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The effects of *Phyllanthus amarus* extract on corrosion and kinetics of corrosion process of aluminum in HCl solution

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Abstract
Inhibitive effect of *Phyllanthus amarus* extract on the acid corrosion of aluminum in 2 M HCl solution was studied by chemical technique. The extract inhibited the acid corrosion of aluminum and the inhibition efficiency increased with increasing concentration of the extract at 30^{o} C. The results obtained revealed that inhibition occurs through the adsorption of the inhibitor molecules onto metal surface and the adsorption accords with Lanqmuir adsorption isotherm.

Keywords: Aluminum, Chemical technique, Acid corrosion, Acid inhibition, *Phyllanthus amarus.*

Introduction
The failure of aluminum equipment due to acid corrosion in industries is widely reported, and the use of chemical inhibitors is the most practical and cost effective means of controlling corrosion of metals in acid solutions [1 – 3]. However, a number of inhibitors of acid corrosion of aluminum are toxic, non-biodegradable and expensive [4 – 6].

As a result of increasing awareness on environmentally friendly practices for sustainable development, the demand for non-toxic inhibitors to replace toxic ones has increased tremendously. Thus, in recent years, several plant extracts [6 – 17] have been investigated for the inhibition of acid corrosion of metals. This is because plants contain naturally synthesized chemical compounds that are biodegradable, environmentally acceptable, inexpensive, readily available and renewable source of materials [13,14,17].

P. amarus extract [15, 16] was found to inhibit the corrosion of mild steel in H_2SO_4 acid solution using weight loss(chemical) technique. Quite recently[17],we reported the value of 76% inhibition efficiency at 20% v/v concentration of *P. amarus* extract for aluminum corrosion in NaOH solution and that the organic compounds in the extract establish their inhibition via adsorption of their molecules in accord with Lanquimuir adsorption model on the metal surface forming a protective barrier.

Presently, there is no reported work on the effects of *P.amarus* extract on aluminum corrosion in HCl solution. Therefore, this study reports on both the inhibition of acid corrosion of aluminum by *P.amarus* extract and its effects on the kinetics of corrosion process of aluminum in 2 M HCl solution using weight loss technique.

2. Materials and methods
2.1. Materials preparation
The chemical composition and the preparation of 3SR aluminum alloy specimens (4 x 2 x 0.04 cm) was as described earlier [21].The 2 M HCl solution, prepared from BDH grade HCl was employed as the aggressive solution for this study.

Stock solution of the plant was prepared by refluxing weighed amount (1g)of the dried powder leaves of *P.amarus* for 1 h in 100 ml 2 M HCl solution. The refluxed solution was allowed to stand for 8 h, filtered and stored. The filtrate was diluted with the appropriate quantity of 2 M HCl solution to obtain inhibitor test solutions of 10, 12, 15, 20 and 25 v/v % concentrations.

2.2. Weight loss determination
The procedure for weight loss determination was similar to that reported earlier [17, 21].

The pre - weighed aluminum coupons were immersed in 50 ml of 2 M HCl solutions (in open beakers) without and with different concentrations (10 – 25% v/v) of the extract at 30 ^{o}C for total period of 7 h immersion period.
The variation of weight loss was monitored at interval of 1 h progressively for a total of 7 h per coupon at 30 ^{o}C. The coupons were withdrawn from the solution at interval of 1 h immersion period, immersed in concentrated (SG 1. 42) nitric acid solution at room temperature, scrubbed with bristle brush under running water, dried and reweighed. The experimental readings were recorded to the nearest 0.0001 g on a Mettler digital analytical balance. Each readings recorded is an average of three experimental readings. The mean weight losses, percentage inhibition efficiency values and standard deviations for triplicate specimens are presented in Table 1 and this indicates good reproducibility.

3. Results and discussion

3.1.Weight loss studies

As presented in Table 1, the amount of material loss (mg $cm^{-2}h^{-1}$) decreased significantly when the extract concentration is increased from 10 – 25% v/v in 2 M HCl solution for 1 h immersion period at 30^{o} C. For instance, addition of 10% v/v extract significantly reduced the weight loss of aluminum in 2 M HCl solutions, with more than 80 – fold reduction in weight loss when compared with that of control.
These results showed that the extract inhibits the acid corrosion of aluminum in 2 M HCl solutions at the specified conditions. The values of percentage inhibition efficiency (% I) were determined for 1 immersion periods using the equation [17]:

$$\% I = [w_u - w_b / w_u] \times 100 \quad (1)$$

where w_u and w_b are the uninhibited and inhibited weight losses , respectively.
Assuming a direct relationship between inhibition efficiency (%I) and surface coverage (θ) for different inhibitor concentrations, the degree of surface coverage (θ) was calculated using the relationship [17]:

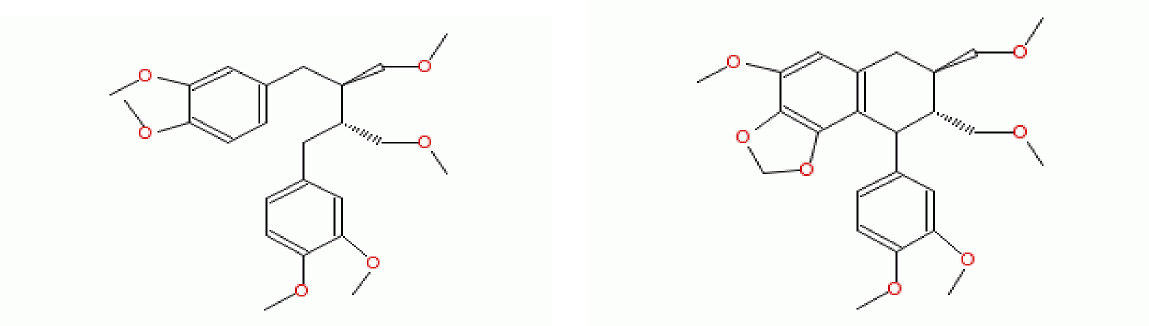
$$\theta = \% I / 100 \quad (2)$$

Table 1: Corrosion rate (mg cm^{-2} h^{-1}), inhibition efficiency and surface coverage of *Phyllanthus amarus* extract on aluminum at 30 ^{o}C for 1 h immersion period.

Concentration (% v/v)	Weight loss(mg cm^{-2} h^{-1})	Inhibition efficiency (%I)	Surface coverage(θ)
0	167.1 ± 7	-	-
10	10.7 ± 2	93.6 ± 5	0.94
12	7.8 ± 0.3	95.3 ± 4	0.95
15	6.4 ± 0.1	96.2 ± 5	0.96
20	3.2 ± 0.2	98.1 ± 2	0.98
25	2.0 ± 0.2	98.8 ± 4	0.99

The inhibition efficiency increases with increasing extract concentration, and reach a maximum value of 98.8% with 25% v/v extract. This indicates that the organic compounds in the extract are adsorbed onto aluminum surface, resulting in the blocking of the reaction sites, and protects the aluminum surface from the attacks of the aggressive ion from the acid solution. Similar view has been reported earlier [17] on inhibition of alkaline corrosion of aluminum by *P.amarus* extract.
P.amarus is rich in several phytochemicals such as phyllathin, hypophyllanthin, saponins, tannins, quercetin, triterpenoids, alkanoids, steroids, flavoids, cyanogenic glycosides,sugars and carbohydrates [15 - 17, 22]. Some of these compounds contain heteroatoms and pie centers in their molecular structures that are regarded as active centers for adsorption on metal surface. For example, phyllathin and hypophyllathin are lignans that consist of heterocyclic organic compounds with 6 or 7 oxygen atoms as shown in Figure 1.
The inhibitive effect of *P. amarus* extract is ascribed to the presence of these organic compounds in the extract. Organic compounds that contain centers for π electrons and O, N or S/or combination of the atoms have been reported as corrosion inhibitors [17]. The inhibitive effect of *P.amarus* cannot be pin pointed to any particular constituents of the plant.
The adsorption of these compounds on the aluminum surface reduces the surface area that is available for the attack of the aggressive ion from the acid solution. As seen in Table 1, the weight losses decrease with increase in extract concentration due to higher degree of surface coverage, θ as a result of enhanced inhibitor adsorption. Also, Figure 2 confirms that the inhibition is due to the adsorption of the active organic compounds onto metal

surface. This is because a straight line is obtained when C/θ is plotted against C (Fig. 2) with linear correlation coefficient of the fitted data close to 1.



Phyllathin hypophyllanthin

Figure 1: Molecular structures of the lignans in *P.amarus*.

This indicates that the adsorption of the inhibitor molecules obey Langmuir`s adsorption isotherm [17] expressed as in Equation 3:

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

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

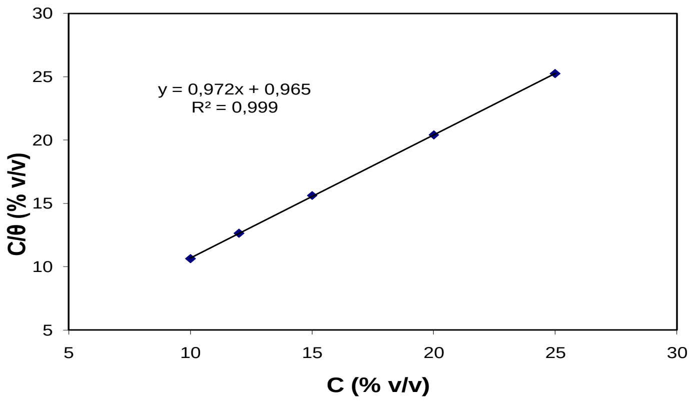


Figure 2: Langmuir adsorption model on the aluminum surface of *P.amarus* extract in 2 M HCl solution for 1 h immersion period at 30^{o} C.

3.2. Kinetics studies

The kinetics of the aluminum corrosion in 2 M HCl and 2 M HCl – extract systems was studied at 30^{o} C by fitting the corrosion data into different rate laws. Figure 3 depicts the dependence of log [W_i - ΔW_t] as a function of time t. The corrosion data fit the rate law for first – order reaction as expressed [21, 23, 24] in Equation 4:

$$\log\,[W_i - \Delta W_t] = -\frac{k}{2.303}t + \log W_i \quad (4)$$

where W_i is the initial weight of aluminum specimen, ΔW_t is the weight loss of aluminum specimen at time t, the term [W_i - ΔW_t] is the residual weight of aluminum specimen at time t and k is the first –order rate constant .

The obtained linear plots with correlation coefficient of almost 1, confirm a first – order kinetics for the corrosion of aluminum in 2 M HCl solution without and with the *P. Amarus* extract.

The linearity of the curves in the absence and presence of the extract implies that its presence does not change the kinetics of the corrosion reaction though it significantly reduces its rate as presented in Table 1. This observation is in agreement with the report on acid corrosion of aluminum in the presence of *Delonix regia* extracts [6].

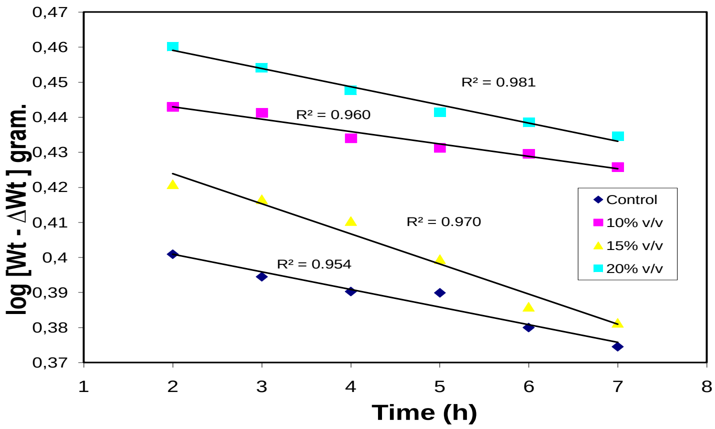


Figure 3: Plot of log [Wi - ΔW_t] versus time for aluminum coupons in 2 M HCl solution with and without *P. amarus* extract at 30 °C.

Conclusion

The present study shows that *P.amarus* leaves extract was very effective in inhibiting the acid corrosion of aluminum in 2 M HCl solutions, with up to 98% inhibition efficiency at optimum concentration and the inhibitory action of the extract is ascribed to the presence of the phytochemicals in the plant. A first- order kinetics relationship with respect to aluminum was obtained from the kinetics treatment of the data.

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