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SHORT COMMUNICATION

GOSSIPIUM HIRSUTUM L. EXTRACT AS GREEN CORROSION INHIBITOR FOR ALUMINUM IN HCl SOLUTION

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ABSTRACT. Inhibitive effect of *Gossipium hirsutum* L. leaves extract on the acid corrosion of aluminum in 1 M HCl solution was studied by weight loss technique. The extract at optimum concentration inhibited the corrosion of aluminum, with about 92% inhibition efficiency and the inhibition efficiency increased with increasing concentration of the extract at 30 °C. The results obtained revealed that the adsorption of the inhibitor molecule onto metal surface accords with Lanqmuir adsorption isotherm.

KEY WORDS: Aluminum, *Gossipium hirsutum* L., Weight loss, Acid corrosion, Acid inhibition

INTRODUCTION

Corrosion inhibitors have continued to play a crucial role in the industry where metals are exposed to acid environment. This is because organic and inorganic compounds are usually added to acid solutions as corrosion inhibitors to reduce metal loss and acid consumption in industrial processes [1] where acid plays important role viz: oil well acidification, metal cleaning, industrial acid cleaning and descaling. But, some of these corrosion inhibitors are expensive, non-biodegradable and toxic to the environment [1-8].

Presently, due to environmental laws on toxic chemicals, the use of heavy metal – based and toxic inhibitors are being curtailed [8]. This has led to several attempts on the development of green corrosion inhibitors from plant extracts [4-12] because plant extracts are rich in natural biodegradable chemicals that are environmentally friendly.

Extracts of *Delonix regia* [12], *Ficus viren* [13], red onion skin [14], *Opuntia* [15], *Vernonia amygdalina* [16], *Carica papaya* and *Azadirachta indica* [5] have been reported to inhibit acid corrosion of aluminum in acid solutions, using chemical and electrochemical techniques. The inhibition action of these extracts was attributed to the presence of organic compounds in their chemical constituents and the blocking of the metal surface via adsorption of these organic compounds onto metal surface in acid solutions.

In our previous effort [17], we studied the effect of *G. hirsutum* L. extract on alkaline corrosion of aluminum in sodium hydroxide solution at 30 °C, using weight loss technique. The *G. hirsutum* L. extract inhibited the alkaline corrosion of aluminum in sodium hydroxide solution with about 93% efficiency at 52% v/v extract concentration and the inhibitive effect was ascribed to the presence of organic compounds in the extract.

Presently, to the best of our knowledge there is no reported work in the open literature on the effects of *G. hirsutum* L. extract on acid corrosion of aluminum and other metals in HCl solution. Therefore, this paper reports the inhibition of corrosion of aluminum in HCl solution using weight loss technique.

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EXPERIMENTAL

Materials preparation. Aluminum 2S alloy samples, the chemical composition of which is given as (in wt. %): Si = 0.1350; Fe = 0.4995; Cu = 0.0020; Mn = 0.0120; Mg = 0.0076; Zn = 0.0057; Ti = 0.00269; Cr = 0.0097; Ni = 0.0038; V = 0.0055; Pb = 0.0048 and the balance Al were used for the corrosion studies. The samples were prepared from a rectangular aluminum 2S alloy plate of thickness 0.04 cm. The plate was mechanically press-cut into specimens of dimensions 4 x 2 x 0.04 cm. The coupons were used as cut without further polishing to ensure a reproducible surface [17, 18]. However, they were degreased in absolute ethanol, dried in acetone and stored in moisture free desiccators before their use. A 1 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 (1 g) of the dried powder leaves of *G. hirsutum* L. for 1 h in 100 mL 1 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 1 M HCl solution to obtain inhibitor test solutions of 0.1, 0.25, 0.5, 1.0, 1.5, 2.0 and 2.5% v/v concentrations.

Weight loss determination. The procedure for weight loss determination was similar to that reported earlier [18]. According to this method [18], previously weighed aluminum coupons were immersed in 100 mL open beakers containing 50 mL of 1 M HCl (blank) and then with addition of different extract concentrations to the 1 M HCl (0.1-2.5% v/v) at 30 ^{o}C. The variation of weight loss was monitored after 30 min immersion per coupon at 30 ^{o}C as presented in Figure 1. After 30 min, the coupons were taken out, immersed in concentrated (SG 1.42) nitric acid at room temperature, scrubbed with a bristle brush under running water, dried and reweighed. The weight loss was calculated in mg as the difference between the initial weight and the weight after the removal of the corrosion product. The experimental readings were recorded to the nearest 0.0001 g on a Mettler digital analytical balance (digital analytical balance with sensitivity of ±1 mg). Triplicate experiments were run for each concentration of inhibitor. The average weight losses of triplicate experiments as presented in Figure 1 were taken as the weight loss of aluminum coupon for each of the concentration.

RESULTS AND DISCUSSION

The plot of material loss (mg per unit area) of aluminum coupon versus extract concentration for 30 min immersion period at 30 ^{o}C for triplicate experiments is presented in Figure 1. There is a gradual decreased in weight loss (mg/cm^2) as a function of extract concentration up to 0.1% v/v concentration but rapidly at 0.25 to 2.5% v/v concentration. This indicates that the inhibition is due to the adsorption of inhibitor's molecule onto the metal surface and the inhibitor acts as an adsorption inhibitor. The introduction of the extract into the HCl solution resulted in noticeable reduction in the amount of material loss from the aluminum surface in comparison with that of control (1 M HCl) at 30 ^{o}C. For example, addition of 2.5% v/v extract significantly reduced the weight loss of aluminum in 1 M HCl solutions, with a factor of about 13 when compared with that of control. This indicates that *G. hirsutum* L. extract inhibits the acid corrosion of aluminum in 1 M HCl solution.

The values of percentage inhibition efficiency (I %) were determined for 30 min immersion period using the equation [17]:

$$I\ \% = [w_u - w_b / w_u] \times 100 \tag{1}$$

where w_u and w_b are the uninhibited and inhibited weight losses, respectively.

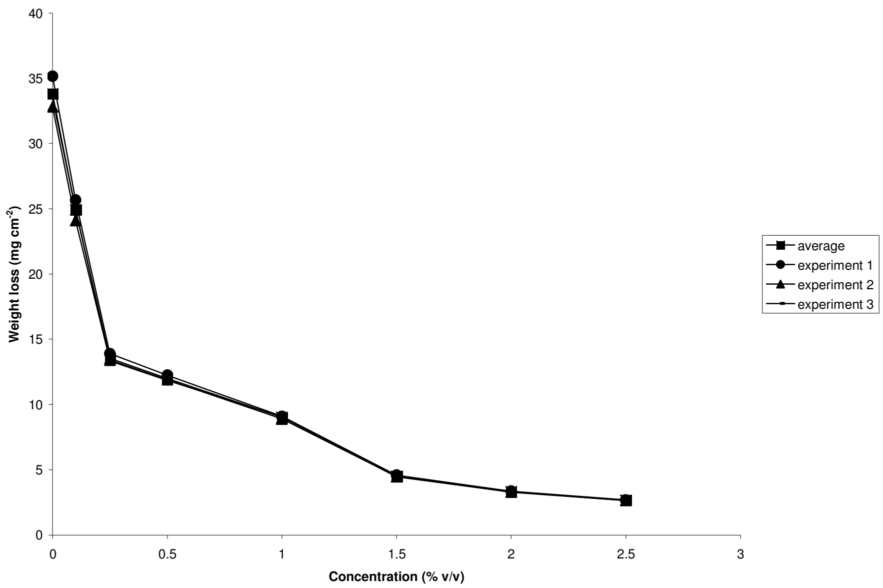

Figure 1. The plots of weight loss of aluminum versus *G. hirsutum* L. extract concentration in 1 M HCl for 30 min immersion period at 30 °C.

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 [20]:

$$\theta = \frac{I\%}{100} \qquad (2)$$

The maximum standard deviation for the observed percentage inhibition efficiency values (Table 1) for 30 min immersion period was calculated to be ±4% and this indicates good reproducibility.

Table 1. Inhibition efficiency and surface coverage of *G. hirsutum* L. extract on aluminum at 30 °C for 30 min immersion period.

Concentration (% v/v)	Inhibition efficiency (%)	Surface coverage (θ)
0.1	26.3 ± 4	0.26
0.25	59.9 ± 2	0.60
0.5	64.5 ± 3	0.65
1.0	73.4 ± 3	0.73
1.5	86.7 ± 1	0.87
2.0	90.2 ± 2	0.90
2.5	92.4 ± 3	0.92

As presented in Table 1, the percentage inhibition efficiency values increase with increasing extract concentration and the highest inhibition efficiency value of 92% was obtained at 2.5% v/v concentration at 30 °C. It can be seen that the inhibition efficiency values increase with increase in extract concentration which suggests that the inhibition is due to adsorption of the inhibitor on the metal surface and *G. hirsutum* L. extract acts as adsorption inhibitor. This indicates that the organic compounds of the extract are adsorbed onto aluminum surface which results in the blocking of the reaction sites, and thereby protects the aluminum surface from the attacks of the aggressive ion from the HCl solution.

G. hirsutum L. contains several organic compounds [17, 20] of high molecular weight with heteroatom and π-centers in their molecular structures. These include tannins, nine different amino acids namely: valine, trytophan, tyrosine, lysine, phenylalanine, methionine, cystine, arginine and threonine. Tannins are water-soluble compounds, esters of an aliphatic and phenolic acids or oligomers and polymers of polyhydroxyflavan-3-ol units with molecular weights between 500 and 3000 [21, 22]. Furthermore, it also contains 5% of a polyphenolic aldehyde called gossypol (1,1', 6,6', 7,7'-hexahydro-3,3'-dimethyl-5,5'-bis(1-methylethyl)-2,2'-binaphthalene-8,8'-dicarboxaldehyde) [17]. Figure 2 shows the molecular structures of gossypol and some amino acids in *G. hirsutum* L. plant.

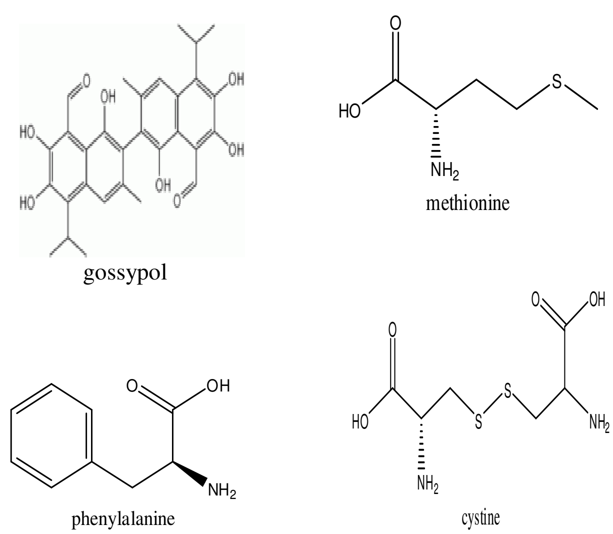

Figure 2. The molecular structures of gossypol and some amino acids in *G. hirsutum* L. plant.

As presented in Figure 2, the molecular structure of gossypol reveals an aldehyde-type organic compound with oxygen and two coplanar naphthalene rings and molecular weight of 518.6.

The inhibitive effect of *G. hirsutum* L. extract may be ascribed to the presence of these organic compounds in the extract but the inhibitive effect of the extract cannot be pin pointed to any particular constituents of the plant. Also, synergistic and antagonistic effects may play an important role on the inhibition efficiency of *G. hirsutum* L. extract due to its complex compositions. Similar views have been expressed in our previous report [20]. Organic compounds that contain centers for π-electrons and O, N or S/or combination of the atoms have been reported as corrosion inhibitors for metals in acid solutions [1, 12, 20].

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 Figure 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 3 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 (Figure 3) with linear correlation coefficient of the fitted data close to 1. This indicates that the adsorption of the inhibitor molecules obey Lanqmuir`s adsorption isotherm [1, 12, 20] expressed as Eq. 3.

$$\frac{C}{\theta} = C + \frac{1}{K} \tag{3}$$

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

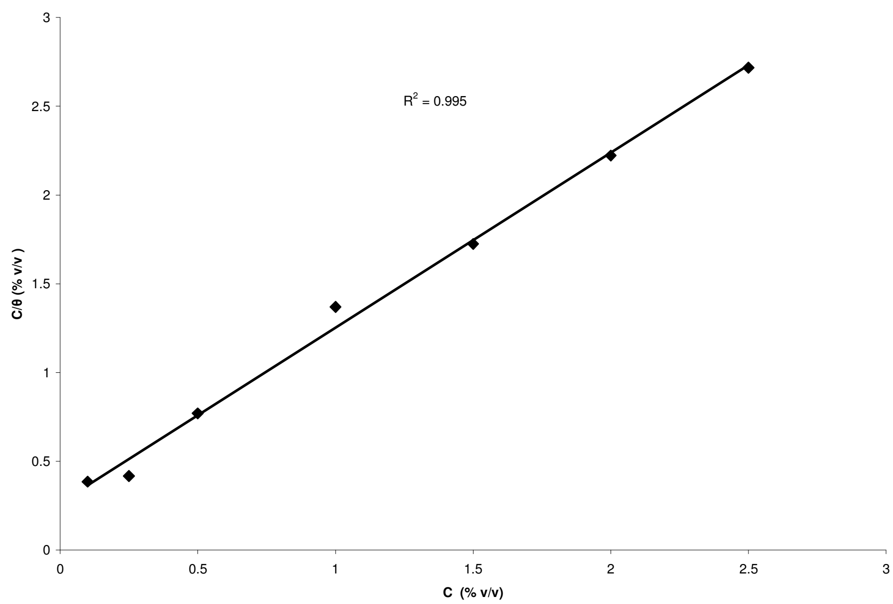

Figure 3. Langmuir adsorption model on the aluminum surface of *G. hirsutum* L. extract in 1 M HCl solution for 30 min immersion period at 30 ^{o}C.

CONCLUSIONS

The present study shows that *G. hirsutum* L. leaves extract was very effective in inhibiting the acid corrosion of aluminum in 1 M HCl solutions, with up to 92% inhibition efficiency at 2.5% v/v concentration and the inhibitory action of the extract is ascribed to adsorption of the organic compounds in the extract. The corrosion inhibition is achieved through the adsorption of the inhibitor on to aluminum surface. The adsorption of the inhibitor molecules was consistent with Langmuir adsorption isotherm. *G. hirsutum* L. extract can be added to HCl solution as non-toxic (green) inhibitor.

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