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Case Report

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Investigation of *Artocarpus Heteropyllus* peel extract as non-toxic corrosion inhibitor for pure copper protection in nitric acid

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ABSTRACT

Artocarpus Heteropyllus Peel as non-toxic fruit waste contained some antioxidants. Peel extract of *Artocarpus heteropyllus* could used as inhibitor to reduced corrosion rate. In this study, *artocarpus heteropyllus* peel extract was used as inhibitor corrosion to protect pure copper in 1 M HNO₃. The inhibitor concentration was varied of 0-800 ppm. The measurement of corrosion rate was conducted by applying potentiodynamic polarization methods. The inhibitor performance, isotherm adsorption the thermodynamic parameter and kinetic activation energy were analyzed. *Artocarpus heteropyllus* peel extract was mixed inhibitor type and tended to anodic inhibitor type. The highest inhibitor efficiency was 98%. It occurred at its concentration of 800 ppm temperature of 25 °C. Isothermic adsorption pattern followed the Frumkin adsorption isotherm equation. Inhibitor molecules were adsorbed on the pure copper surface physically.

1. Introduction

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Copper is used in various applications due to its good mechanical and physical properties [27] is utilized for tube, electronics, alloy, wires production and other. Pipelines in electronic industries, marine industries, power stations, heat exchangers and cooling towers use material from copper too. Copper has corrosion resistance properties, but its use in the industrial sector causes copper to be often exposed to aggressive environments. Passive films are less likely to form on copper surfaces when exposed to highly aggressive environments. The chance is also low if the copper is in an environment containing corrosive ions such as sulfate or chloride. In general, copper has good corrosion resistance, however, copper can seriously damaged when exposed to high temperatures, and aggressive environments containing high salt. Thus, copper being susceptible to corrosion. Nitric acid is the oxidizing acid. The oxygen in nitric acid causes the increase of corrosion rate on copper surface [1]. Therefore, copper protection in nitric acid from corrosion is needed.

Corrosion inhibitor is applied to protect of copper from corrosion. It is chemical compound that can reduce corrosion rate if added into corrosive environment in small quantities [2]. The addition does not change any concentration of corrosive substances significantly. It is more effective when the inhibitor [48] used in small concentration. Inhibitors with inorganic materials are widely used to protect copper from

corrosion. The inorganic inhibitors include chromate, molybdate and tetraborate. These compounds are toxic compounds and do not provide [39] inhibitor efficiency even in an aggressive environment. It is likely due to instability of the protective layer that forms on the copper surface [1]. Thus [6] organic inhibitors do not have optimal inhibitory effect, and it causes negative impact on the environment and humans due to their toxic compounds. Non-toxic and effective corrosion inhibitors are needed to protect copper from corrosion attack.

Therefore, organic inhibitor is an appropriate choice, which is environmentally friend [21] The inhibitory effect of the organic compounds are shown by their adsorption on metal surfaces, The polar functional groups have major role in the adsorption process [3]. Organic inhibitor compound is adsorbed on metal surface and form adsorbate layer. It protects metal surface from its corrosive environment. This is caused by inhibitor compounds that have heteroatomic structures such as N, O, P, S, and atoms, which have free electron pairs. The elements with lone electron pairs as ligands form complex compound with metal. The adsorption layer does not only separate the metal from the corrosive medium, but also improves the energy barrier of the corrosion reaction [4] [16]

Inorganic corrosion inhibitors cannot simultaneously meet the high demand for low cost corrosion resistance and low toxicity. Gradually, organic corrosion inhibitors are replacing the common use of inorganic

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corrosion inhibitors to prevent copper corrosion, being more efficient, less toxic and affordable [5]. Organic inhibitors have been widely used to control corrosion on copper. This has been proven by various studies on the use of plants as corrosion inhibitors. The studies were conducted on the whole parts of the plants. *Thymus vulgaris* [6], *Unused meropenem* [7], *Eugenia caryophyllus* [8], *Withania somnifera* [9], *Zygophyllum coccineum* [10], *Ceratonia siliqua* [11], *Azadirachta indica* [12], *Hyoscyamus muticus* [13], *Euphorbia heterophylla* [14], *Moringa oleifera* [15], *Ricinus communis* [16], *Curcuma longa* [17], *Curcuma* [18].

Artocarpus heterophyllus or jackfruit are aggregate tropical fruit that grow in South Asia countries and Florida. In those countries, *Artocarpus heterophyllus* are more popular as garden plants rather than plants for commercial plantation [19]. In Indonesia, *Artocarpus heterophyllus* are eaten when they are ripe or nearly ripe. Unfortunately, the waste of this fruit has not been utilized maximally. The processing industry of *Artocarpus heterophyllus* is the largest producer of fruit waste. The fruit waste will become a pollution problem for the environment if it is not handled properly. The fruit waste needs to be processed into other useful products. Fruit peel waste can be used as a source of pectin. Pectin is widely used as a thickening agent in the food industry. Fruit peel waste can also be used as an adsorbent for heavy metal (Cd) II in waters and economical activated carbon. The bio-hydrogen produced can also utilize fruit peel waste. Thus, the utilization of fruit peel waste can reduce waste problems, and increase its economic value. Furthermore, it can contribute to the economic improvement of the *Artocarpus heterophyllus* processing industry. The peel waste has been converted commercially into high value products [20]. *Artocarpus heterophyllus* peel contains some antioxidant compounds such as isovitexin, morin, and luteolin [21]. These compounds are also found in other organic inhibitors which have high inhibitor efficiency. *Artocarpus heterophyllus* peel is a non-toxic fruit waste; therefore, it is safe for the environment. It is proven by some research. Pectin from *Artocarpus heterophyllus* peel has been using as raw material in the food industry [22]. *Artocarpus heterophyllus* peel has potential as an adsorbent of various harmful dyes and metal ions from water [20].

Based on the previous explanations, *Artocarpus heterophyllus* peel has several advantages that can be used as a new material. *Artocarpus heterophyllus* peel can be used as a substitute material such as a thickening agent or heavy metal absorbent material, thus it increases its economic value. *Artocarpus heterophyllus* peel also has antioxidant compounds that can be adsorbed on the metal surface, and it can protect the metal from aggressive environmental attacks. In addition, *Artocarpus heterophyllus* peel contains nontoxic compounds that are safe for the environment and humans. Therefore, *Artocarpus heterophyllus* peel can be considered as an environmentally friendly corrosion inhibitor.

The pure copper needs non-toxic inhibitor to protect it from corrosion attack in nitric acid. In this study, *Artocarpus heterophyllus* peel extract (AHPE) was used to reduce corrosion rate of pure copper in nitric acid. The inhibitor performance was investigated by the result of corrosion rate test using potentiodynamic polarization. The characterization of AHPE as corrosion inhibitor and adsorbate was analyzed through IR and UV-Vis spectra.

2. Materials and methods

2.1. The materials

The material of working electrode in this experiment was pure copper. Emery paper with grade 600 to 1200 abraded it. The dimension of specimen was 10 mm × 40 mm × 1 mm with 100 mm² for the exposed square area. In this study, the electrolyte used 1 M HNO₃ solution from Merck. The solution was made using dissolving process of 69 ml of 65% HNO₃ with aquades until 1000 ml solution. AHPE was added into 1 M HNO₃ solution with varied concentration and temperature.

AHPE was made with maceration extraction method. The cleaning process of peel from contaminants was the first stage in *Artocarpus*

heterophyllus peel extraction preparation. The next stage, the clean peel was dried and crushed into powder. The powder mixed with ethanol solvent and produced filtrate. The filtrate was placed into erlenmeyer. The evaporation of filtrate process was done by rotary vacuum evaporator. The result of evaporation process was thick extract.

2.2. The characterization of AHPE

IR and UV-Vis spectra was obtained by Fourier transform infra red (FTIR) and Ultra violet Visible (UV-Vis) spectroscopy. FTIR spectroscopy of Shimadzu 8400 S was used to identify the AHPE functional group. AHPE powder was mixed with KBr salt to form pellets. That was a way to make test samples. The AHPE as adsorbate powder was taken from the layer on the copper surface. Sample preparation for UV-Vis spectroscopy was begun with the process of mixing 1 M HNO₃ solution and a little AHPE. It was divided into two portions. Pure copper was cleaned and polished. It was immersed in one of them at room temperature for 72 hours. The both of solution were samples. The scan wavelength ranged from 300,0 nm to 750,0 nm.

2.3. Corrosion test

Potentiodynamic polarization was the method for corrosion rate measurement. Measurement was done using Autolab PGSTAT 204 N and software Nova 11 Autolab. The test was done to measure corrosion rate of pure copper in 1 M HNO₃ with and without AHPE inhibitor. AHPE was added into 1 M HNO₃ with various concentration of 200 ppm, 400 ppm, 600 ppm, 800 ppm. The temperature variation were 25 °C, 30 °C and 35 °C.

The unexposed surface of copper specimens were coated with epoxy resin. This specimen was used as the working electrode and platinum was the counter electrode. The reference electrode used Ag/AgCl. The scan rate was set at 0.100 V/s and the value of Open Circuit Potential (OCP) ranged from -0.44 V to -0.46 V using average OCP value.

The value of inhibition efficiency (IE) was calculated following the equation [23]:

$$IE = \left(\frac{i_{corr} - i_{corr_i}}{i_{corr}} \right) 100\% \quad (12)$$

Where i_{corr} was the corrosion current density (A/cm²) without inhibitor and i_{corr_i} was the corrosion current density (A/cm²) with inhibitor.

2.4. Isotherm adsorption

Isothermal adsorption is a way for corrosion inhibitors to interact with the pure copper surface. The adsorption pattern of corrosion inhibitors is explained by linear curve plot of isothermic adsorption equations. They are Langmuir, Freundlich, Temkin and Frumkin equations [24]:

Langmuir equation:

$$K_{ads} = \theta / (1 - \theta) C_{inh} \quad (1)$$

Frumkin equation:

$$\text{Log} \frac{\theta}{1 - \theta C_{mh}} = \text{Log} K_{ads} + b\theta \quad (2)$$

Freundlich equation:

$$\text{Log} \theta = \text{log} K_{ads} + n \text{Log} C_{mh} \quad (3)$$

Temkin equation:

$$\exp(2a\theta) = b C_{mh} \quad (4)$$

K_{ads} is the adsorption-desorption balance constant, θ is the surface coverage fraction, C_{inh} is the concentration of inhibitor and b is the parameter of interaction which uses slope of the linear regression equation to calculate it. The attraction of the adsorbed species is

indicated by the value of b which is more than zero. However, the resistance of the adsorbed species is specified by the value of b which is less than zero. The adsorption isotherm pattern is defined by the value of each R2 determinant coefficient.

2.5. Thermodynamic calculation

The parameter of thermodynamic can be used to review the mechanism of inhibition of AHPE on pure copper surface. The changes of free energy of adsorption (ΔG_{ads}^0), enthalpy of adsorption (ΔH_{ads}^0) and entropy of adsorption (ΔS_{ads}^0) are included. The equation for the changes of free energy of adsorption [25] is:

$$\Delta G_{ads}^0 = -RT \ln(K_{ads} A) \quad (5)$$

R is the gas constant with the value of $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$, T is the absolute temperature ($^{\circ}\text{K}$) and A is the water concentration in the acidic solution. The value is 55.5 for concentration in Molar or 1000 for concentration in g/L. The value of ΔG_{ads}^0 indicates physisorption if it is around -20 kJ mol^{-1} . However, the chemisorption indication can be shown with the value of ΔG_{ads}^0 around -40 kJ mol^{-1} [26]. The negative value of enthalpy ΔH_{ads}^0 can be used to determine exothermic adsorption. The magnitude absolute of ΔH_{ads}^0 for physisorption is less than chemisorption. The calculation of ΔH_{ads}^0 was estimated through Van't Hoff equation [25]:

$$\ln K_{ads} = -\Delta H_{ads}^0 / RT \quad (6)$$

T is the absolute temperature and ΔH_{ads}^0 is the enthalpy of adsorption. The value of ΔS_{ads}^0 can be used to identify the adsorption process. If the value of ΔS_{ads}^0 is greater than zero, it indicates the adsorption is exothermic. Its value was calculated following the equation:

$$\Delta G_{ads}^0 = \Delta H_{ads}^0 - T \Delta S_{ads}^0 \quad (7)$$

2.6. Kinetic of activation

The inhibitor adsorption process on pure copper surface in 1 M HNO_3 with the absence and presence of AHPE can be specified by kinetic of activation. There are the energy of activation (E_a), the enthalpy of activation (ΔH^{\ddagger}) and the entropy of activation (ΔS^{\ddagger}). The activation energy (E_a) was calculated using Arrhenius equation [26]:

$$i_{corr} = A \exp\left(\frac{E_a}{RT}\right) \quad (8)$$

i_{corr} is the corrosion current density, A is the Arrhenius constant, and R is the universal gas constant. The equation of transition state is illustrated in the following:

$$i_{corr} = \frac{R}{Nh} \exp\left(\frac{\Delta S^{\ddagger}}{R}\right) \exp\left(\frac{-\Delta H^{\ddagger}}{RT}\right) \quad (9)$$

h is the Constanta of Planck and N is Constanta of Avogadro.

Temperature effect to corrosion inhibition can be explained with Arrhenius Equation (eg. 8). E_a values can be determined from the slope of linear regression result between $\ln i_{corr}$ versus $1/T$ this equation. Values of ΔS^{\ddagger} and ΔH^{\ddagger} were obtained through Linear plotting of $\ln(i_{corr}/T)$ versus $1/T$.

3. Result and discussion

3.1. AHPE characterization

Some peaks of FTIR product was used to identification the AHPE functional groups. It was shown in Fig. 1.

Fig. 1(a) presented the functional group of AHPE based on IR chart [27]. The alcohol functional group with O-H appears in wavenumber

range $3550\text{--}3200 \text{ cm}^{-1}$ and intensity 10%. The aromatic compound functional group with C=C can be indicated in wavenumber range $1625\text{--}1440 \text{ cm}^{-1}$ and intensity until 42.87%. In addition, C-O bonds have been found in the wavelength range of $1320\text{--}1000 \text{ cm}^{-1}$ with an intensity of 37.39%. The bond can be indicated as an ether functional group. The Nitro compound functional group with N=O was read in wavenumber range of $1390\text{--}1300 \text{ cm}^{-1}$ and intensity 45.24%.

Based on the functional groups found in AHPE, the content of flavonoid antioxidant compounds can be predicted. The suspected flavonoid compounds include luteolin (C15H10O6), morin (C15H10O7), phenol (C6H6O), protocatechuic acid (C7H6O4), artocarpone (C16H14O6), artocarpin (C26H28O6) or isovitexin (C21H20O10) [20]. Their molecular structure is shown in Fig. 2. Hydroxyl groups with O-H bonds are always found in these flavonoid compounds [20]. C=C double carbon bonds are also found in the benzene ring of flavonoid compounds [28]. Ether with an R'-O-R arrangement and C-O bonds is found in the methoxy group contained in the artocarpin molecule [29].

The FTIR results (Fig. 1 (a)) indicate that AHPE can be used as a corrosion inhibitor. This is because AHPE functional groups are assumed as the framer of antioxidant molecules. The role of molecules form an adsorption layer to protect copper surface from HNO_3 attack. This role is proven by the results of potentiodynamic polarization testing.

3.2. Potentiodynamic polarization

The effect of AHPE concentration in 1 M HNO_3 solution for pure copper corrosion rate were explained with their potentiodynamic polarization curves. They were shown in Fig. 3.

Corrosion parameters based on tafel extrapolation on the Potentiodynamic polarization curves are presented in Table 1.

The value of the cathodic slope (β_c) of pure copper with APHE concentration of 0 ppm, temperature 25°C is the same as the anodic slope (β_a). This β_c value is smallest from the other. The value of $\beta_c > \beta_a$ in specimens with AHPE concentrations of 600 ppm, 25°C . The value of $\beta_c > \beta_a$ means that the anode ion decomposes into the HNO_3 solution. While the other specimens have a value of $\beta_c < \beta_a$. The value of $\beta_c < \beta_a$ indicates that decomposition of metal ions at the anode does not occur [30]. β_a is at range of 32.7 mV/dec up to 508.7 mV/dec and β_c is at range of 26.8 mV/dec to 97.1 mV/dec . The shift of β_a is bigger than β_c . It indicates that AHPE is mixed inhibitor type. However, it tends to be anodic inhibitor type [30]. The significant shift of Ecorr with and without AHPE inhibitor is in the range of $9.5 \text{ mV--}47 \text{ mV}$. If the values of Ecorr shift is less than 85.0 mV , it is confirmed as the mix inhibitor [31].

The lowest corrosion current density (i_{corr}) was found in specimen with 800 ppm AHPE at a temperature of 25°C ($0.9 \times 10^{-5} \text{ A/cm}^2$). The increase of temperature increased the i_{corr} . At temperature of 30°C , the i_{corr} value increased to $1.7 \times 10^{-4} \text{ A/cm}^2$. When the temperature was increased to 35°C , the i_{corr} value increased to $2.7 \times 10^{-4} \text{ A/cm}^2$. This is caused by the binding reduction between the surface of the copper and the molecules of AHPE. This moment can be called desorption. The desorption occurred parallel to the adsorption and the protection for pure copper lessened. Therefore, the effectiveness of inhibitor reduced gradually [32]. Based on the i_{corr} value, the inhibitor efficiency (IE) was calculated. IE increased when AHPE concentration was increased too at the same temperature. It occurred parallel at the other temperatures. The highest IE was 98%. It appeared at AHPE concentration of 800 ppm and temperature of 25°C .

3.3. Isotherm adsorption

The determinant coefficient (R^2) value from linear curve of the isothermic adsorption equations for AHPE adsorption are shown in Table 2.

R^2 value from Frumkin equations was the higher than the other. It was similar case at each temperature. Their value were 0.819 at 25°C , 0.997 at 30°C and 0.985 at 35°C . It means the isothermic adsorption

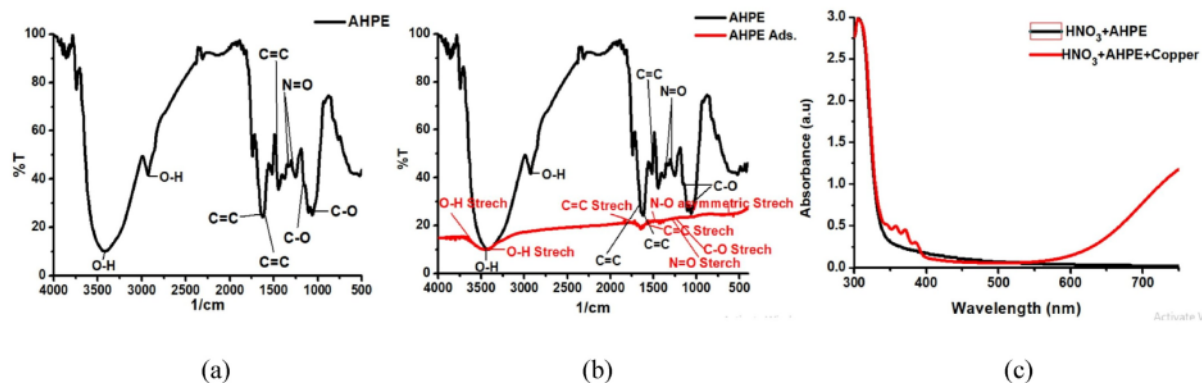


Fig. 1. (a) The results of Fourier transform infrared (FTIR) test on AHPE functional group, (b) The IR spectra of AHPE and the IR spectra of AHPE as adsorbate on pure copper, (c) UV-Vis spectra for 1 M HNO₃ solution contained 800 ppm AHPE before and after copper corrosion.

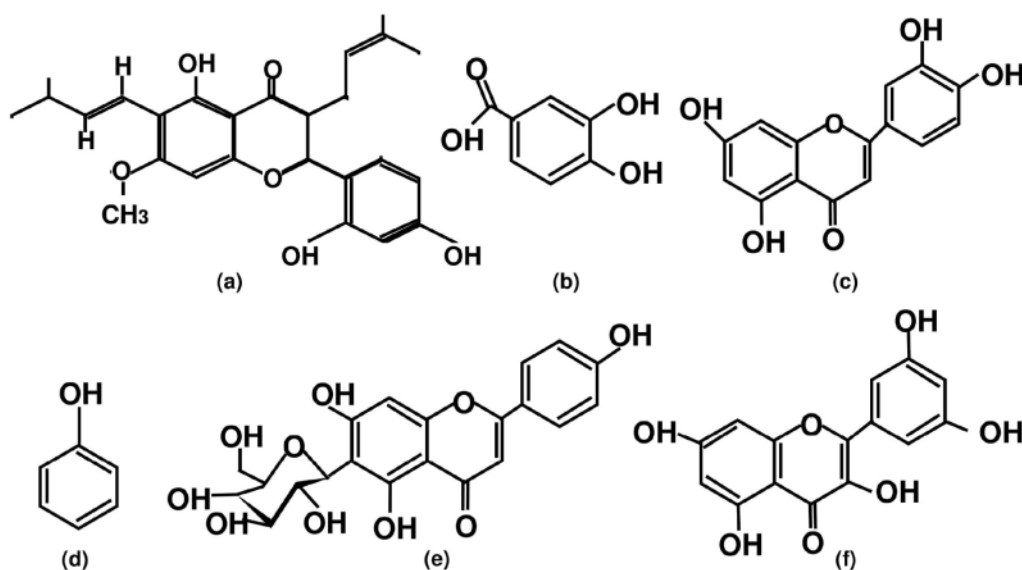


Fig. 2. The molecule structures of artocarpin (a), protocatechuic acid (b), luteolin (c), phenol (d), morin (e) and isovitexin (f).

pattern at each temperature has followed the frumkin adsorption isotherm equation.

3.4. Thermodynamic parameter

AHPE inhibition mechanism can be reviewed through thermodynamic parameter at the concentration with the highest IE as shows at Table 3.

$\Delta G^{\circ}_{\text{ads}}$ values ranges from -15.03 KJ/mol [19] to -7.64 KJ/mol. They are up to -20 KJ/mol. It means that 52 PE molecules are adsorbed onto the pure copper surface physically. The electrostatic interaction occurs between the charged pure copper surface and a charged molecule [33]. Positive values are used to express $\Delta H^{\circ}_{\text{ads}}$ value was positive at each temperature. The positive value of $\Delta H^{\circ}_{\text{ads}}$ indicates that the adsorption process of AHPE is endothermic process. $\Delta S^{\circ}_{\text{ads}}$ value is positive too. It means that the corrosion process is slow due the regularity of energy [34].

3.5. Kinetic of activation

Activation parameters for pure copper corrosion in 1 M HNO₃ with the absence and the presence of AHPE at concentration with the highest IE are shown in Tab. 62.

Table 4 exhibits the values of E_a , $\Delta S^{\#}$ and $\Delta H^{\#}$. E_a values with inhibitor are higher than those without inhibitor. The increase of concentration is shown in line with the increase of E_a value. Positive value is expressed for $H^{\#}$ value but it is the opposite of $S^{\#}$ value.

The increase of activation energy of corrosion in the absence and the presence of AHPE indicates the occurrence of physisorption. This is confirmed by 24 decrease of inhibitor efficiency if the temperature increases [32]. The positive values of $\Delta H^{\#}$ both in absence and presence of AHPE indicate that the react is endothermic. It adsorbs thermal from its surround 49 for the pure copper corrosion process. The activation enthalpies increased with the increase of concentration of AHPE too. The $\Delta S^{\#}$ negative 38 values show that a disordering decrease when occurred movement from reactant to the activated complex [26]. The increase of AHPE concentration caused the increase of $\Delta S^{\#}$ value to more positive,

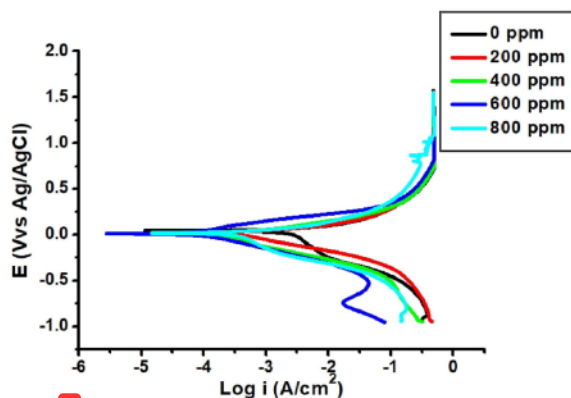


Fig. 3. Potentiodynamic polarization curves for pure copper corrosion in 1 M HNO_3 with the varying of AHPE concentration.

Table 1
The Pure Copper corrosion parameter in 1 M HNO_3 solution with varied AHPE concentration and temperature.

C (ppm)	T (°C)	Slope		E_{corr} (V)	i_{corr} (A/cm ²)	Corrosion rate (mm/year)	IE (%)
		β_a (mV/dec)	β_c (mV/dec)				
0	25	32.7	26.8	46.4	0.000460	10.42	
	30	447.4	53.8	55.1	0.001628	36.94	
	35	208.8	62.7	47.0	0.001679	38.09	
200	25	153.2	47.5	24.1	0.000335	7.60	27.05
	30	227.9	61.8	19.1	0.000545	9.37	10.12
	35	417.0	44.6	26.7	0.000560	9.71	6.87
400	25	71.3	37.3	11.6	0.000103	2.34	77.59
	30	138.7	43.1	23.7	0.000320	7.25	30.42
	35	123.0	624.1	45.8	0.000382	8.66	16.88
600	25	79.9	87.7	13.0	0.000063	1.43	86.23
	30	170.9	57.5	20.6	0.000223	5.07	51.40
	35	508.7	74.3	13.3	0.000344	7.79	25.26
800	25	74.4	51.6	15.2	0.000009	0.20	98.10
	30	74.6	44.4	19.0	0.000172	3.90	62.59
	35	355.2	97.1	9.5	0.000265	6.02	42.28

Table 2
The R^2 value from linear curve of the isothermic adsorption equations at the varied temperature.

Temp. °C	R^2			
	Langmuir	Freundlich	Temkin	Frumkin
25	0.217	0.531	0.659	0.819
30	0.971	0.996	0.987	0.997
35	0.54	0.646	0.802	0.985

Table 3
Thermodynamic parameters of inhibitor adsorption of AHPE.

C ppm	Temp. °C	θ	$\Delta G^{\circ}_{\text{ads}}$ (KJ/mol)	$\Delta H^{\circ}_{\text{ads}}$ (KJ/mol)	$\Delta S^{\circ}_{\text{ads}}$ (KJ/mol K)	
						800
	30	0.23	0.37	-7.64	2.48	0.03
	35	0.23	0.37	-7.73	2.56	0.03

so that a disordering increase too.

E_a value can be used to support the relationship between IE and temperature. IE decreases with increase of temperature is supported with E_a

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Table 4
Activation Parameters for pure copper corrosion in 1 M HNO_3 with the absence and presence of AHPE at temperature between 25 °C and 35 °C.

Concentration ppm	E_a KJ/mol	ΔS° KJ/mol K	ΔH° KJ/mol
0	40.44	-0.24	37.93
200	66.55	-0.16	64.04
400	70.17	-0.15	67.66
600	72.07	-0.15	70.45
800	81.13	-0.14	77.24

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(solution with inhibitor) $> E_a$ (blank solution). The opposite expression increases with increase of temperature. IE does not change with change of temperature is supported with (solution with inhibitor) $= E_a$ (blank solution) [35]. The fact from this research presents that IE decreased with the increase of temperature. It is supported with E_a without AHPE value in 40.44 KJ/mol that lower than E_a with AHPE values.

3.6. Adsorption layer

Comparison between the IR spectra of AHPE as corrosion inhibitor and AHPE as adsorbate on pure copper surface was used to review the change or the shift of functional groups. It is shown in Fig. 1 (b). The figure illustrates the shift of transmittance from AHPE IR spectra to IR spectra as adsorbate. Several wavenumbers shift too. The alcohol functional group wave number shifted from 3416.46 cm^{-1} to 3631.07 cm^{-1} . Their percentage of transmittance shifted from 10% to 14%. The aromatic compound functional group wave number shifted from 1617 cm^{-1} to 1650.99 cm^{-1} with the shift of transmittance percentage from 24.39% to 18.58%.

The wave numbers of 1530.21 cm^{-1} and 1445.35 cm^{-1} which moved to 1633.7 cm^{-1} were the aromatic compound functional group wave number which shifted too. Their percentage transmittance shifted from 42.87% to 35.59%–18.72%. The functional group nitro compound had the movement of wave number from 1329.63 cm^{-1} and 1375.91 cm^{-1} to 1537.96 cm^{-1} with the shift of percentage of transmittance from 40.09% to 45.24%–21.15%. The shift of wavenumber did not change the functional groups because it was still in the wavenumber range. The changes due to the addition of AHPE were also supported by UV-Vis results before and after copper corrosion. It is shown in Fig. 1(c). The insignificant change occurred up to wavelength of 550 nm. After that, the shift of absorbance was more significant.

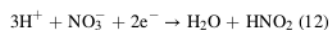
3.7. AHPE adsorption mechanism

Based on the parameters of thermodynamic and activation energy, AHPE was adsorbed on pure copper surface physically. The reactions of electrochemical for copper in HNO_3 solution [7] can be presented as follows:

Anodic reaction:



Cathodic reaction:



The inhibiting effect of AHPE can be explained by AHPE molecules accumulation on pure copper surface in HNO_3 solution [9]. The AHPE molecule was adsorbed on copper surface positively charged in the neutral molecules form. It contained water molecules movement from the copper surface and the share of electrons among nitrogen atoms or oxygen atoms and the copper surface [36]. Antioxidant molecules in AHPE such as luteolin, phenol, morin, artocarpin and others contain a lot of heteroatoms (O atoms), functional groups (OH groups), and

-electrons. The Van Der Waals force occurs between the molecules and the copper surface. In this force, there has been an attraction between the atoms of the molecule and the copper surface, each of which has a charge, but the bond is weak. Thus, the AHPE molecules are adsorbed on the copper surface. These molecules cover the copper surface, thus protecting the copper from the environment [34].

3.8. The practical application and future research

AHPE is an organic material that is non-toxic, easy to obtain and has high economic value. AHPE contains antioxidant compounds that can be adsorbed on the copper surface. Based on the results of this study, it is proven that AHPE can protect copper with inhibitor efficiency up to 98% when added to nitric acid solution at a concentration of 800 ppm. AHPE molecules are physically adsorbed on the copper surface. Copper is a material for industrial equipment including heat exchangers and cooling towers. The cleaning process of the equipment is carried out periodically by using acid. This can cause the copper to corrode. Consequently, it is necessary to add AHPE with a small concentration to protect the equipment from corrosion damage during the cleaning process. AHPE will be adsorbed on the copper surface that has undergone a cleaning process by forming a protective layer.

This study pays special attention to inhibitors derived from the waste of *Artocarpus heterophyllus*. The application is applied to pure copper materials in nitric acid environment. Further research needs to be done to determine the performance of AHPE in protecting materials other than pure copper. Metal materials that are usually used as industrial equipment include copper alloys or aluminium and its alloys. The behaviour of AHPE as a corrosion inhibitor also needs further study if it is used to protect metals in other aggressive environments.

Research development to enrich knowledge also needs to be done. The use of corrosion inhibitors with mixed plant waste materials and their performance also needs further study. The *Artocarpus heterophyllus* peel can be mixed with other plant waste, such as durian peel or mangosteen peel with a certain composition. After the mixture of *Artocarpus heterophyllus* peel, other plant debris were extracted and its characteristics were studied, it was also possible to study its performance as a corrosion inhibitor to protect metals from aggressive environments.

4. Conclusion

Artocarpus heterophyllus peel extract (AHPE) is feasible to use as a non-toxic corrosion inhibitor on pure copper protection in nitric acid. Based on the result of potentiodynamic polarization testing, the inhibitor performance, isotherm adsorption the thermodynamic parameter and kinetic activation energy were analyzed. AHPE was mixed inhibitor type and tended to anodic inhibitor type. The highest IE was 98%. It occurred at AHPE concentration of 800 ppm and temperature of 298 °C. Isothermic adsorption pattern followed the Frumkin adsorption isotherm equation. Further research is needed to know the role of AHPE as a corrosion inhibitor to protect pure copper in other acidic environments. In conclusion, the substantial evidence reported in this paper will benefit us in the development of new organic materials as non-toxic corrosion inhibitors for metals in strong acid environments.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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