Eco-friendly corrosion inhibitors: Effect of Delonix regia extract on corrosion and kinetics of corrosion process of aluminium alloy 2S in HCl solution

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ARTICLE INFO	ABSTRACT
Keywords: Aluminium, Acid corrosion, *Delonix regia*, Kinetic parameters, Weight loss	*The inhibitory effect of Delonix regia leaf extract on acid corrosion of aluminium alloy 2S in 1M HCl solution has been investigated using chemical techniques. The protection efficiency increases with increasing concentration of the extract but decreases with increasing temperature. Adsorption and activation studies were discussed. Adsorption studies showed that the inhibitor adsorbed on the metal surface according to the Langmuir adsorption isotherm. A first-order kinetics relationship with respect to aluminium was obtained with and without the extract from the kinetics treatment of the data.*

This study is a continuation of our previous work (Abiola *et al*., 2007) on eco-friendly corrosion inhibitors for aluminium in acid media. Our previous work (Abiola *et al*., 2007) has shown that *Delonix regia* extract inhibits corrosion of aluminium in HCl solution. It was therefore decided to investigate the effect of *Delonix regia* extract on kinetics of corrosion process of aluminium alloy 2S in HCl solution and the influence of temperature on the protection efficiency of this inhibitor.

A large volume of work has been published over the years on the use of inorganic and organic compounds for metals in acid and other systems (Abdel-Gaber *et al*., 2006; Abiola *et al*., 2004; Abiola *et al*., 2007; Abiola *et al*., 2011a; Abiola *et al*., 2015; Bhawsar *et al*., 2015;Kumar *et al*.,2004; Raja and Sethuramam, 2008; Zaferani *et al.,* 2013). The bio-toxicity of inorganic inhibitors such as chromate, dichromate, nitrite and nitrate is well-known. Their non-environmentally-friendly nature limits their application (Abiola *et al*., 2004;

Abiola *et al*., 2011b; Manimegalai and Majula, 2015; Rajappa *et.al*, 2008).

Recently, due to strict legislation on toxic corrosion inhibitors, the development of non-toxic corrosion inhibitors has been regarded as important. Organic compounds with functional groups containing hetero-atoms are of special interest as corrosion inhibitors (Abiola and Oloba-Whenu, 2015; Dharmalingam *et al*., 2016; Gerengi *et al*., 2016). One promising area of interest is the use of extracts from plants. This is because plants contain phytochemicals having centers for π electrons and functional groups such as O, S or N/ or combination. *Delonix regia* is rich in several biodegradable, eco-friendly heterocyclic compounds with heteroatoms incorporated in their molecular structures.

The aim of the present work is to investigate the effect of *Delonix regia* extract on corrosion and kinetics of corrosion of aluminium in 1 M HCl solution using weight loss.

Experimental details

The chemical composition and preparation of aluminium alloy 2S test specimens of dimensions 5 x 2 x 0.04 cm were as reported in previous communications (Abiola and Otaigbe, 2008a). HCl was of analytical grade and 1 M HCl solution was used as the aggressive solution for this study. Stock solution of the plant was prepared by refluxing weighed amount (1 g) of the dried powder leaf of *Delonix regia* for 2 hrs in 100 ml of 1 M HCl solution. The refluxed solution was allowed to stand for 8 hrs filtered and stored. The filtrate was diluted with the appropriate quantity of 1 M HCl solution to obtain inhibitor test solutions of 1 – 10 % v/v concentrations. The procedure of weight loss determination was similar to that reported previously (Abiola and Otaigbe, 2008a; Abiola *et al*., 2011a). Previously weighed Al coupons were immersed in 50 ml open beakers containing 50 ml of 1 M HCl solution (blank) and with additions of different concentration of *Delonix regia* extract to 1 M HCl (1- 10% v/v) at 30 ℃ . The weight losses of the coupons were monitored for 150 consecutive min at 30 min intervals as presented in Fig. 1. Duplicate experiments were conducted at the same time and the average values were taken.

The effect of temperature on the corrosion rate of Al coupon in 1 M HCl solution for 30 min immersion periods at 40, 50 and 60 ℃ ± 0.3 ℃ was also studied with 5, 8 and 10 %v/v extract. The temperature was thermostatically controlled using thermostat with precision of ± 0.3 ℃.

Results and discussion

The results obtained are presented in Figures 1-3 and Tables 1-3 for different concentrations of *Delonix regia* in 1 M HCl soluton from weight loss measurements.

The plot of weight loss (mg per unit area) of aluminium coupon versus inhibitor concentration at 30 ℃ for 30 min immersion period is shown in Figure 1. Weight loss as a function of inhibitor concentration decreased gradually up to 2% v/v concentration and decreased rapidly at 4% v/v concentration. This indicates that *Delonix regia* inhibits the acid corrosion of aluminium in 1 M HCl solution. The values of percentage inhibition

efficiency (I%) were determined for 30 min immersion periods using the equation:

$$\% \ I = [\ w_0 - w_1 \ / \ w_0 \ ] \ x \ 100 \qquad (1)$$

where w_0 and w_1 are the uninhibited and inhibited weight losses, respectively.

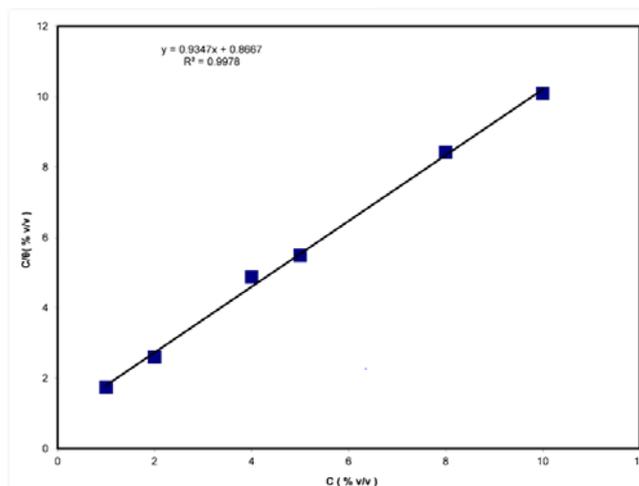$$y = 0.9347x + 0.8667$$
$$R^2 = 0.9978$$

Figure 1: The plot of weight loss of aluminium coupon versus *Delonix regia* extract concentration in 1 M HCl solution for 30 min immersion periods at 30 ℃

Assuming a direct relationship between inhibitor efficiency (I%) and surface coverage (θ) for different inhibitor concentrations, the degree of surface coverage was calculated using the relationship:

$$\theta = \% \ I \ / \ 100 \qquad (2)$$

Table 1 displays the percentage inhibition efficiency at 30 ℃ for inhibitor concentrations of 1 – 10% v/v for inhibitor concentrations of 8 and 10% v/v. As presented in Table 1, the percentage inhibition efficiency values increase with increasing extract concentration. The highest inhibition efficiency of about 98% was obtained at 10% v/v concentration at 30 ℃.

Table 1: Inhibition efficiency and surface coverage of *Delonix regia* extract on aluminium at 30 °C for 30 min immersion periods

Concentration (% v/v)	Inhibition efficiency (I%)	Surface coverage (θ)
0	-	-
1	57.2	0.57
2	77.4	0.77
4	82.1	0.82
5	90.9	0.90
8	95.0	0.95
10	98.8	0.99

This result indicates that increase in exact concentration increases the number of inhibitor molecules adsorbed onto Al surface and reduces the size of the surface area that is available for direct acid attack on the Al surface. *Delonix regia* contains N organic compounds such as alkaloid, amine oxide base, Δ-azetidine-2-carboxylic acids, amino acids amongst others (Chou and Lev, 1992). The inhibition properties of *Delonix regia* is ascribed to the presence of phytochemicals in the extract. Similar view has been reported in our previous communications (Abiola *et al.*, 2007).The phytochemicals in *Delonix regia* are known to contain aromatic compounds (Figure 2) with hetero atoms (N, S or O). These include several biodegradable, eco-friendly heterocyclic compounds of high molecular weight such as kaempferol-3-glucoside, chlorogenic acid, gallic acid cyanidine-3-O-glucoside, cyanidine-3-O-rutinoside and L-azetidine-2-carboxylic acid.
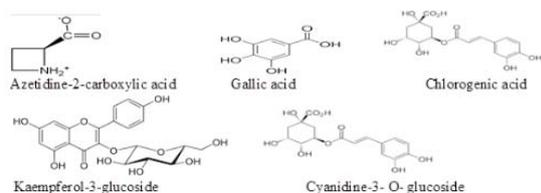

Figure 2: Examples of chemical structures in *Delonix regia*

The inhibitive effect of *Delonix regia* may be due to the presence of these organic compounds in the acid extract. Organic compounds having centers

for π electrons and functional groups of O, S or N/ or combination have been reported as corrosion inhibitors for metal in acid solutions (Abiola *et al.*, 2007; Abiola *et al.*, 2011a; Abiola and James, 2010). A barrier film may not form on the metal surface by the inhibitor molecules during 30 minutes exposure period. However, the increase in % inhibition (Table 1) with increase in inhibitor concentration supports the adsorption rather than barrier layer formation theory. Kumar *et al.* (2004) and Abiola *et al.* (2007) reported similar views for the inhibition of steel and aluminium in HCl solution by plant based inhibitors. Values of θ were tested graphically for fit to Frumkin, Freundlich, Temkin and Langmuir adsorption isotherms. As presented in Fig 3., a straight line is obtained when C/θ is plotted against C and linear correlation coefficient of the fitted data is close to 1, indicating that the adsorption of the inhibitor molecule obey the Langmuir's adsorption isotherm (Abiola and James, 2010) expressed as in equation [3]:

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

where C is the inhibitor concentration and K the equilibrium constant for the adsorption / desorption process of the inhibitor molecules on the metal surface.
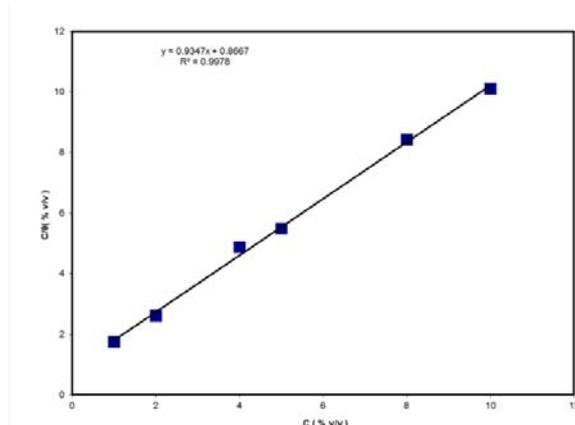

Figure 3: Langmuir adsorption model on aluminium surface of Delonix regia extract in 1 M HCl solution for 30 min immersion period at 30 °C)

The effect of temperature on the corrosion rate of aluminium in HCl solution in the presence of 5, 8 and 10% v/v inhibitor concentrations was investigated at 40, 50 and 60 ± 0.3 oC .

Table 2 shows the dependence of inhibitor efficiency on temperature when different concentrations of inhibitor were added to the acid solution. Inhibitor efficiency decreased as the temperature increased and this suggests physisorption of inhibitor's molecule at the aluminium surface. Desorption of inhibitor molecules with increased temperature is usually observed in cases of physisorption (Abiola *et al.* 2007).

Table 2: Percentage Inhibition efficiency of *Delonix regia* extract on aluminium for 30 min immersion period at different temperatures

Concentration (% v/v)	30o C	40o C	50o C	60o C
0	-	-	-	-
8	95.1	39.2	17.2	8.9
10	98.8	40.4	20.5	10.7

The apparent activation energy, E_a of the corrosion reaction was calculated using the Arrhenius equation:

$$\log \frac{v_2}{v_1} = \frac{E_a}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad (4)$$

where v1 and v2 are corrosion rates at temperature T1 and T2, respectively.

The heat of adsorption, Qads was calculated using Equation 5 (Abiola and James, 2010).

$$Q_{ads} = 2.303R\left[\log\left(\frac{\theta_2}{1-\theta_2}\right) - \log\left(\frac{\theta_1}{1-\theta_1}\right)\right] \times \frac{T_1 T_2}{T_2 - T_1} \qquad (5)$$

where θ_1 and θ_2 are the values of surface coverage at temperatures T_1 and T_2.

The values of E_a and Q_{ads} are presented in Table 3. The observed increase in activation energy in the presence of inhibitor from 9.29 to 39.02 kJ mol^{-1}, with attendance decrease in inhibition efficiency of the inhibitor as temperature increases, suggests physical adsorption of the inhibitor molecules on the metal surface. This result is in agreement with our findings (Abiola and James, 2010; Abiola et al., 2011; Ebenso et al., 2006). The negative value of heat of adsorption process indicates that the adsorption process is exothermic in nature. This observation further confirms physical theory of adsorption for the inhibitor on aluminium surface in 1 M HCl solution.

Table 3: Apparent Ea and Q_{ads} of *Delonix regia* extract on aluminium for 30 min immersion period

Concentration (% v/v)	Ea (40 – 50o C , kJ mol^{-1})	Q_{ads} (40 – 50 o C, kJ mol^{-1})
0	9. 29	-
8	38. 39	-95.68
10	39.02	-77.29

Kinetics of aluminium corrosion in HCl solution with and without inhibitor
Figure 4 shows the dependence of log Wi (weight of aluminium at time t) as a function of time. As presented in Figure 5, the corrosion data fit the rate law for first -order reaction as expressed (Abiola and James, 2010; Abiola and Otagbe, 2008b) in equation [6]:

$$\log [W_i - \Delta W_t] = -\frac{k}{2.303}t + \log W_i \qquad (6)$$

where k is the first – order rate constant, Wi is the initial weight of aluminium sample, ΔWt is the weight loss of aluminium sample at time t and the term (Wi – ΔWt) is the residual weight of aluminium sample at time t and can be designated as Wt as shown in Figure 4.

The obtained plots are linear with correlation coefficient of almost 1, confirm a first – order kinetics for the corrosion of aluminium in HCl solution in the presence and absence of inhibitor.
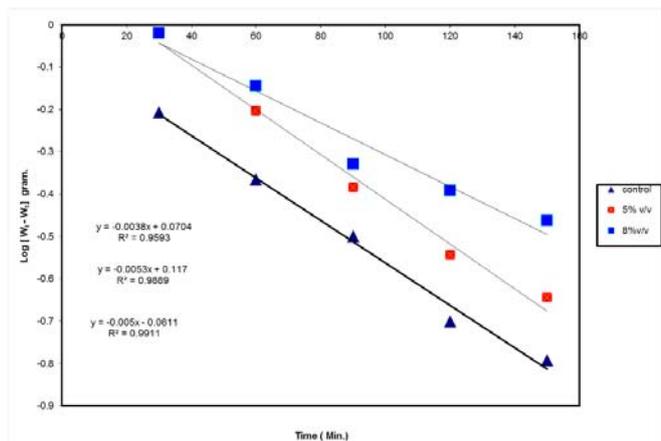
Figure 4: Plot of log [Wᵢ - ΔWₜ] versus time for aluminium coupons in 1 HCl solution with and without *Delonix regia* extract at 30 ᵒC

Figure 4 reflects the anodic reaction order with respect to aluminium i.e., the anodic reaction (Eq. (7)).

$$Al \rightarrow Al^{3+} + 3e \qquad (7)$$

From the results (as presented in Figure 4), the inhibition of acid corrosion aluminium in 1 M HCl solution by *Delonix regia* extract does not influence the anodic reaction order. As seen in Fig.4, similar plot was obtained for aluminium in HCl solution without and with the extract. In our previous communications (Abiola *et al.* 2007), using H_2 evolution technique we have reported similar results on inhibition of acid corrosion of aluminium in 2 M HCl solution by *Delonix regia* extract from kinetic treatment of the H_2 gas evolution data.

Conclusions

This study shows that *Delonix regia* leaves extract inhibits the acid corrosion of in 1 M HCl solution, with inhibition efficiency of about 98% at 10% v/v extract concentration and the % inhibition efficiency decreased with increase in temperature. The corrosion activation energy was higher in the presence of *Delonix regia* extract than in the absence of the extract. The adsorption of inhibitor molecules was consistent with Langmuir adsorption isotherm and a first- order kinetics relationship was obtained from the kinetics treatment of the mass loss measurements. *Delonix regia* can be added to HCl solution as green corrosion inhibitor.

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