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Corrosion Inhibition of Aluminum by Using Nipah (*Nypa Fruticans)* Extract Solutions in Hydrochloric Acid (HCl) Media

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This study examine the effectiveness of Nipah extract solutions to inhibit corrosion of aluminum (Al) in hydrochloric acid (HCl) media by using weight lost technique. Al's concentration in the inhibitor's solution is also detected by inductively coupled plasma (ICP-OES). Each part of Nipah palm consisting of frond (upper and lower), inflorescence stalk and husk was extracted by using wringer machine to provide the extract solution. The inhibition efficiency (% IE) of each solution was measured. The inhibition action of the extracts was discussed in view of Langmuir adsorption isotherm. It was found that the extracts act as a good corrosion inhibitor for Al in 2.0 M HCl solution. Weight loss of Al is decreased as the concentration of inhibitor is increased. Inhibition efficiency of Al corrosion was optimum in the presence of extract from inflorescence stalk which is 51.43 % (at higher concentration). The results obtained proved that extract solution from each part of Nipah palm can be serve as an effective inhibitor of Al in HCl media.

Keywords: Nipah extract solutions; aluminum; corrosion; inhibitor

1. INTRODUCTION

It is well known that aluminum (Al) is metal that has a wide range of applications due to its good properties. It is used in electronics, for production of wires, sheets, tubes, and also to form alloys. Unfortunately, Al and their alloys are exposed to the action of acid in industrial processes where acids play an important roles such as in oil well acidizing, acid pickling, acid cleaning and acid descaling. This can lead to the substantial metal loss due to corrosion [1].

The use of inhibitors is one of the most practical methods to cope with this problem. Currently, organic and inorganic compounds are usually added to HCl solution as corrosion inhibitors, but some of these inhibitor are toxic, non-biodegradable and costly to synthesize [2, 3]. In an attempt to find corrosion inhibitors which are environmentally safe and readily available, there has been a growing trend in the use of natural products such as leaves or plants extract as corrosion inhibitors for metals in acid cleaning process. This is because plants serve as incredibly rich sources of naturally synthesized chemical compounds that are environmentally acceptable, inexpensive, readily available and renewable source of materials [4].

Extracts of some plants such as *Cocus nucifera* [1], *Delonix regia* [5], *Opuntia* [6], *Vernonia amydalina* [7] and *Sansevieria trifasciata* [8] have been reported to inhibit the rate of acid corrosion of Al. Their inhibitive effect has been attributed to the presence of phytochemicals in their chemical constituents and the adsorption of the phytochemicals on the Al surface leads to slowing down of the electrochemical processes on the metal surface [1].

The present work is another trial to find a cheap and environmentally safe inhibitor for Al corrosion in the acidic solution, where the aqueous extracts of *Nypa fruticans* from various parts are tested.

There is no reported work on the effect of aqueous extracts of this species on acid corrosion of Al in HCl solution but previous research reported a successful use of *Nypa fruticans* leaves as corrosion inhibitor [9, 10].

Therefore, it is necessary to study the effect of extracts from other parts of *Nypa fruticans* on the acid corrosion of Al in HCl solution. This is because of its safe to use, low cost, availability, and high solubility in seawater.

2. MATERIALS AND METHODS

2.1 Preparation of aluminum sheet

Aluminum (Al) sheet, with 0.1 cm thickness and 99.98 % purity were cut into 2x2 cm pieces. The sheet were cleaned and scrubbed with sand paper (gred 240) to eliminate aluminum oxide, Al_2O_3 layer on the Al surface and to expose clean shining on the surface. Surface treatment of the Al sheet was done by degreased it in absolute ethanol, rinsed with double distilled water and dried in acetone. Then they were placed in the furnace at temperature of 40°C for about 15-20 minute. Finally, the sheet was allowed to cool overnight in moisture free desiccators before weighing [10].

2.2 Preparation of Nipah extract's solutions

Sampling of Nipah palm including part from frond (upper and lower), inflorescent stalk and husk was conducted at Seberang Perak, Perak. All samples were cut into pieces and squeezed by using wringer machine. Extract solutions with a concentration of 50 ml/L were made by dilution of 50 ml of extracts solution with 2 M HCl . This represents the stock solution from which different concentrations of 10, 20, 30 and 40 ml/L was prepared by dilution with the same acid solution. All reagents were of analar grade and doubly distilled water was used for the preparation of all solutions.

2.3 Weight loss technique

Aluminum (Al) sheet were immersed in 250 ml beaker containing 200 ml of HCl solution at temperature of 40°C. The Al sheet then was retrieved from their corroding solutions at one hour interval for 7 hours. At each interval, the sheet was dipped into saturated ammonium acetate solution at room temperature, to end the corrosion reaction. They were then washed several time with 20 % NaOH and dried in acetone. Further drying was in an oven at 100 °C. The Al sheet was allowed to cool in moisture free desiccators before measuring their weight. The weight loss was evaluated in miligrams. The experiments were performed with triplicate and the mean weight loss was recorded [10]. Similar technique was applied to the aluminum sheet in the present of nipah solution extract's solution inhibitors. Weight lost of Al is measured in one hour interval for 7 hour. The weight lost of Al sheet was evaluated in milligrams as the difference in the weight of the coupons before and after the test:

$$W = (W_i - W_f)\ \text{mg} \qquad (1)$$

Where W = weight loss of Al sheet, W_i = Initial weight of Al sheet, W_f = Final weight of Al sheet. Each reading reported is an average of triplicate. The inhibition efficiency (% IE) of Nipah extract's solutions acting as an inhibitor were calculated by using formula as provide below [3]:

$$\%\ IE = [1 - w_1/w_2] \times 100 \qquad (2)$$

Where w_1 and w_2 are the weight losses (mg) for Al sheet in the presence and absence of inhibitor respectively.

2.4 Determination of aluminum concentration

Concentration of Al in inhibitor's solutions (test solutions) was measured by inductively coupled plasma optical emission spectroscopy (ICP-OES).

2.5 Kinetics study of aluminum corrosion

Corrosion rate (mm/year), inhibitor efficiency, % IE [3] and surface coverage, θ [11] was calculated for 7 hour period by using formula:

$$\text{Corrosion rate (mm/year)} = 87.6W/DAt \qquad (3)$$

$$\text{Surface coverage, } \theta = [1 - w_1/w_2] \qquad (4)$$

Where W = weight loss (mg), D= density of aluminum (g/cm^{-3}), A= surface area of sheet (cm^2) and t = corrosion reaction period.

3. RESULTS AND DISCUSSION

3.1 Corrosion of aluminum in HCl media

Figure 1 represents the corrosion of aluminum (Al) in different hydrochloric acid (HCl) concentration since there was a general weight loss at the end of the corrosion-monitoring process. The weight loss of Al caused by corrosion process was summarized in Table 1. Increasing time of Al exposed in HCl media result in increasing weight loss of Al. Concentration of HCl media affected the corrosion of Al. This is in line with the result yield, which shows the higher concentration of acid, the higher weigh lost of Al. Al corrodes directly proportional to the acid concentration which follow the order 3.0>2.5>2.0>1.5>0.5>0.1 M of HCl concentration. This is in accordance with the general rule guiding the rate of chemical reactions which stated that the chemical reaction increases with increasing concentration. This is due to increasing of absorption and ionization at active species when corrosion processes take place [12]. Similar results were obtained by [9]. Based on Figure 1, the nonuniformity of the plots indicates that the corrosion is not a simple homogenous process but a heterogeneous one consisting of intermediate steps [10]. Moreover, time factor also affected the weight loss of Al. Weight loss of Al is increased with increasing time of Al being exposed to the HCl media.

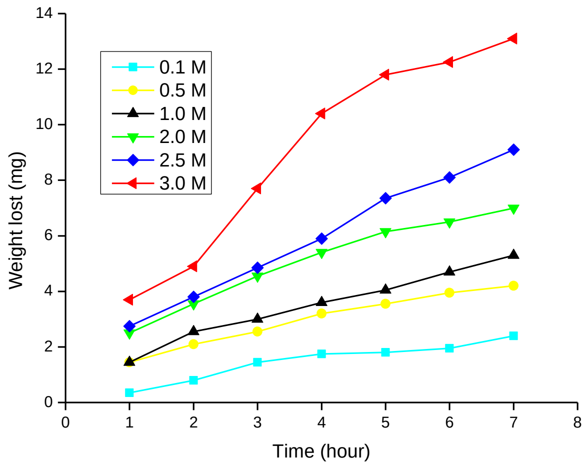

Figure 1. Weight loss of aluminum sheet in different concentrations of HCl for 7 hours

Table 1. Average weight loss of aluminum in differents concentration of HCl in the absence of inhibitor

[HCl] (M)	Range (mg)
0.1	2.00-2.40
0.5	4.00-4.40
1.0	5.30-5.30
2.0	6.80-7.20
2.5	9.00-9.20
3.0	1.30-1.32

3.2 Corrosion of Al in 2.0 M HCl in the present of Nipah extract's solution inhibitors

Overall weight loss of Al affected by corrosion in HCl media in the present of Nipah extract solutions was summarized in Table 2 and Figure 2. Al Nipah extract's solution inhibitors tested in the experiment able to decrease the weight loss of Al compared with in the absence of inhibitor in 2.0 M HCl media. Variation of weight loss with time of Al exposure in HCl solutions containing the inhibitors shows a remarkable decrease in weight loss compared with solutions without inhibitors; signifying corrosion inhibition (Figure 2). The inhibition process is the result of an adsorption of inhibitor's molecule on the Al surface where Nipah extract's solutions act as an adsorption's inhibitor. Reaction between inhibitor and Al surface could limit the occurring of corrosion process. The corrosion rate decreased with the increase of additives concentration in the temperatures studied (Figure 2).

Table 2. Corrosion rate, inhibition efficiency and surface coverage of Nipah extract solutions in of 2.0 M HCl media

Nipah solution extract inhibitor	Inhibitor's volume (ml)	Corrosion rate (mm/year)	Inhibition efficiency, % I.E	Surface coverage, θ
Upper frond	10.00	6.49	15.71	0.157
	20.00	6.14	22.86	0.229
	30.00	5.56	28.57	0.286
	40.00	4.98	35.71	0.357
	50.00	4.40	45.71	0.457
Lower frond	10.00	6.84	20.00	0.200
	20.00	6.26	24.29	0.243
	30.00	5.79	31.43	0.314
	40.00	5.21	38.57	0.386
	50.00	4.40	45.71	0.457
Inflorescent stalk	10.00	5.91	27.14	0.271
	20.00	5.56	31.42	0.314
	30.00	5.10	37.14	0.371
	40.00	4.52	44.29	0.443
	50.00	3.94	51.43	0.514
Husk	10.00	7.53	7.14	0.071
	20.00	6.72	17.14	0.171
	30.00	6.26	22.86	0.229
	40.00	5.68	30.00	0.300
	50.00	4.75	41.43	0.414

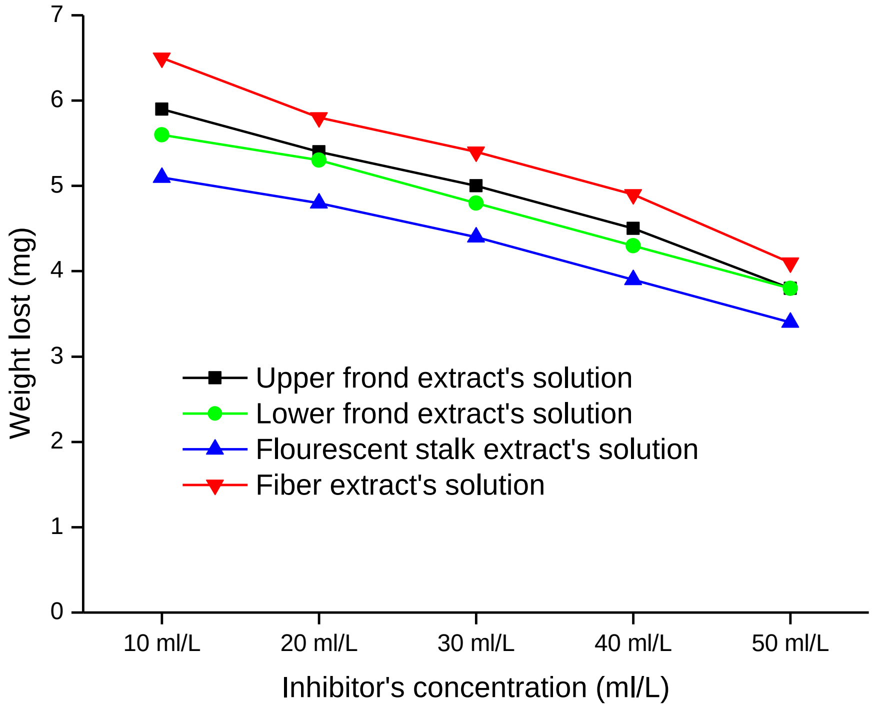

Figure 2. Overall weight loss of aluminum in different concentrations of HCl (after 7 hours)

Figure 3 represents weight loss of Al caused by corrosion in 2.0 M HCl media for every hour interval in the presence of Nipah extract solutions. Compare with extracts from other parts of Nipah tree, the extract solution from inflorescence stalk produced the lowest weight loss of Al for all volume tested. The lowest weight loss and corrosion rate of Al (Table 2) indicates that Nipah extract solution from this part is the most effective inhibitor. Weight loss and corrosion rate of Al was also found decrease with the increasing of Nipah extract concentration. Same result obtained for the other type of inhibitor used. This is due to the higher degree of surface coverage (θ) which enhanced the inhibitor adsorption as already reported by other authors [4, 13, 14]. Value of θ, calculated from inhibitor efficiency (% IE) was used to represent the fraction of Al surface filled by inhibitor's molecule. Value of θ for all Nipah extract solution tested in this experiment is summarized in Table 2. Surface coverage was directly proportional with inhibitor's concentration.

Figure 4 shows that the inhibition process occurred due to adsorption of active organic compounds on the Al surface. This is proved by the linear correlation between C/θ and C, and the linear correlation constant of the fitted data is close to 1, indicate that adsorption of inhibitor molecule closely followed the Langmuir's adsorption isotherm:

$$C/\theta = C + 1/K \qquad (5)$$

Where C is inhibitor's concentration and K is equilibrium constant for inhibitor's molecule absorption on the Al surface.

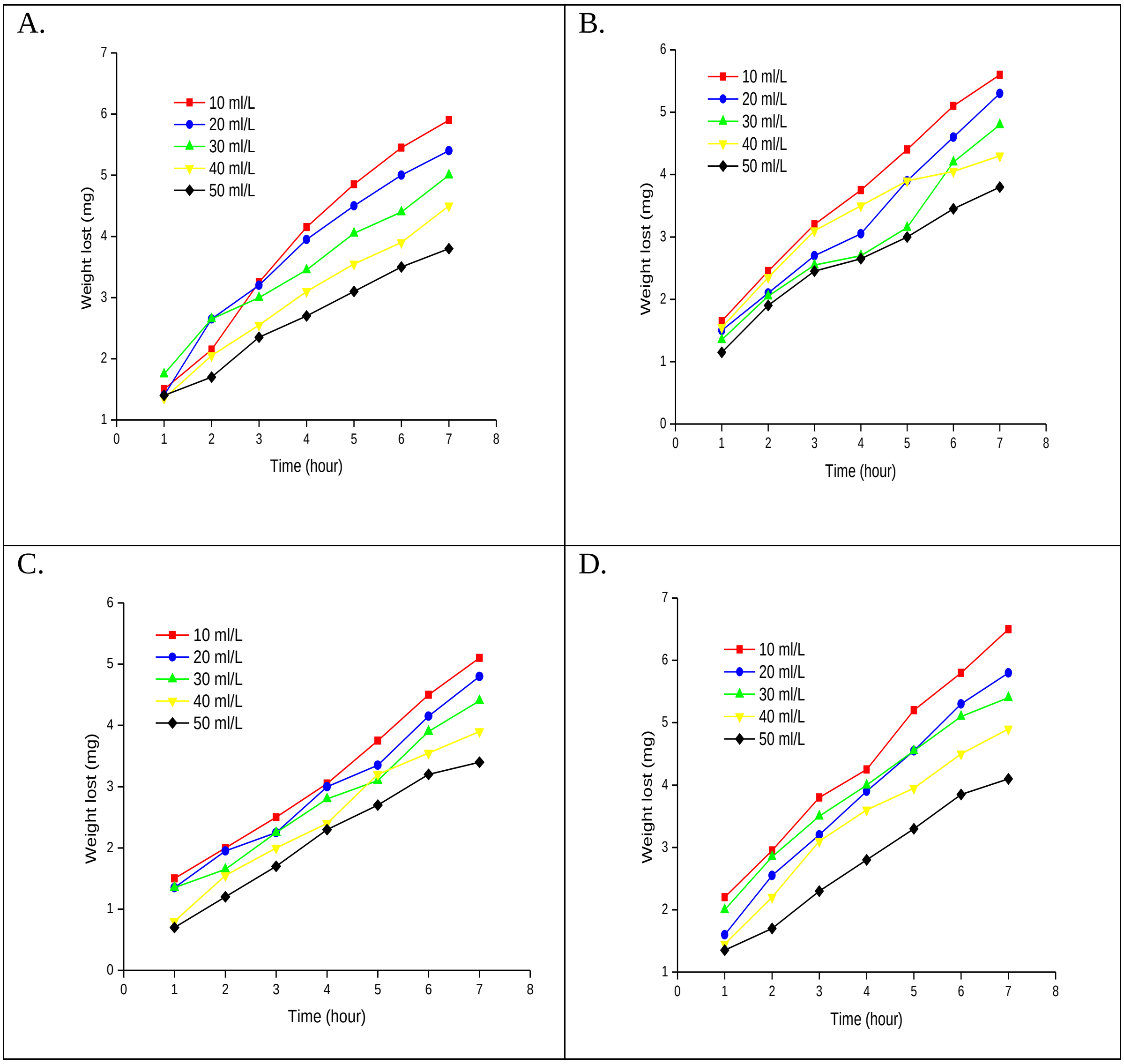

Figure 3. Weight loss of aluminum in different concentration of HCl media for 7 hours in the present of Nipah extract solution *(A= upper frond, B= lower frond, C= inflorescence stalk, D= husk)*

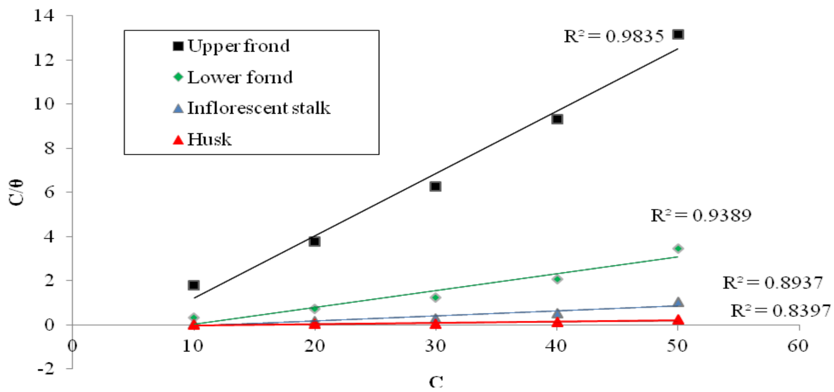

Figure 4. Langmuir adsorption model on Al surface of Nipah extract solution in 2.0 M HCl for 7 hours immersion period.

3.3 Inhibition efficiency (% IE) of Nipah solution extracts in 2.0 M HCl

Inhibition efficiency (% IE) was calculated to compare the effectiveness of all Nipah extract solution as corrosion inhibitor for Al (Table 2). This is measured by their ability to adsorb on Al surface and produce a layer which could prevent corrosion process from occurred. The results obtained indicate that the % IE was increased with the increasing concentration of Nipah extract solutions. Meaning that the weight losses of Al in the presence of inhibitors are decreased compared with weight loss of Al in the absence of inhibitor in HCl media.

The increasing concentrations of Nipah extract solutions resulting in the increasing of inhibitor's molecule that adsorbed on the Al surface. Therefore decreasing the surface area of Al exposed to acid.

The higher % IE value of Nipah extract solution recorded from inflorescence stalk (at higher concentration, % IE= 51.43 %) indicates that Nipah extract solution from this part of Nipah tree is the most effective inhibitor for Al corrosion. This is may be due to the existence of nitrogenous compound in the Nipah extract solution. Effect of inhibition through Al surface occurred when nitrogenous compound produce a bond between the surface and Nypa-Al^{3+} complex. Those absorbed nitrogen atom on the Al surface inhibit corrosion process [10].

The inhibition properties of *Nypa fruticans* also may be due to the presence of tannin which is often in the extract of leaves, bark of trees and seeds [15]. Tannins are complex astringent aromatic acidic glycosides found in various plants. They are made up from polyphenols and their acidic and heterocyclic derivatives. Polar organic compounds containing sulphur, nitrogen and oxygen are good corrosion inhibitors.

They prevent corrosion by the formation of an oriented film layer which essentially blocks discharge of H^+ and dissolution of metal ions [9].

Organic compounds containing –OR, –COOH, NR2 and/or –SR functional group act as a good inhibitor for metal corrosion in acid media [13]. Adsorption of this compound on the Al surface can reduced exposed surface area from being attack by aggressive acidic media [1]. Based on the chemical screening carried out for flavonoid, polyphenol, anthraquinone, tannin and phlobatannin on all Nipah extracts solution revealed that only tannin and polyphenol available in fiber (husk) extract solution while a negative results were recorded for other parts extract solution.

3.4 Concentration of aluminum in the inhibitor's solution

Total weight loss of Al can be viewed in by the concentration of Al in the inhibitor's solutions. This is made by the assumption that corroded Al was fully transferred into the inhibitor's solution. Concentration of Al in the Nipah extract solution is shown in Figure 5. Increasing volume of Nipah extract solution result in decreased of Al concentration in the solution. Same results obtained to all type of inhibitor's solution tested.

Lower concentration of Al was recorded by inhibitor's solution from inflorescence stalk. The lowest weight loss of Al in the presence of Nipah extract solution from inflorescence stalk as discussed earlier was an evident of this result.

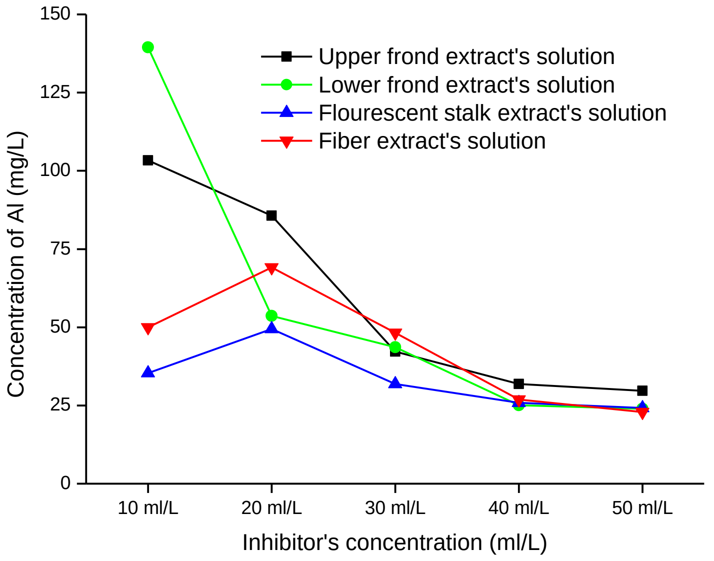

Figure 5. Concentration of aluminum in Nipah extracts solution 2.0 M HCl media

4. CONCLUSIONS

Nipah extract solution inhibits corrosion effectively. Inhibitor from inflorescence stalk extract solution was the most effective inhibitor from nypa palm species. Inhibition was maximum at an optimum concentration. Concentration of Al detected in inhibitor's solutions is consistent with the weight loss of Al at each concentration used. Behavior of the adsorption of the inhibitor molecules was consistent with Langmuir adsorption isotherm.

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