

## Effectiveness of a Cassava Peel Adsorbent on the Absorption of Copper (Cu<sup>2+</sup>) and Zinc (Zn<sup>2+</sup>) Metal Ions

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**Abstract** — Cassava peel waste can be used as an adsorbent to remove heavy metal pollution from industrial liquid waste. This study aims to determine the effect of the mesh size and operational temperature of a cassava peel adsorbent on the adsorption of heavy metal ions of copper (Cu<sup>2+</sup>) and zinc (Zn<sup>2+</sup>). This study concerns on the ability to absorb the heavy metals copper (Cu<sup>2+</sup>) and zinc (Zn<sup>2+</sup>), the characteristics of the adsorbent (functional group), and the adsorption capacity for isothermal adsorption using the Langmuir and Freundlich models. The cassava peels were crushed, dried, ground and sieved with 80, 100 and 120 mesh sieves. The cassava peel powder was activated with HNO<sub>3</sub> and used to absorb metal ions from the model liquid waste at different temperatures of 35°C, 45°C and 55°C. The cassava peel adsorption process was analyzed using AAS, SEM and FT-IR analyses. The results of the study showed that the optimum conditions for the cassava peel adsorbent to absorb copper (Cu<sup>2+</sup>) and zinc (Zn<sup>2+</sup>) metal ions are 120 mesh in size and an operating temperature of 35°C to obtain adsorption values of 55.19% for copper (Cu<sup>2+</sup>) and 41.7% for zinc (Zn<sup>2+</sup>). Functional groups present in the cassava peel adsorbent include O-H, N-H, C=O, and C-N. Among the two widely used isotherms tested (i.e., Langmuir and Freundlich models), the experimental data were found to mostly closely resemble the Freundlich isotherm.

**Keywords** — natural adsorbent; cassava waste; heavy metal; industrial pollutant; langmuir and freundlich models.

### I. INTRODUCTION

Heavy metals are generally toxic to living things, although some are required in small quantities [1]. Electroplating waste is derived from metal coating activity by precipitation of a metal coating on metal or electrolytic plastics. In an industrial process, many chemicals are used, especially heavy metals, resulting in very dangerous and toxic industrial waste. The heavy metals found in electroplating industry waste include copper (Cu<sup>2+</sup>), zinc (Zn<sup>2+</sup>), nickel (Ni<sup>2+</sup>), lead (Pb<sup>2+</sup>), silver (Ag<sup>2+</sup>), cadmium (Cd<sup>2+</sup>) and chromium (Cr<sup>6+</sup>) [2], [3]. The inlet fitting test of metal and galvanized coating industry activities showed that the concentrations of copper (Cu<sup>2+</sup>), zinc (Zn<sup>2+</sup>), nickel (Ni<sup>2+</sup>), lead (Pb<sup>2+</sup>), silver (Ag<sup>2+</sup>), cadmium (Cd<sup>2+</sup>) and chromium (Cr<sup>6+</sup>) can reach approximately 2020, 15, 683, 1, 0.06, 0.002 and 0.003 mg/L, respectively [4], which are much higher than the standard limit of inlet fitting quality set by the government, i.e., 0.5, 1, 0.1, 0.5, 0.05 and 0.0 mg/L, respectively [3].

One method to separate heavy metals from industrial waste is adsorption. This is a promising method for treating

industrial waste because it is cheap and has a high absorption capacity [5], [6]. Adsorption is a process that occurs when a fluid (liquid or gas) bonds to a solid and ultimately forms a film (thin film) on the surface of the solid. The process of adsorption of metal ions involves intermolecular forces such as van der Waals interactions or hydrogen bonds. The van der Waals force is also called the electrostatic force and is a force that occurs due to the interaction between dipoles, which will lead to the formation of ionic bonds. This electrostatic force occurs due to the presence of a polar active group, such as a hydroxyl (-OH), in an adsorbent. Thus, there will be an attraction between the positive metal ion and the negative ion of the hydroxyl group, which will lead to the metal ions present in solution interacting with the adsorbent [7], [8].

Indonesia is the third largest producer of cassava after Brazil and Thailand and has 1,205,440 hectares of embedded areas. In 2015, cassava production in Indonesia reached 21,801,415 tons, including cassava production in Banten Province, which reached 74,163 tons [9]. Cassava peel is contained in each cassava tuber and makes up 16% of the weight of cassava tubers, meaning that the potential of

cassava leaf in Indonesia reaches 3.5 million tons/year [10]. The percentage of outer peel waste amounts to 0.5-2% of the total weight of fresh cassava, and the inner skin waste is 8-15% [11].

Cassava peel waste can be utilized as a material to reduce dangerous heavy metal content or absorb metal ions. Cassava peel has high carbohydrate, nonreducing cellulose, and coarse fiber contents and HCN (cyanide acid). These components contain -OH, -NH<sub>2</sub>, -SH and -CN functional groups that can bind metals. The levels of C, H, O, N and S in cassava peel are approximately 59.31, 9.78, 28.7, 2.06, and 0.11%, respectively. In addition, cassava peel also contains 459.56 ppm HCN (cyanide acid) [12]. The cellulose in cassava peel when both chemically and physically activated has an increased surface area and can be used as an adsorbent. This increase is due to the breakdown of organic compounds that takes place very quickly and uncontrollably, thereby damaging the arrangement of the existing carbon hexagon rings [11]. This study aims to determine the potential preparation of metal adsorbents from cassava peels using different mesh sizes and operational temperatures and to measure their ability to absorb heavy metal ions of copper (Cu<sup>2+</sup>) and zinc (Zn<sup>2+</sup>) in industrial liquid waste.

## II. MATERIALS AND METHODS

### A. Materials

Cassava peels were supplied by a farmer from the Banten Province area. Chemicals used during the adsorbent preparation and analysis, such as HNO<sub>3</sub>, copper (Cu<sup>2+</sup>) and zinc (Zn<sup>2+</sup>), were supplied by local suppliers.

### B. Adsorbent Preparation

The cassava peels were washed and cleaned using deionized water and crushed. The crushed cassava peels were then dried at 100°C for 24 hours, ground using a ball mill and sieved with 80, 100 and 120 mesh sieves. The cassava peel powder was then activated by immersion in a 0.3 M HNO<sub>3</sub> solution for 24 h, followed by neutralization with deionized water. Chemical modifications were made by adding 1.5 g of cassava peel powder (80, 100 and 120 mesh size) to 100 ml water containing 10 mg/l of copper (Cu<sup>2+</sup>) and zinc (Zn<sup>2+</sup>) metal ions. The solution was then mixed using a magnetic stirrer for 80 min at different temperatures of 35°C, 45°C and 55°C. The filtrate was passed through filter paper, collected and analyzed.

### C. Analysis of Cu<sup>2+</sup> and Zn<sup>2+</sup> Absorption

The filtrate was analyzed using an atomic absorption spectrophotometer (AAAnalyst 400 Spectrometer, PerkinElmer, Waltham, USA) to determine the amount of metal ions adsorbed from a solution containing copper metal ions (Cu<sup>2+</sup>) and zinc (Zn<sup>2+</sup>) using a cassava peel adsorbent [13].

### D. Functional Group Analysis (FTIR)

The functional groups of the sorbents were analyzed using FT-IR (IRPrestige-21 spectrophotometer, Shimadzu, Japan) to determine the functional groups present in the adsorbent before and after immersion in a HNO<sub>3</sub> solution. Functional group analysis was also carried out on adsorbents with

adsorbed heavy metals to determine which functional groups bind to the heavy metals copper (Cu<sup>2+</sup>) and zinc (Zn<sup>2+</sup>).

### E. Morphology Analysis (SEM- Scanning Electron Microscopy)

Analysis using scanning electron microscopy (ZEISS, Germany) was used to measure the morphology and pore size of the cassava peel adsorbent.

### F. Langmuir Linearity Test Adsorption

The adsorption isotherm is the equilibrium relationship between the concentration in the fluid phase and the concentration inside adsorbent particles at a certain temperature.

The Langmuir isotherm theoretically assumes only an adsorbed gas monolayer, in addition to the adsorption of localized solute molecules; i.e., once adsorbed, the molecules cannot move on the surface of the solid. The Langmuir isothermal adsorption equation is as follows [14].

$$\frac{C}{q} = \frac{K}{q_0} + \frac{1}{q_0} C \quad (1)$$

where:

C = concentration of the solute at equilibrium

q = the period of solute adsorbed per adsorbent period

K = the adsorption constant obtained from the experiment (intercept)

q<sub>0</sub> = maximum adsorption power

### G. Freundlich Linearity Test Adsorption

The Freundlich isotherm equation is derived empirically assuming multicomponent adsorption occurs. The equation can be derived from the adsorption of solids in water or a solid-aqueous system. The form of the equation is as follows:

$$\frac{x}{m} = K. C^{1/n} \quad (2)$$

where:

X = number of substances absorbed

m = weight of the adsorbent

C = concentration of the substances after adsorption

n and k = the constants obtained from the experiment

If the above equations are applied to the algorithm, then:

$$\log \frac{x}{m} = \frac{1}{n} \log C + \log K \quad (3)$$

## III. RESULTS AND DISCUSSION

### A. Effect of the Particle Size and Operating Temperature

The effect of the mesh size and operating temperature on the absorption of copper metal ions (Cu<sup>2+</sup>) and zinc (Zn<sup>2+</sup>) is presented in Table 1. It can be observed that the effectiveness of 120 mesh size to absorb copper (Cu<sup>2+</sup>) and zinc (Zn<sup>2+</sup>) metal ions at temperatures of 35, 45 and 55°C is generally higher than that of the mesh sizes 100 and 80 mesh. This result agrees with the theory that the smaller the size of the particles used, the greater the ability of the adsorbent due to the larger contact surface area between the adsorbent and the adsorbate [15]. A mesh size of 120 will produce

adsorbents with particle sizes of 125 microns, while mesh sizes of 100 and 80 will produce adsorbents with particle sizes of 150 and 180 microns, respectively [16]. From these

data, it can be stated that the adsorption ability for copper ( $\text{Cu}^{2+}$ ) and zinc ( $\text{Zn}^{2+}$ ) metal ions increased with decreasing particle size of the adsorbent.

TABLE I  
EFFECT OF MESH SIZE AND TEMPERATURE OF CASSAVA PEEL ADSORBENT ON  $\text{Cu}^{2+}$  AND  $\text{Zn}^{2+}$  ADSORPTION

Mesh size (mesh)	Temperature ( $^{\circ}\text{C}$ )	Initial [ $\text{Cu}^{2+}$ ] (ppm)	Adsorbed [ $\text{Cu}^{2+}$ ] (ppm)	% Absorption	Adsorbed [ $\text{Zn}^{2+}$ ] (ppm)	% Adsorbed
80	35	10.000	4.214	42.14	2.669	26.69
	45	10.000	3.276	32.76	1.649	16.49
	55	10.000	2.460	24.60	1.33	13.30
100	35	10.000	4.371	43.71	3.012	30.12
	45	10.000	3.342	33.42	2.768	27.68
	55	10.000	2.581	25.81	1.966	19.66
120	35	10.000	5.519	55.19	4.17	41.70
	45	10.000	4.294	42.94	2.79	27.90
	55	10.000	3.383	33.83	2.02	20.20

The adsorption of metal ions at  $35^{\circ}\text{C}$  is better than that at temperatures of 45 and  $55^{\circ}\text{C}$ . The adsorption of copper metal ions ( $\text{Cu}^{2+}$ ) and zinc metal ions ( $\text{Zn}^{2+}$ ) with the 120 mesh size adsorbent at 35, 45 and  $55^{\circ}\text{C}$  was 55.19, 42.94 and 33.83%, respectively. Similar trends were observed for the 80 and 100 mesh sizes. The results obtained are similar to the adsorption process for  $\text{Cu}^{2+}$  metal ions at  $35^{\circ}\text{C}$  reported by [15] and [17]. A study by [15] reported that the optimum temperature for the adsorption process of metal ions  $\text{Co}^{2+}$ ,  $\text{V}^{3+}$  and  $\text{Cr}^{3+}$  is  $40^{\circ}\text{C}$ . The adsorption will decrease with increasing temperature, and after reaching the optimum temperature, the adsorption will decrease. Theoretically, an increase in the adsorption ability is due to other chemical reactions, which are influenced by the temperature, and the higher the temperature is, the faster the reaction. However, in this study, this did not occur due to a reduction in the adsorption capacity of cassava peel at high temperatures because the cassava peel begins to rupture, starting the process of desorption and releasing metal ions from the active sites of the cassava peels [15]. High temperatures are

also thought to damage the active metal-binding sites contained in cassava peels.

The maximum absorption of metal ions ( $\text{Cu}^{2+}$ ) and zinc ( $\text{Zn}^{2+}$ ) found with the 120 mesh size at an operation temperature of  $35^{\circ}\text{C}$  is 55.19% and 41.70%, respectively. The resultant absorption level is quite low compared to the absorption levels of cassava peel found for  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$ , which are 98.9% and 99.8%, respectively [18].

#### B. Functional Group Analysis

The identification of functional groups of cassava peel adsorbent through infrared spectral analysis (IR) is shown in Figures 1 and 2. Analyses were performed using an FT-IR spectrophotometer to identify functional groups on the cassava skin adsorbent. The infrared spectra of the cassava peel adsorbent before and after activation with  $\text{HNO}_3$  are shown in Figure 1. Additionally, the infrared spectra before and after adsorption of copper ( $\text{Cu}^{2+}$ ) and zinc ( $\text{Zn}^{2+}$ ) metal ions are shown in Figure 2. The interaction that occurs during the adsorption process of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  metal ions by the cassava peel adsorbent involves the functional groups as the active sites present in the adsorbent.

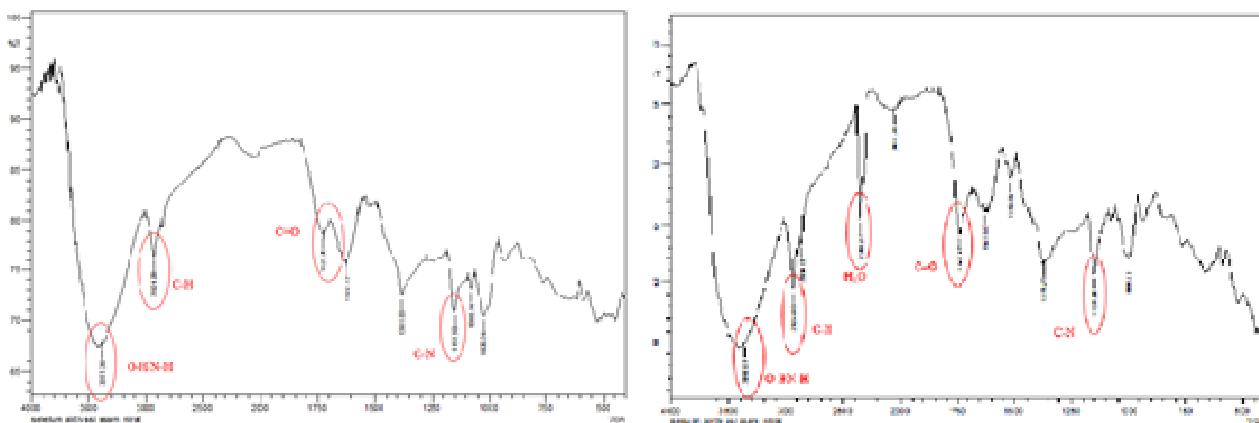


Fig.1 Ftir spectra of cassava peel adsorbent before (left) and after (right) activation

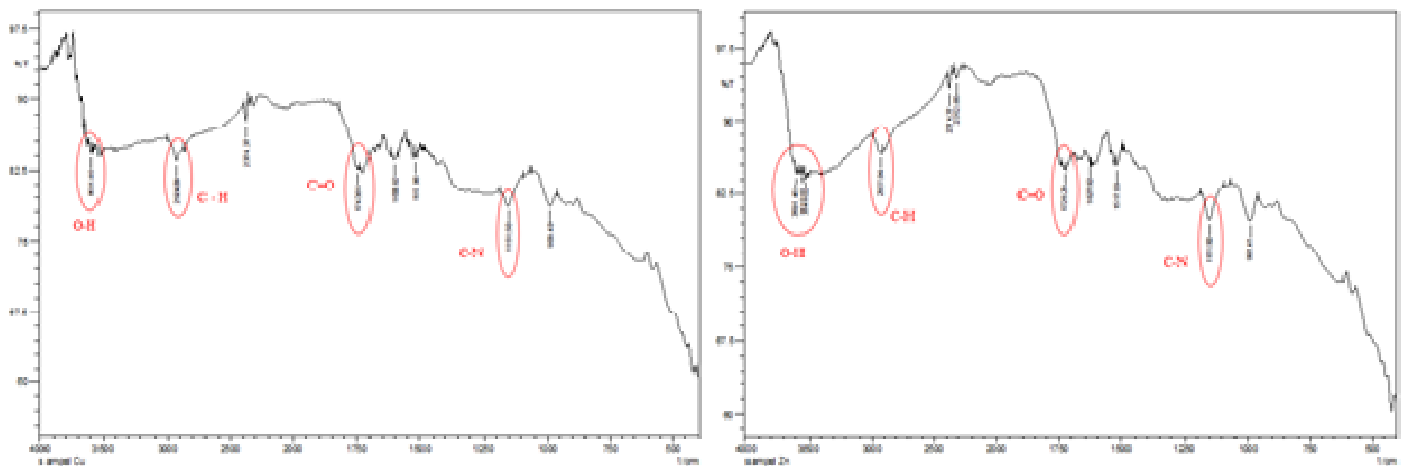


Fig.2 ftir spectra of the cassava peel adsorbent after adsorption of copper (cu2+) (left) and zinc metal ions (zn2+) (right)

From the infrared spectra in Figure 1, it appears that the functional group O-H or N-H appears as the band at  $3377.36\text{ cm}^{-1}$ , the C-H group appears as a band at  $2924.09\text{ cm}^{-1}$ , the C=O group appears as a band at  $1724.36\text{ cm}^{-1}$  and the C-N functional group appears as the band at  $1151.50\text{ cm}^{-1}$ . These functional groups can bind metal ions. The infrared spectrum is also shown after the activation process, which aims to remove the impurities present in the cassava peel adsorbent. The functional group O-H or N-H appears as the band at  $3358.07\text{ cm}^{-1}$ , the C-H group appears as the band at  $2924.09\text{ cm}^{-1}$ , the C=O group appears as the band at  $1741.72\text{ cm}^{-1}$  and the functional group C-N appears as the band at  $1151.50\text{ cm}^{-1}$ . After activation with  $0.3\text{ M HNO}_3$ , the intensity of the carbonyl and hydroxyl groups increased in the infrared spectrum and other functional groups appeared. This result is demonstrated by the broader valley size and the appearance of new peaks, proving that the activation process using nitric acid can remove impurities on cassava peel adsorbents. A similar result was also reported by [18], which mentioned the FTIR spectrum of cassava peel after adsorption of metal ions. The spectrum revealed bands at  $2858$ ,  $3223$  and  $1600\text{ cm}^{-1}$ , which were assigned to C-H, O-H and C-O stretching vibrations, respectively.

In the adsorption process, there is a bond between the functional group and the metal ions ( $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$ ), as shown in Figure 2. The bonding of O-H, N-H, C=O and C-N occurs because the functional groups bind to the metal ion. The FT-IR spectrophotometer cannot detect the metal ions, and thus, the functional groups that bind to the metal ions will not be detected and will form small valleys. The absorption of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  metal ions shows different results in the infrared spectra, with more adsorption of  $\text{Cu}^{2+}$  metal ions than  $\text{Zn}^{2+}$  metal ions. As shown in Figure 2, the valley size in the copper metal spectrum is larger than that in the Zn metal ion spectrum.

### C. Morphology and Size of the Adsorbent

The morphology of the cassava peel adsorbent at a magnification of  $1000\times$  is shown in Figure 3. The results show that the heterogeneous pores of the adsorbent have pore sizes of  $3,909\text{ }\mu\text{m}$ ,  $3,574\text{ }\mu\text{m}$ ,  $2,904\text{ }\mu\text{m}$ ,  $3,127\text{ }\mu\text{m}$  and

$0,9004\text{ }\mu\text{m}$ . Similar heterogeneous morphology and very noticeable pore space development within the biomass of a cassava peel adsorbent have also been reported by [18].

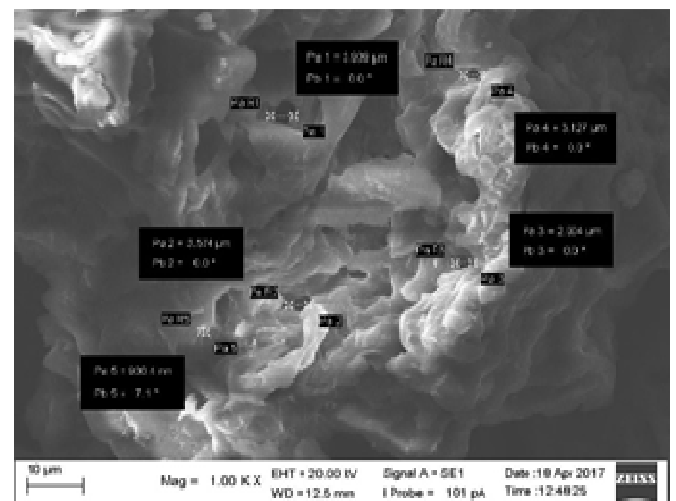


Fig. 3 SEM micrograph of the cassava peel adsorbent at magnification 1000x

### D. Langmuir and Freundlich Linearity Test of the Adsorption of $\text{Cu}^{2+}$ and $\text{Zn}^{2+}$ ions

To determine the isotherm pattern of adsorption of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  ions, the characteristics of adsorption and the adsorption power optimum by cassava peels activated with  $\text{HNO}_3$  were modelled with the Langmuir and Freundlich isotherms. The adsorption model is determined by comparing the linearity of the curve fitting, as indicated by the value of  $R^2$ . An acceptable  $R^2$  value is  $\geq 0.95$ . [19]

The Langmuir isotherm adsorption model is tested by plotting  $C / (x / m)$  versus  $C$  ( $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  equilibrium ion concentrations). The maximum adsorption power of the Langmuir isotherm pattern is determined from the  $\max 1 / (x / m)$  value obtained from the slope of the curve  $C / (x / m)$  versus  $C$  on the Langmuir isotherm adsorption pattern test (Figure 4).

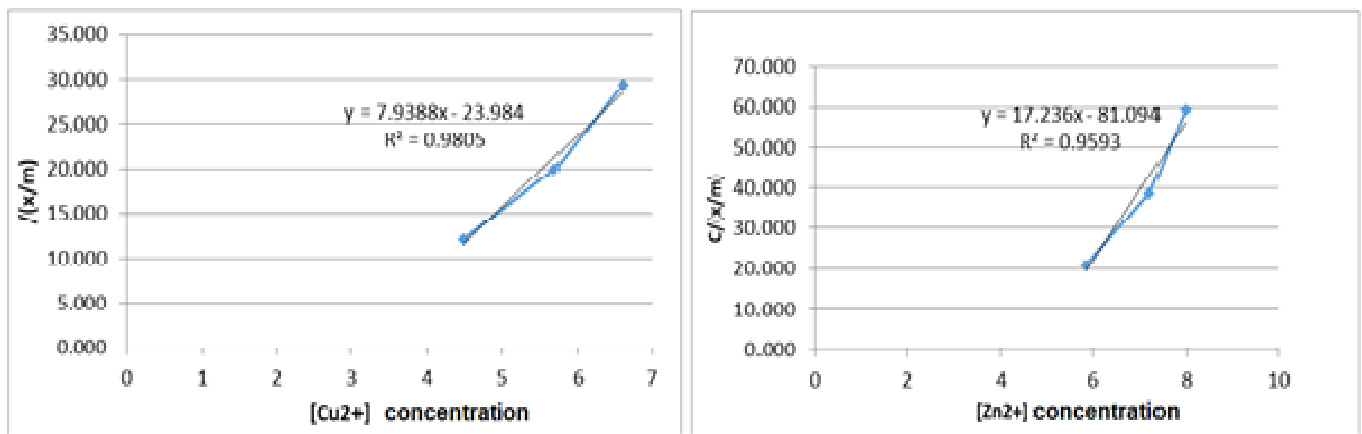


Fig. 4 Langmuir model fit for cu<sup>2+</sup> (left) and zn<sup>2+</sup> (right) adsorption by hno<sub>3</sub>-activated cassava peels

As shown in Figure 4, the linear regression coefficient R<sup>2</sup> for the Langmuir adsorption model for Cu<sup>2+</sup> on HNO<sub>3</sub>-activated cassava peels is 0.9805 with the straight-line equation  $C / (x / m) = 7.9388x - 23.984$ , which has a gradient of  $1 / (x / m)_{\max} = 7,9388$ . Thus, the value  $(x / m)_{\max} = 0.126$  mg / g. The maximum adsorption value of Cu<sup>2+</sup> ions by cassava peels activated by HNO<sub>3</sub> is 0.126 mg/g. Figure 3 also shows that the linear regression coefficient R<sup>2</sup> for the Langmuir adsorption model for Zn<sup>2+</sup> on the cassava peel activated by HNO<sub>3</sub> is 0.9593 with the straight-line equation  $C / (x / m) = 17.236x - 81.094$ , which has a gradient of  $1 / (x / m)_{\max} = 17.236$ . Thus, the value  $(x / m)_{\max} = 0.0580$  mg / g; i.e., the maximum adsorption value of Zn<sup>2+</sup> ions by cassava peels activated by HNO<sub>3</sub> is 0.0580 mg/g.

Based on the value of R<sup>2</sup>, the adsorption of Cu<sup>2+</sup> and Zn<sup>2+</sup> ions from cultivated cassava peels by HNO<sub>3</sub> match the Langmuir isotherm pattern. This suggests that the uptake of Cu<sup>2+</sup> and Zn<sup>2+</sup> ions by cassava peel occurs at a homogeneous specific site in the adsorbent and that there is a uniform distribution of the adsorption sites. Consequently, once the adsorbate molecule occupies the surface of the

adsorbent, no more absorption may occur at the site, so the adsorption will be confined to the formation of a single layer (monolayer) on a limited number of surface sites. [19] Adsorption of Cu<sup>2+</sup> and Zn<sup>2+</sup> metal occurs both physically through pores and chemically through the interactions of carbonyl (CO) and hydroxide (OH) groups. These clusters can bind copper and zinc metal through bonding with ions or polar ions. [20]

As shown in Figure 5, the value of the linear regression coefficient R<sup>2</sup> for the Freundlich adsorption isotherm model of Cu<sup>2+</sup> on HNO<sub>3</sub>-activated cassava peel is 0.9954 with the straight-line equation  $y = 2.2345x - 0.3755$ , which has a value of  $1 / n_{\max} = 0.4475$ . Thus, the value of  $1 / n_{\max} = 0.4475$  mg / g, and the maximum adsorption value of Cu<sup>2+</sup> ions by cassava peels activated by HNO<sub>3</sub> is 0.4475 mg / g; if  $\log k = 0.3755$ , then  $k = 2.3741$ . From both these constants, we obtained the Freundlich equation for the experiment under the best conditions, that is,  $(x / m) = 2.3741 C^{1 / 0.4475}$ . The equation can be used to determine the amount of adsorbent needed to adsorb certain metal ions under the same operating conditions.

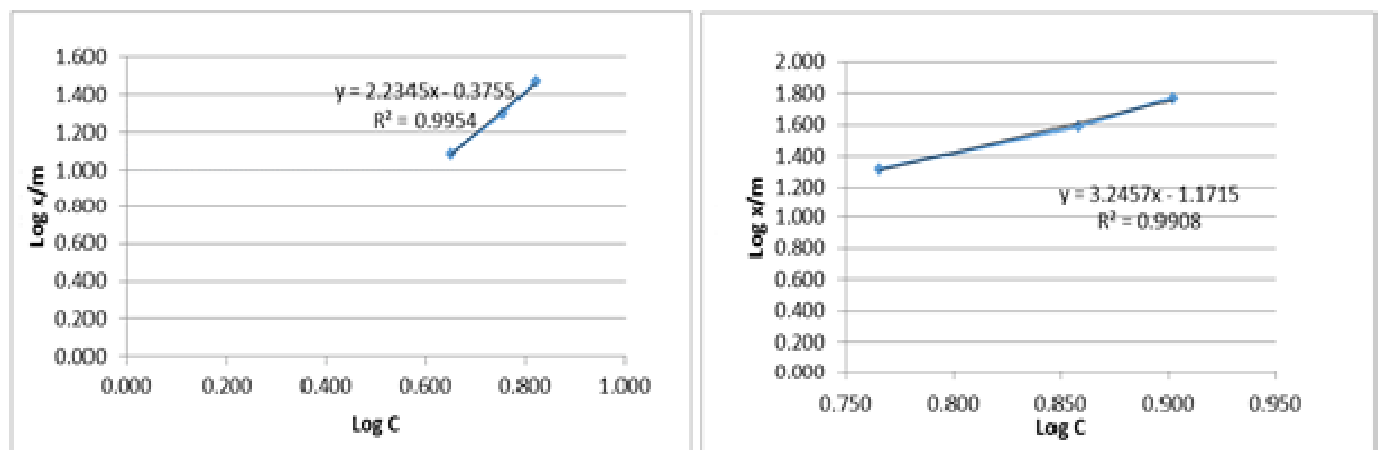


Fig.5 Freundlich linearity curve of cu<sup>2+</sup> (left) and zn<sup>2+</sup> (right) metal adsorption by hno<sub>3</sub>-activated cassava peel, 120 mesh

Figure 5 also shows that the value of the linear regression coefficient R<sup>2</sup> for the Freundlich adsorption isotherm model of Zn<sup>2+</sup> on HNO<sub>3</sub>-activated cassava peel is 0.9908 with the straight-line equation  $y = 3.2457x - 1.1715$ , which has a

value of  $1 / n_{\max} = 0.3081$ . Thus, the value of  $1 / n_{\max} = 0.3081$  mg / g, and the maximum adsorption value of Zn<sup>2+</sup> ions by cassava peels activated by HNO<sub>3</sub> is 0.3081 mg / g; if  $\log k = 1.1715$ , then  $k = 14.842$ . From these two constants,

we obtained the Freundlich equation for the experiments under the best conditions ( $x / m$ ) = 14.842 C<sup>1</sup> / 0.3081. The equation can be used to determine the amount of adsorbent required to adsorb certain metal ions under the same operating conditions. The Freundlich isotherm theory considers a heterogeneous surface with nonuniform adsorption distribution on the surface and states that the ratio of the amount of solids adsorbed on the amount of the adsorbent mass to the final concentration of the solid is not constant at the initial concentration of the solution. [21] The Freundlich equation can be applied to the adsorption process of copper metal ions (Cu<sup>2+</sup>) and zinc (Zn<sup>2+</sup>) by using cassava peel adsorbent because the adsorbent has a heterogeneous surface according to the heterogeneous SEM morphology of the adsorbent.

#### IV. CONCLUSION

Based on the research that has been done, we obtained the following conclusions. The optimal particle size for the cassava adsorbent to absorb copper metal ions (Cu<sup>2+</sup>) and zinc (Zn<sup>2+</sup>) is 120 mesh, and the optimal operating temperature is 35°C. Under the optimal condition, adsorption of 55.19% for copper metal ions (Cu<sup>2+</sup>) and 41.7% for zinc metal ions (Zn<sup>2+</sup>) can be obtained. The functional groups present in the cassava peel adsorbent are O-H, N-H, C=O, and C-N, and these functional groups can bind metal ions. The Langmuir isotherm adsorption model maximum adsorption values of Cu<sup>2+</sup> and Zn<sup>2+</sup> ions by cassava peels activated by HNO<sub>3</sub> were 0.126 mg / g and 0.0580 mg / g, respectively. While the Freundlich adsorption isotherm adsorption model indicated the maximum adsorption values of Cu<sup>2+</sup> and Zn<sup>2+</sup> ions adsorbed by cassava peels activated by HNO<sub>3</sub> were 0.4475 mg / g and 0.3081 mg / g, respectively. The Freundlich model can be applied to the adsorption process of copper metal ions (Cu<sup>2+</sup>) and zinc (Zn<sup>2+</sup>) by using the cassava peel adsorbent.

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