Aceh Int. J. Sci. Technol., 12(2) 297-303
August 2023
doi: 10.13170/aijst.12.2.27947

Aceh International Journal of Science and Technology
ISSN: p-2088-9860; e-2503-2398
Journal homepage: http://jurnal.usk.ac.id/aijst

Isotherm and Kinetic Adsorption of Cadmium (Cd) onto Biosorbent Made from *Kepok* Banana Peel (*Musa Acuminata balbisian*): The Effect of Activator Type and Biosorbent Dosage

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Received : September 06, 2022
Received in revised from July 24, 2023
Accepted : August 30, 2023
Online : August 31, 2023

Abstract - The present study determined the isotherm and kinetics model of the cadmium adsorption process onto a biosorbent made from *kepok* banana peel (*Musa Acuminata balbisian*). The experiments were carried out in batch process, laboratories scale, room temperature, pH of Cadmium of 4, volume of Cd solution of 20 ml, and biosorbent size particle of 60 mesh—the biosorbent produced using chemical activation method onto dry banana peel. The variation in this research was the type of activator (H_3PO_4 and H_2SO_4) and the biosorbent dosage (1, 1.5, and 2 g). The experimental data was used to calculate the Langmuir and Freundlich isotherm—Kinetics analysis based on pseudo-first-order and second-order kinetics models. The best condition of the cadmium removal occurred at 90 minutes of contact time and 2 g dosage for H_2SO_4 and H_3PO_4 activators. Cadmium biosorption was in accordance with the Langmuir isotherm and pseudo-second-order kinetic model. The linear equation obtained is positive, with the maximum adsorption capacity and the affinity constant. Cadmium adsorption onto banana peel biosorbents followed the Langmuir adsorption isotherm pattern, so chemical adsorption occurred in this study. Cadmium adsorption kinetics onto biosorbent that activated with an acid activator of H_3PO_4 and H_2SO_4 followed the pseudo-second-order kinetic model. The best condition of the cadmium removal occurred at 90 minutes of contact time and 2 g dosage for H_2SO_4 and H_3PO_4 activators. Cadmium biosorption in this study was in accordance with the Langmuir isotherm and pseudo-second-order

Keywords: Cadmium, Dosage, Activator, Isotherm, Kinetic

Introduction

Heavy metals contaminate various industrial wastes such as the textile industry, materials, mining, metal coating and mixing, the petrochemical industry, and the oil and gas processing industry (Kaewsarn, Saikaew, and Wongcharee 2008). Heavy metals in small amounts are dangerous because of their carcinogenic effect. Among the various types of heavy metals, cadmium is a dangerous heavy metal based on Indonesian Government Regulation No. 85 year of 1999 concerning B3 waste treatment. Cadmium metal has contaminated paddy soil in Jelegong Village, Bandung, producing liquid waste generated by the local textile industry equal to 0.02-0.17 mg/l (Komarawidjaja 2017). The case of cadmium pollution in Japan (*itai-itai disease*) was caused by mining carried out by Mitsui Mining and Smelting Co., Ltd. in 1967 with a total cadmium metal of 1-6.88 mg/l. *Itai-itai* disease causes chronic kidney and bone disease. Referring to the case, the grade II heavy metal content of cadmium based on Indonesian Government Regulation No. 82 year of 2001 concerning water quality management and water pollution control must not exceed 0.01 mg/l(Republik Indonesia 2001).

Some of the existing heavy metal waste processing technologies include precipitation, ion exchange, membrane separation, electrolysis, and solvent extraction (Nilanjana et al. 2008). These processes generally require high costs and are less effective when applied to low concentrations of waste (Ashraf, Maah, and Yussof 2010)—An alternative treatment to process cadmium waste that is low cost and efficient is the biosorption process. The biosorption process uses biomass to absorb heavy metals. One biosorbent was made from *kepok* banana (*Musa Acuminata balbisian*) peels. Banana peels have not been used effectively daily, making them a waste to the surrounding environment.

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Sanjaya and Agustine (2015) researched the ability of activated charcoal from banana peels to absorb lead (Pb) waste. The maximum adsorption capacity was 1.4582 mg/g with a gram of adsorbent dosage and followed the Langmuir isotherm and second-order kinetics model (Sanjaya and Agustine 2015). Kurniati et al. (2019) studied the kinetic adsorption of activated carbon from *kepok* banana peels to adsorb methylene blue in the textile industry waste. The adsorption kinetics of this study used pseudo-first and pseudo-second-order models. The pseudo-first-order model produced k1 adsorption constants for the ratio of NaOH activators of 0.1 N and 0.5 N, which were 0.0066 and 0.0033 $min^{-1,}$ respectively. The second pseudo-order model produced a k2 adsorption constant of 1.8172 and 1.2539 min^{-1} (Kurniati, Putri Prastuti, and Lutfi Septiani 2019). Deshmukh et al. (2017) adsorb cadmium solution using banana peels as biosorbents. The maximum condition is pH 4-7, with 85% cadmium metal absorption. This study follows the Langmuir isotherm model (Deshmukh et al. 2017).

The biosorption process in conditions that are not optimum can cause excessive use of reagents and spend much time for results that are not optimal. Therefore, efficiency in the process is important in the biosorption process. One parameter affecting the process is the kinetics rate of adsorption. The kinetics rate of adsorption is the adsorption rate of adsorbent by contact time. This is useful to know the adsorption kinetics constant so that the adsorption process in batches can be carried out continuously with the adsorption column for industrial scale. Kinetic analysis is based on a pseudo-first-order and pseudo-second-order kinetics model. The absorption pattern of biosorbents also needs to be known to calculate the maximum capacity and determine the type of adsorption that occurs. This study aims to determine the appropriate isotherm and kinetic models in the cadmium adsorption process by looking at the adsorption capacity in the biosorbent doses and acid activator variation.

Materials and Methods

Tools and Materials

The tools were Atomic Absorption Spectroscopy (AAS), Erlenmeyer, measuring cup, beaker glass, measuring flask, stirring rod, spatula, oven, magnetic stirrer, filter paper, funnel, blender, 60 mesh sieve, pH meter, and analytical balance.

The materials were *kepok* Banana peel (*Musa acuminata balbisian L.*), aqua dest, 6M H_3PO4 technical solution, 2M H2SO4 technical solution, and 2 ppm Cd (Cadmium) solution.

Procedures

Production of biosorbents was as follows: separated the layer insides of the banana peels, washed the banana peels with water, then dried under the sun for 2 days. After that, the banana peels were crushed in a blender, and then reduced the particle size to 60 mesh. Dried banana peel powders were mixed with an activator, which was a weight and volume ratio between the activator to the biosorbent of 2:1. The mixtures were stirred by using a magnetic stirrer at a speed of 90 rpm for 30 minutes, washed the biosorbent with aqua dest until neutral, and then dried the biosorbent by using the oven at temperature 105^{o}C.

The method of making cadmium solution according to SNI 6989.16: 2009 standard with a pH of 4. The adsorption process was carried out by mixing 1 g, 1.5 g, and 2 g of activated biosorbent into 20 ml cadmium solution at pH 4. Then, the solution was stirred using a magnetic stirrer at 90 rpm for 10, 45, 90, and 120 minutes. The solution was filtered to take the filtrate and then analyzed with an Atomic Absorption Spectroscopy (AAS).

Adsorption Isotherm

The Langmuir and Freundlich determined the adsorption isotherm model. Research data is plotted based on equation (1) and equation (2), respectively. C_e is the concentration of the solute, q_m is the maximum adsorption capacity, q_e is the absorbed solute value, b is the affinity constant, K_f is the Freundlich constant, and $\frac{1}{n}$ is the heterogeneity factor.

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m b} \quad (1)$$

$$\text{Log } q_e = \text{Log } K_f + \frac{1}{n} \text{ Log } C_e \quad (2)$$

Aceh Int. J. Sci. Technol., 12(2) 297-303
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Adsorption Kinetic

Determination of the adsorption kinetics was done to determine the final concentration value (C_A) by using the pseudo-first-order at equation (3) and pseudo-second-order at equation (4), making a graph of the relationship between time (*t*) and C_A, and determining the coefficients of the constant k1 and k2 from the linear equation slope. C_A is the final concentration, C_{Ao} is the initial concentration, k is the adsorption kinetic constant, and t is the adsorption time.

$$\text{Ln } C_A = \text{ln } C_{Ao} - kt \quad (3)$$

$$\frac{1}{Ca} - \frac{1}{Cao} = kt \quad (4)$$

Result

Adsorption Isotherm

The Langmuir and Freundlich isotherms determined the adsorption isotherm model in this study. The activator in this study was an acid solution, which is a weak acid of H_3PO_4 and a strong acid of H_2SO_4. The Langmuir Isotherm model for the biosorbent that activated with H_3PO_4 can be seen in Figure 1. Cadmium metal biosorption with biosorbent *kepok* banana peel, as shown in Figure 1, was excellent, where the R^2 value at each biosorbent dose was 1. With this linear equation, the maximum adsorption capacity (q_m) and the affinity constant (b) can be determined, as shown in Table 1.

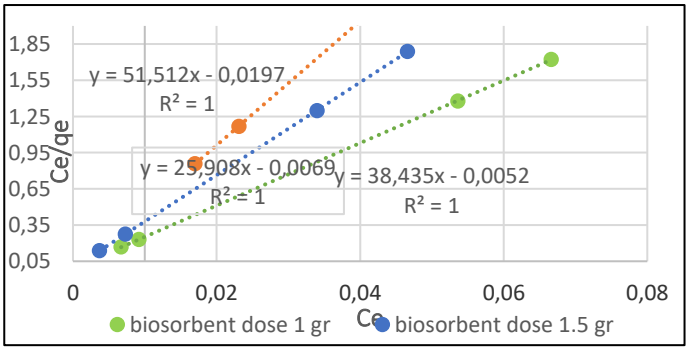

Figure 1. Langmuir isotherm model for cadmium solution onto *kepok* banana peel biosorbent that activated with H_3PO_4

Table 1. Langmuir isotherm constant of cadmium removal onto *kepok* banana peel biosorbent that activated with H_3PO_4

Biosorbent Dosage	R^2	q_m (mg/g)	b
1 g	1	0.0260	7391
1.5 g	1	0.0385	3754
2 g	1	0.0196	12755

The Langmuir Isotherm model of the biosorbent of *kepok* banana peel that activated with H_2SO_4 can be seen in Figure 2. The regression value of Figure 2 showed a similar trend to Figure 1; cadmium metal adsorption on biosorbent with H_2SO_4 activator, as shown in Figure 2, was excellent, where the R^2 value at each biosorbent dose was 1. The linear equation obtained is positive, with the maximum adsorption capacity (q_m) and the affinity constant (b), as shown in Table 2.

Referring to Tables 1 and 2, it can be seen that the maximum adsorption capacity with H_3PO_4 activator was 0.0385 mg/g takes place when the mass of the adsorbent was 1.5 grams, and the H_2SO_4 activator was 0.0380 mg/g at the mass of 1 gram adsorbent.

Aceh Int. J. Sci. Technol., 12(2) 297-303
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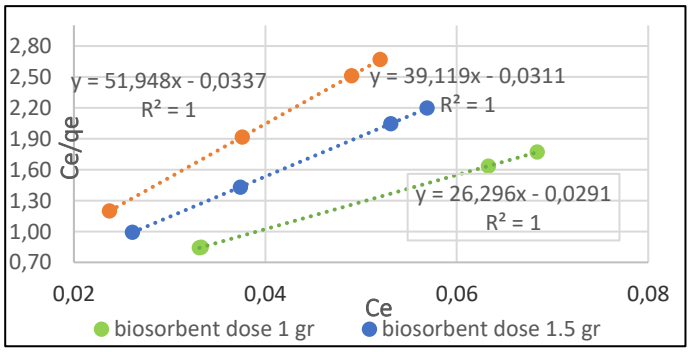
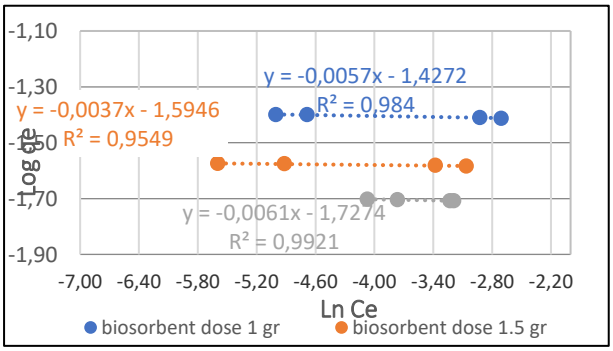


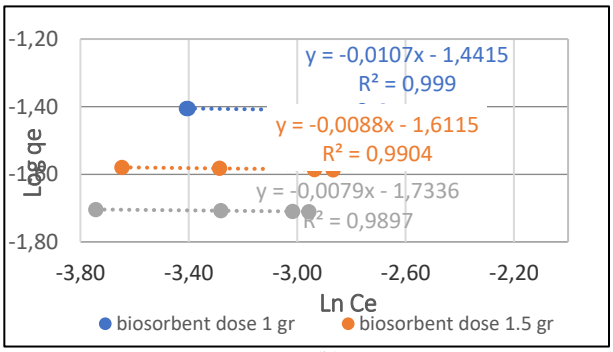
Figure 2. Langmuir isotherm model for cadmium solution onto *kepok* banana peel biosorbent that activated with H_2SO_4

Table 2. Langmuir isotherm constant of cadmium removal onto *kepok* banana peel biosorbent that activated with **H_2SO_4**

Biosorbent Dosage	R^2	q_m (mg/g)	b
1 g	1	0.0380	903.643
1.5 g	1	0.0255	1257.85
2 g	1	0.0192	1542.55



(a)



(b)

Figure 3. Freundlich isotherm model for cadmium solution onto *kepok* banana peel biosorbent that activated with (a) H_3PO_4 (b) H_2SO_4

The Freundlich isotherm model can be seen in Figures 3(a) and 3(b) for the biosorbent of *kepok* banana peel-activated H_3PO_4 and H_2SO_4 solution. Adsorption of Freundlich isotherms takes place on heterogeneous and multilayer surfaces. The solid nature of the adsorbent and temperature depend on the K_f and n values. In addition, the K_f value defines the adsorption capacity in the Freundlich isotherm model because it reflects the number of cavities available in the adsorbent (Singh and Allowai 2006). The constant of Freundlich isotherm is shown in Tables 3 and 4.

Table 3. Freundlich isotherm constant of cadmium removal onto *kepok* banana peel biosorbent that activated with H_3PO_4

Adsorbent Dosage	R^2	K_f	n
1 g	0.9840	0.04	-76.34
1.5 g	0.9549	0.03	-117.65
2 g	0.9117	0.02	-172.41

Table 4. Freundlich isotherm constant of cadmium removal onto *kepok* banana peel biosorbent that activated with H_2SO_4

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Adsorbent Dosage	R^2	K_f	n
1 g	0.9999	0.04	-40.82
1.5 g	0.9904	0.02	-49.50
2 g	0.9897	0.02	-54.95

Adsorption Kinetic

The determination of first-order in the cadmium adsorption process with banana skin biosorbents was carried out by linear regression using first-order equations presented in Figure 4. The determination of second-order in the cadmium adsorption process with banana skin biosorbents was done by linear regression using second-order equations, which can be seen in Figure 5.

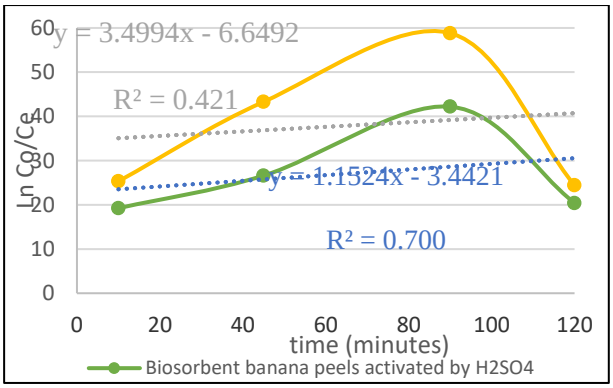

Figure 4. First-order Kinetics Model

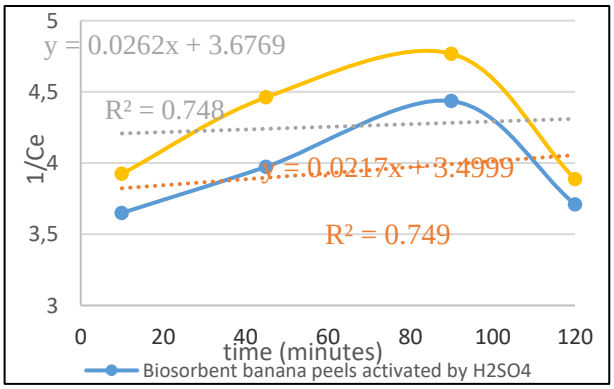

Figure 5. Second-order Kinetics Model

Table 5. Kinetic adsorbent constant

Subject	Activated biosorbent of H_3PO_4		Activated biosorbent of H_2SO_4	
	first	second	first	second
R^2	0.421	0.748	0.700	0.749
Constant	3.4494	0.0262	1.152	0.0217

Discussion

Adsorption Isotherm

The adsorption isotherm in the adsorbent is one of the important parameters to determine the characteristics of an adsorbent in determining the kinetics of the adsorption rate of an adsorbate on the surface of the adsorbent (Holle, Wuntu, and Sangi 2013). The kinetics rate is used to determine the kinetics constant of adsorption so that the adsorption process in batches in this study can be carried out continuously with the adsorption column for the industrial scale. The adsorption isotherm is also used to determine the energy produced by the adsorption process of an adsorbate on the surface of the adsorbent so that the interaction between the adsorbate and the adsorbent can be known, whether the interaction is physical or chemical. Adsorption isotherm is also used to determine the absorption pattern of biosorbents using several isotherm models.

The Langmuir and Freundlich isotherms determined the adsorption isotherm model in this study. Figure 1 and 2 shows the Langmuir Isotherm model for the biosorbent that activated with H_3PO_4 and H_2SO_4. The linear equation obtained is positive, with the maximum adsorption capacity (q_m) and the affinity constant (b), as shown in Tables 1 and 2. The low adsorption capacity is due to this study's initial concentration being too low. The affinity constant (b) showed the strength of the adsorbate molecule bound to the surface of the adsorbent (Sanjaya and Agustine 2015). A large value of b indicates that the bond is not quickly broken. Activated charcoal from banana peels was used to absorb lead (Pb) waste, the maximum adsorption capacity was 1.4582 mg/g, which is with 1 gram of adsorbent dosage and adsorption isotherm following Langmuir isotherm model (Sanjaya and Agustine 2015). The biosorption of dyes with activated and inactivated banana skin biosorbents has an

doi: 10.13170/aijst.12.2.27947

adsorption capacity of 19.671 mg/g and 18.647 mg/g, and the isotherm model that fitted the experimental data with Langmuir isotherm (Amela, Hassen, and Kerroum 2012). The research on the biosorption of lead metal (Pb) and cadmium (Cd) using banana skin biosorbents with a maximum adsorption capacity of 2.18 mg/g for lead and 5.71 mg/g for cadmium (Anwar et al. 2010). Based on previous studies, it can be stated that the biosorbent of *kepok* banana peel has a good ability to absorb heavy metals or dyes.

Figure 3 (a) and (b) shows the Freundlich isotherm model for biosorbent of *kepok* banana peel activated H_3PO_4 and H_2SO_4 solution. The linear equation obtained is negative, although the R^2 value obtained in the Freundlich isotherm model is close to 1. A negative slope value produces negative n, so the cadmium metal biosorption follows the Langmuir isotherm model. Langmuir isotherm model has a negative slope and intercept value, so the study's adsorption processors do not follow the Langmuir isotherm model (Kiurski et al. 2013). The results of the Freundlich isotherm equation in this study have negative slope (n) and intercept (log K_f) values. This indicates that the adsorption of cadmium metal in this study does not follow the Freundlich isotherm model.

This study's cadmium metal adsorption process follows the Langmuir isotherm model, indicating that chemical adsorption occurs (Sanjaya and Agustine 2015; Deshmukh et al. 2017). Chemical adsorption occurs because adsorbates form chemical bonds with the surface of the adsorbent. This was proven by the results of FTIR analysis in this study, where there was a change in the absorption band in the functional group due to an ion-exchange event between the functional groups in the biosorbent of *kepok* banana peel with cadmium metal ions. The chemical bond in the adsorption process causes a high-affinity constant (b) value so that the bond between the adsorbate and the adsorbent is not easily separated. Although there are chemical bonds and a high rate of affinity constants, the adsorption of cadmium metal with biosorbent banana peels is not very stable because of the bonds formed by covalent bonds shown in the graph where the percentage of adsorption trends is still up and down.

Chemical adsorption also occurs because the adsorbent is given a certain treatment; in this case, it is activation with a solution of H_3PO_4 and H_2SO_4, which aims to activate the surface site, remove impurities in the biosorbent and create an acidity atmosphere appropriate for the cadmium adsorption process that is sensitive to pH changes. Besides, the activation process in chemical adsorption causes the adsorbate to have minimum energy so that it can be absorbed by the surface of the adsorbent so that the percentage of absorption of cadmium metal in this study is very high, namely 99.91%. Chemical adsorption only forms one layer (monolayer) because the surface of the adsorbent can only bind to one metal ion, following the working principle of ion exchange.

Adsorption Kinetic

The adsorption kinetics study was carried out to determine the adsorption velocity, which was marked by changes in the concentration of the adsorption substance, analyze the value of k (slope), and find out the adsorption mechanism that occurred. Experimental data were tested using pseudo-first-order (Equation 3) and pseudo-second-order (Equation 4). Determination of the adsorption kinetics model using the optimum conditions of the study, namely at pH 4 and a dose of 2 grams for biosorbent banana peels activated by H_3PO_4 and H_2SO_4. Referring to Figures 4 and 5, the alignment between the predicted value and experimental data was expressed by the regression coefficient (R^2). The highest regression coefficient value on experimental data of adsorption kinetics rate is considered the most suitable model. From the data in Table 5, it can be concluded that cadmium adsorption with both H_3PO_4 and H_2SO_4 activated banana skin biosorbents follows the pseudo-second-order kinetic model based on the value of linear correlation coefficient, which is close to 1. The pseudo-second-order kinetics states that the adsorption mechanism depends on the adsorbent and adsorbate; in this case, the nature of the adsorbent and the functional group on the adsorbent influences the kinetics of pseudo-second-order (Masoumi, Ghaemy, and Bakht 2014). The rate-limiting step in the mechanism of the adsorption process is chemisorption, where there is an electron exchange or ion exchange in the adsorption process (Vimonses et al. 2009). This is following the Langmuir isotherm model principle. Other studies using banana peel biosorbents followed the pseudo-second-order kinetics model (Sanjaya and Agustine 2015; Deshmukh et al. 2017; Amela, Hassen, and Kerroum 2012; Anwar et al. 2010).

Conclusion

The adsorption isotherm in the adsorbent is one of the important parameters to determine the characteristics of an adsorbent in determining the kinetics of the adsorption rate of an adsorbate on the surface of the adsorbent. The Langmuir and Freundlich isotherms determined the adsorption isotherm model for the biosorbent that activated with H_3PO_4 and H_2SO_4. The linear equation obtained is positive, with the maximum adsorption capacity and the affinity constant. Cadmium adsorption onto banana peel biosorbents followed the Langmuir adsorption isotherm pattern, so chemical adsorption occurred in this study. Cadmium adsorption kinetics onto biosorbent that activated with an acid activator of H_3PO_4 and H_2SO_4 followed the pseudo-second-order kinetic model. The best condition of the cadmium removal occurred at 90 minutes of contact time and 2 g dosage for H_2SO_4 and H_3PO_4 activators. Cadmium biosorption in this study was in accordance with the Langmuir isotherm and pseudo-second-order

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