagrenee, M (2005). Thermodynamic characterization of metal dissolution and inhibitor adsorption processes in mild steel/2,5-bis(n-thienyl)-1,3,4-thiadiazoles/hydrochloric acid system. Corrosion Sci 47(12): 2915-2931.

Eddy, N O; Odoemelam, S A; Ekwumemgbo, P (2009). Inhibition of the corrosion of mild steel in H_2SO_4 by penicillin G. Sci Res Essay 4(1): 33-38.

Ejikeme, P M; Umana, S G; Onukwuli, O D (2012). Corrosion Inhibition of Aluminium by Treculia Africana Leaves Extract in Acid Medium. Portugal. Electrochim. Acta. 30(5): 317-328.

El-Maghraby, A A (2009). Corrosion inhibition of aluminum in hydrochloric acid solution using potassium iodate inhibitor. The Open Corrosion J 2: 189-196.

El-Etre, A Y (2003). Inhibition of aluminum corrosion using opuntia extract. Corrosion Sci 45: 2485-2495.

FAO (Food and Agriculture Organization of the United Nations). Worldwide dates production statistics (2006). http:// faostat/servlet.

Gerengi, H (2012). Anticorrosive properties of of date palm (*Phoenix dactylifera L.*) fruit juice on 7075 type aluminum alloy in 3.5% NaCl solution. Ind Eng Chem Res 51:12835-12843.

Juhany, L I (2010). Degradation of date palm trees and date production in Arab countries: causes and potential rehabilitation, Austral. J. Basic Appl. Sci. 4(8): 3998-4010.

Kesavan, D; Gopiraman, M; Sulochana, N (2012). Green inhibitors for corrosion of metals: A review. Chem Sci Rev Letters 1(1):1-8.

Nguyen, T H; Foley, R T (1982). The Chemical Nature of Aluminum Corrosion: II. The Initial Dissolution Step. J. Electrochem. Soc.129(1): 27-32.

Obot, I B; Obi-Egbedi, N O; Umoren, S A (2009). Adsorption characteristics and corrosion inhibitive properties of clotrimazole for aluminium corrosion in hydrochloric acid. Inter J Electrochem. Sci. 4: 863-877.

Oguzie, E E (2007). Corrosion inhibition of aluminum in acidic and alkaline media by Sansevieria trifasciata extract. Corrosion Sci 49(3):1527-1539.

Rehan, H H (2003). Corrosion control by water-soluble extracts from leaves of economic plants. Mat.-wiss. u. Werkstoffech 34: 232-237.

Sahin, M; Bilgic, S; Yilmaz, H (2002). The inhibition effects of some cyclic nitrogen compounds on the corrosion of the steel in NaCl mediums. Appl Surf. Sci 195:1-7.

Sangeetha, M; Rajendran, S;Sathiyabama, J; Krishnaveni, A (2013). Inhibition of corrosion of aluminum and its alloys by extracts of green inhibitors. Portugal. Electrochimia Acta 31(1):41-52.

Shalabi, K; Fouda, A S; Elewady, G Y; ElAskalany, A (2014). Adsorption and Inhibitive Properties of *Phoenix dactylifera L.* extract as a Green Inhibitor for Aluminum and Aluminum Silicon Alloy in HCl. Protec of Metals & Phys Chem of Surf. 50(3): 420–431.

Sharma, A.; Choudhary, G; Sharma, Ar; Yadav, S (2013). Effect of Temperature on Inhibitory Efficacy of Azadirachta indica Fruit on Acid Corrosion of Aluminum. Inter. J. Innovative Res. in Sci. Eng. & Technol. 2(12): 7982-7992.

Sultan, A.A.; Ateeq, A A; Khaled, N I; Taher, M K; Khalaf, M N (2014). Study of Some Natural Products as Eco- Friendly Corrosion Inhibitor for Mild Steel in 1.0 M HCl Solution. J. Mater. Environ. Sci. 5(2): 498-503.

Trabanelli, G (1987). Corrosion Inhibitors. In Mansfeld, F. (ed.) Chemical Industries: Corrosion Mechanism, Chapter 3. Marcel Dekker, New York, pp. 28-120.

Umoren, S A (2008). Inhibition of aluminum and mild steel corrosion in acid medium using Gum Arabic. Cellulose 15: 751-761.

Umoren, S A; Gasem, Z M; Obot, I B (2013). Natural Products for Material Protection: Inhibition of Mild Steel Corrosion by Date Palm Seed Extracts in Acidic Media. Ind. Eng. Chem. Res. 52(44):14855–14865.

Umoren, S A; Obot, IB; Ebenso, E E; Okafor, P C (2008). Eco-friendly Inhibitors from Naturally Occurring Exudate Gums for Aluminum Corrosion Inhibition in Acidic Medium. Portugal Electrochem Acta 26: 267-282

Wang, L (2001). Evaluation of 2-Mercaptobenzimidazole as Corrosion Inhibitor for Mild Steel in Phosphoric Acid. Corrosion Sci 43: 2281-2289.

Yurt, A; Ulutas, S; Dal, H (2006). Electrochemical and theoretical investigation on the corrosion of aluminum in acidic solution containing some Schiff bases. Appl Surface Sci. 253(2): 919–925