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Pb(II) Removal from Aqueous Solutions Using Citric Acid Modified Kepok Banana Peel: Batch and Kinetic Studies

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Industrial processes are the main source of Pb(II) contamination of natural water bodies. Pb(II) is a non-biodegradable heavy metal and carcinogen. The recent study explored the ability of citric acid-modified-kepok banana peel (CA-BP) to remove Pb(II) from an aqueous solution using the batch method. The adsorption capacity of kepok banana peel (BP) was also investigated for comparison. The optimum conditions for Pb(II) removal using kepok banana peel were achieved at pH 5, initial concentration of 600 mg l^{-1}, contact time of 75 min, and agitation speed of 100 rpm, with an adsorption capacity of 36.478 mg g^{-1}. Meanwhile, the adsorption capacity of citric acid modified-kepok banana peel was 64.088 mg g^{-1}, which was reached at pH 5, initial concentration of 850 mg l^{-1}, contact time of 75 min, and agitation speed of 150 rpm. The adsorption of Pb(II) onto both sorbents followed the Langmuir isotherm model and pseudo-second-order model, indicating monolayer adsorption with chemical interaction as a rate-limiting step. A Fourier Transform Infra-Red (FTIR) analysis was conducted to identify the functional groups present in the biosorbent and demonstrate a change in the wave number. The surface morphology of the biosorbent was examined using Scanning Electron Microscopy (SEM) before and after the absorption of Pb^{2+} metal ions. The objective of Energy Dispersive X-ray (EDX) is to quantify the elemental composition of the biosorbent derived from the surface of the kepok banana peel. An X-ray fluorescence (XRF) analysis was conducted to determine the chemical composition of the surface of the kepok banana peel biosorbent. Thermogravimetric Analysis (TGA) was conducted to observe the decrease in mass of the biosorbent as the temperature increased.

Keywords: Citric acid, Isotherm, Kepok banana peels, Kinetic, Pb(II)

INTRODUCTION

Natural resources that are carried out carelessly can have an impact on the environment. Types of pollutants, such as organic, inorganic, metal, gas, and others can pollute the environment [1]. Wastewater produced by various industries is made up of harmful compounds. Those compounds enter the aquatic environment, including heavy metals, pesticides, detergents, particulates, and so on. Heavy metals are the second most dangerous and toxic pollutant that induce reactive oxygen species (ROS) formation, causing lethal diseases [2]. The electroplating process, wood, batteries, *etc.* Generate significant quantities of heavy metals (such as cadmium, zinc, lead, chromium, nickel, copper, vanadium, platinum, silver, and titanium) [3]. Industries that produce inorganic pigments also discharge chromium and cadmium sulfide [4].

Lead Pb(II) is a toxic heavy metal that is dangerous and threatens the life of living creatures [5,6]. For humans, Pb(II) will harm tissue and organs, causing cancer and organ failure [7-9]. According to the WHO, the maximum allowable limit for drinking for Pb(II) is 0.01 mg l^{-1} [10], and based on the Ministry of Environment and Forestry of the Republic of Indonesia's methodology and requirements for waste management B3, the standard quality of metal wastewater Pb(II) is 0.1 mg l^{-1} [11]. Consequently, it is

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mandatory to remove Pb(II) from wastewater. The distribution of Pb(II) is originally associated with mining, pesticides, municipal sewage sludge, fertilizers, and industrial wastes that are released into aquatic ecosystems [12].

Various methods have been employed for handling this issue, such as chemical precipitation, ion exchange, electrodialysis, and membrane separation [13,14]. However, these methods are expensive and ineffective and cost a lot to maintain. Therefore, an efficient, easy, and low-cost method such as adsorption is required [15-17]. Biosorption is an eco-friendly and inexpensive method that is used for the extraction of metal ions from contaminated water [1,18]. The adsorption method utilized low-cost adsorbents such as sago bark as an adsorbent for Pb(II) removal with an absorption capacity of 31.4375 mg g^{-1} [19], reduced graphene oxide [20], zeolite [21] and activated carbon [22].

In this research, kepok banana peel was used to remove Pb(II) from aqueous solutions. Kepok banana peel is an agricultural by-product of banana plantations. Kepok banana peel contains useful functional groups such as carboxyl and hydroxyl. Those functional groups can bind heavy metals, reducing their concentration in solution [23-25]. Moreover, recent research aims to enhance the adsorption capacity of kepok banana peels using citric acid as a modifier. Previous studies have utilized citric acid-modified lemon grass leaves to remove methylene blue in an aqueous solution. The citric acid addition to lemon grass leaves could increase the adsorption capacity of lemon grass leaves from 43.1556 mg l^{-1} to 122.1211 mg l^{-1}. Citric acid is claimed to encourage esterification of hydroxyl and carbonyl groups [26]. Thus, this study will evaluate the citric acid modified-kepok banana peel's ability to reduce Pb(II) concentration in an aqueous solution. The batch method is employed to examine the parameters that affect the adsorption capacity of the adsorbent. The mechanism of adsorption is also observed using isotherms and kinetic models.

EXPERIMENTAL

Materials and Reagents

Kepok banana peel was taken from a local market in Padang City, West Sumatera, Indonesia. The adsorbate employed was $Pb(NO_3)_2$ (Merck), whereas citric acid ($C_6H_8O_7$) (Merck) was used as a modifier for the kepok banana peel. The utilization of sodium dihydrogen phosphate (NaH_2PO_4) (Merck) was catalyzed to expedite the contact process. Nitric acid (HNO_3 pro analysis 65%) (Merck) was used for the activation of the biosorbent. The pHpzc analysis utilized potassium chloride (KCL 99%) (Merck) and sodium hydroxide (NaOH) (Merck) as pH regulators.

Sample Preparation and Modification

The preparation was carried out by washing the banana peel and cutting it into small pieces. The banana peel is dried at 60 ºC for 24 h. The sample was then mashed using a blender and sieved through a 180 µm sieve. The activation process was done by soaking 50 g of kepok banana peels in 350 ml of 0.1 M HNO_3 for 2 h [15,27]. Then it was washed with distilled water until a neutral pH was reached and air-dried.

The modification process was conducted by mixing 2 g of kepok banana peel with 0.3 g of citric acid, 0.25 g of sodium dihydrogen phosphate, and 30 ml of distilled water. After being homogeneous, the mixture was ultrasound for 15 min and then heated in a water bath for an hour. After that, it was dried at 140 ºC for 4 h. After heating and cooling to room temperature, the mixture was rinsed with 500 ml of distilled water to remove citric acid residue and sodium dihydrogen phosphate. The sample was then filtered using a vacuum pump and dried at 60 ºC until a constant weight was obtained. It was then stored in a desiccator and labeled citric acid modified-kepok banana peel (CA-BP) [28].

Batch Adsorption Studies

The batch adsorption process was carried out at different parameters such as pH (2-7), initial concentration (150-1000 mg l^{-1}), contact time (45-125 min), and agitation speed (50-250 rpm). 0.2 g of citric acid modified-kepok banana peel was put into a Pb(II) solution and shaken for a particular contact time. The concentration of Pb(II) was measured using an Atomic Absorption Spectrophotometer (AAS). The amount of metal ions Pb(II) adsorbed was determined by the following Eqs. (1) and (2):

$$q = \frac{(\mathrm{Co-Ce})}{\mathrm{m}} \times V \tag{1}$$

$$\%R = \frac{(Co - Ce)}{Co} \times 100\% \quad (2)$$

q (mg l^{-1}) is the adsorption capacity, %R is the removal efficiency, C_0 and Ce (mg l^{-1}) are the initial and final concentrations of Pb(II), m (g) is the mass of citric acid modified-kepok banana peel (CA-BP), and V (l) is the volume of the Pb(II) metal solutions.

The adsorbent was characterized using a shaker (Edmun Buhler 7400 Tubingen), a mortar grinder (Fritsch, Germany), a pH meter (Metrohm), an analytical balance (Kern & Sohn GmbH), an electric oven (Memmert), and a sieve (Fritsch, Germany). The instruments used were the Atomic Absorption Spectrophotometer (AAS) (Thermo Scientific iCE 3000), Fourier Transform Infrared (FTIR) (IRTracer-100-Shimadzu), Scanning Electron Microscope-Energy Dispersive X-ray (SEM-EDX) (Hitachi FLEXSEM 1000), X-Ray Fluorescence (XRF) (Panalytical Epsilon 3), and Thermogravimetric Analysis (TGA).

Point of Zero Charge

0.5 g of adsorbent was added to KCl 0.1 M with different pH. The mixture was shaken for 24 h, and the final pH was measured for point of zero charge plotting [29].

RESULTS AND DISCUSSION

Effect of pH

pH provides a significant effect on the adsorption capacity and the ionization of the active site on the biosorbent. The pH point of zero charge (pH_{PZC}) is the pH value at which the surface charge is equal to zero. If the pH of the solution is lower than pHpzc, the surface charge on the adsorbent becomes positive, and protonation of the functional groups occurs due to the adsorption of excess H^+. Conversely, if the pH of the solution is greater than pHpzc, the surface charge of the adsorbent becomes negative, and deprotonation of the functional groups occurs due to the adsorption of excess OH^- [29].

Figure 1 shows that the optimum pH was obtained at pH 5, with an adsorption capacity of 31.632 mg g^{-1} for BP and 31.723 mg g^{-1} for CA-BP. At a lower pH value, minor adsorption capacity was obtained because, in an acidic condition, the solution contains a lot of H^+ ions, which

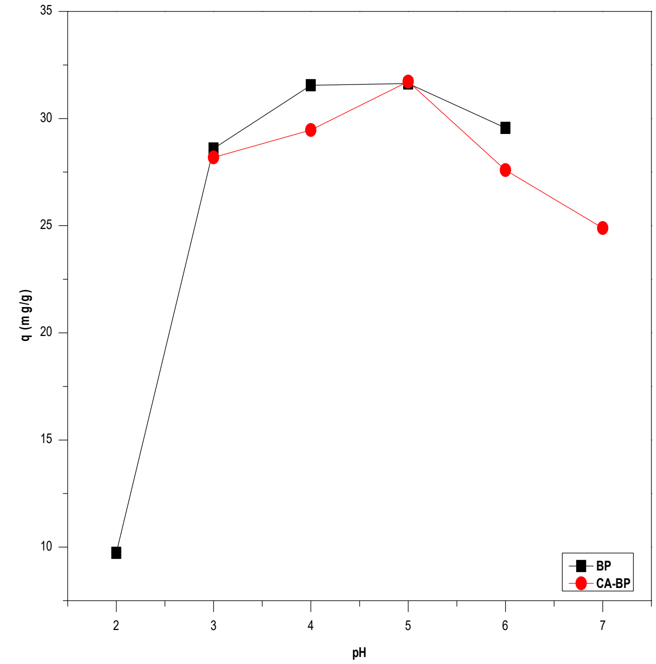

Fig. 1. Effect of pH BP and CA-BP on Pb(II) sorption (initial concentration 250 mg l^{-1}; contact time 60 min; agitation speed 100 rpm; and adsorbent mass 0.2 g).

inhibits interaction between Pb(II) and H^+, The high concentration of OH- ions causes the formation of precipitates of metal ions such as Pb(II), and metal ions cannot interact properly with the active site [30]. Higher pH initiates heavy metal precipitation and hinders Pb(II) from binding to the active site, resulting in lower adsorption capacity. The results of the pH obtained are at pH 5, and the value of pHpzc is 3.68 (pH > pHpzc) (Fig. 2), meaning that the surface of the biosorbent is negatively charged and can interact with Pb(II) [29,31].

Effect of Initial Concentration and Isotherm Evaluation

The concentration of heavy metals greatly affects the adsorption capacity of the adsorbent. The optimum concentration of Pb(II) that could be removed by banana peels was 600 mg l^{-1} and 850 mg l^{-1}, with an adsorption capacity of 50.563 mg g^{-1} and 62.088 mg/g for citric acid modified-kepok banana peel (Fig. 3). The initial adsorption process takes place quickly because of the availability of the biosorbent surface to bind metal ions both chemically and

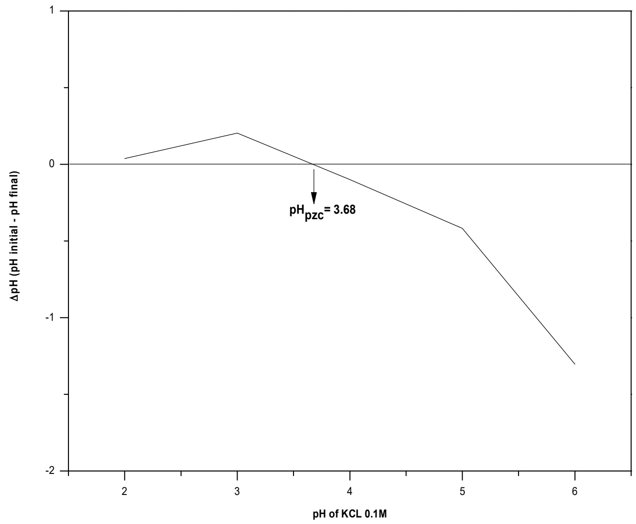

Fig. 2. pHpzc CA-BP.

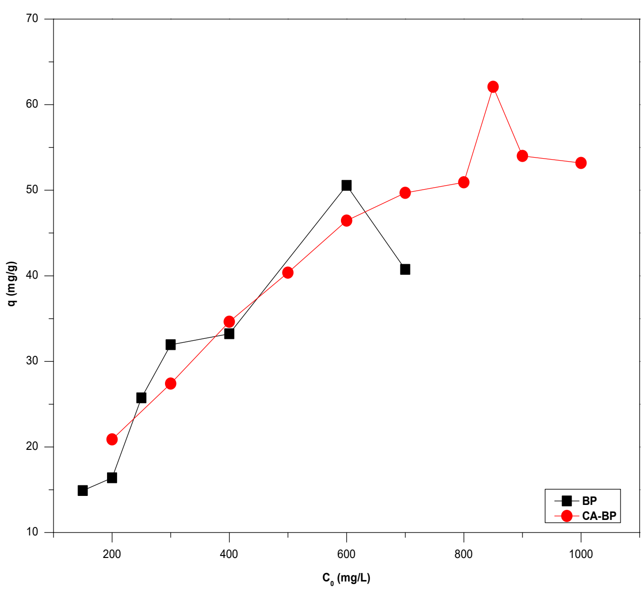

Fig. 3. Effect of initial concentration BP and CA-BP on Pb(II) sorption (pH 5; contact time 60 min; agitation speed 100 rpm; and adsorbent mass 0.2 g).

physically [30]. Based on the results, the higher the concentration, the more metal ions are present in the solution, so that more Pb(II) metal ions will be adsorbed and the adsorption capacity will continue to increase. However, the number of available active sites will gradually decrease, so that the adsorption rate becomes slower until it reaches equilibrium. Higher levels of metal ions can make the active site more saturated, which lowers its ability to bind molecules. This is because all of the biosorbent's active sites are now bound to Pb(II) metal ions in solution, which is called saturation. If the active sites of the adsorbent are saturated, increasing the metal ion concentration will not increase the absorption of metal ions [32].

The purpose of studying adsorption isotherms is to find out what kind of layer forms on the biosorbent's surface, how stable the interaction between the adsorbent and the adsorbate is, how the molecule adsorbs, and how the adsorption works. In addition to looking for the effect of concentration, adsorption isotherms are also carried out to observe the interactions that occur between the biosorbent and metal ions. Langmuir and Freundlich isotherm models are used to evaluate the effect of concentration on the adsorption mechanism of Pb(II) onto kepok banana peel (Fig. 4). The Langmuir isotherm model focuses on the adsorption monolayer of adsorbate on the surface of the adsorbent and the homogeneity of the adsorption sites. The interactions that occur on the surface are chemical interactions [33]. The Langmuir model is expressed by the following Eq. (3):

$$\frac{C_e}{q} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \tag{3}$$

Where qm is the maximum monolayer adsorption capacity of the adsorbent (mg g^{-1}), q is the adsorption capacity at equilibrium (mg g^{-1}), and K_L is the Langmuir adsorption constant (l mg^{-1}).

Meanwhile, the Freundlich isotherm model exhibits multilayer absorption and a heterogeneous distribution of active sites. The linear equation of the Freudlich model can be seen as the following Eq. (4):

$$\log q = \log K_F + \frac{1}{n} \log C_e \tag{4}$$

Where q is the adsorption capacity (mg g^{-1}), K_F (l mg^{-1}), n (l mg^{-1}) is the Freundlich isotherm constant, and C_e is the concentration of the solute in solution (mg l^{-1}).

The separation factor (R_L) indicates whether the adsorption process is favorable or unfavorable in Table 1. If the value of R_L = 0, then the adsorption process tends to be

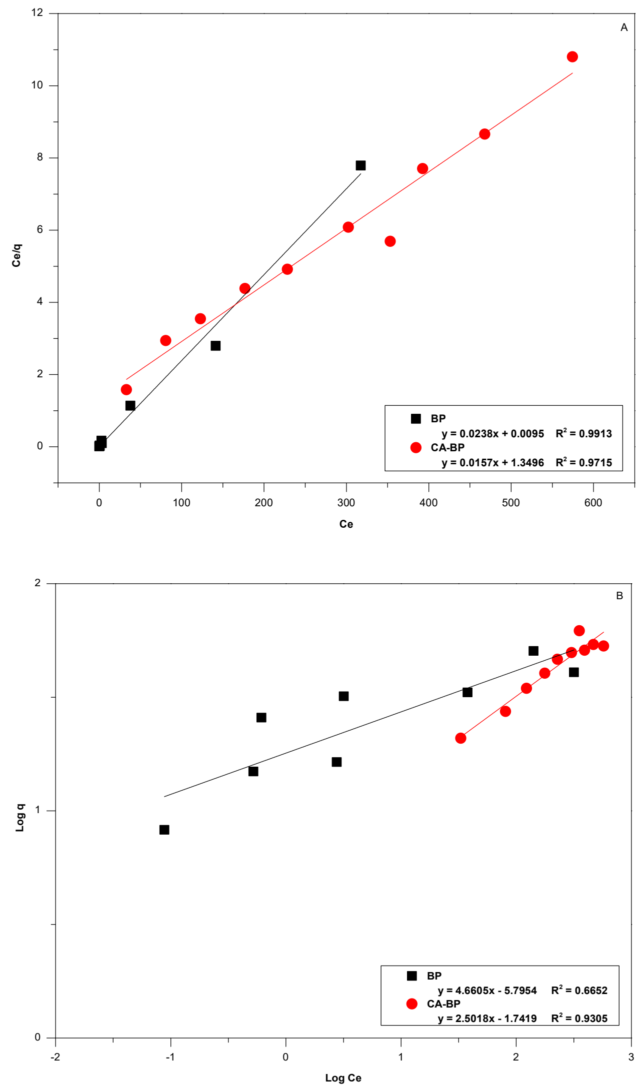

Fig. 4. Isotherm model (A) Langmuir and (B) Freundlich BP and CA-BP of Pb(II) sorption.

Table 1. Isoterm Models of Kepok Banana Peels of Pb(II)

Isotherm models	BP	CA-BP
Langmuir		
K_L (l mg^{-1})	2.5053	0.0181
qm (mg g^{-1})	42.0168	60.2410
R_L	0.0027	0.2164
R^2	0.9913	0.9715
Freundlinch		
K_F (l g^{-1})	0.8042	0.6963
n_F	0.2146	0.5741
R^2	0.6652	0.9305

irreversible. R_L ($0 < R_L < 1$), the adsorption process tends to be favorable, if $R_L = 1$, the adsorption process is linear; and if $R_L > 1$, the adsorption is unfavorable. The results show that the R_L value of Pb(II) adsorption on kepok banana peel activation was <1, which indicated a favorable process. The adsorption of Pb(II) follows the Langmuir isotherm model, presenting monolayer adsorption on the surface of BP and CA-BP [34,35].

Effect of Contact Time and Kinetic Study

Contact time aims to determine the required time to remove and bind Pb(II) optimally. The absorption capacity of metal ions in banana peels increases as the contact time increases until the optimum time of 75 min is obtained for both adsorbents, with an adsorption capacity of 39.534 mg g^{-1} for BP and 59.088 mg g^{-1} for CA-BP (Fig. 5). The longer the interaction between the solution and the biosorbent, the more active sites that were previously available begin to decrease and compete to bind to the vacant active sites.

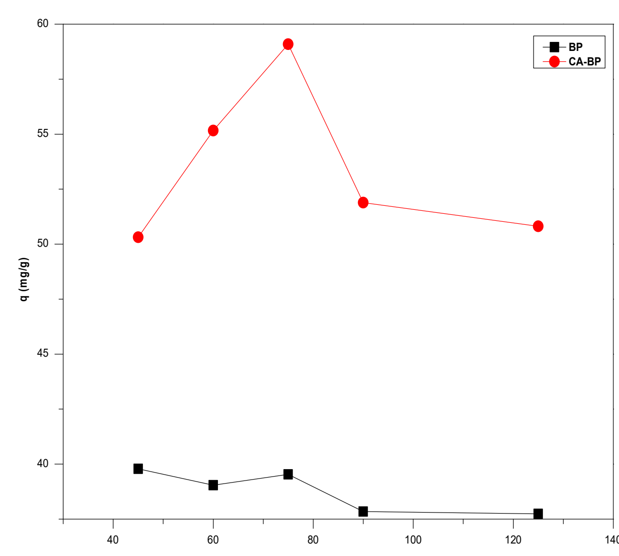

Fig. 5. Effect of contact time BP and CA-BP on Pb(II) sorption (pH 5; initial concentration 850 mg l^{-1}; agitation speed 100 rpm; and adsorbent mass 0.2 g).

Absorption begins to decrease and reaches a saturation point because of active site number reduction [36]. The bond between the biosorbent and the metal ions is becoming less stable, which is another reason why the amount of metal ions that are adsorbed is going down. This means that some of the metal ions will be released again. [26].

Influence the contact time on the absorption carried out to investigate the results of the adsorption kinetics model. Adsorption kinetics on the effect of contact time is used to measure the level of adsorption that occurs [26]. Adsorption kinetics is the study of how fast sorbate is held on to or released from a water-based solution at the interface with a solid. Kinetic models, namely pseudo-first order and pseudo-second order, are utilized to analyze the further effect of contact time [37]. The pseudo-first-order model is calculated by the following Eq. (5):

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \tag{5}$$

Where k_1 is the pseudo-first-order reaction rate constant, t is the time (min), q_e is the adsorption capacity (mg g^{-1}) at equilibrium, and q_t is the amount adsorbed at a certain time. The plot of $\log(q_e - q_t)$ *versus* t gives a linear relationship from which kt and qe can be determined from the slope and intercept of the plot. Whereas the pseudo-second-order model can be expressed as Eq. (6):

$$\frac{t}{q_t} + \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{6}$$

Where k_2 is the pseudo-second-order constant, q_e is the adsorption capacity at equilibrium, and q_t is the amount adsorbed at a certain time. The parameters of the adsorption kinetics model are listed in Table 2.

In pseudo-first-order, the kinetic model looks at the rate of change in adsorbate absorption over a certain amount of time. This rate is directly related to the difference in concentration and rate. This model is to describe the rate of physical adsorption (physsorption) in a solid-liquid phase system. Pseudo-second-order model is related to the Langmuir isotherm chemically (chemisorption). The value of the correlation coefficient (R2) in Table 2 indicates that the adsorption of Pb(II) for the two adsorbents follows the second-order pseudo-kinetic model because the second-order kinetic equation has the highest value when compared to the first-order pseudo-kinetic model. The interactions that occur in the adsorption process are chemical interactions, where the cationic exchange in the gas or liquid phase adsorption process follows a pseudo-second-order kinetic model.

Table 2. Kinetic Parameter of Pb(II) Sorption

Kinetic models	BP Pb	CA-BP Pb
q (exp)	39.534	59.088
Pseudo Orde-1		
k_1 (min^{-1})	0.0759	0.0124
q (calc) (mg g^{-1})	1691.718	2.306
R^2	0.5389	0.0093
Pseudo Orde-2		
k_2 (min^{-1})	-0.0066	-0.0039
q (calc) (mg g^{-1})	36.496	49.505
R^2	0.9990	0.9806

Effect of Agitation Speed

The agitation speed allows an opportunity for Pb(II) and the adsorbent to react properly, preventing the agglomeration of the adsorbent on the bottom of the flask.

Figure 6 indicates that the adsorption capacity of BP reached its optimum point at 100 rpm, with an adsorption capacity of 36.478 mg g^{-1}. Meanwhile, CA-BP achieved its peak at 150 rpm with an adsorption capacity of 64.088 mg g^{-1}. Increased capacity can occur because the stirring movement is more effective so that the adsorbent can absorb more adsorbate. At high speed, the ability to adsorb metal ions decreases, and the adsorbent begins to saturate because the structure of the adsorbent starts to break down. Moreover, the adsorbate that has been attached will be released back into the solution, so that the adsorption process becomes less than optimal [38]. The optimal adsorption of Pb(II) by modified banana peels was higher than that of unmodified banana peels. It is proven that the addition of carboxyl, hydroxyl, and carbonyl groups by citric acid can serve as additional groups for the adsorption of Pb(II) to the surface of the biosorbent. The addition of the active group can provide the ability to push metal ions to the active group of the biosorbent so that more Pb(II) metal ions

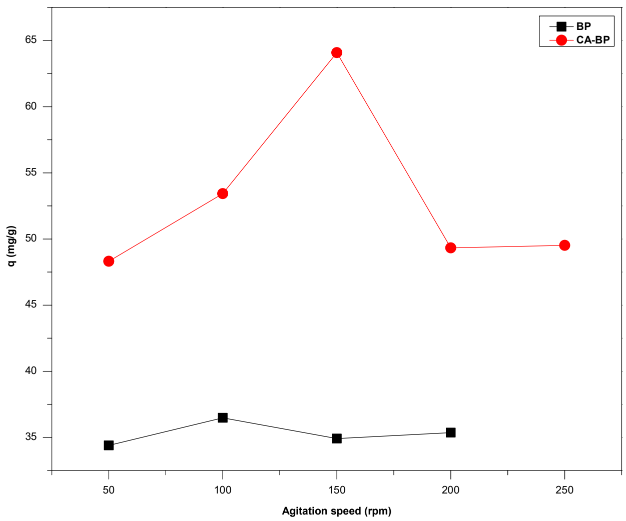

Fig. 6. Effect of agitation speed BP and CA-BP on Pb(II) sorption (pH 5; initial concentration 850 mg l^{-1}; contact time 75 min; and adsorbent mass 0.2 g).

can interact with the functional groups of banana peels that have been modified with citric acid.

Application of Kepok Banana Peel from the River

The biosorbents that have been analyzed are then applied to river water in optimal conditions. This test is done by comparing the original pH condition of the river with the previously obtained optimal pH condition in Table 3.

The results in the original condition and the optimal conditions, respectively, are pH 7 and pH 5. From the data, it can be seen that the percentage of adsorption processes performed in the optimal condition is higher than in the initial condition. The determination of the pH is very influential in the adsorption process, so it is well known that banana peel can be a good absorber in river water determination applications.

Adsorbent Characterization

Analysis of Fourier Transform Infra-Red (FTIR) of kepok banana peels. You can see the functional groups in BP and CA-BP in Fig. 7. It also shows how the adsorption process changes the wavenumber of each functional group. The wavenumber of some functional groups, such as functional groups O-H, C-H, C=O, C=C, and C-O, was shifted, which indicates an interaction between the

Table 3. Application of Original and Optimal CA-BP Conditions to Pb Metal Ions

Metal ion	Sample code	pH	Co (mg l^{-1})	Ce (mg l^{-1})	%R
Pb	Original	7	0.070	0.027	61.43
	Optimal	5	0.052	0.018	65.39

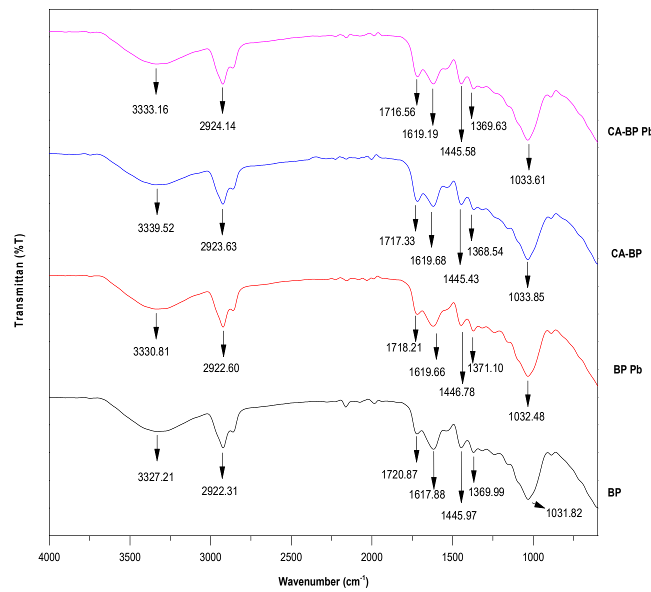

Fig. 7. FTIR characterization banana peels and modification kepok banana peel before and after Pb absorption.

functional groups and citric acid and Pb(II) [17,26]. Kepok banana peel will interact with citric acid to form esters, and the results show that there is a shift in the wave number of the C=O functional group from 1720.87 to 1717.33 cm^{-1}. Apart from the C=O group, the O-H group also experienced a shift in wave numbers from 3327.21 to 3339.52 cm^{-1}, where the OH group is a hydroxyl group in organic compounds such as cellulose, hemicellulose, and lignin [26]. Other functional groups include C-H from 2922.31 to 2923.63 cm^{-1}, C=C from 1617.88 to 1619.68 cm^{-1}, and C-O from 1031.82 to 1033.61 cm^{-1}.

Scanning Electron Microscopy (SEM) of kepok banana peels. SEM characterization is carried out to observe the surface morphology of the kepok banana peel before and after adsorption. The structure of the two samples is also uneven, indicating that the two biosorbents have many pores and are therefore good at adsorbing metal ions [39]. From the picture after absorption, the surface looks smooth and no cavities are visible. This happens because the functional groups on the surface of the banana peel biosorbent are bound to metal ions (Fig. 8) [26,32].

Energy Dispersive X-ray (EDX) of kepok banana peels. The chemical composition of the kepok banana peel also changes. It can be seen that Pb(II) has reacted with kepok banana peel, not only physically but also chemically through complexion, ion exchange, or electrostatic [30]. EDX analysis aims to determine the abundance of elements on the surfaces of both adsorbents. From Table 4, it can be seen that before absorption, C 44.24%, O 52.23%, Si 0.68%, and Ca 1.48% were obtained, where these elements act as ion exchangers and can interact with Pb(II). After adsorption, the BP contained 5.29% Pb(II), 38.14% C, 55.42% O, 0.60% Si, and 0.23% Ca. Meanwhile, in CA-BP, the percentage of Pb(II) was 6.90%, C 41.16%, O 49.17%, Si 0.64%, and Ca 0.28%. The obtained result showed that citric acid modified-kepok banana peel contained a higher amount of Pb(II) because the addition of citric acid has successfully increased adsorbent performance [27].

X-Ray Fluorescence (XRF) of kepok banana peels. Table 5 above shows that several elements and metal oxides

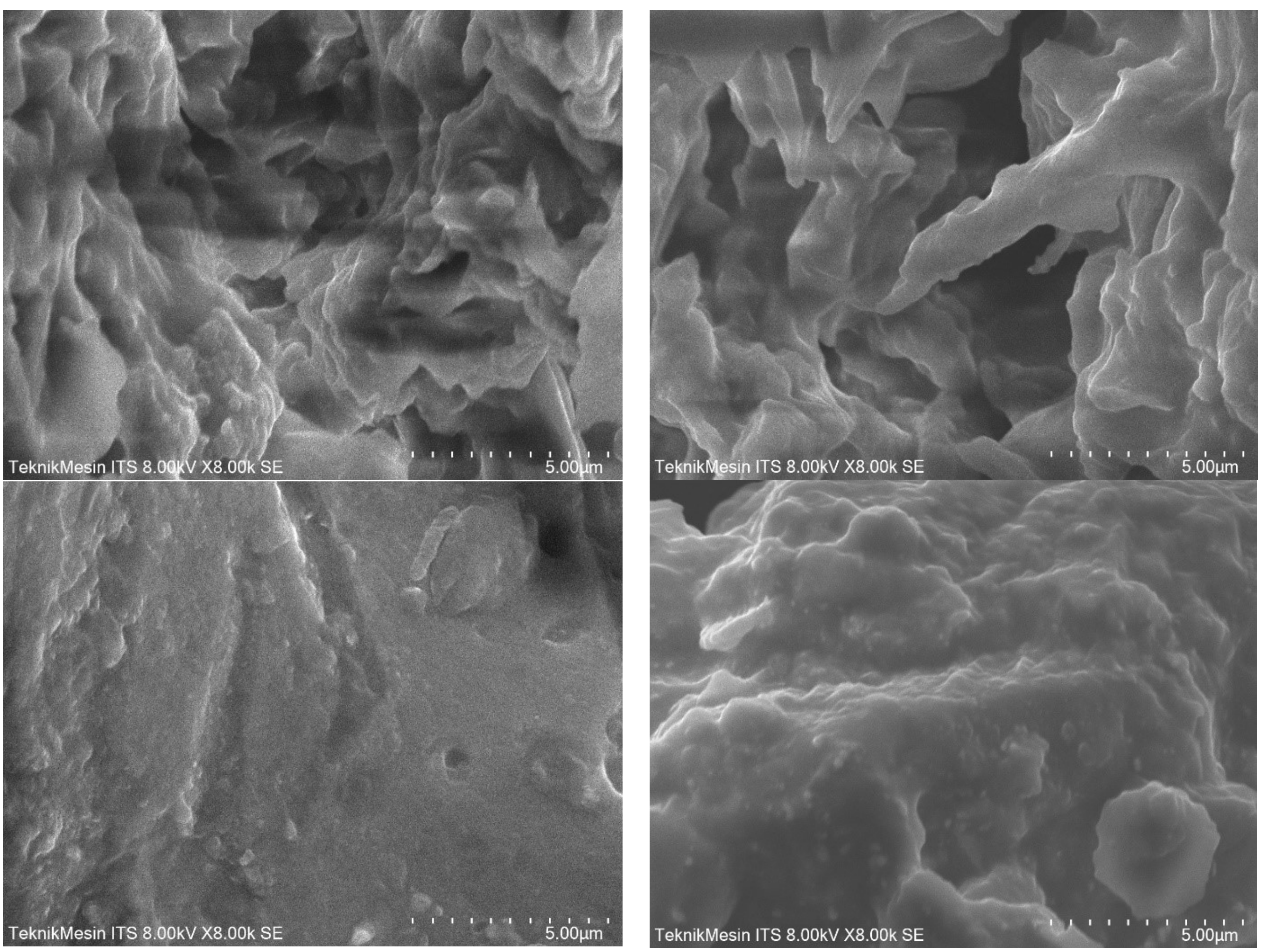

Fig. 8. SEM banana peel and modification kepok banana peel with citric acid (A) BP, (B) CA-BP, (C) BP Pb(II), (D) CA-BP Pb(II), 8000 magnification.

are present in the adsorbent before and after adsorption. BP consisted of Ca 71.862%, CaO 61.105%, Mn 2.956%, MnO 2.069%, Fe 1.26%, and Fe_2O_3 0.974% before adsorption.After adsorption, elemental and metal oxide concentrations decreased. This is due to the formation of complex compounds with functional groups and ion exchange between Pb(II) and Ca, Si, Mn, and Fe on the surface of the bioadsorbent [32]. Before the metal ions were absorbed, the percentages of elements and metal oxides could not be seen. However, the levels after adsorption showed that the biosorbent's surface was well absorbed. There was a decrease in adsorption on elements due to cation exchange with Pb(II). The increase in the percentage of Pb(II) indicates the binding of the kepok banana peel biosorbent.

Table 4. EDX Before and After Adsorption

Biosorbent	Element	Before Adsorption Pb (%)	After Adsorption Pb (%)
BP	C	44.24	38.14
	O	52.23	55.42
	Si	0.68	0.60
	Ca	1.48	0.23
	Pb	-	5.29
CA-BP	C	43.24	41.16
	O	51.79	49.17
	Si	1.03	0.64
	Ca	1.02	0.28
	Pb	-	6.90

Thermogravimetric Analysis (TGA) of kepok banana peels. Thermogravimetric analysis (Fig. 9) is conducted to see the mass reduction of the biosorbent with increasing temperature. In general, it can be seen that the higher the heating temperature of the biosorbent, the lower the weight of the biosorbent, as evidenced by the reduced adsorption capacity

Table 5. XRF Before and After Adsorption

Biosorbent	Element and Metal Oxides	Before Adsorption Pb (%)	After Adsorption Pb (%)
BP	Ca	71.862	3.529
	CaO	61.105	4.551
	Si	3.261	-
	SiO_2	5.312	-
	Mn	2.956	0.036
	MnO	2.069	0.043
	Fe	1.26	0.165
	Fe_2O_3	0.974	0.217
	Pb	-	91.362
	PbO	-	90.351
CA-BP	Ca	58.168	2.81
	CaO	42.90	3.629
	Si	3.803	-
	SiO_2	5.719	-
	Mn	1.359	0.016
	MnO	0.809	0.02
	Fe	1.013	0.113
	Fe_2O_3	0.666	0.149
	Pb	-	95.269
	PbO	-	94.376

of the biosorbent due to damage to functional groups or the presence of compounds that evaporate after heating.

In the adsorption process, Pb(II) with BP (without modification) was found to start weight loss considerably from 250 °C to 430 °C, as much as 85%-33%. When CA-BP was used to adsorb Pb(II), the weight started to drop from 86% to 35% at temperatures 230-430 °C (Fig. 9). According to [40], there are two stages of thermal degradation. The first stage is mass loss, which causes damage to the active groups contained in cellulose and hemicellulose. The decomposition of the active carboxyl and hydroxyl groups causes the glycoside bond to break and the C=O and C–C bonds to form [32]. The second stage is lignin degradation when the temperature has passed 430 °C [41].

Modification of cellulose by citric acid is carried out through esterification between the hydroxyl groups of cellulose and the carboxyl groups of citric acid. Because the modification of cellulose with citric acid will form ester bonds, the temperature is regulated until it reaches the boiling point to ensure the reaction is in the solid phase[25,42]. So, citric acid will stick to the kepok banana peel and add more functional groups, like hydroxyl and carbonyl, to help get rid of the Pb(II) (Fig. 10).

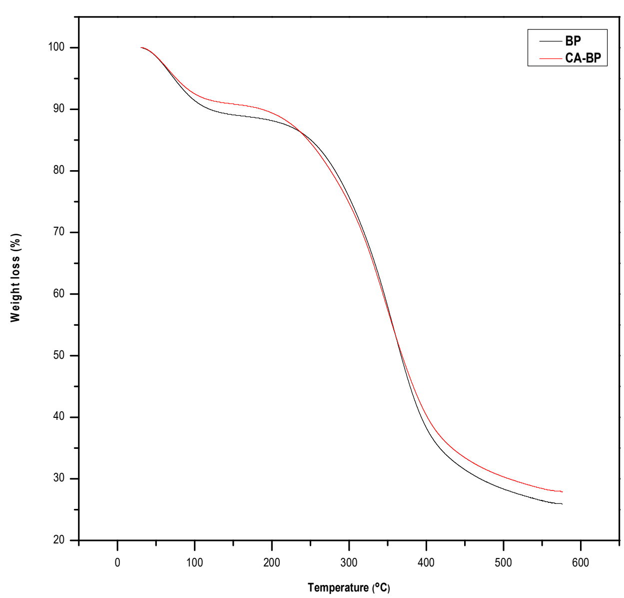

Fig. 9. Weight loss of banana peel (BP) and citric acid modified-kepok banana peel (CA-BP).

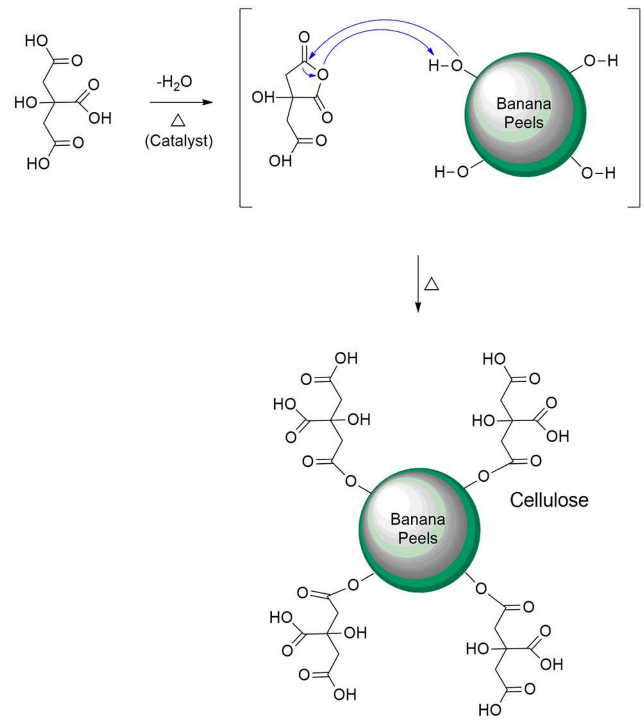

Fig. 10. Schematic illustration of citric acid modification of kepok banana peel.

CONCLUSION

Citric acid modified-kepok banana peel (CA-BP) has the potential to remove Pb(II) properly. This adsorbent is environmentally friendly and easy to obtain. Based on the research, the adsorption capacity of BP was 36.478 mg g^{-1}, and CA-BP was 64.088 mg g^{-1}. The CA-BP adsorption process followed the Langmuir isotherm model and pseudo-second-order model. In these models, Pb(II) molecules form a single layer on the surface adsorbent, and chemical interactions happen while the molecules stick to the surface. The characterizations of the adsorbent support the fact that the adsorption of Pb(II) onto BP and CA-BP was chemically and physically occurring through electrostatic interaction and pore trapping. Modification of BP using citric acid has increased the adsorption capacity of Pb(II) removal by 76%. In the application of the river water condition, the original condition of 0.070 mg l^{-1} was obtained, where the permissible limit according to WHO is 0.01 mg l^{-1}, and according to the Regulations of the Minister of Environment and Forestry, 0.1 mg l^{-1} is still a reasonable limit.

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