Madras Journal Series Pvt Ltd Advanced Materials & Applications
Adv.Mater. App 2 (2019) 16-22

An investigation of the inhibitive effects of Aspilia africana leaves extract on the corrosion of aluminium alloy AA8011 in sulphuric acid

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Received 10 January 2019, Received in final form 04 March 2019, Accepted 06 March 2019

Abstract

In the present work, the inhibitive effects of Aspilia africana leaves extract on the corrosion of aluminium alloy AA8011 in sulphuric acid was investigated using weight loss method at room and elevated temperatures respectively. The leaves extract had a good corrosion penetration inhibition on aluminium alloy in 0.5M sulphuric acid with inhibitor efficiency of optimum values of 59.41% at room temperature and 80% at elevated temperature. The inhibition process was attributed to the formation of an adsorbed film of inhibition on the metal surface which protected the metal against corrosion. The inhibition efficiency and surface coverage (ϴ) of extract from Aspilia africana leaves increased with increase in inhibitor concentration, but decreased with increasing temperature. The adsorption of extract of Aspilia africana leaves on the aluminum metal surface was found to obey Langmuir's adsorption isotherm. The Corrosion activation energies increased in the presence of the extract. The negative free energy value (- Gads) indicated that the adsorption of inhibitor molecule was of physical adsorption and the reaction was spontaneous. Extract from Aspilia africana leaves could serve as an excellent corrosion inhibitor owing to the nature that it is eco-friendly, cheap, biodegradable and highly acceptable by environmental regulation.

Keywords: *Adsorption, Effects of temperature, Acidic medium, Aspilia africana, Corrosion*

1. Introduction

In practical terms, the effectiveness of engineering materials is influenced by the interaction with its environment in many ways. The result of this is usually the degradation of such material. Therefore, corrosion is the wearing a way of materials due to chemical reactions. Apart from metals that primarily suffer electrochemical attack, corrosion can also refer to other materials such as ceramics and polymers. The other materials can only be deteriorated by direct chemical attack. Corrosion of metals therefore can be regarded in some ways reverse extractive metallurgy. Most metals exist in nature in the combined state, for example, as oxides, sulphides, carbonates, or silicates. In this combined states, the energies of the metals are lower. In the metallic state, the energies of the metals are higher, and thus, there is a spontaneous tendency for metals to react chemically to form compounds [1-3].

Protection by inhibitors is widely used for metals in corrosive environment. A corrosion inhibitor is a chemical additive, which, when added to a corrosive aqueous environment, reduces the rate of metal wastage. It can be categorized as anodic inhibitor, cathodic inhibitor, mixed inhibitor, and adsorption type corrosion inhibitor. Many organic inhibitors work by an adsorption mechanism. The adsorption mechanism can be physical or chemical adsorption mechanism. For instance, the resultant film of chemisorbed inhibitor is responsible for protection either by physically blocking the surface from the corrosion environment or by retarding the electrochemical processes. The main functional groups capable of chemisorbed bond with metal surfaces are –NH2, -COOH, and –PO_3H, although other functional groups or atoms can form co-ordinate bonds with metal surface. Aluminium is being considered as the metal sample.

Aluminium is a silvery white member of the boron group of chemical elements. It has the symbol Al, and its atomic number is 13. It is not soluble in water under normal circumstances. Aluminium is the third most abundant element (after oxygen and silicon) and the most abundant metal in the Earth's crust. It makes up about 8% by weight of the Earth's solid surface. Aluminium metal is too reactive chemically to occur natively. Instead, it is found combined in over 270 different minerals. The chief ore of Aluminium is bauxite. Aluminium is a good thermal and electrical conductor, having 59% of the conductivity of copper, both thermal and electrical. Aluminium is capable of being a superconductor, with a superconducting critical temperature of 1.2 K and a critical magnetic field of about 100 Gauss (10 milliteslas) [4].

Aluminium is 100% recyclable without any loss of its natural qualities. Corrosion resistance can be excellent due to a thin surface layer of Aluminium oxide that forms when the metal is exposed to air, effectively preventing further oxidation. The strongest Aluminium alloys are less corrosion resistant due to galvanic reactions with alloyed copper [5]. It is lighter than all other engineering metals except magnesium and beryllium. Aluminium is not widely used for chemical resistance, but for applications involving atmospheric corrosion resistance. It is probably the most widely used metallic material. The alloying elements of aluminum are Iron, Magnesium, Silicon, Copper, Manganese, Zinc, Chromium, Titanium, Lead/Bismuth, Zirconium, and Lithium.

Tetraoxosulphate VI acid is a heavy chemical. Concentrated Sulphuric acid is a thick colourless viscous liquid, which used to be called 'oil of vitriol'. It has specific gravity of about 1.84gcm^{-3}. In concentrated form, it is very corrosive and causes serious burns when it gets in contact with the skin. As an acid, it reacts with metals found above hydrogen in the activity series to liberate a gas. H_2SO_4 acid is often used metal processing such as pickling and decaling of steel and non-ferrous metal plating and purification.

$$Al + 3H_2SO_4 \longrightarrow Al(SO_4)_3 + 3H_2$$

Aspilia africana (Fig. 1) is a tropical shrub which grows widely at roadsides in Nigeria and popularly used as fodder for grazing goats in most villages and also has been established as an effective medicinal plant. It is commonly known as 'urinyun' by the Yoruba, as 'orangila' by Igbos, 'Tozakin' by Hausas, and 'Edemedong' by Efiks. The leaf extract of Aspilia Africana effectively arrests bleeding from fresh wounds. The potentials of the leaves of the haemorrhage plant, Aspilia africana (Compositae) in wound care was evaluated using experimental models. A. africana, which is widespread in Africa, is used in traditional medicine to stop bleeding from wounds, clean the surfaces of sores, in the treatment of rheumatic pains, bee and scorpion stings and for removal of opacities and foreign bodies from the eyes.

Fig. 1. *Aspilia Africana leaves*

Phytochemical analysis of the extract indicates the presence of tropical plant constituents such as alkaloids, saponins, sterols, terpenoids, carbohydrates, glycosides, and tannins. The fatty acids compositions of Aspilia africana are palmitic acid, stearic acid, oleic acid, linoleic acid, behenic acid, and some others but in trace amount. [6-18]. These metabolites are usually responsible for the pharmacological activities of medicinal plants. α-pinene, one of the terpenoids in A. africana leaves, is known to possess anti-inflammatory activity [19] and may contribute to the wound healing activity by suppressing inflammatory reactions invoked by the injured tissues. In addition to this, the documented identification of the abundant presence of saponins and tannins in the leaves of this plant [19] is implicating for these constituents in the activities of the leaves extracts, especially tannins, which have been implicated in the haemostatic activity of plants where they arrest bleeding from dam- aged or injured vessels by precipitating proteins to form vascular plugs. To a reasonable extent, going by the quantified relative presence in the leaves of this plant and documented role in haemostatic activity, we may safely assume that the tannins in the extracts partly contribute to the activity since mechanisms other than vascular plugs formation are likely involved [6].

Due to high cost of using metals that form naturally protective films and also the toxic nature of some chemicals currently in use, we investigated how we could still achieve similar purpose by using natural inhibitors. This is because possible replacements of some expensive chemicals as corrosion inhibitors for metals are the organic inhibitors. Therefore, this investigation can be a good source of developing environmentally acceptable and less expensive inhibitors. Hence, this study focused on the ability of the extract of Aspilia africana leaves to inhibit the effect of a corrosive medium on Aluminium alloy AA8011, and why it possessed such inhibitive property.

2. Materials and Methods.

2.1 Methodology

The experimental technique used was the weight loss method. This is a simple immersion in a beaker test used to test for uniform and pitting corrosion. Similarly, it was used for the inhibition experiment using different concentrations of inhibitor on the acid medium at room and elevated temperatures respectively. The coupons were completely immersed in each corrosive medium by using a nylon twine supported with a stick.

2.2 Preparation of Specimen

The test coupons of Aluminium alloy AA8011 were dimensioned 3 cm by 3 cm using trisquare and scriber. They were cut and shaped using guillotine machine, and hand filed respectively. A 2mm diameter hole was drilled on the test coupons to allow polystyrene thread to pass through. The coupons were weighed to obtain their initial masses which were used to calculate their densities and weight loss after corrosion or inhibition using the dimensions of the coupons.

2.3 Preparation of the Corrosive Medium and Inhibitor Extract

The corrosive medium used was sulphuric acid solution. The corrosion penetration rate of the acidic medium on the Aluminium alloy is calculated as follows:

$$\mathrm{C.P.R} = \frac{\mathrm{KW}}{\mathrm{DAt}} \qquad (1)$$

where C.P.R is corrosion penetration rate (mpy), W is weight loss (mg), D is density of specimen (g/cm^3), A is exposed specimen area (inch^2), K is constant (534 for mpy), t_e is time of exposure (Hr). The Aspilia africana leaves were dried for 3days using the solar drier, and then grinded to fine powder using electric grinding machine. The method used for the extraction of the inhibitor was reflux method. Here, the Aspilia africana leaves powder was put in 1000 mL ethanol and heated for about 3 hr, after which the solution was filtered into a separate beaker using a handkerchief.

The inhibitor efficiency of the Aspilia africana leaves extract on the acidic medium was determined as follows:

$$\text{Inhibitor Efficiency} = \frac{W_b \quad W_i}{W_b} \text{X } 100\% \qquad (2)$$

where W_b is weight loss for blank (g) and W_i is weight loss for inhibited (g). The change in Gibb's free energy adsorption for each temperature is derived as follows:

$$\Delta G = \quad \mathrm{RTIn55.5b} \qquad (3)$$

where ΔG is the change in Gibb's free energy adsorption (KJ/Mol), R is the universal gas constant (8.314J/Mol K), b is the intercept of the Langmuir Plot and T is the Temperature of the medium (K)

2.4 Experimental techniques

2.4.1 Weight Loss Technique at Room Temperature

For the set up without inhibitor at room temperature, 8 coupons were each immersed in 8 beakers containing 300 mL of 0.2 M sulphuric acid solution as a medium. Every 24 hr, a coupon was removed from a beaker. This lasted for 8days when the final coupon was removed. After each removal, further coupon corrosion was quenched using ethanol, rinsed with water, immersed in acetone for easy drying and weighed with digital weighing balance.

Similarly, 8 coupons were each immersed in 8 beakers containing 0.5M H_2SO_4 as medium. Each beaker contains 300mL of the medium. Every 24hr, a coupon was removed from a beaker till the 8th day, when the last coupon was removed. After each removal, further coupon corrosion was quenched using ethanol, rinsed with water, immersed in acetone for easy drying and weighed in digital weighing balance.

For the set up with and without inhibitor, using 0.5M H_2SO_4 on Aluminum AA8011, 64 coupons were immersed in 64 beakers, each containing 350mL solution of inhibitor and acid solution except the non-inhibited beakers containing only 350mL acid solution. The beakers were divided into 8. Each set has the following inhibitor concentrations: 0g/L to 0.7g/L. Each set has 8 coupons on 8 beakers in which 8 coupons were removed after each 24 hr. This lasted for 8 days when the last eight coupons were removed. After each removal, the coupons were cleaned, dried and weighed.

2.4.2 Weight Loss Technique at Elevated Temperature

In this set up, 8 coupons of inhibitor concentration 0mg/L to 700mg/L were immersed in acidic medium for about 3 hr. Furthermore, 3 sets of 8 coupons were heated separately at temperatures 40°C, 50°C, and 60°C respectively with the same inhibitor concentrations in acidic medium for about

3 hr each. After each removal, the coupons were cleaned, dried and weighed.

3. Results and discussions

3.1 Result Analysis

The tables and figures below describe the results obtained using the weight loss technique for inhibited and non-inhibited at room and elevated temperatures.

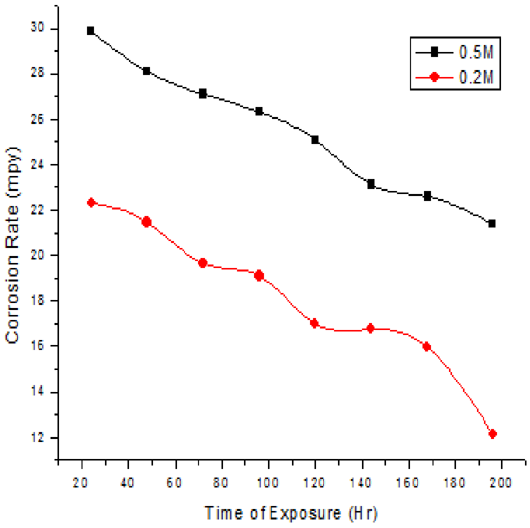

Fig. 2. *Variation of corrosion penetration rate with time of exposure for 0.2M and 0.5M of sulphuric acid on Aluminium Alloy AA8011 for 8Days*

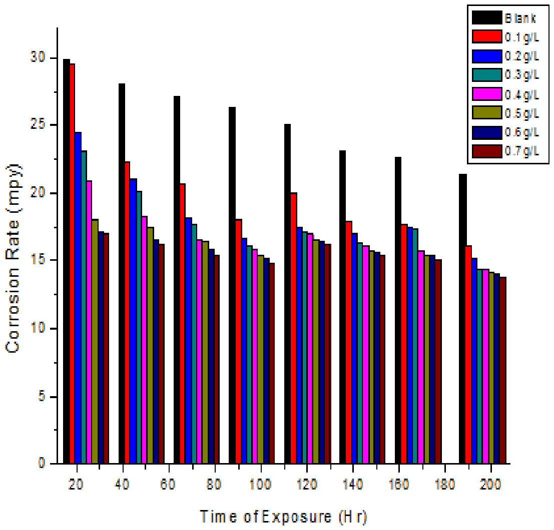

Fig. 3. *Variation of corrosion penetration rate with time of exposure for different inhibitor concentrations of Aspilia Africana leaves extract for Aluminium Alloy AA8011 in 0.5M Sulphuric acid for 8 Days*

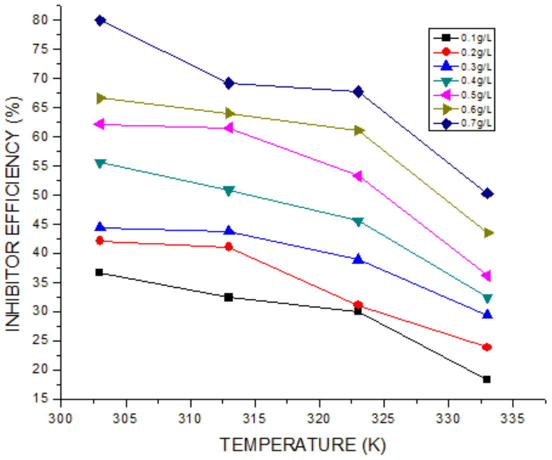

Fig. 4: *Variation of Inhibitor Efficiency with Temperature for different inhibitor concentrations of Aspilia Africana leaves extract for Aluminium Alloy AA8011 in 0.5M Sulphuric acid at 303K, 313K, 323K, and 333K for 3 hr*

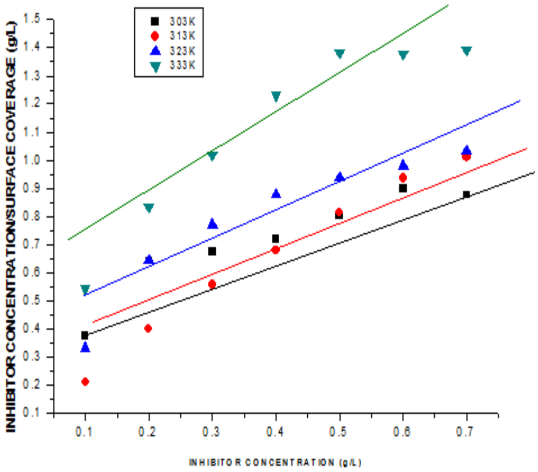

Fig. 5: *Langmuir plot for inhibition corrosion of Aspilia africana leaves extract for Aluminium Alloy AA8011 in 0.5 M Sulphuric acid at 303 K, 313 K, 323 K, and 333 K for 3 hr*

3.2 Data Analysis and Discussion of Findings

3.2.1 Results of Weight Loss Technique at Room Temperature

Fig. 2 shows that the corrosion rate of the Aluminium alloy AA8011 increases with increase in the molarity of sulphuric acid solution. For the inhibited samples, it was also observed from the data in table 1 that as the concentration of inhibitor rises, inhibitor efficiency of sample rises. The same was also observed for the rate of corrosion which decreased as concentration of inhibitor rises. This was consistently observed for the 8 days respectively.

Table 1: *Variation of Inhibitor Efficiency with Inhibitor Concentration of Aspilia Africana leaves extract for Aluminium Alloy AA8011 in 0.5M Sulphuric acid for 8 days*

Inhibitor Concentration (g/L)	Inhibitor Efficiency (%) for 8 Days							
	1	2	3	4	5	6	7	8
0	10.89	20.53	23.64	31.46	20.28	22.17	21.68	21.97
0.1	17.82	25.26	33.09	36.52	30.19	26.44	22.43	26.47
0.2	22.77	28.42	34.91	39.04	31.60	29.21	23.18	30.45
0.3	31.68	34.74	38.91	39.89	32.31	30.06	30.09	30.80
0.4	39.60	37.89	39.27	41.29	33.73	31.77	31.59	31.66
0.5	42.57	41.05	41.45	42.42	34.20	32.41	31.78	32.53
0.6	59.41	42.11	43.27	43.54	35.38	33.48	33.64	33.22
0.7	10.89	20.53	23.64	31.46	20.28	22.17	21.68	21.97

Table 2: *Variation of Inhibitor Efficiency with Inhibitor Concentration of Aspilia Africana leaves extract for Aluminium Alloy AA8011 in 0.5 M Sulphuric acid at 303 K, 313 K, 323 K, and 333 K for 3 hr*

Inhibitor Concentration (g/L)	Inhibitor Efficiency (%)			
	303K	313K	323K	333K
0.1	36.67	32.44	30.00	18.40
0.2	42.11	41.00	31.11	23.93
0.3	44.44	43.85	38.89	29.45
0.4	55.56	50.97	45.56	32.52
0.5	62.22	61.54	53.33	36.20

Table 3: *Calculated Values of Corrosion Rate, Apparent Activation energy (Ea) and Surface Coverage for different inhibitor concentrations of Aspilia africana leaves extract for Aluminium Alloy AA8011 in 0.5 M Sulphuric acid at 303 K and 333 K*

Inhibitor Concentration (g/L)	Corrosion Rate (mpy)		Ea (KJ/ Mol.)	Surface Coverage	
	303 K	333 K		303 K	333 K
0.00	106.37	385.31	36.45		
0.10	78.01	314.40	39.48	0.27	0.18
0.20	73.28	293.12	39.26	0.31	0.24
0.30	59.10	271.85	43.22	0.44	0.29
0.40	47.28	260.03	48.28	0.56	0.33
0.50	40.19	245.84	51.29	0.62	0.36
0.60	35.46	217.48	51.37	0.67	0.44
0.70	21.27	191.47	62.23	0.80	0.50

Table 4: *Adsorption parameters obtained from temperature and isotherm plots of the corrosion rate values for Aluminium Alloy AA8011 in 0.5 M Sulphuric acid at 303K, 313 K, 323 K, and 333 K for 3 hr*

Temperature (K)	R^2	Slope	Change in Gibb's free energy (KJ/Mol.)
303	0.84	0.77	-7.85
313	0.98	1.33	-5.05
323	0.84	1.05	-7.91
333	0.86	1.42	-8.85

The table of inhibitor efficiency versus inhibitor concentration (Table 1) shows that as the inhibitor concentration of the medium increases, the efficiency of inhibitor increases as well. These results show that the corrosion rate of the Aluminium alloy in 0.5 M sulphuric acid solution decreased with increasing concentration of Aspilia africana leaves extract in inhibited solutions compared with the uninhibited solution. This suggests that the inhibiting action is concentration-dependent. As a function of time, the corrosion rate of Aluminium in the test solutions decreased with increase in time of exposure. The corrosion rates for Aluminium plotted against time for different concentrations of the extract in 0.5 M sulphuric acid solution is shown Fig. 3. Inspection of the plot reveals high corrosion rate of Aluminium in 0.5M sulphuric acid solution. The plot also illustrates the decreased corrosion rate on introduction of the Aspilia africana leaves extract into the corrodent, indicating that Aspilia africana leaves extract actually affords corrosion inhibition of Aluminium in sulphuric acid solution.

3.2.2 Results of Weight Loss Technique at Elevated Temperature

Effect of Temperature on Inhibition Efficiency

The effect of temperature on the inhibition efficiency for the Aluminium alloy in 0.5 M sulphuric acid solution in the absence and presence of different concentration of Aspilia Africana leaf extract at temperature ranging from 303 K to 333 K was obtained by weight loss measurements as displayed graphically in Fig. 4. The inhibition efficiencies are found to decrease with increasing the solution temperature from 303 to 333 K. This behaviour can be interpreted on the basics that at relatively high temperature, the increase in temperature results in the desorption of the inhibitor molecules from the surface of Aluminium alloy. Previous investigators showed that the corrosion rate increases with increase in temperature, which results into a decrease in the inhibition efficiency, Therefore, decreasing the reaction temperature favours the inhibition efficiency of acid extracts of Aspilia africana leaves extract on Aluminium in sulphuric acid.

Adsorption Parameters

Adsorption isotherms are very important in determining the mechanism of organoelectrochemical reaction. The inhibition of the corrosion of aluminum alloy in 0.5 M sulphuric medium with addition of different concentrations of the extract can be explained by the adsorption of the components of the plant extract on the metal surface. The principal step in the accomplishment of inhibitor action in acid solution is usually established to be the adsorption on the metal surface. This leads to the assumption that the corrosion reactions are prohibited from occurring over the area (or active sites) of the metal surface enclosed by adsorbed inhibitor species, whereas these corrosion reactions take place on the inhibitor free region. The surface coverage (Θ) data, in Table 3, are very useful in 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 evaluated at equilibrium condition. The best isotherm fit was obtained with Langmuir isotherm as suggested by the plot between C/Θ and C (as shown in Fig. 5) and the linear correlation coefficient of the fitted data was close to 1,indicating that the adsorption of the inhibitor molecules obey the Langmuir's adsorption isotherm.

Free Energy of Adsorption

Results obtained, as presented in Table 4, indicate that the values of ΔG° are negative in all cases, showing that the reaction is spontaneous and that the Aspilia africana leaves extract are strongly adsorbed on the aluminum surface by physical adsorption. Previous investigators showed that the values of ΔG° up to -20 KJ/Mol. are consistent with electrostatic interaction between charged molecules and a charged metal (which indicates physical adsorption), while those more negative than -20 KJ/Mol. involve charge sharing or transfer from the inhibitor molecules to the metal surface to form a co-ordinate type of bond (which indicates chemisorption). This observation also supports the earlier assertion that a physical adsorption is proposed as a result of electrostatic attraction between charged metal surface and charged species in the bulk of the solution. The ΔG values which are less than 10.5 kJ/ Mol. for various inhibitor concentrations (Table 4) revealed the decreased rate of corrosion reaction which is also substantiated by other studies.

4. Conclusions

The acid extract of Aspilia africana leaves acts as good and efficient inhibitor for the corrosion of aluminum alloy AA8011 in sulphuric acid medium. Inhibition efficiency increases with the increase of extract concentration and decreases with rise in temperature. The adsorption of different concentrations of the plant extract on the surface of the aluminum alloy in 0.5 M sulphuric acid followed Langmuir adsorption isotherm. The values of standard free energy of adsorption suggest that the adsorption of inhibitor on Aluminium surface occurred by physical adsorption mechanism. The negative sign of the Free Energy of adsorption indicates that the adsorption of the inhibitors on the Aluminum surface is a spontaneous process.

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