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Green Corrosion Inhibitor of Aluminum in Artificial Acid Rain by Rambutan Peel Extract

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Abstract The inhibitive action of methanolic Rambutan Peel Extract (RPE) as green corrosion inhibitor of aluminum was investigated in artificial acid rain (AAR) using potentiodynamic polarization. The results revealed that RPE was an effective eco-friendly inhibitor for aluminum. The results also showed the inhibition efficiency increased with increase extract for Al and it reached maximum IE 93.18% at 8 g/L, and the values of IE decreased with temperature. The inhibitive action is attributed to the adsorption of the inhibitor molecules on the metal surface following Langmuir adsorption isotherm. Standard free energy of adsorption ΔG_{ads} (-12.81 to -15.107 kJ mol^{-1}), a physical adsorption mechanism is proposed for the adsorption of the inhibitor on the surface of aluminum.

Keywords: Corrosion, Green inhibitor, Acid rain, Electrochemical, Polarization, Adsorption.

تثبيط تآكل الالومينوم في وسط مطر حامضي اصطناعي باستخدام قشور الرامبوتان كمثبط أخضر

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الملخص أجريت عملية تثبيط تآكل الالومينوم في وسط حامضي اصطناعي باستخدام مستخلص قشور الرامبوتان Rambutan Peel Extract (RPE) وذلك باستخدام الطريقة الكهروكيميائية المتمثلة في استقطاب الجهد الديناميكي potentiodynamic polarization. وقد أظهرت النتائج أن RPE كان مثبطًا فعالًا للألمنيوم. كما بينت النتائج أيضًا أن كفاءة التثبيط inhibition efficiency (IE) تزداد مع زيادة تركيز المستخلص حيث بلغت 93.18% عند أقصى تركيز 8 جم / لتر ، وكذلك انخفضت كفاءة التثبيط مع ازدياد درجة الحرارة. إن عملية التثبيط تعزى إلى ادمصاص جزيئات المثبط على سطح المعدن وقد وجد انها تتبع الادمصاص الحراري من نوع Langmuir، كما أن الطاقة الحرة القياسية للادمصاص ΔG_{ads} (-12.81 الى -15.107 كيلومول/جول)، وقد أستنتج من خلال الدراسة ان آلية ادمصاص المثبط على سطح الألومنيوم كان أدمصاص فيزيائي.

الكلمات المفتاحية: التآكل، التثبيط الأخضر، المطر الحامضي، الكهروكيميائي، الاستقطاب، الادمصاص.

1. Introduction

Corrosion of metal has been received great attention worldwide, because of its negative impacts on profits and costs (Tasdemiroglu, 1991; Ivaskova et al., 2015), it will be very important to mitigate this issue using several techniques include cathodic protection (Barbalat *et al.*, 2012), coating (Elkais et al., 2013; George *et al.*, 2012) and inhibition (Akpan & Offiong, 2014; Cang *et al.*, 2013; EL Quadi et al., 2015). The former is a significant method to mitigate corrosion, but unfortunately, many commercially available inhibitors are harmful to both the environment and human beings and therefore must be replaced with environmentally friendly, safe, non-toxic green inhibitors (Paul & Kar, 2012) and ecological acceptable (Prabhu & Rao, 2014).

Recently, researchers have shown an increased interest in using a natural product as a promising green inhibitor. The literature on eco-friendly inhibitors for aluminum has highlighted several plant products, which have the potential to be extracted into corrosion inhibitors includes *Piper longum* (Singh & Quraishi, 2012), *Albizia lebbeck* (Petchiammal & Selvaraj, 2013), *Garcinia indica* (Prabhu & Rao, 2014) and *Apuim graveolens* (Al-moubaraki et al., 2017) In addition, enormous amounts of agricultural-food waste are produced worldwide, which can be used as green corrosion inhibitors. Agricultural waste, such as seeds and peel of fruit has been evaluated as a rich source of natural products (Jayaprakasha *et al.*, 2001; Thitilertdecha *et al.,* 2010). Rambutan (*Nephelium lappaceum*) is a tropical fruit belonging to family Sapindaceae and native to Southeast Asia, particularly in Peninsular Malaysia (Norzila *et al.*, 2014) and in the eastern and southern regions of Thailand (Thitilertdecha *et al.*, 2010). This fruit is consumed fresh, canned, or processed and its consumption results in the production of vast amounts of waste from seeds and peels of the fruit. Thitilertdecha *et al.,* (2010) proved that the peel waste has significant potential due to its powerful antioxidant properties and the large amounts of peel-materials being generated. The previous studies on Rambutan waste, the antioxidant and phenolic contents, amino acids, alkaloids and pigments were evaluated. This study aims to use a methanolic extract of *Nephelium lappaceum* (Rambutan) as a green corrosion inhibitor for aluminum in artificial acid rain solution using electrochemical technique.

2. Materials & Methods

2.1. Preparation of Aluminum Coupons

Aluminum specimen was cut in small pieces of about 1.0 cm^2, and placed in blocks using resin cold mounting, with just one side having a specific area exposed to the tested medium. Aluminum specimen of composition (0.05% C, 0.015% Mn, 0.027% P, 0.003% Zn, 0.32% Si and balance Al) was used in the study.

2.2. Plant Extraction

Fresh peels of Rambutan were obtained from traditional markets (Bazar Malam), Serdang, Selangor, Malaysia. The peels were washed with tap water and rinsed with distilled water, then allowed to air dry at room temperature for 15 days and one day in the oven with 50 C. The dried peels were grinding. 500g of dried and ground peels were extracted by using one liter of 99.8% methanol for 48 hours at room temperature as stated by Norzila *et al.,* (2014), with some modification. The extract was filtered and solvent was removed by using a rotary evaporator model EYELA. The resultant is red brown crude of methanol extract was stored at 4°C for further purposes.

2.3. Electrochemical Test

Electrochemical method is used characteristically for evaluation of the inhibition efficiency (IE). The current-potential curves were measured using a conventional three- electrode cell including a working electrode involves aluminum, the counter electrode is platinum sheet and the reference electrode is Ag/AgCl. These electrodes were equipped with a potentiostat (μ- AUTOLAB type III), which connected to a host computer so that the entire process could be run via computerized software (NOVA 1.11 Software) (Ghamarian et al., 2013). The electrolyte was prepared as cited in (Zabawi *et al.,* 2008) with modification, The simulated acid rain solution was then adjusted to the desired pH (pH= 4.5) using 0.05 M (HCl) and 0.5 M (NHO_3). The experiments were performed in the absence and presence of 0.25, 0.5. 2 & 8 g/L of the inhibitor. The experiments were run at different temperature (300, 313 & 323 K), which were maintained in a water bath equipped with a thermostat. Corrosion rate (*Cr*) was estimated from intercept of cathodic and anodic Tafel lines, and the inhibition efficiency (*EI %*) was calculated by using the following equation:

$$\theta = \frac{Cr^{0} - Cr}{Cr^{0}} \quad (1)$$

where, θ is the degree of surface coverage of the metal surface, and *Cr* and Cr^0 are the corrosion rate with and without the inhibitor, respectively. The inhibition efficiency (*IE %*) can be calculated from the following equation:

$$IE\% = \theta \times 100 \quad (2)$$

3. Result & Discussion

3.1. Effect on Aluminum

Corrosion rate, degree of surface coverage, inhibitor efficiency, resistance polarization and corrosion current were determined using linear polarization. Table 1 provides the obtained results of aluminum from the preliminary analysis of the former parameters in absence and presence of inhibitor extract. The effect of RPE on the corrosion rate of aluminum in artificial acid rain, conducted at different temperatures. It can be observed from table 1 that the corrosion rate in the absence of inhibitor increased with increasing of temperature, and this is a chemical-kinetic effect and behaviour of most metals under corrosion attack. The corrosion rates reach 23.54, 24.16 and 29.01μm/year for 300, 313, and 323 K, respectively. After adding the inhibitor, the corrosion rate decreased with raising the concentration of the inhibitor, with successive increases in concentration of extract, the potential corrosion moved further toward positive areas, (see Fig. 1).

In 300 K, following the addition of inhibitor from 0 to 8 g/L, the corrosion rate decreased significantly from 23.54 to 1.605 μm/year, also, it can be seen the degree of surface coverage (θ) and inhibitor efficiency (IE) were increased with increase of concentration of inhibitor and the maximum IE reached 93.18% at 8 g/L. Figure (1) shows the effectiveness of inhibitor on the corrosion rate and inhibitor efficiency. Moreover, polarization resistance (Rp) increased with increasing the concentration of inhibitor is caused by chemical reactions between the electrodes and the electrolyte. It can be seen the inhibitor also has an effect on other polarization measurements such as corrosion current, corrosion potential.

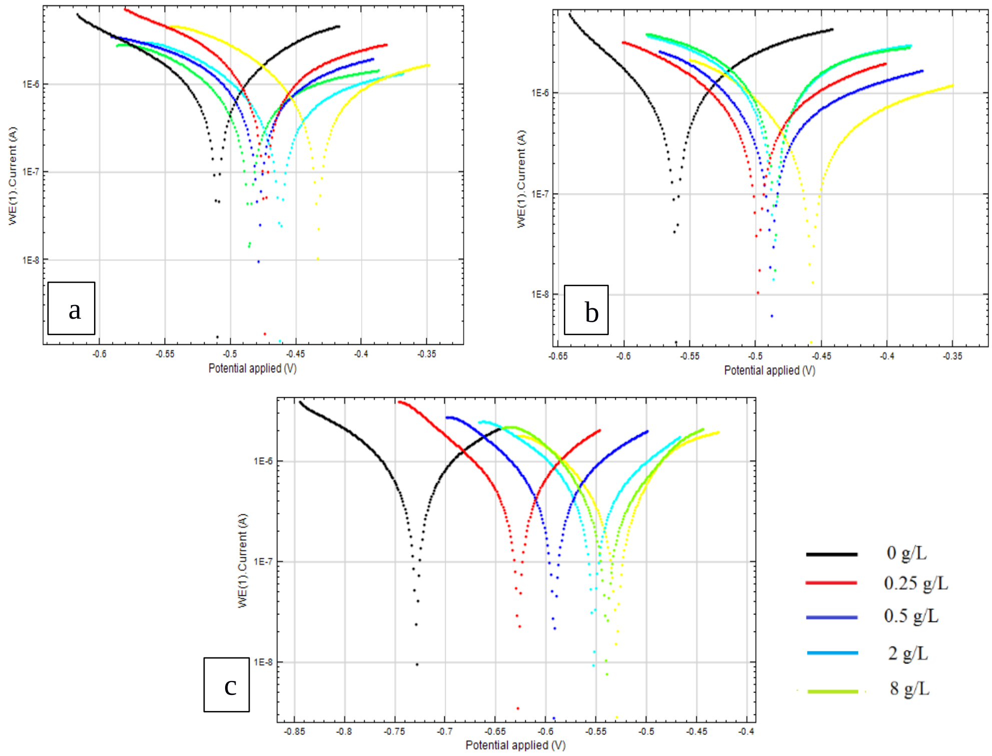

Figure 1. Tafel polarization curves for aluminum in artificial acid rain at different concentrations of inhibitor RPE at (a) 300, (b) 313, (c) 323

In addition, a similar circumstance happened with the inhibition at 313 K, but with higher level compared with 300K, in this case, the corrosion rate decreased significantly from 24.16 to 2.318 µm/year, and the maximum IE achieved 90.41% at 8 g/L. Fig. 1 illustrates the effectiveness of inhibitor on the corrosion rate, inhibitor efficiency and resistance polarization of aluminum at 313K. As shown in table 1, the resistance increased with the raise of concentration of inhibitor. These results indicate that the inhibition efficiency and degree of surface coverage increased with increasing concentration of the extract. This trend is most probably due to the number of available reaction sites has been reduced and blocked by complex chemical composition extracts. Consequently, aluminum is more effectively separated from the corrosive medium. Moreover, Table 1 showcases the effect of RPE on the corrosion rate and other polarization measurements of aluminum at 323 K, the corrosion rate was ranged between 29.01 to 2.992 µm/year at 0 and 8 g/L of concentration inhibitor. In addition, the inhibition efficiency achieve maximum value (89.69%) at 8 g/L.

Table 1. Effect of RPE on the aluminum corrosion in artificial acid rain (AAR) solution

T **(K)**	***C*** **(g/L)**	I_{corr} **(µA)**	E_{corr} **(mV)**	R_p **(kΩ)**	***CR*** **(µm/year)**	θ	***IE*** **(%)**
300	0	2.147	-510.2	20.92	23.54		
	0.25	0.974	-493.8	22.87	14.68	0.37638	37.63
	0.5	0.727	-490.1	23.73	10.97	0.53398	53.39
	1	0.4881	-484.0	27.81	5.351	0.77268	77.27
	2	0.3993	-467.5	34.11	2.377	0.89902	89.90
	8	0.2376	-440.6	60.28	1.605	0.93182	93.18
313	0	2.204	-560.7	22.80	24.16		
	0.25	1.077	-481.4	27.23	16.81	0.30422	30.42
	0.5	0.6551	-495.2	43.59	7.857	0.67479	67.48
	1	0.5592	-477.3	53.60	6.603	0.72669	72.67
	2	0.481	-468.2	67.04	5.273	0.78174	78.17
	8	0.330	-457.7	63.21	2.318	0.90406	90.41
323	0	2.646	-728.8	34.23	29.01		
	0.25	1.181	-627.5	41.86	12.95	0.55360	55.36
	0.5	1.379	-591.8	44.63	8.346	0.71230	71.23
	1	0.9062	-552.7	49.59	7.526	0.74057	74.06
	2	0.3564	-539.7	59.13	4.907	0.83085	83.09
	8	0.2364	-529.6	59.48	2.992	0.89686	89.69

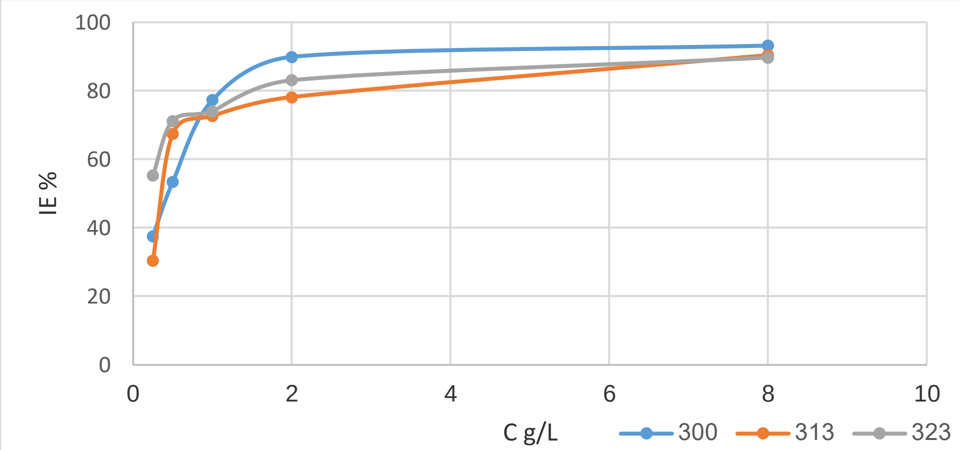

Fig. 2. Inhibition efficiency of aluminum in AAR in the presence and absence of RPE at different temperatures

3.1.1. Effect of Temperature

Figure 2 shows that increase in temperature will decrease the inhibition efficiency values and considerably increase the corrosion rate. The decreasing of the inhibition efficiency might attribute to the increase of average kinetic energy of the components of extracts (Song, 2012). This will make the adsorption between aluminum surface and components of extracts insufficient to maintain the species at binding site and could lead to desorption or cause species to bounce off the surface of aluminum (El Quadi *et al.,* 2015). Hence, the temperature will affect the stability of the aluminum surface complex components. In addition, the decreasing of IE with increase temperature may suggest that the adsorption is physical adsorption. Similar results obtained for inhibition of aluminum in acidic media by Rambutan peels (Norzila *et al.*, 2014).

More recent attention has focused on the effect of the temperature on adsorption process in acidic media, but there is a lack study in the artificial acid rain. Anozie *et al.*, (2011) found that IE decreased at high temperature at all concentration of *Euphorbia hirta* and *Dialum guineense*. Fares *et al.*, (2012) used pectin as a green inhibitor for aluminum in acidic medium. Ladha *et al.*, (2015) evaluated the effect of fenugreek seed extract on the corrosion inhibitory activity of aluminum in acidic solution, and the findings reveal that with increase in temperature there is a decrease in inhibition efficiency. Norzila *et al.*, (2014) concluded that Rambutan peel extract was an attractive candidate for the green corrosion inhibitor. In general, from literature studies, direct effect is caused by chemisorption, while the inverse relationship is meaning the adsorption is attributed to physisorption. In the current study, the mechanism adsorption of studied extract is caused by physisorption.

3.1.2. Adsorption Isotherm

The adsorption behaviour of the inhibitor on the electrode surface was investigated to understand its role in corrosion control. (Kamal & Sethuraman, 2013; Maayta & Al-Rawashdeh, 2004). As cited in (Verma & Khan, 2016), the Adsorption mechanism is commonly considered as a process of substitution of water molecules that adsorbed at the metal–solution interface by the inhibitor molecules. Langmuir adsorption isotherm is the best fit was obtained model, wherein the degree of surface coverage (θ) values are plotted against the concentration (C) of the RPE (Fig. 3):

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

where θ is the surface coverage, K_{ads} is adsorptive equilibrium constant, and C is the equilibrium inhibitor concentration. K_{ads} values were calculated from the intercepts of the straight lines C/θ-axis, and are given in Table (2). The positive values of adsorption equilibrium constant K_{ads} imply better adsorption, which leads to an increase in the inhibition efficiency (Abboud *et al.*, 2009). Furthermore, the Temkin $(\theta\ vs. \log C)$ and Frumkin $(\log C \frac{\theta}{(1-\theta)C}\ vs. \theta)$ isotherm was calculated.

The equilibrium constant of adsorption of methanol extract of rambutan peel is related to the free energy of adsorption (ΔG_{ads}) according to the following equation:

$$\Delta G_{ads} = -RTln(55.5 \times K_{ads}) \quad (4)$$

where R is the universal gas constant, T is the absolute temperature, K_{ads} is the equilibrium constant of adsorption, and 55.5 is the molar concentration of water in solution. From the calculated values (Table 2), the free energies are negatively less than the threshold value of -40 kJ mol^{-1} required for chemical adsorption, therefore, the adsorption of methanol extract of rambutan peel on aluminum surface is spontaneous and supports the mechanism of physical adsorption. In fact, physical adsorption consequences from electrostatic interaction between the charged centers of inhibitor and charged aluminum surface (Umoren *et al.,* 2009). Moreover, this adsorption may obey the Temkin adsorption isotherm, but cannot follow the Frumkin isotherm based on the R^2 values (Table 2).

Table 2 Adsorption parameters for the adsorption of RPE in AAR on aluminum at different temperatures

T K	Langmuir				Temkin		Frumkin	
	ΔG_{ads} KJ/mole	K_{ads} KJ/mole	Slope	R^2	Slope	R^2	Slope	R^2
300	-12.81	3.07	1.03	0.999	0.1662	0.8507	0.1384	0.0425
313	-12.96	2.62	1.06	0.9986	0.1494	0.7779	-0.1481	0.026
323	-15.07	4.93	1.09	0.9999	0.0931	0.9046	-1.8056	0.7533

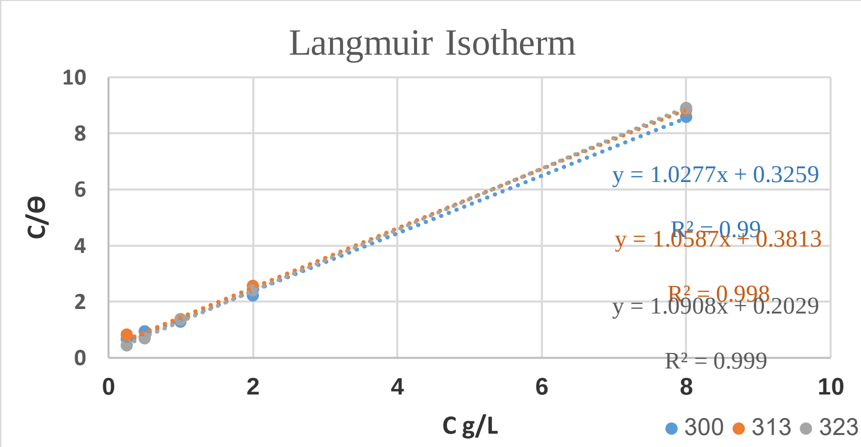

Figure 3. Langmuir isotherms for adsorption of Inhibitor RPE on aluminum at 300, 313, and 323K

Conclusion

From the study it can be concluded that the methanolic Rambutan Peel Extract (RPE) acted as effective green corrosion inhibitor for aluminum in artificial acid rain. The results indicated that the corrosion rate decreased with increasing extract concentration, and inhibition efficiency (IE) increases with the inhibitor concentration. In addition, the inhibition efficiency values increased with rising temperature, which suggested the adsorption is physisorption. The former results proved by adsorption isotherm, which demonstrated the adsorption is followed the Langmuir adsorption isotherm and the adsorption of the inhibitor is spontaneous and followed the mechanism of physical adsorption. In addition, this adsorption may obey the Temkin adsorption isotherm, but cannot follow the Frumkin isotherm.

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