Potential of Honey as Corrosion Inhibitor for Aluminium Alloy in Seawater

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Abstract: The inhibition action of natural honey was investigated with two concentrations by using weight loss method, potentiodynamic polarization technique and electrochemical impedance spectroscopy techniques. 75g and 150g of honey of were diluted in 14 litres of tropical seawater in order to produce two different concentrations. The weight loss of aluminium alloy was increased with respect to time. It was found that at higher concentration (150g), the weight loss is lower compared to 75g of honey with the corrosion inhibition efficiency increases to 76%. Potentiodynamic polarization method indicates that honey which was used as inhibitor is a mixed-type inhibitor with predominantly control of anodic reaction. The presence of honey significantly decreases the values of corrosion current density. Electrochemical impedance spectroscopy shows reduction in double layer capacitance and increase polarization resistance. Inhibition efficiency increases with the increase of concentration.

Key words: Aluminium alloy • Electrochemical technique • Honey • Polarization resistance • Weight loss

INTRODUCTION

Aluminium and its alloys represent an important category of materials due to their high technological value and wide range of industrial applications including marine industry such as ships, offshore structure, pipelines and marinas. For marine application, cathodic protections are normally used to reduce corrosion. Aluminium alloys are preferentially used cathodic protection of metal objects due to its low cost, high current efficiency and low specific weight of the metal [1]. During cathodic protection, the sacrificial anode, for example aluminium, is disposed to the environment into seawater as its ion. Nevertheless, the problems arise when the metal is directly in contact with the seawater where this aggressive media can initiate corrosion process. For this reason, the use of inhibitor to slow down the corrosion process is essential.

Organic compounds could inhibit the corrosion process where these compounds possess hetero atoms such as nitrogen, sulphur or oxygen and an aromatic ring in their molecules. However, the synthesis of the compounds usually expensive and they are toxic and hazardous to human and environment [2]. Results showed

that organic compounds especially those containing nitrogen or sulphur gave a very good inhibition for copper corrosion in different media [3].

Currently, there are rises in interest of using natural occurring substances which exhibit the ability to inhibit corrosion. The previous research on using honey as inhibitor shows that it is effectively reduce the corrosion rate and hence inhibit the corrosion process [4]. Natural honey was used as the inhibitor because it contains a mixture of organic and inorganic compounds. The presence of nitrogen, sulphur, oxygen and -C=C- makes honey as an excellent corrosion inhibitor [5]. In addition, it is not expensive and not hazardous to environment.

The purpose of this study is to investigate the corrosion inhibition of honey for aluminium in seawater. Actual seawater experiment has also been done on mild steel by other researchers [6].

MATERIALS AND METHODS

Sample Preparation: The coupons employed in this research are aluminium alloy (AA7631). They were cut into 25mm x 25mm x 3mm and then polished using 600, 800 and 1200 emery paper. After the polishing process,

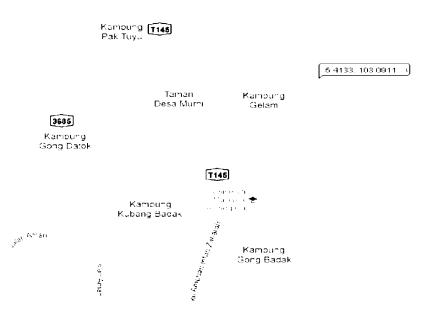


Fig. 1: Location of sampled area of seawater

Table 1: The composition of natural honey

Comp.	Water	Fructose	Glucose	Sucrose	Dextrin	Minerals	Acids	Unknown
%	17.7	40.5	34.0	21.9	1.15	0.18	0.08	4.9

the coupons were cleaned with acetone and rinsed with distilled water. Then the coupons were dried in air and stored in desiccators. The composition of natural honey was given in Table 1 [5]. Natural honey used in this study was bottled under Agromas brand name and distributed by Federal Agricultural Marketing Authority (FAMA). This honey was obtained from *Apis Dorsata* bee variety found in forests areas of Malaysian northern region. Seawater was taken from Kuala Terengganu shore line area shown in Figure 1. Honey was diluted in seawater where 75g and 150g of honey were diluted in 14 liters of seawater to produce two different types of concentration.

Weight Loss Analysis: Before the coupons were cleaned with acetone, the coupons were weighed for the original weight by using Sartorius Cole-Polmer analytical balance (readability: 0.0001g) and hung in the aquarium containing seawater for 60 days. One sample was taken out from the aquarium in 10 days interval for 6 weeks. Before weighing, the sample was cleaned with distilled water and dried. Then the sample was immersed in nitric acid (HNO₃) to remove the corrosion products. Finally, the sample was washed with distilled water, dried and weighed in order to obtain the final weight.

The inhibition efficiency, IE (%) was calculated by using the following equation where w_1 and w_2 are the corrosion weight loss in the presence and absence of inhibitors [2]:

$$IE(\%) = \frac{(w_2 - w_1)}{w_2} \tag{1}$$

Polarization Scan: It is the most common polarization method used for measuring corrosion resistant [7]. The cell used is a conventional three electrodes with a platinum wire counter electrode (CE) and a saturated calomel electrode (SCE) as reference to which all potentials are referred. The working electrode (WE) is in the form of a square cut so that the flat surface would be the only surface in the electrode. The potentiodynamic current-potential curves will record the data after the electrode potential was automatically changed from $-200 \, \text{mV}$ to $+200 \, \text{mV}$ with the scanning rate of $10 \, \text{mVs}^{-1}$. The results were analyzed using the GPES fit program. Corrosion current (I_{corr}) was calculated by using the Stern-Geary where b_a is anodic Tafel slope [8], b_c is cathodic Tafel slope and R_p is polarization resistance:

$$I_{corr} = \frac{b_c \times b_a}{2.303 R_p (b_c + b_a)}$$
 (2)

In this method the inhibition efficiency, IE (%), was calculated by using the following equation where I_2 and I_1 are the double layer capacitances in the absence and presence of inhibitors [2]:

$$IE(\%) = \frac{(I_2 - I_1)}{I_2} \times 100$$
 (3)

Electrochemical Impedance Spectroscopy (EIS): For EIS measurements, the test was conducted by using AC signal of impedance measurements by using Autolab PGSTAT302N and run at the corrosion potential. All the potentials referred were relative to SCE. The impedance measurements were conducted over a frequency range of 1 MHz down to 10 mHz. The results were analyzed using the fit program FRA. The inhibition efficiency, IE (%) was calculated by using the following equation where C_2 and C_1 are the double layer capacitances in the absence and presence of inhibitors [2]:

$$IE(\%) = \frac{(C_2 - C_1)}{C_2} \times 100$$
 (4)

RESULTS AND DISCUSSION

Weight Loss Analysis: The weight loss measurement is a classical way to determine the corrosion rate of aluminium alloy. The result for the weight loss measurement was summarized in Figure 2. The graph shown in Figure 2 reveals that there was an increasing in weight loss with respect to immersion time. The weight loss of coupons immersed in seawater in the presence of honey was lower compare in absence of honey which indicates that honey has retarded the corrosion process of AA7631.

Different concentration of honey influences the value of inhibition efficiency, IE. The inspection of Table 2 reveals that as the concentration of inhibitor increase, the inhibition efficiency also increases. With the presence of 150 g honey the IE increases to 75.76%. As the concentration increase, the weight loss decreases. There are rises in surface area covered by adsorbed molecules of honey during the increment of concentration [9]. The existences of various compounds like oxygen (polyphenols) as well as nitrogen and sulphur

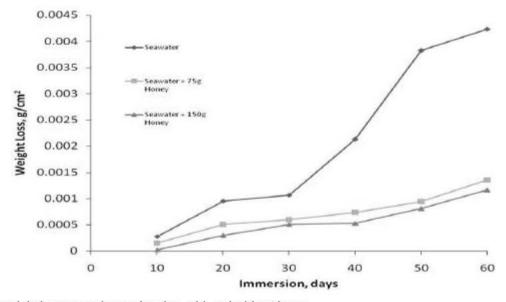


Fig. 2: The weight loss versus immersion time with and without honey

Table 2: The inhibition efficiency of honey using weight loss method

Concentration	Initial weight (g)	Final weight (g)	Weight loss (g)	IE (%)
Seawater	2.0265	2.0100	0.0165	15%
Seawater + 75g honey	1.6432	1.6377	0.0055	66.67
Seawater + 150g honey	2.0552	2.0512	0.0040	75.76

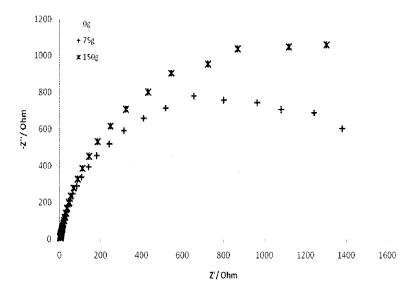


Fig. 3: Nyquist plots for AA7631 inhibited by 75g and 150g of honey in seawater

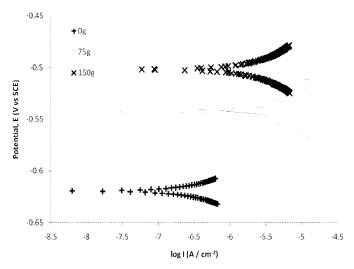


Fig. 4: Potentiodynamic polarization curves for AA7631 inhibited by 75g and 150g of honey in seawater

Table 3: R_P and C_{dl} value of AA7631 in seawater

Concentration	$R_P(\mathrm{k}\Omega)$	$C_{dl}\left(\mathrm{\mu F} ight)$	IE(%)
Seawater	1.52	166.86	-
Seawater + 75g honey	1.59	14.44	91.35
Seawater + 150g honey	2.45	13.81	91.72

Table 4: Electrochemical parameters: corrosion potentials (E_{corr}), corrosion current density (i_{corr}) and Tafel slopes (b_a and b_c) of AA7631 in seawater

Concentration	E_{corr} (mV)	$i_{corr}(\mu \text{Acm}^{-2})$	$b_a(\mathrm{Vdec}^{-1})$	$b_c(\mathrm{Vdec^{-1}})$	IE(%)
Seawater	-619	0.50	0.99	0.98	-
Seawater + 75g honey	-541	0.33	0.19	0.36	34.00
Seawater + 150g honey	-502	0.14	0.14	0.22	72.00

(glucosinate), it is hard to determine which components inhibit the metal from corrosion [4]. It may be one or all of them involve in synergism action [10]. There was considerable reduction in weight loss and hence reduces the corrosion rate with the introduction of inhibitor in corrosive media [8]. Higher concentration of honey was effectively inhibiting the corrosion compares to lower concentration of honey.

Electrochemical Impedance Spectroscopy: The data for the electrochemical was summarized in Table 3 and Figure 3. The presence of honey causes the formation of extra protective film through the adsorption of their molecules on the metal surface where the protective film formed is responsible for the corrosion resistance. As seen, when the concentration increases, the value of polarization resistance, R_p increases while the double layer capacitance, C_{dl} decreases. The inhibition efficiency increases as the concentration increase. The capacitive loop in Figure 3 is due to the charge transfer reaction and time constant of the electric double layer as well as surface inhomogeneity of structural or interfacial origin. This behavior commonly found in adsorption process [11, 12]. The decrease in double layer capacitance, C_{dl} is due to a decrease in local dielectric constant and/or an increase in the thickness of the electrical double layer [11]. This process shows that the addition of honey as inhibitor acts by an adsorption at the aluminium and solution [13]. The changes in C_{dl} values can be a sign that there is gradual replacement of water molecules by the adsorption of the organic molecules on the metal surface. Thus, it decreases the extent of metal dissolution [14].

Polarization Scan: The effects of natural honey on the corrosion reactions were determined by polarization measurements. The changes observed in the polarization curves after the addition of the corrosion resistant were usually used as the criteria to classify inhibitor as cathodic, anodic, or mixed [16]. Figure 4 and Table 4 represent the anodic and cathodic polarization cuves of AA7631 in seawater in the absence and presence of honey. From the figure, the corrosion potential, E_{corr} shifted toward more positive direction and toward lower current densities which indicates that honey is a mixed-type inhibitor with predominantly control of anodic reaction [5]. The process of shifting towards more positive value indicates that the inhibitor influence the dissolution of aluminium and the hydrogen evolution process as the inhibitor behaves as mixed-type inhibitor [15]. The change of E_{corr} is assumed to be related to the growth of a passive layer at the surface electrode [16]. The value of cathodic Tafel slopes decrease upon addition of inhibitor which indicates that there are variation of inhibition mechanism occurs in the corrosion process.

CONCLUSION

The following conclusion can be made base on the basis of the results obtained:

- Natural honey in seawater acts as corrosion inhibitor for aluminium alloy.
- Inhibition efficiency increase with the increase of their concentration
- Honey can be used in petroleum fields to reduce the corrosion rate of steel pipelines.
- The inhibiting efficiencies obtained by polarization, EIS and weight loss measurements are still in acceptable agreement.

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