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BIOSORPTION OF Fe (II) IONS FROM AQUEOUS SOLUTION USING KEPOK BANANA PEEL (Musa acuminate)

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ABSTRACT

The present study used adsorbents from Kepok banana peel to remove Fe (II) from an aqueous solution. The effect of adsorbent dose and initial metal concentration was investigated at room temperature to evaluate the maximum adsorption and adsorption capacity of Kepok banana peels. The adsorption parameters studied were adsorbent mass [0.5-2.5 g], and initial Fe (II) concentration [30-70 mg/L], where the operating conditions were 50 ml of Fe metal solution was added to each adsorbent, the pH value of the mixture was adjusted to 6. Then the mixture was stirred at 250 rpm for 30 minutes. In the adsorption process, it was found that 2.5 grams of mass adsorbent and 60 mg/L as initial metal concentration gave the highest adsorption and adsorption capacity, with 57.99% and 0.644 mg/g, respectively. FTIR spectra of adsorbent showed hydroxyl, carboxylic, and amine groups in Kepok banana peels. This study showed that Kepok banana peels had good potential for removing Fe (II) ions and could be used as a good adsorbent for removing the Fe (II) from water and wastewater at very little concentration.

Keywords: Kepok Banana Peels, Adsorption, Fe(II), Adsorption Capacity

INTRODUCTION

Metal contamination is considered to be one of the most common and complex environmental problems. The accumulation of heavy metals in soil and water is essential because it can impact human health through possible contamination of the food consumed [1], [2]. Although iron in the form of Fe (II) and Fe (III) ions is one of the micro-nutrients for humans, animals, and plants, at high concentrations. it can cause unwanted problems in both ecosystems and industrial processes [2], [3]. High iron levels can cause an unpleasant taste or odor in drinking water and cause blockage of pipes or transmission lines in the process industry due to the formation of iron hydroxide. Therefore, a large amount of wastewater containing iron must be treated before being discharged into the environment [3].

According to research conducted by [4], Banjarbaru well water used by the community still contains some heavy metals that can be harmful to health if exceeding the quality standard. Even if boiled for consumption, the heavy metals in the water will not be lost because this method only eliminates bacteria in the water. content of iron metal in Banjarbaru well water[5]. In the North Banjarbaru subdistrict, the iron content was 19.875 mg/L; in the South Banjarbaru sub-district, the iron content was 26.125 mg/L, in the Cempaka sub-district, the iron content was 59.875 mg/L. According to the Regulation of the Minister of Health No. 419 of 1990, these results are far above the quality standard for iron metals, which is 1 mg/L.

The conventional methods for removing metals from water include precipitation [6], coagulation [7], ion exchange [8], [9], electrochemical reduction [10], and reverse osmosis [11]. Most of these methods require high capital costs and are not suitable for small scale industries. Research on processing waste containing metals has stated that the adsorption method is effective [12].

Materials derived from agriculture are currently receiving growing attention as adsorbents to remove heavy metals from water. Adsorbents derived from agriculture have polymer groups, such as cellulose, hemicellulose, pectin, lignin, and protein, as active centers for metal binding [13]. In Indonesia, many types of banana plants can grow, one of which is the Kepok banana. Kepok bananas are widely used as food raw materials ranging from home industries to large-scale industries, so the availability of waste associated with Kepok bananas is quite large, especially those that cause waste disposal problems. Kepok bananas are widely used because of their relatively large size with a dense fruit texture or not being easily crushed. Banana peels are waste that can be processed into adsorbents. The advantages of banana peel waste are cheap, easy to obtain, harmless, natural material, and environmentally friendly [14]. The average mass is 125 g, where 25% of it is dry matter, and the rest is water [13].

In Indonesia, from year to year, banana production continues to increase. From the cultivation and production analysis, bananas are in the first place [15], [16]. Banana is one of the potential commodities being managed by the government, which aims to increase regional income so that it is possible to assist the regional development process [17]. Based on the department of statistics (BPS) [18], in 2018, banana production in Indonesia was 7,264,379 tons and reaching 7,280,658 tons in 2019. The growth value of banana production 2019 over 2018 was 0.22%, spread in 34 provinces in Indonesia.

Banana is one of the fruits with the highest consumption rate in the world. It is becoming the main problem since the peel is useless and causes agro-waste production. Several tons of banana peels are produced every day in the market and as household waste causing environmental pollution. Banana peels are tested as adsorbents for toxic metals from industrial wastewater [13].

Table 1. Application of Banana Peels as Adsorbent on Several Types of Metals

Metals		References				
Cu, F	Ъ,	Y. Li, J. Liu, Q. Yuan, H. Tang, F. Yu,				
Cd, a	nd	and X. Lv [19]				
Cr						
Cu		P. D. Taralgatti [20]				
Cd		P. D. Deshmukh, G. K. Khadse, V.				
		M. Shinde, and P. Labhasetwar [21]				
Pb		S. Jena and R. K. Sahoo [22]; P.				
		Kumari [23]; G. A. Wardani and W.				
		T. Wulandari [24]				
Cu and Pb		G. Vilardi, L. Di Palma, and N.				
		Verdone [25]				
Cu, Z	Zn,	G. R. Dukare, A. Bhoir, S. Raut, P.				
Co,	Ni,	Parkar, S. Deshpande, and K.				
and Pb		Thomre [26]				
Cd and Pb		M. Sirilert and K. Maikrang [27]				

Research on heavy metal adsorption using agricultural waste from banana peels has been carried out (Table 1). However, research on the application of banana peels for iron metal adsorption is still limited, and only a few have carried it out [28]. Iron metal contamination in the environment also needs to be watched. Therefore, this study reported the potential of Kepok banana peels as an adsorbent to remove iron metal from water, based on the parameters of the adsorbent mass and initial metal concentration.

Banana peels residue can be processed and transformed into adsorbents because it has a large surface area, high swelling capacity, excellent mechanical strength, and great potential to absorb harmful contaminants, such as heavy metals [12]. Based on research by [29], with a similar method of preparation of banana peel adsorbent, the surface area of the dried material was measured using the BET method was found to be 13 m²/g.

METHODS

1. Materials

The materials used included FeSO₄·7H₂O metal (Merck), HCI (Merck), NaOH (Merck), and deionized water (WaterOne). All the materials mentioned above were guaranteed reagents and Kepok banana peels, which were collected from the waste of traders and home industries that used Kepok bananas as raw material.

The method used in this study included the preparation of the adsorbent. The adsorption process was carried out based on the variation of the adsorbent mass. The adsorbent mass with the highest percent adsorption value was used for the adsorption process based on the effect of variations in the initial metal concentration to calculate the value of the adsorption capacity.

2. Preparation of the Adsorbent

Kepok banana peel waste was separated from the stem, cut into small pieces, then washed with running water to remove dust and other impurities. Subsequently, the Kepok banana peel was dried under the sun for five days and dried again in the oven for three hours at 70°C afterwards. Finally, the dried Kepok banana peels were softened in a blender and sieved with a mesh size of 100. This preparation method was adopted from research by [27] and [30].

3. Preparation of Fe (II) Solution

FeSO₄·7H₂O was weighed in a certain amount to make a stock solution of Fe (II) with a concentration of 1000 mg/L. Later, the Fe (II) stock solution was diluted to obtain Fe (II) 's working solution in several concentrations according to the needs of mass variation and adsorption capacity variations, namely 30, 40, 50, 60, and 70 mg/L. Finally, the dissolution and dilution of this solution were carried out using deionized water.

4. Effect of Adsorbent Mass Variations

The usage of variation in the adsorbent mass was aimed to discover the optimum dose of Fe (II) metal adsorption. The adsorbent mass variations used were 0.5, 1, 1.5, 2, and 2.5 grams. Later, 50 ml of Fe metal solution 50 mg/L was added to each adsorbent. The pH value of the mixture was adjusted to 6 by adding 0.1 M HCl or NaOH.

The mixture was then stirred at 250 rpm for 30 minutes. The adsorption results were filtered, where the filtrate obtained was then analyzed to identify the remaining metal Fe (II) concentration. Replication was conducted three times. The highest average adsorption percentage was the optimum adsorbent mass data.

5. Effect of Initial Fe (II) Metal Concentration Variations

Analysis of variations in initial metal concentrations was carried out to calculate the adsorption capacity of Fe (II) metal from the Kepok banana peel adsorbent. First, this optimization was carried out by varying the initial Fe (II) metal concentrations by 30, 40, 50, 60, and 70 mg/L. This parameter was done by weighing the number of adsorbents obtained from the adsorbent mass optimization. Next, the adsorbent powder was mixed with a Fe (II) metal solution with the initial concentration, as mentioned above. Subsequently, the pH of the mixture was adjusted to a value of 6, and an adsorption process was carried out for 30 minutes at a speed of 250 rpm. After the adsorption results were filtered, the filtrate obtained was then analyzed to identify the remaining concentration of Fe (II) metal. The Fe (II) concentration shown was then used to calculate the adsorption capacity. Replication was conducted three times.

6. Data Analysis

Fe (II) metal data obtained from each parameter was calculated to get the adsorption percentage and adsorption capacity through the following equation [22]: $\%Adsorption = \frac{C_0 - C_t}{C_0} \times 100\%$ (1)

$$q_t = \frac{C_0 - C_t}{m} \times V \tag{2}$$

Where q_t was the adsorption capacity (mg/g), C_0 and C_t were the initial and final metal ion concentrations (mg/L), respectively, V was the volume of solution (L), and m was the adsorbent mass of the Kepok banana peel used.

RESULTS AND DISCUSSION

The method used in this study included the preparation of the adsorbent. The adsorption process was carried out based on the variation of the adsorbent mass in the range of 0.5-2.5 grams. The adsorbent mass with the highest percent adsorption value was used for the adsorption process based on variations in the initial metal concentration in the range of 30-70 mg/L to calculate the value of the adsorption capacity.



Figure 1. Adsorbent preparation

Adsorbent preparation in this study was a simple and easy preparation because it did not require a very high temperature. The preparation was begun with the cleaning

process of the Kepok banana peels, which had been obtained as waste. This treatment aimed to remove dust and other contaminants sticking to the peel to minimize the possibility of other factors that interfere with the adsorption process. Subsequently, Kepok banana peels were cut into small pieces to increase the contact area and dried in the sun for five days to remove the moisture. The results obtained were in the form of changes in the color and texture of the banana peels, from yellow to dark brown and shrinking. The dried banana peels were then dried over in an oven at 70°C for three hours to ensure no remaining moisture content. The banana peels were then mashed to increase the surface area and sieved to equalize the size of the adsorbent powder (Figure 1). Finally, the prepared Kepok banana peel adsorbent was stored in a closed container filled with silica gel to prevent mold growth.

1. Effect of Adsorbent Mass Variations

In this study, the adsorbent mass was varied from 0.5 to 2.5 grams (Figure 2 and Table 2). It was shown in Figure 1 that the greater the adsorbent mass added, the higher the %Adsorption obtained. It was in line with the prediction that the more available surface areas were correlated, the more active sides due to the increased adsorbent mass [14].

Table 2. Results of % Adsorption and Adsorption Capacity

Adsorbent Mass (gram)	0.5	1	1.5	2	2.5
Average % Adsorption	11.92	21.75	33.66	39.13	57.99
Initial Fe (II) Concentration (mg/L)	30	40	50	60	70
q (mg/g)	0.313	0.618	0.576	0.644	0.576



Figure 2. Graph of the Effect of Adsorbent Mass Variations on %Adsorption

Based on the results obtained, the use of the lowest adsorbent mass, which was 0.5 grams, had shown its ability to absorb Fe (II) metal with a %Adsorption value of 11.92%. Then along with the addition of the adsorbent mass dose, the highest adsorbent mass was 2.5 grams, with a %Adsorption value of 57.99%. However, adsorption was considered to be a phenomenon that occurs on the surface. Thus, adsorbents with a higher surface area should present faster adsorption than adsorbents with a lower surface area. This correlation was also closely related to the use of adsorbent doses [1]. In addition, the more adsorbents used, the greater the possibility of the abundance of active sites from the active groups on the surface available to bind to metals. The increase in the adsorption percentage value and the increase in the adsorbent's mass also indicate that under these operating conditions, there is no overlapping and partial aggregation [27].

This study also has the same trend as the [22] study, which used banana peel adsorbents for heavy metal adsorption, where the larger the mass of the adsorbent used, the higher the adsorption percent. It also shows that after a certain adsorbent dose, maximum adsorption will be reached, so that the number of ions bound to the adsorbent and the number of free ions will remain constant even with the addition of more adsorbent doses [22], [31].

2. Effect of Initial Fe (II) Metal Concentration Variations

The adsorption rate was a function of the initial concentration of metal ions, which made it an essential factor for an effective biosorption process [32]. From Figure 3, in general, the data showed that the adsorption capacity of the adsorbent increased with the increase in the initial metal concentration. These characteristics indicated that the surface saturation depended on the equilibrium concentration of the metal. Thus, at low concentrations, the active site of the adsorbent absorbed metal ions more quickly. Whereas at higher concentrations, metal ions had to diffuse on the adsorbent surface through intraparticle diffusion, and metal ions, which were effortlessly hydrolyzed, would diffuse at a gradual rate [33]. This statement was fitting with the results of this study.

It was shown in Figure 3, at low concentrations, namely 30 mg/L, the adsorption capacity obtained was 0.313 mg/g. Whereas at higher concentrations, namely 40-70 mg/L, the adsorption capacity value was twice the value of the original adsorption capacity. It indicated that at concentrations above 30 mg/L, the adsorbent surface began to saturate properly with Fe (II) metal ions. It was also proved by the fluctuating value of the weak bond between

the active sides of the adsorbent and the Fe (II) metal ion so that the Fe (II) metal ion encountered desorption and returned to the system [30].



Figure 3. Graph of the Effect of Initial Fe (II) Metal Concentration Variations on Adsorption Capacity

In this study, the highest adsorption capacity obtained was 0.644 mg/g. However, this result is smaller than the previous study by [30], which obtained an adsorption capacity of 1.44 mg/g, which in this study used a solution of Fe (II) with an initial concentration of 50 mg/L.

3. Functional Group Analysis using FTIR





Figure 4 showed the FTIR spectrum of adsorbent before and after the adsorption process. It was proved that the Kepok banana peel adsorbent contained several functional groups in the biomass and showed the complex nature of the biosorbent. In addition, the adsorbent spectrum showed transmission absorption at various frequencies, indicating the presence of different functional groups.

In the Kepok banana peel adsorbent before and after adsorption, the strong absorption due to the hydroxyl group stretching at a frequency of 3269.22 and 3336.49 cm⁻¹ indicated the presence of a hydroxyl group free of polymer compounds, such as lignin or pectin, which contained phenol, and carboxylic alcohol. acid functional groups. A wide frequency range (3600-2800 cm⁻¹) was defined as a free hydroxyl group (-OH), indicating the presence of polymer compounds [21], [34]. The absorption due to primary amines' N-H bending vibration was observed at 1601.15 and 1624.22 cm⁻¹. The uptake in the area around 1700 cm⁻¹ was caused by the vibration of the C=O strain of the carboxylic groups (-COOH, -COOCH₃), which could be attributed to the carboxylic acids or their esters.



Figure 5. Interactions between the metal ion (M²⁺) and the chemical groups present in the banana peel; (a) carboxyl, (b) hydroxyl [35]

The difference in transmittance of the adsorbent bonded to the Fe (II) metal after adsorption indicated that the carboxylate aroup was involved in the bindina mechanism. The uptakes at 1438.52 and 1443.48 cm⁻¹ were probably due to vibrations of the lignin aromatic ring. The absorption at wavenumbers 1315.04 and 1318.67 cm⁻¹ could be associated with cellulose, hemicellulose, or lignin polymers [21]. The absorption at the 2919.92 and 2919.27 cm⁻¹ areas indicated the strain movement of the C-H bond [22], [36]. The absorption at 1031.20 and 1035.82 cm⁻¹ were determined for the vibration of the C-N bond strain of the aliphatic amine. The FTIR spectrum of adsorbent before and after adsorption showed that the Kepok banana peel consisted of functional groups, such as hydroxyl, carboxyl, and amine groups [21].

Changes in transmittance and small deflection in the frequency band after adsorption on absorption showed the contribution of this functional group in the adsorption process [21]. According to research [1], the adsorption process is strongly influenced by the carboxyl functional group in the galacturonic acid polymer, the main constituent of pectin, where pectin is the compound with the highest proportion in banana peels. In the solution system, the carboxyl functional group in the galacturonic acid polymer is ionized into negative ions (-COO⁻), which causes banana peels to adsorb positively charged heavy metals. Other functional groups that contribute to the heavy metal adsorption process are amine (-NH), carboxyl (-OH), and carbonyl (=O) functional groups [37].

CONCLUSION

Based on the research that had been done, it was known that the highest adsorption of 57.99% was obtained when using the adsorbent mass of 2.5 grams. Besides, at the initial Fe (II) metal concentration of 60 mg/L, the highest adsorption capacity was obtained, 0.644 mg/g. Furthermore, the Kepok banana peel adsorbent was also characterized by FTIR. Several identified functional groups, namely carboxylic acid and hydroxyl groups of polyphenols and polysaccharides, could play a crucial role in reducing metal cations.

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