POTENTIAL OF CASSAVA PEEL AS Cr METAL BIOSORBENT IN LABORATORY COD WASTE

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ABSTRACT
Cassava peel is an agricultural residual waste that can be found from industrial processing in Indonesia. Cassava peel contains cellulose which can be used as a biosorbent. The aim of this study was to optimize the adsorption of cassava peel waste on chromium metal ions and then to determine the adsorption capacity and adsorption constant values of the Langmuir model and the Freundlich model. The research was divided into four stages, namely manufacture, optimization conditions, maximum capacity, and application to waste. Optimization conditions for weight ratio, optimum concentration, pH, and contact time. Determination of chromium content, standard series, and testing using the APHA method SSA ed. 23\textsuperscript{rd} 3030 D & 3111 B, 2017 at a wavelength of 357.78 nm. Determination of adsorption isotherms of Langmuir and Freundlich models. The optimum condition results at a weight ratio of 1 gram in 10 ml of solution, a concentration of 10 ppm, pH 2, and a contact time of 180 minutes. The adsorption capacity is 0.10216 mg Cr/gram cassava peel biosorbent. Application to chrome contamination laboratory waste obtained an adsorbed concentration of 20.681 ppm. In the Langmuir and Freundlich isothermal model, the $R^2$ value is 0.9668 and 0.9985, the $n$ value is 0.73964.

Keywords: Biosorbent; Cassava peel; COD; Isotherm

1. INTRODUCTION
Cassava peel is a residue of agricultural products or waste of the mocaf flour production industry, tapioca flour, fermentation industry, chips industry and others. Based on the data of the Ministry of Agriculture, the Agricultural Research and Development Agency, in 2013, cassava production was 18.9 million tons per year. Based on this amount of production, the white inner cassava peel waste reached 1.5-2.8 million tons. While the brown outer peel reached 0.04-0.09 million tons per year. Cassava peel as waste is very easy to obtain and the price is low so it has the potential to use as an adsorbent material [1].

Cassava peel has ability to adsorb organic and inorganic compounds useable to reduce Cr concentrations in laboratory waste. Cr metal is a heavy metal that we must reduce or eliminate in laboratory waste complying with the Minister of Environment Regulation Number 5 of 2014 concerning wastewater quality standards [2]. Utilization of cassava peel as an adsorbent to reduce Cr metal content in waste is an alternative use for cassava peel. Therefore, it is necessary to test the adsorption performance of the cassava peel biosorbent for Cr metal in laboratory wastewater.

Cassava peel can be usable as an alternative adsorbent. It refers to [3] suggesting that, based on laboratory analysis, we know that cassava peel contains 56.82% α-cellulose, 21.72% lignin, and fiber length of 0.05 – 0.5 cm [3]. Cassava peel has good potential if used to adsorb heavy metals because it contains cellulose which is quite effective in binding metal ions [4]. According to Zubair et al (2018), cassava peel can be used as an adsorbent to reduce Cr metal in COD wastewater with an adsorption capacity of 0.6911 mg/g [5]. According to [6], cassava peel can be used as an adsorbent to reduce Cr in COD wastewater with an adsorption capacity of 0.0707 mg/g [6]. In previous studies, it
was found that the value of Cr absorption capacity was small. This is because in this study not all optimization of cassava peel biosorbents was carried out beforehand such as optimum contact time, optimum weight ratio, and optimum pH. According to [7], the test results from the start of the COD testing waste showed problems such as dissolved solids (TDS) of around 1415 mg/L, metal Iron (Fe) 105.309 mg/L, metal Manganese (Mn) 85.450 mg/L, metal Total Chromium (Cr-T) 45.750 mg/L and Ammonia (NH\textsubscript{3}-N) 45.809 mg/L. These levels are outside the provisions of the Ministry of Environment's wastewater quality standards No. 05 of 2014 concerning wastewater quality standards for industry and/or other business activities. Appropriate wastewater treatment is required to reduce the levels of pollution load parameters contained in laboratory wastewater [7]. Based on the description above, this study aimed to make, characterize, and optimize the adsorption of Cr metal against pH; contact time; as well as weight ratio, determine maximum capacity of Cr metal and its absorption constant, and end with testing of laboratory COD waste.

2. METHODS

The tools used include erlenmeyer, volumetric pipette, volumetric flask, stirring rod, magnetic stirrer, oven, furnace, vacuum pump, sieve 60 mesh, analytical balance and the instrument used is AAS, FTIR, and SEM. The materials used include cassava peel, KOH 0.3 N, and water, K\textsubscript{2}Cr\textsubscript{2}O\textsubscript{7} (Merck) concentration of 1000 mg/L, distilled water, HNO\textsubscript{3} p.a. (Merck), and 0.45 µm filter paper.

2.1. Production of Biosorbent

As much as 5 kg of cassava peel is washed clean. Then do the drying in the sun until dry. Dry cassava peel as much as 2 kg cut into small pieces. Then the cassava peel biosorbent was ground and blended and then sieved through a 60 mesh sieve. Obtained 1.5 kg of cassava peel biosorbent measuring 60 mesh. Then 1 kg of cassava peel biosorbent was activated using 3 liters of KOH 0.3 N then homogenized using a stirrer for 1 hour at 50 °C then the biosorbent was left to soak for 24 hours. The biosorbent is then filtered and then washed with distilled water and a small addition of 0.5 N HCl or 0.5 N NaOH until the pH reaches 6.5 – 7. The activated biosorbent is then dried in an oven at 110 °C for 2 hours. The biosorbent is cooled in a desiccator and is ready for use.

2.2. Determination of Weight Ratio and Optimum Concentration

Put 50 ml of distilled water into a 250 ml glass cup. Then in the glass cup, 1 gram of cassava peel biosorbent is added continuously until agglomeration occurs. The ratio of the weight of the cassava peel biosorbent to the volume of water was recorded. Then the maximum ratio weight was put into four glass beakers containing 1.0 ppm chromium standard solution; 2.0 ppm; 5.0 ppm and 10.0 ppm. Each cup was stirred using a stirrer speed of 150 rpm for 60 minutes. Then the solution was filtered and the chromium content was measured using an atomic absorption spectrophotometer. Recorded as the ratio of weight and optimum concentration.

2.3. Determination of Optimum pH

50 mL of chromium solution with optimal concentration was added to each of six glass beakers. In each glass cup, the pH of the solution is pH 2; 3; 4; 5; 6; and 7 by adding 0.1 N H\textsubscript{2}SO\textsubscript{4} solution or 0.1 N NaOH into a glass cup containing chromium solution. Then, in each glass cup, cassava peel biosorbent is added according to the optimum weight ratio that has been determined. Then stir with a stirrer at 150 rpm for 15 minutes. Then it was filtered and the chromium content was measured using an atomic absorption spectrophotometer.

2.4. Determination of Optimum Contact Time

The cassava peel biosorbent was added as much as the optimum weight ratio which had been determined and then put into five glass beakers. Enter as much as 50 ml of optimum concentration Cr solution. Adjust the pH according to the results of determining the optimum pH. Stirred at 150 rpm for 1 hour using a stirrer then allowed to stand for the specified contact time, namely 30, 60, 120, 180, 360 minutes. When it reaches the contact time limit, the
mixture is then filtered and the chromium content is measured using an atomic absorption spectrophotometer.

2.5. Determination of Maximum Capacity

Cassava peel biosorbent was added as much as the optimum weight ratio that has been determined to be put into a 250 mL glass cup. Then put as much as 50 mL of concentration 2.0; 3.0; 4.0; 5.0; 6.0; 7.0; 8.0 ppm Cr into the beaker earlier. The mixture was then stirred at 150 rpm for 1 hour and then allowed to stand for the optimum contact time obtained from determining the optimum contact time. The mixture was filtered and the filtrate was measured for chromium content on an atomic absorption spectrophotometer. Then the data obtained, processed data with graphical methods.

2.6. Waste Water Treatment Application

The homogenized laboratory COD waste solution from one of the testing laboratories in the city of Bogor was pipetted 50 mL into a 100 mL glass cup. Added 5 mL of concentrated HNO₃. Heated on an electric heater until the solution is almost dry. 50 mL of distilled water was added, then filtered, put into a 100 mL volumetric flask and adjusted with distilled water, then homogenized. The chromium content was measured using an atomic absorption spectrophotometer (AAS). The activated cassava peel biosorbent was then tested on a laboratory waste solution. 50 ml of waste water is put into a 250 mL glass cup. The pH was adjusted to the optimum pH that had been determined by adding 0.1N NaOH or 0.1N H₂SO₄. Then the biosorbent was added in the amount of the weight ratio that had been determined. Then stir with a stirrer at 150 rpm for 1 hour. Then allowed to stand in accordance with the determination of the optimum contact time. Then filtered, pipette the filtrate as much as 50 ml into a 100 mL glass cup. Added 5 mL of concentrated HNO₃. Heated on an electric heater until the solution is almost dry. 50 mL of distilled water was added, then filtered, put into a 100 mL volumetric flask and adjusted with distilled water, then homogenized. The chromium content was measured using an AAS.

2.7. Data Analysis

Determination of chromium content of chromium metal and adsorption effectiveness in COD wastewater were determined using an AAS. Determination of % adsorption efficiency can be calculated using the equation:

\[ \% \text{ Efficiency} = \frac{C_i - C_e}{C_i} \times 100 \]

Where \( C_i \) is the initial concentration (mg/L) and \( C_e \) is the final concentration (mg/L). Calculation of adsorption capacity (qe) can be calculated using the equation:

\[ qe = \frac{C_i - C_e}{m} \times V \]

Where \( qe \) is the Cr adsorbed by the adsorbent (mg/g), \( C_i \) is the initial concentration of Cr (mg/L), \( C_e \) is the final concentration of Cr (mg/L), \( m \) is the mass of the adsorbent (g), and \( V \) is the volume of the solution absorbed (L).

3. RESULTS AND DISCUSSION

3.1. Production of Cassava Peel Biosorbent

The cassava peel biosorbent produced from cassava peel waste has a blackish brown color with a fine texture and has a size of 60 mesh. The yield produced from 5 kg of cassava peel waste is 1.55 kg or 31%. The ingredients in cassava peel are generally cellulose, hemicellulose, and lignin. Cellulose is an organic compound consisting of carboxyl and hydroxyl. The carboxyl and hydroxyl in cellulose can reduce metal content in a waste [8]. In addition to the cellulose content, cassava peel also contains lignin. Lignin can bind to cellulose and form lignocellulose. Lignocellulose must reduce or even eliminate if a biomass is to be usable as an adsorbent. Lignocellulose can be removable using alkaline solutions such as NaOH or KOH. The alkaline solution used for the delignification process in this study was KOH, where OH⁻ could break the lignocellulosic bonds [9].

3.2. Characterization of Cassava Peel Biosorbents

Characterization of cassava peel biosorbents used FTIR and SEM.
Based on Figure 1, several functional groups were found in the cassava peel biosorbent, including the O-H functional group stretching at wave number 3272.75 cm$^{-1}$, the C-H group aliphatic stretching at absorption wave number 2923.08 cm$^{-1}$ [10], the C=O ester group at absorption wave number 1598.29 cm$^{-1}$, and the C-O ester group at absorption 1007.41 cm$^{-1}$. The results of the FTIR qualitative test on this cassava peel biosorbent match the spectrum of cellulose [11].

The characteristic results using SEM at a magnification of 2,500 times can show that the surface area of the biosorbent after activation is greater than before activation. The larger the surface of the adsorbent, the greater the metal absorption results that will be carried out by the biosorbent is.

3.3. Optimum Biosorbent Weight Ratio and Optimum Concentration

The results of the study on the optimum weight ratio of the cassava peel biosorbent were then compared to the various test concentrations. This weight ratio is obtained by adding a number of biosorbents to distilled water continuously to form lumps. Then, this result is tested on variations in concentration to find out the optimum concentration of this weight ratio works.

Figure 3 shows that, with a weight ratio of 1 gram of cassava peel biosorbent in 10 ml of chromium standard solution, the adsorption efficiency reached 71.55% at a concentration of 10 ppm. It shows that the adsorption efficiency for cassava peel biosorbent with a ratio of 1 gram of cassava peel biosorbent in 10 ml of standard Cr solution was effective at concentrations of around 10 ppm or more. At concentrations of 1 ppm and 2 ppm, the efficiency was only 0.9% and 1.9%. This can happen due to the lack of interaction time between the adsorbent and the chromium solution. So that the adsorption process at this concentration has not been completely adsorbed [14].
3.4. Optimum pH of Cassava Peel Biosorbent

Based on Figure 4, the optimum pH for the cassava peel biosorbent was obtainable at pH 2 where the adsorbed chromium was 7.9363 ppm with an efficiency value of 77.13%. At pH 6 and 7, the amount of adsorbed concentration decreased significantly compared to pH below 4. It was because, at low pH, the H⁺ ions on the adsorbent surface increased resulting in a strong electrostatic bond between the positive charge on the adsorbent surface and the dichromate ion.

Figure 4. Graph of Optimum pH

Meanwhile, with increasing pH, the adsorption of Cr metal ions would decrease. It was because, at high pH, the concentration of OH⁻ ions in solution increased so that the cell surface slowly became negatively charged. It caused the strength to bind Cr ions to be smaller and reduced the adsorption ability. At high pH there is also precipitation of Cr ions into Cr(OH)₃ which reduces the solubility of Cr ions in solution resulting in a reduced amount of Cr ions that can be absorbed by the cell surface [15].

3.5. Optimum Time of Cassava Peel Biosorbent

Contact time is the time needed for cassava peel biosorbent to obtain the highest concentration of adsorbed chromium. The longer the contact time, the higher the chromium concentration that will be adsorbed by the biosorbent is. Therefore, it is necessary to test the contact time in the adsorption process.

Figure 5. Graph of Optimum Time

Figure 5 shows that the longer the contact time occurring in the adsorption process, the more metal ions that will be adsorbed by the cassava peel biosorbent is. In this study, the optimum contact time occurred at 180 minutes, with an efficiency value of 79.03%. At a contact time of 360 minutes, the concentration of chromium absorbed did not increase. It was because, after passing the contact time of 180 minutes, the absorption capacity of the adsorbent began to decrease. It was because the adsorbent was already in a saturated condition. Saturated conditions are conditions where the ability of the adsorbent to absorb metal ions has greatly reduced. It is because the adsorbent pores are filled with adsorbed metal ions [16].

3.6. Maximum Capacity and Adsorption Isotherms

In Figure 6 it can be shown that the increase in the amount of adsorbed metal is directly proportional to the increase in the initial concentration. This is because the higher the concentration of Cr, the more Cr molecules that interact with the biosorbent so that the adsorption increases [17].
The determination of the isotherm model was carried out to determine the adsorption equilibrium model occurring in a test. Determination of the type of adsorption isotherm by cassava peel biosorbent used data of the calculation of adsorption capacity at various concentration variations. Then, a graphic table was made to determine that the linear regression of the cassava peel biosorbent followed the linear regression of the Langmuir’s isotherm model or the Freundlich’s isotherm model.

The Freundlich’s equation model explains that there is more than one surface layer (multilayer) and the sides are heterogeneous, namely, there is a difference in binding energy on each side where the adsorption process on each adsorption side follows the Langmuir’s isotherm. Therefore, the determination of the maximum adsorption power of the cassava peel biosorbent in the chromium metal absorption process was calculated by using the Langmuir’s adsorption equation as in the research of reference [19]. Because it was carried out on a single layer of adsorbed substance of chromium metal ions on each surface of the cassava peel biosorbent in units of mg of adsorbed chromium metal ions/gram of biosorbent. The calculation results show that the maximum adsorption capacity is 0.10216 mg/gram.

### Table 1. Constant Values on Langmuir and Freundlich Isotherms

<table>
<thead>
<tr>
<th>Isotherm</th>
<th>Constant</th>
<th>Value</th>
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<tbody>
<tr>
<td>Langmuir</td>
<td>a</td>
<td>0.10216</td>
</tr>
<tr>
<td></td>
<td>b</td>
<td>0.34250</td>
</tr>
<tr>
<td>Freundlich</td>
<td>k</td>
<td>18.6509</td>
</tr>
<tr>
<td></td>
<td>n</td>
<td>0.73964</td>
</tr>
</tbody>
</table>

Figure 7 and Table 1 show that test of the data obtained by the cassava peel biosorbent using the Langmuir’s isotherm model and the Freundlich’s isotherm model shows a good R² value and has an R² coefficient ≥ 0.9 [18]. Figure 7 shows that the adsorption equation for Cr ions by the cassava peel biosorbent satisfies the Langmuir’s adsorption equation with R² as much as 0.9668 and also the Freundlich’s adsorption equation with R² as much as 0.9985.

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### 3.7. Laboratory COD Waste Application

COD waste is waste analysis results of COD analysis using a large amount of chromium in the analysis process. COD waste is taken from the...
laboratory. The COD waste is then subjected to preliminary testing and the initial concentration of chromium before adsorption by the cassava peel biosorbent using an atomic absorption spectrophotometer (AAS) with the equation of the line \( y = 0.059564x + 0.0063220 \) with \( R^2 = 0.9994 \).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Observation</th>
</tr>
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<tbody>
<tr>
<td>Cr</td>
<td>24,011 ppm</td>
</tr>
<tr>
<td>pH</td>
<td>0.11</td>
</tr>
<tr>
<td>Form</td>
<td>Liquid</td>
</tr>
<tr>
<td>Color</td>
<td>Green</td>
</tr>
</tbody>
</table>

Table 2. Initial Concentration of COD Waste

After obtaining the initial concentration of the preliminary test, the COD waste was adsorbed by cassava peel biosorbent. In this study, it was known that the chromium content of COD waste was 24.011 ppm. The waste used for the adsorption process was 50 ml with a weight ratio of 1 gram of cassava peel biosorbent in 10 ml of the solution and then set to optimum conditions according to the optimization carried out. The pH obtained is very low, this is because at low pH the \( \text{H}^+ \) ions on the adsorbent surface increase resulting in a strong electrostatic bond between the positive charge on the adsorbent surface and the dichromate ion [15].

Figure 8. Graph of Biosorbent Application to COD Waste

Figure 8 shows the decrease in chromium concentration in COD waste after adsorption with cassava peel biosorbent. The decrease in chromium concentration in COD waste from 24.0111 ppm to 3.33 ppm with an efficiency of 86.13%. The maximum capacity in this test is 0.2060 mg Cr/g cassava peel biosorbent.

4. CONCLUSION

The cassava peel biosorbent which was activated using 0.3 N KOH was blackish brown with a size of 60 mesh. The characteristics of the functional groups obtained from the FTIR test are the O-H alcohol functional group, the aliphatic C-H functional group, the C=O ester functional group and the C=O ester functional group. The characteristic results from SEM show that the surface area of the cassava peel biosorbent after activation has a larger size than the cassava peel biosorbent before activation. The optimum condition of the cassava peel biosorbent obtained was the maximum weight ratio of 1 gram of cassava peel biosorbent: 10 ml of solution, at pH 2, contact time of 180 minutes with 10 ppm chromium concentration. The adsorption isotherm model obtained includes the Langmuir isotherm model and the Freundlich isotherm model with an \( R^2 \) value of more than 0.9 each. So that the maximum adsorption capacity in this study can refer to the \( a \) of the Langmuir isotherm model, which is 0.10216 mg Cr/g biosorbent and \( b \), which is 0.34250. Cassava peel biosorbent can reduce Cr levels in COD analysis service laboratory wastewater from 24.0111 ppm to 3.33 ppm with an efficiency of 86.13% and a maximum capacity of 0.2060 mg Cr/g biosorbent.

REFERENCES


