

pH Effect, Isothermal Adsorption, and Adsorption Kinetic Study of Copper(II) Ion into PVA/Alginate Beads Containing Banana Peels

Pasjan Satrimafitrah,¹ Nov Irmawati Inda,^{1*} Ni Ketut Sumarni,¹ Veky Sarapun¹, Natasya Fridian Aprilia¹ and Koichiro Shiomori²

¹Department of Chemistry, Faculty of Mathematics, and Natural Sciences, Tadulako University, Indonesia

²Department of Applied Chemistry, University of Miyazaki, 1-1 Gakuenkibanadai-nishi, Miyazaki 889-2192, Japan

*Corresponding email: nov_chemuh@yahoo.co.id

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ABSTRACT

Banana peels have been widely used as a biosorbent for metal ion adsorption. However, the small size of banana peels as a biosorbent leads to difficulty in the separation process of banana peels from the aqueous solution. Thus, the banana peels were impregnated into PVA/Alginate beads to increase the biosorbent size using the (W/O) emulsion process. Various amounts of banana peels were impregnated into beads. The obtained beads were used to adsorb copper(II) ions from aqueous solutions. The result shows that beads could extract the copper(II) ion from an aqueous solution containing 0.7875 ppm copper(II) ion at pH 4 with the quantity of extraction was 0.729 mmol/g. The effect of contact time and initial concentration indicates that the adsorption process of copper(II) ion from aqueous solution using beads follows the Langmuir isothermal adsorption and the adsorption kinetic follows the pseudo-second-order equation. Hence, the adsorption mechanism follows a chemisorption process with monolayer formation on the PVA/Alginate containing banana peels. Further investigation was carried out and found that the surface reaction and film diffusion occurred at initial stage of contact time, adsorptive diffusion through pores occurred at the later stage.

Keywords: PVA/Alginate Beads, Banana Peels, pH, Isothermal Adsorption, Kinetic Adsorption

INTRODUCTION

An abundance of banana peels can be found in Indonesia, particularly in Palu, Central Sulawesi. Banana peels ended up in the garbage can of the household without further processing. To minimize banana peel waste, many researchers have utilized the banana peel as a biosorbent [1], [2], [3], [4]. However, the small size of the banana peel powder leads to the suspension of banana peel powder in the aqueous solution. Hence, the difficulty in the separation process of banana peel powder from the aqueous solution would have occurred. In order to improve the performance of banana peels as a biosorbent, the impregnation process of banana peels into PVA/Alginate beads is needed [5]. PVA/Alginate beads have been widely used as an encapsulant to impregnate various organic for drug delivery [6], [7], [8], [9] and inorganic materials [10]. In this study, we used PVA/Alginate beads to impregnate banana peel powder and apply the beads as biosorbent for copper(II) ion adsorption. There are many

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researchers reported that PVA/Alginate itself could adsorb metal ions owing to their active site attached to the molecule [11], [12], [13]. However, the active site is crosslinked with each other thus leading to a decrease in the adsorption ability of the beads. Hence, the PVA/Alginate beads are impregnated with banana peel powder to improve the adsorption ability of the beads [5].

As copper demand is increasing and copper waste is also increasing owing to many electronic devices discharged into the environment, the recovery of copper(II) ions from the discharged electronic are more important than copper mining. Therefore, the development of biosorbent PVA/Alginate containing banana peel powder is one of the promising biosorbents to accelerate the increasing of copper demand.

In order to understand the adsorption ability and the adsorption mechanism of copper(II) ion adsorbed into PVA/alginate beads containing banana peel powder, isothermal adsorption and adsorption kinetics were investigated. There are many reports relating to isothermal adsorption and adsorption kinetic studies [14], [15], [16], [17]. However, the isothermal adsorption and adsorption kinetic study of PVA/Alginate containing banana peel powder has not been reported. Thus, the focus of this study is investigating the pH effect, isothermal adsorption process, and adsorption kinetic process of copper(II) ion adsorbed into PVA/Alginate containing banana peel powder beads and the proposed adsorption mechanism that probably occurred during the adsorption process.

EXPERIMENT

Chemicals and instrumentation

Chemicals used in this study are the obtained PVA/alginate beads containing banana peels from a previous study [18], which consists of polyvinyl alcohol (Sigma), Alginate (Sigma), and banana peels (*Musa paradisiaca*). Other chemicals used are Cu(SO₄) 5H₂O, (NH₄)₂SO₄ 0.5 M, H₂SO₄ 1 M, NaOH 1 M, and distilled water. The instrumentation applied for analysis is the atomic absorption spectrophotometer (PG Instrument Model 990).

The pH effect procedure

A 0.2 g of PVA/Alginate beads containing banana peels was put into the vial bottle containing 30 mL of CuSO₄ 5 H₂O solution at various pH of extraction. The pH of extraction was controlled using H₂SO₄ 1 M and NaOH 1 M and was adjusted using ammonium sulfate. The extraction process was carried out by shaking the vial bottle using a shaker at 100 rpm for 24 hours. After the extraction process, the solutions were filtered and the copper(II) ion concentration before and after extraction was measured using an Atomic Adsorption Spectrophotometer (PG Instrument Model 990).

Isothermal adsorption procedure

A 0.2 g of PVA/Alginate beads containing various amounts of banana peel powder was put in 30 mL of Cu(SO₄) 5H₂O solution in vials with various concentrations of copper(II) ion solutions were 5, 10, 50, 100, 200, and 500 ppm. The extraction process was carried out using a shaker at room temperature for 24 hours. The solution was filtered and measured using an Atomic Adsorption Spectrophotometer (PG Instrument Model 990). The obtained data were analyzed using the following equations:

$$\text{Langmuir equation: } \frac{C_{eq}}{q_{eq}} = \left(\frac{1}{q_{max}} \right) C_{eq} + \frac{1}{K_{max}} \quad (1)$$

Where C_{eq} is an equilibrium concentration, q_{eq} is an equilibrium quantity amount of copper(II) ion extracted into the beads, q_{max} is the maximum quantity amount of copper(II) ion extracted into the beads, and K_{max} is the maximum constant of Langmuir.

$$\text{Freundlich equation: } \log q_e = \log K_f + \frac{1}{n} \log C_e \quad (2)$$

Where q_e is the adsorption quantity amount of copper(II) ion into the beads at equilibrium, C_e is the copper(II) ion concentration in the aqueous solution, K_f is the maximum constant of Freundlich, and n is an adsorption intensity.

Adsorption kinetic procedure

2 g of PVA/Alginate beads containing various amounts of banana peel powder was added into 600 mL of $\text{Cu}(\text{SO}_4) \cdot 5\text{H}_2\text{O}$ 500 ppm solution in 1000 mL of beaker glass. 20 mL of copper(II) ion solution was pipetted with intervals of contact time 0, 2, 5, 8, 11, 14, 17, 20, 30, 60, 180, 360, and 720 minutes. Furthermore, each solution was measured using an atomic adsorption spectrophotometer, and the obtained data were analyzed using the following equation:

$$\text{Pseudo-first Order [19]: } \log (q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (3)$$

Where q_e is the adsorption quantity amount at equilibrium, q_t is the adsorption quantity amount at a time, K_1 is the pseudo-first order constant, and t is time.

$$\text{Pseudo-second Order [20]: } \frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

Where K_2 is a pseudo-second-order constant.

$$\text{Intraparticle Diffusion [21]: } q_t = K_{id} t^{1/2} + C \quad (5)$$

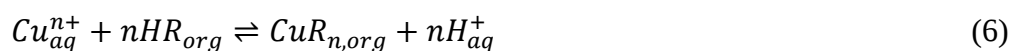
Where K_{id} is an intraparticle Diffusion constant and C is adsorbate concentration.

RESULT AND DISCUSSION

The pH effect on copper(II) ion from aqueous solution using PVA/Alginate beads containing banana peel

Copper(II) ion successfully adsorbed from aqueous solution using PVA/Alginate beads containing 2.5 g of banana peel in the range of pH 1-10 and reached the highest percentage content of copper(II) ion extraction into the beads was 72.32%. The quantity of copper(II) ions extracted into the beads increased as the pH range increased and reached the maximum quantity of copper(II) ions extracted into the beads at pH 4.

Considering the banana peels as a monomer with abundant active sites attached to the banana peels, the extraction equilibrium can be written as follows:



Where HR is banana peel, “aq” is the aqueous phase and “org” is organic phase. From equation 1, we can determine the equilibrium constant as follows:

$$K_{eq} = \frac{[CuR_n]_{org}[H^+]_{aq}^n}{[Cu^{n+}]_{aq}[HR]_{org}^n} \quad (7)$$

Considering the equilibrium concentration of banana peel in the organic phase is equal to its initial concentration because of the metal concentration in the organic phase are much lower than that of the initial ligand concentration, thus:

$$[HR]_{0,org} \approx [HR]_{org} \quad (8)$$

Using the mass balance equation for metal ions,

$$[Cu^{n+}]_{0,aq} = [Cu^{n+}]_{aq} + [Cu^{n+}]_{org} \quad (9)$$

here,

$$[Cu^{n+}]_{org} = [CuR_n]_{org} \quad (10)$$

and combining equation (9) and (10) thus the variation of metal ions in the organic phase as a function of pH in the aqueous phase can be calculated using equation (11).

$$[Cu]_{org} = \frac{K_{ex}[Cu^{n+}]_{0,aq}[HR]_{org}^n}{[H^+]_{aq}^n + K_{ex}[HR]_{org}^n} \quad (11)$$

If distribution ratio is:

$$D = \frac{[CuR_n]_{org}}{[Cu^{2+}]_{aq}} \quad (12)$$

Thus,

$$\log D = \log K_{eq} + n \log [HR]_{0,org}^2 + npH \quad (13)$$

By plotting log D and pH, we will obtain the value of n and K_{ex} . Value of n is indicating the active site of banana peel bonding with Cu(II) ion and K_{ex} is an equilibrium extraction constant. The plot between log D and pH (Figure 1) gives a straight line with slope (n) was 2.9233 which indicates that the adsorption process of copper(II) ion into the beads occurred by releasing $[H^+]$ ion with equilibrium constant was $6.91 \times 10^{-9} \text{ Kg}^2/\text{mol.dm}^3$.

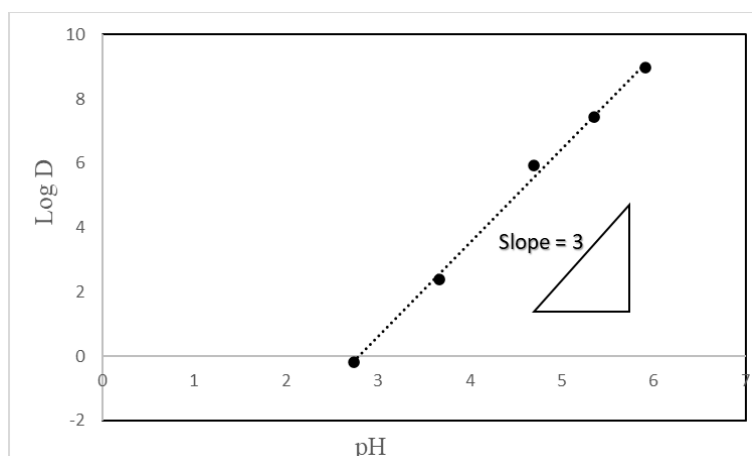


Figure 1. Log D versus pH

To be approved, the theoretical data was normalized to the experimental data using the obtained K_{ex} value and n value as shown in Figure 2.

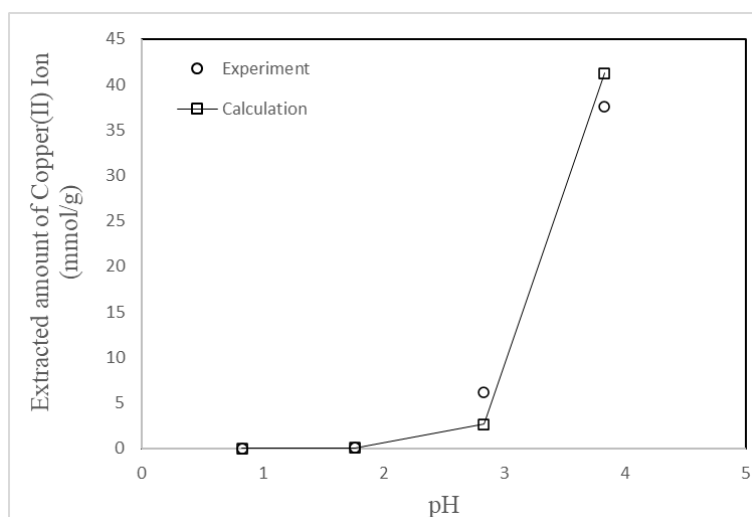


Figure 2. pH vs Extracted amount of copper(II) ion into the beads

The obtained slope and intercept from Figure 1 was used for further analysis using logarithm equation in equation 13 and the result shows that both experiment and calculation using the suggested equation give an optimum amount of copper(II) ion extracted into the beads was at pH 4.

In order to approve the above analysis which is $n = 3$, further analysis was carried out by analyzing the effect of initial concentration of the copper(II) ion towards the copper(II) ion adsorption into the beads. Effect of initial concentration of copper(II) ion in the extraction process of copper(II) ion into the beads containing various amount of banana peels is shown in Figure 3 by plotting $\log [HR]/[H^+]$ with $\log D/[H^+]$.

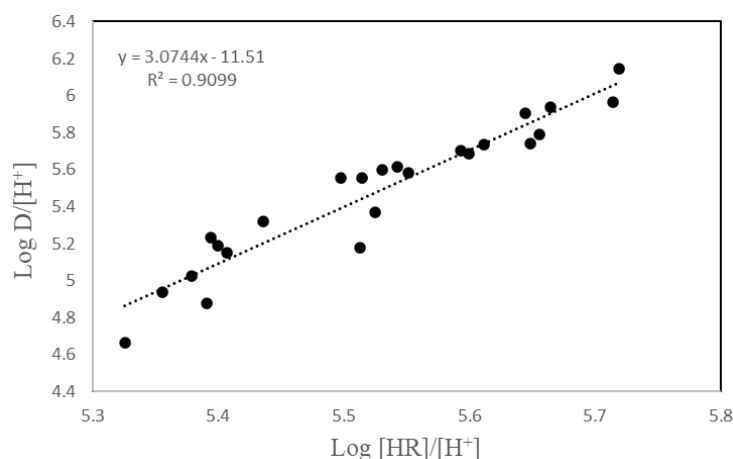


Figure 3. Log [HR]/[H⁺] vs log D/[H⁺] at various of initial concentration of copper(II) ion

The obtained slope is 3,0744 which indicating that n value in the above suggested equation (Eq. 13) is 3. The obtained experimental data of initial concentration effect was also analysis for further investigation and the calculation results are shown in Figure 4.

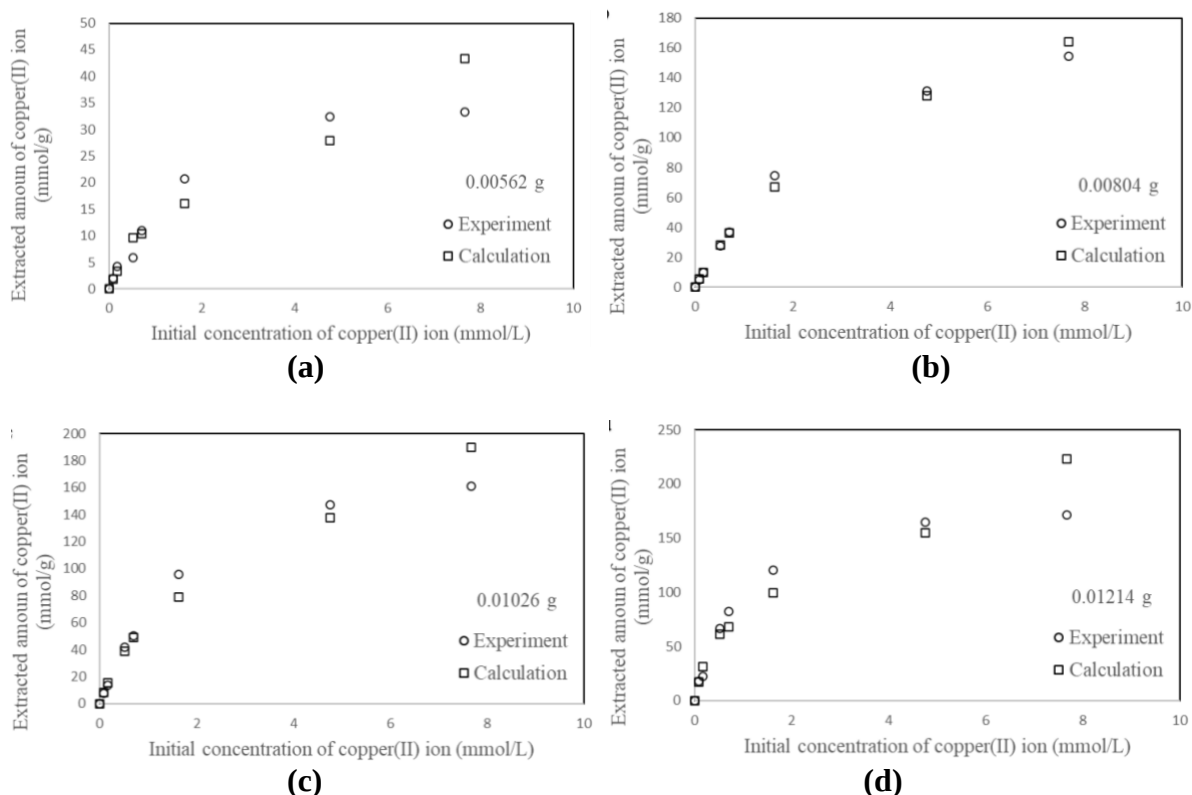


Figure 4. Initial concentration effect of copper(II) ion on copper(II) ion extraction using PVA/Alginate beads containing various amount of banana peels (a) 0.00562 g; (b) 0.00804 g; (c) 0.01026 g, (d) 0.01214 g

Figure 4 shows that the obtained experimental data and calculation data using equation 13 fits well with $n = 3$ which means that 3 mole of HR (banana peels) reacts with one copper(II) ion and form a complex compound. As shown in Figure 4, the amount of banana peels impregnated into the beads affected the amount of copper(II) ion extracted into the beads. As

the amount of banana peels impregnation in the beads increase, the amount of copper(II) ion extracted into the beads was also increased and reached the constant value at high initial concentration of copper(II) ion in the aqueous solution. At high initial concentration, the amount of copper(II) ion extracted into the beads increased and reached the constant value owing to the occurrence of the saturation condition of the beads. It means that all of the active site attached to the beads containing banana peels have occupied by the copper(II) ion.

Isothermal adsorption of copper(II) ion into PVA/Alginate containing banana peels

Further study was carried out in order to gain more information in adsorption mechanism of copper(II) ion from aqueous solution into the beads. Langmuir isotherm and Freundlich isotherm are common isotherm that have been used to analyzed the adsorption mechanism of adsorbate into adsorbent. As reported elsewhere [22], [23], Langmuir isotherm is describing a chemisorption process and forming a monolayer adsorption. Whereas Freundlich isotherm is describing a physisorption process and forming a multilayer adsorption. In order to understand the adsorption mechanism of copper(II) ion extracted from aqueous solution into the beads, whether chemisorption or physisorption, both isotherms were applied in this study.

The obtained experimental data was analyzed using Eq. 1 and Eq. 2 for Langmuir and Freundlich isothermal adsorption, respectively and the results are grouped in Table 1.

Table 1. Langmuir and Freundlich Isothermal Adsorption of Copper(II) Ion into PVA/Alginate Beads Containing Various of Banana Peels

Amount of impregnated banana peels (g)	Langmuir Isothermal Adsorption			Freundlich Isothermal Adsorption		
	R ²	q _{max}	K	R ²	n	K _f
0.00562	0.9551	0.0054	0.482	0.9576	1.5611	0.0014
0.00804	0.9951	0.0290	0.268	0.9786	1.2933	0.0051
0.01026	0.9966	0.0262	0.461	0.9631	1.4521	0.0066
0.01214	0.9978	0.0245	0.986	0.9349	1.8746	0.0095

Table 1 shows that R² value either in Langmuir isothermal adsorption or Freundlich isothermal adsorption are linear, closed to 1. However, the R² value of Langmuir isotherm is more linear than Freundlich isotherm. To be approved, the experimental data was substituted to the Eq. 1 and Eq. 2 to see the compatibility of experimental data with Langmuir or Freundlich isothermal adsorption as shown in Figure 5 and Figure 6, respectively.

Either Langmuir or Freundlich isothermal adsorption data show a compatibility with the experimental data. However, Figure 5 (b) and 6 (b) show that the experimental data fits well with the obtained data from Langmuir isothermal adsorption equation rather than the data obtained from Freundlich isothermal adsorption equation.

Eventhough the obtained experimental data give a straight line with a linearity closed to 1, however the theoretical analysis data by substituting the obtained experimental data into the Eq. 1 shows the obtained experimental data is following the Langmuir equation owing to the suitable point between the experiment and calculation using Langmuir equation as shown in Figure 5(b). Therefore, it can be concluded that the reaction mechanism of copper(II) ion extracted into the beads is chemisorption and forming a monolayer with covalent bonding. As reported elsewhere [22], [23], if the adsorption process is following a Langmuir equation, the reaction mechanism is chemisorption, the interaction between adsorbate and adsorbent is a

covalent interaction and formed a monolayer. In addition, by considering the linearity of Freundlich equation was closed to 1, thus the kinetic adsorption study was also investigated to ensure the reaction mechanism of copper(II) ion adsorption into the beads.

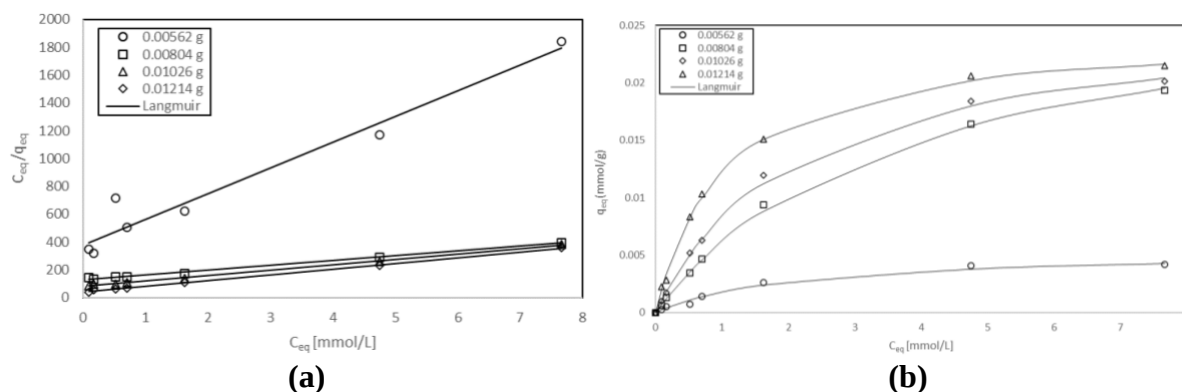


Figure 5. Langmuir Isothermal Adsorption of copper(II) ion into the beads: (a) plot C_{eq}/q_{eq} , (b) C_{eq} vs q_{eq}

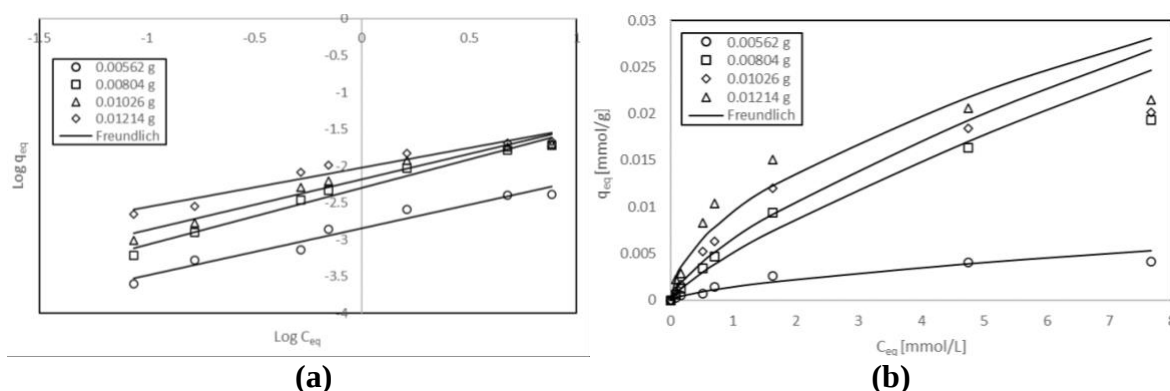


Figure 6. Freundlich Isothermal Adsorption of copper(II) ion into the beads: (a) $\text{Log } C_{eq}$ vs $\text{Log } q_{eq}$, (b) C_{eq} vs q_{eq}

Adsorption kinetic of copper(II) ion into PVA/Alginate containing banana peels

The adsorption kinetic study is conducted in purpose to investigate the reaction mechanism of copper(II) ion adsorption into PVA/Alginate beads containing banana peels. Three types of simple adsorption kinetic equation are applying in this study to analyze the obtained experimental data and identify the rate-controlling mechanism in copper(II) ion adsorption into the beads. The three most of adsorption kinetic models that have been widely used are pseudo-first order (PFO), pseudo-second order (PSO) and intraparticle diffusion (ID). The adsorption kinetic model can be analyzed in separate set of experimental adsorption process at constant temperature within time, thus the adsorption rate of copper(II) ion from the aqueous solution into the beads can be quantitatively calculated using PFO and PSO.

Pseudo-first order adsorption kinetic model

Pseudo-first order adsorption kinetic model was obtained by plotting the contact time (t) against $\log(q_e - q_t)$ and give a straight line where the q_e value is a slope and k is an intercept. The obtained q_e value and k value from the linearity of PFO equation as shown in Table 2 then used for further analysis.

Table 2. The q_e and K value obtained from Pseudo first-order and Pseudo-second order equation

Pseudo-first order Kinetic Adsorption Model			Pseudo-second order Kinetic Adsorption Model		
R^2	q_e [mmol/g]	K [min ⁻¹]	R^2	q_e [mmol/g]	K [g/mmol.min]
0.8479	54.459	0.0056	0.9988	109.877	6.97×10^{-4}

Figure 7 (a) and (b) represents how the suitability of the obtained experimental data with the PFO kinetic adsorption model by substituting the experimental data into the PFO equation. Figure 7(a) is a plot between contact time (t) against $\log(q_e - q_t)$ and Figure 7(b) is a plot between contact time (t) against quantity amount of copper(II) ion extracted into the beads (q_t). The results show that the obtained theoretical data from PFO equation by substituting the experimental data into PFO equation does not fit well with the whole range of contact time.

According to Ho and Mckay, 1998 [25] the PFO equation is applicable towards the obtained experimental data. However, it generally differs from the valid first order equation. First, the parameter of $k(q_e - q_t)$ does not describe the number of the available active site in the adsorbent. Second, the obtained value of $\log(q_e)$ is found to be not equal with the obtained intercept of a plot between t versus $\log(q_e - q_t)$. In the valid first order equation, the value of $\log(q_e)$ must be equal or closed to the plot between t versus $\log(q_e - q_t)$. Additionally, the value of q_e must be known in order to fit the theoretical data with the experimental data.

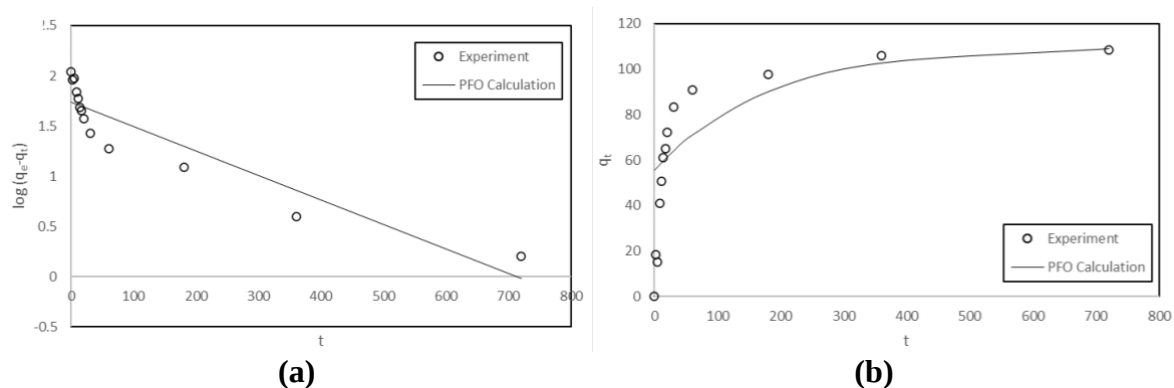


Figure 7. Pseudo-first order adsorption kinetic model

In most cases, the value of q_e is unknown and by considering the chemisorption process tends to be unmeasurably slow, thus the amount of copper(II) ion adsorbed into the beads is smaller than the equilibrium amount. Gerente, et. al. (2007) [26] reported that PFO equation does not fit well with the whole range of contact time and PFO generally applicable with the range of contact time at initial 30 minutes, thus, we try to analyze the experimental data separately for the initial 30 minutes and after 30 minutes of contact time using PFO equation. The result shows in Figure 8 and the q_e value is grouping in Table 3.

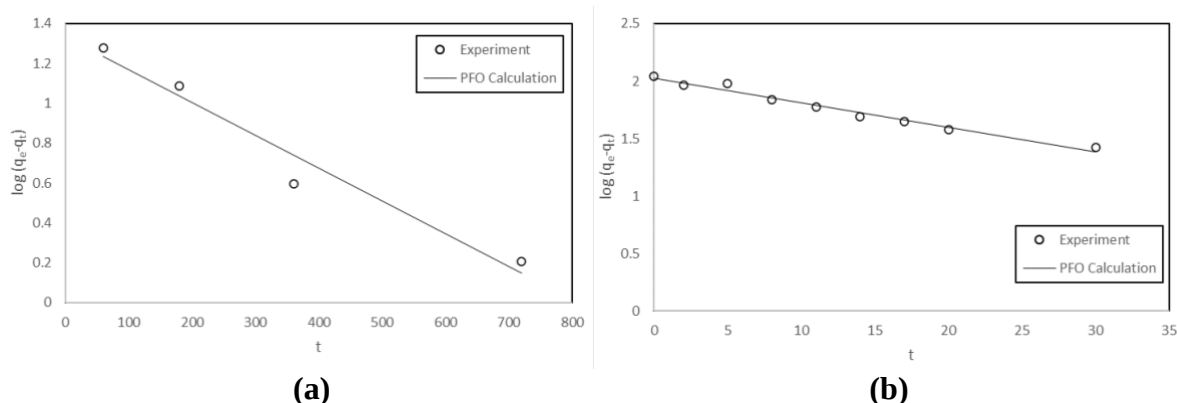


Figure 8. Pseudo-first order kinetic adsorption model (a) within 30 minutes of contact time, (b) after 30 minutes of contact time

Table 3. The q_e and K value obtained before and after 30 minutes of contact time using PFO equation

0-30 minutes of contact time			Over 30 minutes of contact time		
R^2	q_e [mmol/g]	K [min^{-1}]	R^2	q_e [mmol/g]	K [min^{-1}]
0.9756	105.2327	0.0488	0.9591	21.6735	0.0038

The experimental data was tested using the obtained PFO linearity equation and the result is shown in Figure 9. As shown in Figure 9, the experimental data fits well with the theoretical data by separately analyzing the contact time within 30 minutes and over 30 minutes. However, the obtained q_e value from the initial 30 minutes of contact time is closed to the q_e value obtained from PSO equation as discuss in the next section. It can be concluded that there are two steps in adsorption process of copper(II) ion into the PVA/Alginate beads containing banana peel.

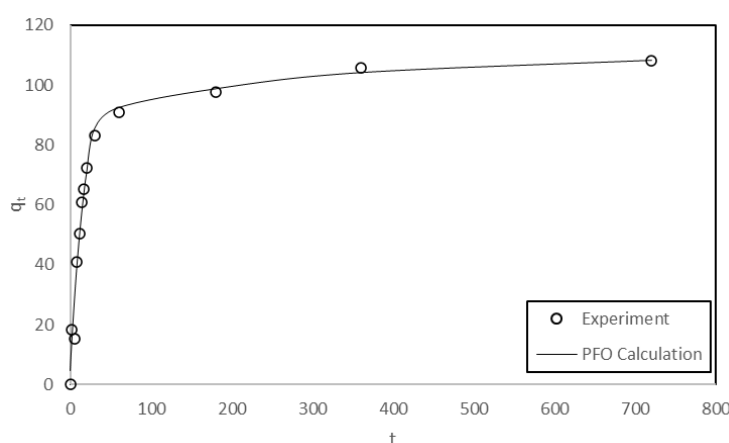


Figure 9. The compliance between experimental data with PFO calculation

Pseudo-second order adsorption kinetic model

Pseudo-second order adsorption kinetic model was carried out by plotting the contact time (t) against t/q_t and give a straight line with slope and intercept are q_e and k value, respectively. The obtained theoretical data by substituting the experimental data into PSO

equation (Figure 10) shows a perfect compliance between the experimental and theoretical data for the whole range of contact time. Therefore, the adsorption mechanism of copper(II) ion from aqueous solution into the PVA/Alginate beads containing banana peels follows the PSO equation and give a straight line with q_e and k value as shown in Table 2.

As reported by Zaini, et. al., (2022) [28], banana peel contains organic compounds that have an active polar sites such as fatty acids, amino acids, dietary fiber and also phenolic compounds that can be considered as a chelate agent to form a complex compound with copper(II) ion. These groups can be chemically involved in chemical bonding formation between banana peel and copper(II) ion. Therefore, these groups can consider to be responsible for cation exchange of banana peels with the copper(II) ion adsorption process.

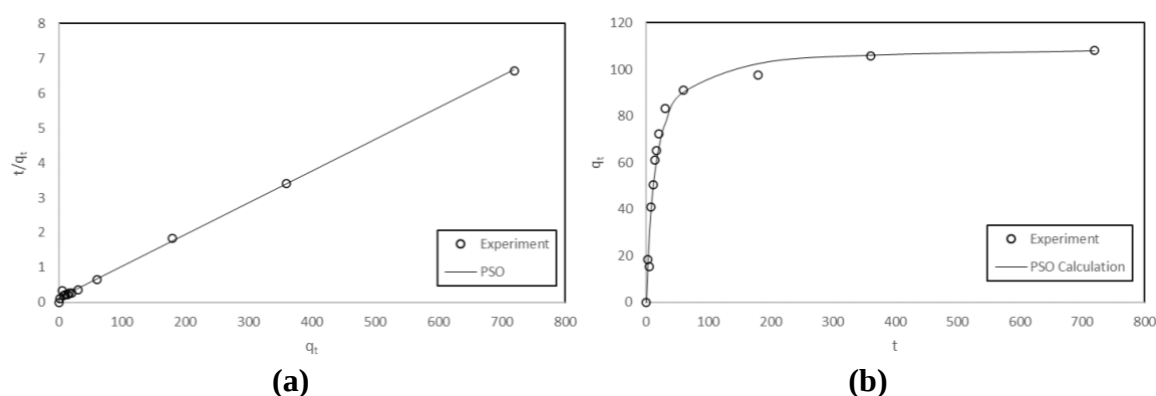


Figure 10. Pseudo-second order kinetic adsorption model

As the adsorption process of copper(II) ion into the beads follows the PSO adsorption kinetic model of the whole range of contact time, we can assume that the adsorption process of copper(II) ion into the beads is chemical adsorption or chemisorption by involving the valency forces through sharing or electron exchange between the active group in the banana peel with copper(II) ion as covalent forces and formed a copper(II) ion complex compound. The obtained q_e value from PSO linearity equation is 109.877 mmol/g and this value closed to the q_e value obtained from PFO linearity equation within initial 30 minutes of contact time. We can assume that during the adsorption process of copper(II) ion on the surface of the beads by chemisorption process, the adsorption through diffusion also occur through the interface. Thus, intraparticle diffusion also applied in this study for further adsorption kinetic mechanism analysis.

Intraparticle diffusion model

As a PVA/Alginate bead containing banana peels is a porous sorbent, it can be considered that there are four stages of adsorption process that probably take place. They are bulk diffusion, film diffusion, intraparticle diffusion and adsorption process of adsorbate on the sorbent's surface. Bulk diffusion and film diffusion in general are going fast, therefore it might be not assumed as a rate-determining step. In the aqueous phase, the surface of the pore in the sorbent probably hydrated and form a water layer on the surface wall. In addition, the water content presence in the beads leads to form a small pore inside the beads. Therefore, we can consider that pore and surface may play an important role in the adsorption process of copper(II) ion from aqueous phase into the beads.

According to Weber and Moris (1963) [21], if the rate-determining step in the adsorption process of adsorbate into the sorbent is intraparticle diffusion, then the plot between q_t versus

$t^{1/2}$ will give a straight line passing through the experimental data with R^2 value closed to 1. However, two scientists, McKay and Allen in 1980 [24], suggested that there are probably two or three stages occurred during the adsorption process. The first stage is an external adsorption stage or known as an instantaneous stage, second stage is gradual adsorption stage where the intraparticle diffusion is a controlling factor and the third is the final stage or known as equilibrium stages where the intraparticle diffusion starts to slow down owing to the low concentration of adsorbate in the aqueous phase.

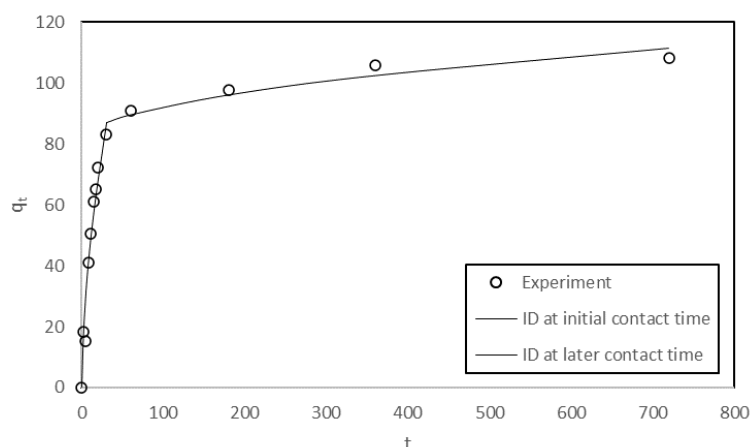


Figure 11. Intraparticle diffusion model

Figure 11 is a result of a compliance between experimental data and theoretical data by substituting the experimental data into the intraparticle diffusion equation. The experimental data was analyzed by separating the initial contact time as the first and second stage (0-30 minutes) and the final stage (30 – 720 minutes of contact time). By separating the adsorption stage into two stages, we therefore obtained 2 values of k_{id} and C for each stage. The values of k_{id} and C for each stage are grouping in Table 4.

Table 4. The K_{id} and C value obtained from Intraparticle diffusion equation

0-30 minutes of contact time			Over 30 minutes of contact time		
R^2	K_{id}	C	R^2	K_{id}	C
0.9479	16.6621	-5.947	0.9065	1.1432	80.641

Adsorption mechanism of copper(II) ion from aqueous phase into PVA/Alginate beads containing banana peel

By analyzing the obtained experimental data in all suggested equation above, we can assume that the adsorption mechanism of copper(II) ion from aqueous solution into the beads following the Langmuir equation and PSO adsorption kinetic model. However, by separating the data analysis at initial stage and later stage of contact time, we found that the adsorption process of copper(II) ion from aqueous solution into the beads was more complex. As shown in Table 4, the C value at initial stage of contact time was negative. According to Rudzinski and Plazinski (2008) [27], the negative value of C describes a combined effect of surface reaction control and film diffusion. Therefore, it can be assumed that either surface reaction and film diffusion were occurred at initial stage of contact time. Furthermore, the adsorption mechanism of copper(II) ion from aqueous solution into the beads can be described as follows:

(1) copper(II) ion was moved from aqueous solution into the surface area of beads through film diffusion process (external diffusion) and formed a covalent bonding with an active site attached on the surface of the beads, assuming a monolayer formation between adsorbate and adsorbent on the surface area; (2) there was a possibility of copper(II) ion transport from the external surface into the beads through the pores, (3) copper(II) ion reacted with the active group attached on the internal surface of beads, (4) the copper(II) ion adsorption reached their equilibrium condition at the later stage, assuming the diffusion of the copper(II) ion into the beads was decelerate. The illustration of copper(II) ion adsorption mechanism is shown in Figure 12.

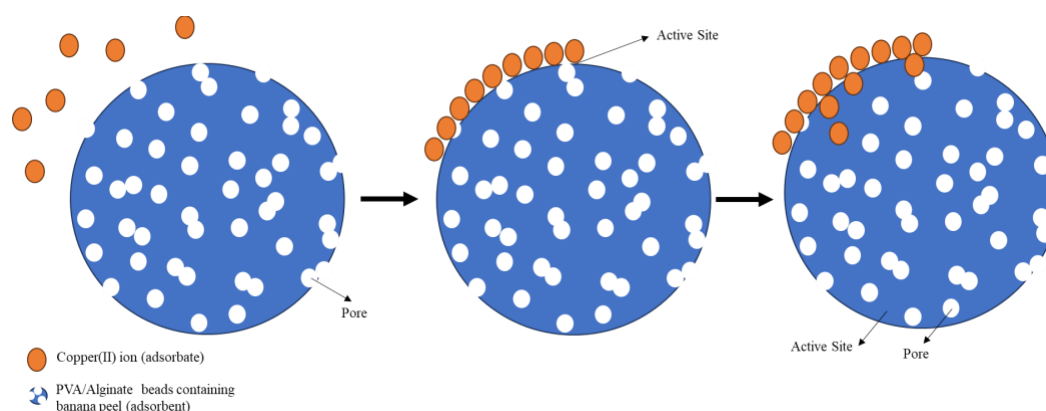


Figure 12. Adsorption mechanism of copper(II) ion into the PVA/Alginate beads containing banana peel

Following the Langmuir isothermal equation in adsorption thermodynamics equation using Gibbs free energy:

$$(\Delta G^0) = -RT \ln K \quad (14)$$

the value of Gibbs free energy was calculated using equation 14 by substituting the equilibrium constant (K) to the equation 14 thus the value of ΔG^0 for 0.00562 g, 0.00804 g, 0.01026 g, 0.01214 g banana peel content in PVA/Alginate beads were -1.836 kJ/mol, -3.319 kJ/mol, -1.982 kJ/mol, and -0.036 kJ/mol, respectively. The obtained ΔG^0 value show that the adsorption mechanism of copper(II) ion from aqueous solution into the beads was spontaneous. As reported elsewhere that the negative value of Gibbs free energy means the adsorption mechanism is spontaneous [29-31].

CONCLUSION

PVA/Alginate beads containing banana peels can be used for copper(II) ion adsorption from aqueous solution. The optimum adsorption pH of copper(II) ion was 4 with the amount of copper(II) ion adsorbed into the beads was 0.729 mmol/g. Based on the distribution ratio, the proposed mechanism of copper(II) ion adsorbed into the beads was 1:3 which means that 1 copper(II) ion reacted with 3 active groups attached on the banana peels and formed a complex. The obtained experimental data follows a Langmuir isothermal equation and Pseudo-second order kinetic adsorption model. Furthermore, the complexity of the copper(II) ion adsorption process into the beads was observed by separating the initial stage of contact time and later

stage of contact time. The obtained data shows that surface reaction and film diffusion occurred at initial stage of contact time and the diffusion of adsorptive substances into the internal surface of the beads occurred at the later stage. Thus, we can assume that surface reaction, film diffusion and pore diffusion have an important role in copper(II) ion adsorption into the beads at different contact time.

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