The reduction of heavy metals Cd and Cr levels in wastewater using bagasse charcoal as an adsorbent

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Abstract. The utilization of charcoal from bagasse as adsorbent is an alternative way to reduce heavy metal of Cd and Cr in Wastewater. Bagasse is one of the agricultural wastes that potentially obtained with an abundant amount. This research aims to identify the full time and the adsorption capacity of charcoal with a continuous column method and downflow. Activation of charcoal used is Chloride Acid 2N in 24 hours soaking. Metal solution concentration of Cd and Cr were 2 ppm and 5 ppm, respectively. The results of this study are that full time for charcoal for Cd occurred on minutes of 480 for 2 ppm and minutes of 300 for 5 ppm. Meanwhile, saturated time for Cr occurred on minutes of 360 for 2 ppm and minutes of 240 for 5 ppm. The significant efficiency of metal ion adsorption to Cd concentrations for 5 ppm and 2 ppm were 28.05% and 26.75%.

1. Introduction

The development of the industry is quite rapid currently to make an essential contribution to humans and the environment. Although it provides a sizeable contribution to humans, it also harms humans and the environment. With the industrialization process that produces liquid, solid and gas waste and the release of toxic heavy metals in the water stream can cause environmental problems and disrupt human health.

Waste products from industrial activities sometimes release heavy metals in water, such as chromium (Cr) and cadmium (Cd). The chemical is wastes of hazardous and toxic substances (B3) that require extraordinary treatment. Several methods for removing heavy metals in wastewater are physical or chemical such as precipitation, coagulation, and ion exchange. However, these methods require quite expensive costs. Therefore, currently, there have been various efforts to control metal ion waste, which leads to efforts to find ways that are cheap, effective and efficient [1].

One of the most widely used methods in the industry is the adsorption process. The adsorption process is more economical, able to remove organic materials, and does not cause toxic side effects. Activated carbon can be made from various raw materials if it contains carbon. In this research, activated carbon is used as the result of sugarcane grinding. Sugarcane bagasse is a natural material. It contains functional groups, including carboxyl, amino, sulfate, plainaccharide, lignin, and sulfhydryl. They are useful in adsorption capability. Also, sugarcane bagasse is one of the materials that are quite potential to be developed in Indonesia because of its abundant availability. In the last ten years, the area of sugar cane plantations in Indonesia has continued to increase with an average growth of 3.75% per year from only 388,500 hectares in 2000, rising to 443,800 hectares in 2009 [2].
This research is to identify how much the ability of bagasse charcoal to absorb toxic heavy metal ions against Cd and Cr metals. By using the column method continuously, it is hoped that this research can be useful in the treatment of industrial waste. As a result, it can reduce the level of environmental pollution caused by dangerous and toxic metals.

2. Methodology

2.1. Location
This research was conducted at the Laboratory of Water Quality, Faculty of Engineering, Hasanuddin University, Gowa. Whereas the sample test was held at the Makassar Health Laboratory Center.

2.2. Research Implementation
This research was conducted by collecting data (literature study). The preparation phase, the stage of determining the saturation time based on the concentration, then the data obtained were analyzed to get a conclusion. 1. Adsorbent preparation is that washing sugarcane bagasse and drying in the sun. Then sugarcane bagasse is cut to a specific size and made into a furnace at 300 0C for 1.5 hours. 2. Activation of sugarcane bagasse charcoal: soaking for ± one day using 2 N HCl, washed to get neutral pH, then dried in an oven at 250 0C for 4 hours. Furthermore, for the manufacture of Cd and Cr 25 L metal solution concentrations of 2 and 5 ppm, respectively.

2.2.1. Determination of the length of time saturated. 25,000 ml of Cd metal solution is put into a container or pipe column. The solution flowing through the bagasse charcoal is passed following the settings of the tap opening discharge 50 ml/min with a variation of the time taken to produce the first 30 minutes filtrate and the next 1 hour. The filtrate yield was then measured using an Atomic Absorption Spectrophotometer (AAS).

Figure 1. Adsorption column method
The method used in this study is the column method [3]. The design of the device consists of a 3-inch pipe, bucket and valve, filter cloth which is in a tube, and a sample bottle. The framework for this research is as follows:

**Figure 2.** Research framework

### 2.3. Data Analysis

The formula can calculate the concentration of Cd and Cr ions adsorbed:

\[
C_{\text{adsorption}} = C_{\text{first}} - C_{\text{end}}
\]  
\[\text{(1)}\]

Where,

- \(C_{\text{adsorption}}\) = Accumulated concentration after the adsorption process (ppm)
- \(C_{\text{first}}\) = Concentration of wastewater before adsorption
- \(C_{\text{end}}\) = Sewage concentration after adsorption

The adsorption kinetics can be done by Thomas equation. The Thomas equation is derived from the Bohart Adams formula. The Thomas model is one of the most widely applied models in determining ion concentrations [3,4,5]. The experimental data adjusted for the Thomas model are shown from the R2 value of the plot results of data between \(\ln (C_0 / C_t - 1)\) to the operating time. A high R2 value indicates that the Thomas model matches the experimental data so that it can be used as a design reference parameter [3, 4, 5]. The value of R2 is a correlation coefficient that indicates whether there is a relationship between one data with other data. If the value of R2 approaches the value of 1, then the data obtained is suitable for use in the Thomas prediction model [3,4,5]. On the other hand, if the value of R2 is much closer to 1, then, the possibility of the data obtained is not following the Thomas model but by other prediction models [3,4,5].

The kinetic parameters of the Thomas model can be determined by equating the regression equation of the plot results with the linear equation, which is explained as follows:
so, to determine the kinetic parameters of the Thomas model in the form kTh and q0 can be obtained through the following equation:

\[ K_{Th} = \frac{-a \times 1000}{C_o} \]  

(4)

Intercept = \( b = \frac{K_{Th} q_0 X}{Q} \) 

(5)

\[ q_0 = \frac{b \times Q}{K_{Th} X} \]  

(6)

The parameters obtained are then used to obtain \( C_t / C_0 \) data to create breakthrough curves. The Thomas model equation follows:

\[ \frac{C_t}{C_0} = \frac{1}{1 + \exp(\frac{K_1}{Q}(q_0 M - C_0 V_{eff}))} \]  

(7)

Where, 

- \( K_{Th} \) is Thomas's rate constant (ml.minute\(^{-1}\) mg\(^{-1}\)), 
- \( q_0 \) is the adsorption capacity (mg/g), 
- \( X \) is the amount of adsorbent in column (g), 
- \( V_{eff} \) is the effluent volume (ml), 
- \( C_0 \) is the influent concentration (mg/l), 
- \( C_t \) is the effluent concentration at time t (mg/l), 
- \( K_1 \) is rate concentration, 
- \( M \) is adsorbent mass (g), and 
- \( Q \) is the flow rate (ml.minute\(^{-1}\)).

Calculation of total mass adsorbed by metal as follows:

\[ q_{total} = \frac{Q C_0 A}{1000} \]  

(8)

The estimate of the total mass of metal ions that pass through a column as follows below:

\[ M_{total} = \frac{C_0 q T_{total}}{1000} \]  

(9)

Calculation of percentage of metal ion removal as below:

\[ R\% = \frac{q_{total}}{M_{total}} \times 100 \]  

(10)

Calculation of adsorption capacity \( (q_e) \) as following below:

\[ q_e = \frac{q_{total}}{X} \]  

(11)

Where, 

- \( Q \) the discharge (ml/minutes), 
- \( C_0 \) is the influent concentration (µg/l), 
- \( X \) the mass of absorbent used in column (g), 
- total saturation time (minutes), 
- \( Z \) bed height (cm), 
- \( t_b \) and \( t_e \) breakthrough time of 10% and a saturation of 90% (minutes).
3. Results and Discussions
This chapter discusses the results of adsorption of Cd and Cr metal ions in a column with the continuous top-down flow using activated charcoal from bagasse waste as an adsorbent. It aims to adsorb Cd, and Cr metal ions, which are adopted by using activated charcoal from bagasse waste is based on variations in the concentration of the metal solution. The reading of the results of the level of metal ions Cd and Cr using Atomic Absorption Spectrophotometer (AAS). Industrial or artificial wastewater is obtained from the effect of mixing the metal solution with distilled water of 2 ppm and 5 ppm, respectively. Taking or checking samples is done every first 30 minutes and 60 minutes after that to find out the saturation time.

3.1. Determination of the saturation time of Cd and Cr metal adsorption based on Breakthrough Curves.
The Breakthrough curve can explain the parameters of the contact time (x-axis) in minutes to the ratio of final concentration ($C_t$) and initial level ($C_0$) (y-axis). If the comparison value of final concentration and initial concentration reaches the value of 1, it can be said that at that time, the adsorbent condition has reached its saturation point. The saturation time is the time needed by the effluent to reach 90% of the initial concentration. It takes time so that 90% is chosen as a practical value in this research to achieve a value of 100%.

3.1.1. Breakthrough curves based on the influence of metals on the same concentration.
Breakthrough curves with concentrations of 2 ppm for Cr and Cd metals.

![Figure 3](image)

Figure 3. The relationship between time and $C_t/C_0$ based on the effect of Cd and Cr metals at a concentration of 2 ppm.

Based on figure 5, the effect of concentration on the metal Cd and Cr can be seen at the same level of 2 ppm, metals for cadmium (Cd) and Chromium (Cr) have different saturation times. 90% $C_t/C_0$ Cd metal occurs at 480 minutes with a $C_t/C_0$ value of 0.9082, while for chrome metal (Cr) occurs at 360 minutes with an amount of $C_t/C_0$ of 0.9108. It indicates that the Cr metal is saturated faster than the Cd metal. It can also be seen from the steep curve shape on the Cr metal and the gentle curve on the Cd metal.

3.1.2. Breakthrough curves with a concentration of 5 ppm for Cr and Cd metals
The same result occurs at a concentration of 5 ppm (figure 6), where the saturation time of Cr metal occurs earlier than that of Cd metal. The saturation time of Cr metal arises at 240 minutes with $C_t/C_0$ value by 0.937, while for Cd at 300 minutes by 0.948. The resulting curve shape is also steep on Cr metal and ramps on Cd metal. It can happen because Cr metal has a low electronegativity so that it is
weak in the bonding process between metal ions. It is following a study by [5], which indicates that a column with high concentration has a breakthrough curve with a sharp slope.

**Figure 4.** The relationship between time and Ct/Co based on the effect of Cd and Cr metals at a concentration of 5 ppm.

3.1.3. **Breakthrough curves based on the effect of different concentrations on one metal.**

**Figure 5.** The relationship between time and ct / c0 based on the influence of concentrations of 2 and 5 ppm on Cadmium metal (Cd).

Figure 7 shows Cadmium (Cd) breakthrough curves with different concentrations. The Cd metal with a variant of 2 ppm concentration and 5 ppm concentration, there is a difference in saturation time. At a level of 2 ppm, saturation time occurs at 480 minutes with Ct/Co 0.908. It is because the metal solution has a lower concentration so that the time needed to adsorb sugarcane bagasse is longer. Whereas at a level of 5 ppm, the adsorption process occurs at a time of 300 minutes with Ct/Co 0.948, which is faster to reach the saturation point. Because of the higher concentration solution results in the quicker metal ion binding process.
3.1.4. Chromium metal (Cr) Breakthrough curves with different concentrations

![Figure 6](image)

Figure 6. The relationship between time and ct / c0 based on the influence of concentrations of 2 and 5 ppm on Chromium metal (Cr).

Whereas in Cr metal, which can be seen in figure 8, the same results were obtained at 2 ppm and 5 ppm concentration variants. The saturation time at a concentration of 2 ppm occurred at 360 minutes with ct / co 0.911, while for the concentration of 5 ppm, the saturation time occurred at 240 minutes with ct / co 0.937. The higher the concentration of a solution, the faster the adsorbent reacts, conversely the smaller the concentration of a solution, the slower the time required for active adsorbent binding. As a result, when the frequency is low, less amount of metal can be absorbed. So, the saturation time obtained is more prolonged, which can also be seen from the shape of the steep curve on the Cr metal. From the breakthrough curve, parameters can be obtained, which explain the adsorption efficiency presented in Table 8 below:

| Parameter Breakthrough adsorb ion Logam Cd & Cr. | Co (mg/L) | total (minute) | T₀.1 minute | T₀.9 minute | MTZ (cm) | qtotal (mg) | Mtotal (mg) | %R | qe (mg/g) |
|-----------------------------------------------|-----------|----------------|-------------|-------------|----------|-------------|-------------|----|----------|
| Cd                                            | 2         | 600            | 6,382       | 460         | 29,58    | 16.05       | 60          | 26.75 | 0.064    |
|                                               | 5         | 300            | 5,882       | 250         | 29,29    | 21.0375     | 75          | 28.05 | 0.084    |
| Cr                                            | 2         | 600            | 5,084       | 345         | 29,55    | 10.995      | 60          | 18.325 | 0.044    |
|                                               | 5         | 300            | 5,084       | 200         | 29,23    | 16.3875     | 75          | 21.85 | 0.065    |

Based on table 8, it is known that increasing the concentration of a solution is followed by the increases in the total mass of the absorbed metal (qtotal). And the mass of metal ions that pass through the column (mtotal), the adsorption capacity (qe), and the absorption efficiency (% R). In addition to the value of the mass transfer zone (MTZ) shows that the greater the concentration of a solution, the value of the Mass Transfer Zone (MTZ) becomes smaller.
3.2. Application of the Thomas model

The Thomas model is one of the most common and widely used theoretical methods to describe column performance. Column biosorption data is adjusted by plotting data between \( \ln \left( \frac{C_0}{C_t} - 1 \right) \) and time. Following is the linearization of the Thomas equation below:

3.2.1. Thomas model plot for Cadmium metal (Cd)

Based on the above plot, it can be explained that a regression equation is obtained for each variation of the inlet concentration. The results of the regression values for the metal Cd at concentrations of 2 and 5 ppm are 0.9958 and 0.9912. While the results of regression values for Cr metal at concentrations of 2 and 5 ppm are 0.9945 and 0.9911. The regression value obtained is close to 1, which shows that the Thomas model is eligible or can be used in the column method.

With this regression equation, the Kostanta Lomas Thomas (KTH) value and the maximum solute concentration during solid \((q_0)\) in Table 9 can be used as a comparison of the adsorption capacity of the experimental data \((q_e)\).

\[
y = -0.0053x + 0.3189 \\
R^2 = 0.9958
\]

\[
y = -0.0102x + 0.2742 \\
R^2 = 0.9912
\]

**Figure 7.** The Thomas Model plot for the adsorption of Cr Metal Charcoal from Bagasse with a concentration of 2 ppm and 5 ppm.

3.2.2. Thomas model plot for Chromium metal (Cd)

Based on the Thomas Model parameters, it can be explained that the adsorption capacity \((q_0\text{Thomas})\) for Cd metal inlet concentration of 2 ppm is 0.02407 mg / g. The concentration of 5 ppm has increased by 0.02688 mg / g. It is consistent with the study by [6,7], which states that the rate constant \((K_{th})\) decreases, and the adsorption capacity \((q_0\text{Thomas})\) increases with increasing concentration.

For Cr metal, the results of adsorption capacity \((q_0\text{Thomas})\) based on the calculation of the Thomas model at 2 ppm concentration is 0.00168 mg / g. At a level of 5 ppm adsorption capacity \((q_0\text{Thomas})\) obtained is 0.00117 mg / g. It is due to several factors during the study, one of which is the standard flow rate so that the flow is sometimes not constant.
Figure 8. The Thomas Model plot for the adsorption of Cr Metal Charcoal from Bagasse at 2 ppm and 5 ppm.

Table 2. Thomas Model Parameter for Cd & Cr metal Adsorption with Concentration Variation

| Metal Variations | Co (mg/l) | Z (cm) | X (g) | K_{TH} (ml/minute.mg) | q_{0 \text{ thomas}} (mg/g) |
|------------------|----------|-------|-------|-----------------------|-----------------------------|
| Cd               | 2        | 30    | 250   | 2.65                  | 0.02407                     |
|                  | 5        | 30    | 250   | 2.04                  | 0.02688                     |
| Cr               | 2        | 30    | 250   | 3.3                   | 0.00168                     |
|                  | 5        | 30    | 250   | 2.3                   | 0.00117                     |

References

[1] Kundari N A dan Wiyuniati S 2008 Tinjauan kesetimbangan adsorpsi tembaga dalam limbah pencuci PCB dengan zeolit In Seminar Nasional IV SDM Teknologi Nuklir Yogyakarta 25-26
[2] Jakarta B P D 2010 Hasil Sensus Penduduk 2010 Data Agregat per Kabupaten/Kota–Provinsi DKI Jakarta
[3] Kumar U and Bandyopadhyay M 2006 Fixed bed column study for Cd (II) removal from wastewater using treated rice husk Journal of hazardous materials 1-3 253-259
[4] Borba C E, da Silva E A, Fagundes-Klen M R, Kroumov A D and Guirardello R 2008 Prediction of the copper (II) ions dynamic removal from a medium by using mathematical models with analytical solution Journal of Hazardous Materials 1 366-372
[5] Calero M, Hernáinz F, Blázquez G, Tenorio G and Martín-Lara M A 2009 Study of Cr (III) biosorption in a fixed-bed column Journal of Hazardous Materials 1-3 886-893
[6] Han R, Zhang J, Zou W, Xiao H, Shi J and Liu H 2006 Biosorption of copper (II) and lead (II) from aqueous solution by chaff in a fixed-bed column Journal of Hazardous Materials 1-3 262-268
[7] Han R, Wang Y, Zou W, Wang Y and Shi J 2007 Comparison of linear and nonlinear analysis in estimating the Thomas model parameters for methylene blue adsorption onto natural zeolite in fixed-bed column Journal of Hazardous Materials 1-2 331-335