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Kepok Banana Peels as Biosorbent for Mercury Sorption from **Artificial Wastewater**

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ABSTRACT

The present study used adsorbents from Kepok banana peel to remove Hg (II) from artificial wastewater. Kepok banana peels are the most abundant waste from several products bananas processed. On(3)f the ways to reduce that waste is by using it as an adsorbent. This study utilizes the adsorbent from kepok banana peels to remove Hg (II) from artificial wastewater. This is besize Hg(II) is a heavy metal that is harmful A previous study showed a high amount of Hg(II) in Kuantan River, one of the River in Riau Province. The efficient of initial metal concentration, adsorbent mass, and contact time was investigated to evaluate the maximum removal percentage and adsorption capacity of Kepok banana peels. The adsorption parameters studied were initial Hg (II) concentration [6.84, 7.02,8.38, and 10.05 mg/L], adsorbent mass [10,20,30 and 40 g], and contact time variations (3,5,7 and 9 hours) where the operating conditions were 250 ml of Hg metal solution was added to each adsorbent. FTIR spectra of adsorbent showed hydroxyl, carboxylic, and amine groups in Kepok bananatipels. The adsorption process found that the metal concentration variation under 6.84 mg/L initial [6] (II) concentration conditions gave the highest removal percentage of 99.7% and the highest adsorption capacity of 0,0758 mg/g under the condition of 10.05 mg/L initial Hg (II) concentration. Then at adsorbent mass variation, the highest removal percentage was 94.8% with 40 grams adsorbent mass, and the highest adsorption capacity was 0.1587 mg/g when using 10 grams adsorbent. The contact time variations gave the highest removal percentage, 95.2 %, and the highest adsorption capacity, 0.0542 mg/g, during contact for 5 hours. This 15 udy showed that Kepok banana peels had good potential for removing Hg (II) ions and could be used as a good adsorbent for removing the Hg (II) from wastewater.

Keyword: Kepok Banana Peels, Adsorption Hg(II), Adsorption Capacity, the Removal percentage

INTRODUCTION

Heavy metals have contaminated our ecosystems with high concentrations produced by various human activities such as industrial activities, energy production, construction, sewage treatment, and vehicle waste caused by high amounts of heavy metals in the atmosphere, water, and soil [1]. Heavy metals become dangerous caused of the bioaccumulation system, which increases the concentration of chemical elements in the body. Heavy metals can cause lossless health effects for humans depending on where the heavy metal is bound in the body. The poison will work as a barrier to enzyme work to disconnect the body's metabolic processes [2]. Heavy metals Hg, Cd, and Pb, are called non-essential metals and, at certain levels, will become toxic metals for living things [3]. Therefore, continued research must be carried out in an effort to handle heavy metals so that pollution environment can be managed.

The accumulation of heavy metals in soil and water is essential because it can impact human health through possible contamination of the food consumed [4]. Heavy metals are usually present in trace amounts in natural waters, but many of them are toxic even at very low concentrations, especially mercury. According to [3], One way of processing gold is an amalgamation. The process used mercury (Hg). Mercury is commonly used as an auxiliary chemical suitable for its properties to bind the gold grains for easy separation from other particles. Then, the waste is discharged into the water. Based on several previous studies. mercury levels exceeded the limits in the waters. The mercury-contaminated environment is eventually dangerous for the biota in these waters and humans' food chains. Mercury accumulates from the river biota, where mercury waste enters the waters and will react with methyl microorganisms mercury, which small fish then eat. It accumulates in the fish's body then to humans. The diseases it will cause include: hair and teeth damage, memory loss, and nervous system disorders [5]. Mercury is one of the most toxic elements among heavy metals, and if exposed to high concentrations, it will cause permanent brain and kidney damage [6].

The data Central Bureau of Statistics Riau Province in 2018 explained that there was an increase in the environmental pollution in villages, where the most pollution was water pollution, followed by air and soil pollution. Water pollution is found in 454 villages, air pollution in 248 villages, and soil pollution in 32 villages [7]. Previous study in Singingi River, Taluk Kuantan, showed a high Hg from illegal gold mining [8] [9]. The same thing happened in Rokan Hilir, Siak, and Dumai. The water in this area contains many heavy metals such as Fe, Pb, Cd, Cr, and Cu [10], [11]. Some chemical methods that have been studied to remove the content of heavy metals include ion exchange, membrane filtration, chemical oxidation process, precipitation chemical process, and coagulation-flocculation. Reduction for Hg has also used this method [12],[13]. However, this method is less effective because it causes secondary waste production, expensive operational costs, a long time and is not able to eliminate the level of heavy metal metal metal ions [14].

From these problems, the researchers tried to produce a quality product in biosorbens that can be applied to overcome pollution, especially in the Riau area, with much higher effectiveness and a much lower production price than the usual filtration process using the principle of absorption.. Research on processing waste containing metals has stated that the adsorption method is more effective [4]. The advantages of banana peel waste are cheap, easy to obtain, harmless, natural material, and environmentally friendly. Research related to the use of bio sorbents from banana peels to reduce heavy

metals that have been done including. [14-20].

The bio sorbents used are made from banana peels. That is because Indonesia is included in the top 10 in the sixth position as the world's largest producer of bananas, with a total production of 5,814,580 tons per the year 2010 [21]. In 2013 increased to 6,279,290 tons, but so far, banana peels have not been widely utilized, especially in Riau. It only becomes waste and a source of considerable environmental pollution because many businesses are currently being developed using bananas as raw materials. However, the waste is considered to have no economic value.

However, research on the application of banana peels for mercury metal adsorption is still limited, and only a few have carried it out [12], [13], [22]. Therefore, this study reported the potential of Kepok banana peels as an adsorbent to remove mercury metal from artificial wastewater, based on the parameters of the adsorbent mass, contact time, and metal ion concentration. Based on the results of previous studies related to the content of banana peels. Kepok banana peel contains vitamin C, vitamin B, calcium, protein, cellulose, hemicellulose, chlorophyll pigments, fats, arabinose, galactose, rhamnose, and galacturonic acid that can bind metals in water. Banana peel waste can also be considered for reducing turbidity levels and heavy metal ions in water contaminated [15]. The structure of the material contains cellulose and lignin naturally will provide a porous structure and has the potential to be used as a filtration medium that can adsorb without being explained [23]. Cellulose is one of the ingredients contained in banana kepok's peels. We know cellulose is a simple polymer that forms chemical bonds with a uniform cellulose chain surface and forms a porous layer. This porous solid material absorbs materials harmful to the environment [24].

METHODS

1. Materials and Tools

The materials used included HgCl₂ (Merck), HCl (Merck), deionized water, and Kepok banana peels, which were collected from the waste of traders and home industries that used Kepok bananas as raw material.

Figure 1. Schematic of Filtration Equipment (Doc.Personal)



- 1. Raw Water Source
- 2. Filter Box
- 3. Filtration Pipe
- 4. Pipe to Reservoir
- 5. Filtration Reservoir Box

2. Preparation of the Adsorbent

Kapok banana peel waste, which was collected from the waste of traders and home industries washed with running water to remove dust and other impurities. Then Kepok banana peel was dried under the sun for 2-3 days. Finally, the dried Kepok banana peels were mashed in a blender and put into a filter bag. This preparation method was adopted from research by [4].

3. Preparation of Hg (II) Solution

HgCl₂ was weighed in a cartain amount to make a stock solution of Hg (II) with a concentration of 1000 mg/L. Later, the Hg (II) stock solution was diluted to obtain Hg (III) 's working solution in several concentrations according to concentration, mass variation, and adsorption capacity variations, namely 5,7,9 and 11 mg/L. Finally, the dissolution and dilution of this solution were carried out using deionized water.

4. Effect of Initial Hg (II) Metal Concentration Variations

Analysis of variations in initial metal concentrations was carried out to calculate the adsorption capacity of Hg (II) metal from the Kepok banana peel adsorbent. First, this optimization was performed by varying the initial Hg (II) metal concentrations by 5, 7, 9, and 11 mg/L. This variation used 30 grams of kepok banana peel and a contact time of 5 hours. After the filtrate was obtained was then analyzed to identify the remaining Hg (II) metal concentration.

The Hg (II) concentration was then used to calculate the adsorption capacity and percentage removal.

5. Effect of Adsorbent Mass Variations

The usage of variation in the adsorbent mass was aimed at discovering the optimum dose of Hg (II) metal adsorption. The adsorbent mass variations used were 10, 20, 30, and 40 grams. Later, 250 ml of Hg metal solution 5 mg/L was added to each adsorbent for 5 hours. After the filtrate was obtained was then analyzed to identify the remaining Hg (II) metal concentration. The Hg (II) concentration was then used to calculate the adsorption capacity and percentage removal. The

highest average adsorption percentage was the optimum adsorbent mass data.

6. Effect of Contact Time Variations

The usage of variation in the contact time aimed to discover the optimum contact of Hg (II) metal adsorption. The contact time variations used were 3,5,7, and 9 hours. Later, 250 ml of Hg metal solution 5 mg/L was added to each adsorbent. In this variation, used 30 grams of kepok banana peel. After the filtrate was obtained was then analyzed to identify the remaining Hg (II) metal concentration. The Hg (II) concentration was then used to calculate the adsorption capacity and percentage removal. The highest average adsorption percentage was the optimum contact time data.

7. Data Analysis

Hg (II) metal data obtained from each parameter was calculated to get the removal percentage through the following equation:

% E =
$$\frac{(c_{A0} - c_{Af})}{c_{A0}} \times 100\%$$
(1)

Where:

E = removal percentage (%)

 $C_{A0}=$ the initial metal ion concentrations (mg/L), $_{\overline{33}}$

 $C_{Af}=$ final metal ion concentrations (mg/L) and adsorption capacity through the following equation :

$$Q = \frac{(C_{A0} - C_{Af})}{m} x V$$
(2)

Where Q= the adsorption capacity (mg/g), ${\it C}_{A0}$ and ${\it C}_{Af}$ 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 [4].

RESULTS AND DISCUSSION

The preparation was begun with the cleaning 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.



Figure 2. Preparation of the Adsorbent a).

Banana peel drying; b). mashed of banana peel samples; c and d) filter bag filled with banana peel

Subsequently, Kepok banana peel is dried for 2-3 days to remove the water content. Then after drying, the banana peel is mashed first with a blender so that it can be expanded and touched surface so that the absorption process can be maximized because more that can bind impurities in artificial waste used[4]. Express the same

that sample refinement is to increase the surface area of the biosorbent. The adsorption contact opportunity will be even greater [25].

Banana peel powder put into the filter bag is then used directly as a biosorbent. Banana peels were used directly without being used as activated carbon or chemically and physically activated. The effectiveness of banana peel without any mixture is because it contains a variety of secondary metabolite compounds that can bind even heavy metals. According to the one on previous research. banana peel waste can be considered to reduce turbidity levels and heavy metal ions in water contaminated. Then [23] also revealed that the structure of the material containing cellulose and lignin would naturally provide a porous structure and the possibility of being used as an absorbent that can adsorb without being heated[15]. which revealed that the content of Kepok including vitamin C, vitamin B, calcium, protein, cellulose, hemicellulose, pigments chlorophyll, fat, arabinose, galactose, rhamnose, and galacturonic acid.

1. Functional Group Analysis using FTIR

The selection of kapok banana peels as an adsorbent; Currently, many businesses use kepok banana as the basic ingredient for banana processing, so this kepok banana peel waste is much easier to obtain available in large quantities compared to other types of banana peels. Based on previous research, banana peels contain various active components, so in this study, the FTIR characterization of banana peels was carried out to see the functional groups contained in the kepok banana peel.

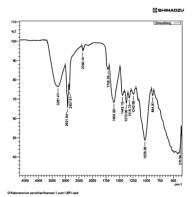


Figure 3. Kepok Banana Peel Spectra

The absorption peaks detected on the banana peel of kepok were 3281.47 cm⁻¹, indicating the presence of free hydroxyl (OH) groups from polymers such as lignin and pectin contained alcohol, phenol, and carboxylic acid functional groups. Overlap with the amine group (NH). The absorption at 2921.94 cm⁻¹ and 2857.61 cm⁻¹ indicates the presence of vibrations from the (C-H) bond, which may originate from the carboxyl ester group. The absorption at 1708.28 cm-1 showed the presence of C=O bonds, which indicated compounds such as hemicellulose and a carboxylic acid group (-COOH). Absorption at 1443.10 cm⁻¹; 1373.06 cm⁻¹, and 1318.73 indicated the stretching vibration of the C-H bond of the carbon atom attached to the hydroxyl group of cellulose, hemicellulose or lignin. The absorption at 1243.68 cm⁻¹ indicates the presence of C-O bonds, which indicate lignin bonds. The absorption at 1029.26 cm-1 indicates the presence of aliphatic amine bonds. The absorption at 884.87 cm⁻¹ indicated the presence of glycosidic bonds from carbohydrate compounds. This is following the banana peel characterization analysis that has been carried out by other studies from [14] [26], [27], and [28].

The presence of functional groups that indicate some of the compounds contained in banana peels is what makes banana peels have the ability as biosorbents. Biosorbents are adsorbents from natural materials that can absorb certain components from a fluid phase [29], known as adsorption. The same stated [28] that the carboxyl functional group strongly influences the adsorption process in the galacturonic acid polymer, which is the main compound of pectin, where we know that banana peels contain large amounts of pectin. This galacturonic acid compound is ionized into negative ions (-COO-), which can bind metals. Other functional groups also affect the metal-binding process, as stated [18] that the presence of cellulose is what makes banana kepok peels able to absorb metal ions well.

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

The variations carried out in this study were with concentrations of 5,7,9, and 11 mg/L. However, after using AAS (Atomic Adsorption Spectroscopy), the initial metal concentration in the artificial waste was measured at 6.84; 7.02; 8.38; and 10.05 mg/L. There is a slight difference in concentration, but the difference is not too significant due to possible errors during the solution preparation process to storage and sample measurement. The results obtained from the treatment using 30 grams of kepok banana peel with an adsorption process cycle

time of 5 hours showed there was a significant decrease in mercury levels, with the largest absorption percentage 99.7%.

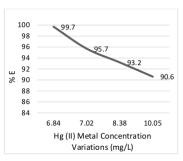


Figure 4. The effect of metal concentration for removal percentage

For the effect of metal concentration on the effectiveness of absorption, it can be seen that the higher the metal concentration to be adsorbed, the lower the percentage of banana peel absorption. This happens because the active group on the banana peel that functions to bind the metal is less than the amount of metal to be adsorbed so that the amount of metal that can be bound is limited and lowers the percent absorption. This is following research by [12] that with a higher metal concentration The adsorbent pores have been closed by the adsorbate in other words, the active site of the adsorbent has reached the saturation point in absorbing metal ions. In line with research [24] that the addition of the concentration of adsorbate or metal to be adsorbed will increase the amount of adsorbate that is adsorbed if the active sites of the adsorbent are not saturated adsorbed.

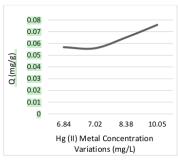


Figure 5. The effect of metal concentration for absorbtion capacity

The results obtained from the treatment using 30 grams of kepok banana peel with a cycle time of 5 hours for each adsorption process contained the largest absorption capacity at a concentration of 10.05 mg/L of 0.0758 mg/g. The absorption capacity is still low at low metal ion concentrations and increases with increasing metal ion concentration. This is because the higher the concentration of metal ions, the binding process will be evenly distributed over the entire surface of the adsorbent. This follows what [4] stated that with an increase in the concentration of metal ions, there is an increase in the absorption capacity until the equilibrium state, which will decrease when it reaches the saturation point. In this study, there was an increase to the highest concentration range, which means that the adsorbent can absorb above concentration.

3. Effect of Adsorbent Mass Variations

The amount of banana peel adsorbent also affects the percentage of the effectiveness of metal absorption. In this variation, 10,20, 30, and 40 grams of

adsorbent were used with a metal concentration of mercury of 6.84 mg/L and a contact time of 5 hours. The highest effectiveness reached 94.8%. The graph of the effect of increasing the amount of adsorbent can be seen in Figure 6.

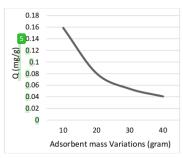


Figure 6. The effect of adsorbent mass variations for removal percentage

It can be seen that the more banana peel Simplicia powder used, the higher the absorption percentage. This happens because if there is an increase in the number of adsorbents, it means that there are more active components such as hydroxyl and carboxyl groups that can bind mercury metal so that the percentage of absorption also increases. This is following the research [30] that the more adsorbents used, the more active sites (C=O and -OH) contained in the adsorbent that can adsorb metals. This active site is used for the chemical adsorption process by forming metal complexes with the active site of the adsorbent. The increase in the percentage of absorption according to the increase in the dose of biosorbent due to the diffusion process towards the adsorbent [13].

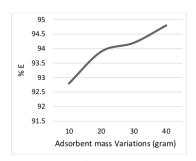


Figure 7. The effect of adsorbent mass variations on absorbtion capacity

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The amount of banana peel adsorbent also influences the absorption capacity. The variations were 10, 20, 30, and 40 grams of adsorbent with a metal concentration of mercury 6.84 mg/L and a contact time of 5 hours. The highest capacity in the amount of adsorbent was 10 grams, which was 0.1587 mg/g and decreased with the increase in the amount of banana peel absorbent used. This is because the increase in absorbents means that more active sites are available, but not all of them are filled with absorbate. This causes the absorption capacity to decrease because we know that the absorption capacity is the capacity of the absorbate that can accumulate on the surface of the absorbent. Therefore, the lower absorption capacity because not all active sites of the absorbent are filled with adsorbate [31].

4. Effect of Contact Time Variations

The contact time between the adsorbent and the effectiveness of metal absorption. Before reaching the optimum condition, the longer the contact time, the greater the absorption efficiency. When contact occurs, the metal absorption process will also occur to the

active sides of the banana peel. In the variation of contact time, the optimum percentage was obtained at 5 hours of contact, with the percentage of effectiveness reaching 95.2%. The graph of changes in the effect of contact time on the percent metal absorption can be seen in Figure 8.

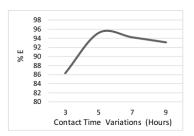


Figure 8. The effect of Contact Time Variations for removal percentage

There was an increase in the percentage of metal absorption along with the addition of adsorption contact time. However, this only lasts until the optimum conditions for the absorption process are reached. When the contact time between the adsorbent and metal continues to grow longer, there is a decrease in absorption effectiveness. This decrease in the percentage of metal absorption can be caused by the active side of the banana peel, which has been saturated and can no longer bind the metal, and the metal bond with the active site on the banana peel is in the form of chemical bonds. Weak so that continuous movement for a long time can cause the bond to break loose again. This is following what has been stated [28] that at the beginning of the contact, the absorption process was still low because the functional groups on the absorbent had not interacted maximally with the metal; then increased, and after reaching the optimum condition, the percentage of absorption decreased. Due to desorption or the release of adsorbate ions that have been bound to the adsorbent into the solution system due to weak bonds. [30] also revealed the same thing that metals can be physically adsorbed (reversible), which causes the longer contact time to cause the metal to be released back into the sample solution

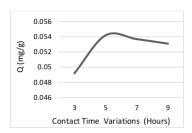


Figure 9. The effect of Contact Time Variations for absorbtion capacity

The contact time between the adsorbent and the metal affects the amount of metal absorption capacity. Before reaching the optimum condition, the longer the contact time, the higher the absorption capacity. In the variation of contact time, the absorption capacity at 5 hours of contact was 0.0542 mg/g. At longer contact times, the absorption capacity decreases. This can be because the solution has reached the saturation point and this can occur due to the release of bonds that have been previously formed. This is in line with what was stated [31] that the initial to optimum contact time will show a high increase in absorption due to the opening of the adsorbent pores by the activator, the condition of the adsorbent is still new and there are still many cavities capable of

catching pollutants. However, when passing the optimum conditions, the adsorbent no longer works. This condition can happen because of the desorption process, which releases heavy metals into the water because of prolonged contact so that the bound metal is released again.

This is also following what was stated [28] that at the beginning of the contact, the absorption process was still low because the functional groups on the absorbent had not interacted maximally with the metal then increased. After reaching the optimum condition the percentage of absorption decreased due to desorption, namely the release of adsorbate ions that have been bound to the adsorbent into the solution system due to weak bonds [30] also revealed the same thing that metals can be physically adsorbed (reversible) which causes the longer contact time to cause the metal to be released back into the sample solution.

CONCLUSION

Kepok banana peels have a very significant effect on decreasing levels of metallic mercury. The optimum removal percentage resulted from variations in mercury concentration was 99.7%, then for variations in the amount of biosorbent was 94.8% and from variations in contact time was 95.2%. The absorption capacity of the kepok banana peel can be influenced by the concentration of mercury metal ions, the amount of absorbent used and the contact time that occurs. Based on the results of a fairly large effectiveness, it means that the kepok banana peel is very suitable to be used as a biosorbent, especially in this case as a

biosorbent for heavy metals such as mercury

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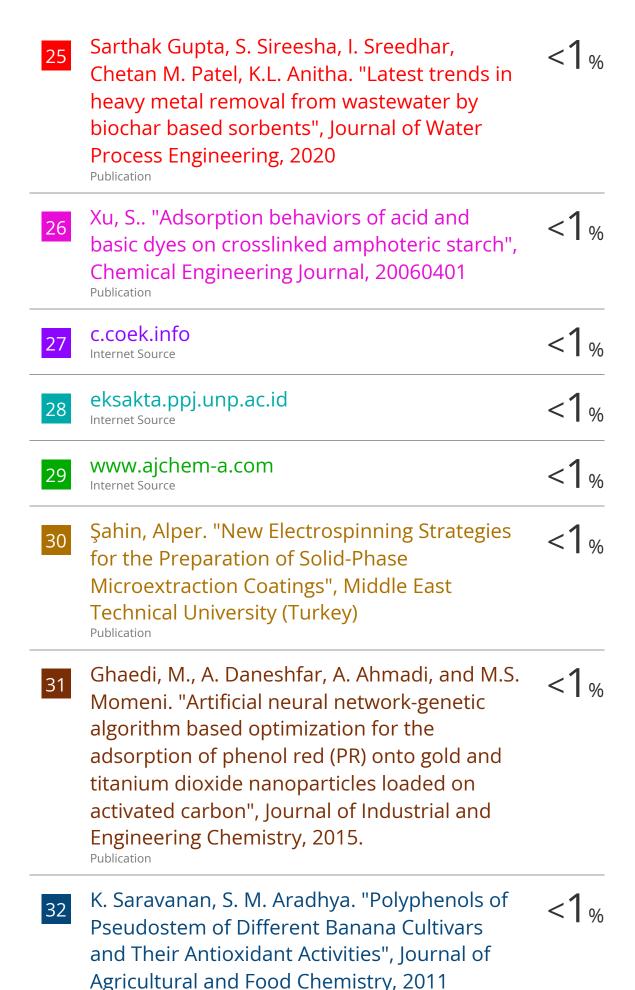
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