The utility of cocoa pods husk M45 (*Theobroma cocoa*) as adsorbent of heavy metals, iron (Fe) and copper in the laboratory wastewater

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Abstract. Adsorption is one of the alternative media for processing wastewater. The study aims to use cocoa pods husk M45 (*Theobroma Cacao*) as a biosorbent in reducing Fe (III) and Cu (II) ions content in the laboratory liquid waste. This research was carried out through two systems, batch and continuous systems. The batch system was conducted to determine optimum contact time, optimum pH, and adsorption capacity, whereas the continuous system was intended to determine the adsorbent height and the maximum flow rate of laboratory liquid waste. The methods used in this study were adsorption and filtration. The adsorption results were analyzed by Atomic Absorption Spectrophotometer (AAS). The results found that the optimum contact time and the optimum pH for the adsorption of metal ions by cocoa pods husk M45 were 90 minutes and 6, respectively. The optimum flow rate of the wastewater in the continuous system was 6.166 mL/sec with an adsorbent height of 15 cm in the 2-inch adsorption column. The adsorption capacity of adsorbent based on the Langmuir isotherm was 11.074 mg/g for Fe (III) and 28.4091 mg/g for Cu (II).

1. Introduction
Cocoa (*Theobroma cacao L.*) is one of the mainstay commodities of Indonesia's national plantations as a provider of employment, a source of income, and foreign exchange [1,2]. Indonesia is the third-largest producer of cocoa in the world after Ivory Coast and Ghana [3].

Cocoa pods contain 36.23% cellulose, 1.14% hemicellulose and 20-27.95% lignin. The high cellulose content in the skin of this cocoa fruit has the potential to be further processed as an adsorbent to handle water pollution waste [4]. The results of the FT-IR analysis showed the presence of C-H, O-H (hydroxyl) and C = C-H (aromatic-H) groups [5]. Proximate composition of cacao plant waste specifically on dry compositions containing ash of 12.20%; crude protein of 7.16%; the fat of 0.80%; Ca of 0.58.5% and P of 0.18% [6]. The utilization of cocoa fruit skin is as an alternative source of nutrition in animals by fermentation [7]. The fruit skin of cocoa is also used as an adsorbent for blue dyes [4].

Environmental pollution is a condition that occurs due to changes in environmental conditions (land, water, and air) that are unfavorable due to the presence of foreign matter so that the environment does not function as before [8]. Water pollution is the inclusion or insertion of other components into the water, causing water to not function according to its designation [9]. A serious cause of seepage into groundwater is the collection of chemical waste and landfills [9]. Therefore,
environmentally friendly products, such as coconut shell waste, are needed to replace chemical pesticides.

A laboratory is a place where the testing process is carried out to obtain accurate test results. Many laboratories use heavy metals which are generally classified as B3 waste. Heavy metals that are often found in laboratory waste include chromium (Cr), iron (Fe), cadmium (Cd), copper (Cu), cobalt (Co), manganese (Mn), zinc (Zn), lead (Pb), and nickel (Ni) \[10, 11\]. Even though some of the heavy metals are essential for human beings, the existence of the metals in the water environment can be dangerous for them. Therefore, it is required to reduce or remove them from the wastewater discharged from the laboratory.

The use of adsorbents is an alternative method of treating waste, both heavy metals and dyes. Biosorption is an alternative way of removing heavy metals from water or liquid waste because the cost required is cheap, the method is easy and efficient to be operated, and raw materials are available \[12-14\]. This study aims to determine the optimum contact time, the pH optimum, and the capacity in adsorbing Fe (III) and Cu (II) ions from the laboratory liquid waste in the batch system. In the continuous system, it aims to determine the flow rate of wastewater, the adsorbent height in a column. The general objective of this study is to utilize agricultural waste as an alternative media for the treatment of wastewater.

2. Materials and methods

2.1. Equipment and materials

The equipment used in this study was Atomic Absorption Spectrophotometers, AAS (Perkin Elmer 900F), magnetic stirrer (VITLAB, 9 x 25 mm), hotplate (VELP SCIENTIFICA), and oven (Memmert). The adsorption column was made of PVC pipe with a diameter of 5 cm and a length of about 50 cm, taking into account the average diameter of the adsorbent around 0.01 - 0.5 cm so that the minimum diameter of the column was 10 times of the adsorbent diameter to avoid wall effects \[15\].

The raw material for purple-cocoa pods husk comes from Posi Village, Bua Subdistrict, Luwu Regency. The laboratory waste was obtained from Chemical Laboratory waste in the State Polytechnic of Ujung Pandang. All chemicals (CuSO\(_4\) . 5 H\(_2\)O, (NH\(_4\))\(_2\)Fe(SO\(_4\))\(_2\) . 12 H\(_2\)O, HNO\(_3\), and NaOH) were purchased from Merck.

2.2. Preparing adsorbent

Cocoa pods husk was dried under the sun, cleaned from specks of dirt and blended to reduce the size. Cocoa husk powder produced was sieved so obtained size of about 100 mesh and heated in an oven at a temperature of 105 °C for approximately 24 hours.

2.3. Determining the optimum contact time in adsorption of Fe (III) and Cu (II) ions

Cocoa pods husk adsorbent was weighed (0.1 g), put into each 100 mL Erlenmeyer, and added 20 mL of Fe (III) ion solution with a concentration of 100 ppm. The solution was stirred using a magnetic stirrer for 30, 60, 90, 120, and 150 minutes. The mixture was then filtered, and the content of ions in the filtrates was measured using an Atomic Absorption Spectrophotometer (AAS). Each experiment was carried out in duplicate. This procedure also applies to Cu (II) ions.

2.4. Determining the optimum pH in adsorption of Fe (III) and Cu (II) ions

Cocoa pods husk adsorbent was weighed (0.1 g), put into each 100 mL Erlenmeyer, and added 20 mL of Fe (III) ion solution with a concentration of 100 ppm at pH of 2, 3, 4, 5, 6, 7.8 and 9. The mixture was stirred at the optimum time and filtered. The experiments were also applied to Cu (II) ions. AAS measured the absorbance of the filtrate. Each experiment was carried out in duplicate. The optimum pH is the pH at which the adsorbed concentration is the greatest.
2.5. Determining the adsorption capacity of cocoa pods husk in adsorption of Fe (III) and Cu (II) ions
Cocoa pods husk adsorbent was weighed (0.1 g) into each 100 mL Erlenmeyer, added 100 mL of Fe (III) ion solution with concentrations of 25, 50, 75, 100, 125, 150 and 200 ppm at the optimum pH and contact time obtained. The mixture was then filtered, and the filtrate was analyzed using an Atomic Absorption Spectrophotometer. This procedure was also performed for Cu (II) metal ions.

2.6. Determination of the optimum pH in adsorption of Fe (III) and Cu (II) ions
Cocoa pods husk adsorbents were inserted into the adsorption column with a constant height of adsorbent, and then the laboratory waste was drained at various flow rates. After the optimum flow rate was obtained, experiments were continued with various adsorbent heights. The results of the processes were tested using an Atomic Absorption Spectrophotometer. The test was carried out to determine the amount of Fe (III) and Cu (II) metal ions adsorbed, so that the laboratory waste discharged into the environment has decreased in concentration to fulfill the standard quality.

3. Result

3.1. Result of determining the optimum contact time
From the experimental results, the optimum contact time for the adsorption process of Fe (III) and Cu (II) metal ions was 90 minutes (Table 1).

| Time (min) | Ion   | C_e (mg/L) | q_e (mg/g) | Adsorption efficiency (%) | Ion   | C_e (mg/L) | q_e (mg/g) | Adsorption efficiency (%) |
|------------|-------|------------|------------|---------------------------|-------|------------|------------|---------------------------|
| 30         | Fe(III) | 46.32      | 10.74      | 53.7                      | Cu (II) | 41.05      | 11.79      | 59.0                      |
| 60         | Fe(III) | 45.53      | 10.89      | 54.5                      | Cu (II) | 38.03      | 12.39      | 62.0                      |
| 90         | Fe(III) | 31.42      | 13.72      | 68.6                      | Cu (II) | 36.52      | 12.70      | 63.5                      |
| 120        | Fe(III) | 38.49      | 12.30      | 61.5                      | Cu (II) | 36.79      | 12.64      | 63.2                      |
| 150        | Fe(III) | 39.24      | 12.15      | 60.8                      | Cu (II) | 37.05      | 12.59      | 63.0                      |

3.2. The effect of contact time
From the experimental results obtained, the optimum pH in the adsorption process of Fe (III) and Cu (II) metal ions was pH 6 (Table 2).

| pH | Ion   | C_e (mg/L) | q_e (mg/g) | Adsorption efficiency (%) | Ion   | C_e (mg/L) | q_e (mg/g) | Adsorption efficiency (%) |
|----|-------|------------|------------|---------------------------|-------|------------|------------|---------------------------|
| 2  | Fe(III) | 91.01      | 1.80       | 9.0                       | Cu (II) | 88.32      | 2.34       | 11.7                      |
| 3  | Fe(III) | 52.90      | 9.42       | 47.1                      | Cu (II) | 42.97      | 11.41      | 57.0                      |
| 4  | Fe(III) | 39.35      | 12.13      | 60.7                      | Cu (II) | 43.36      | 11.33      | 56.6                      |
| 5  | Fe(III) | 44.48      | 11.10      | 55.5                      | Cu (II) | 41.90      | 11.62      | 58.1                      |
| 6  | Fe(III) | 31.42      | 13.72      | 68.6                      | Cu (II) | 36.52      | 12.70      | 63.5                      |
| 7  | Fe(III) | 40.29      | 11.94      | 59.7                      | Cu (II) | 50.28      | 9.94       | 49.7                      |
| 8  | Fe(III) | 40.54      | 11.89      | 59.5                      | Cu (II) | 52.38      | 9.52       | 47.6                      |
| 9  | Fe(III) | 41.42      | 11.72      | 58.6                      | Cu (II) | 52.79      | 9.44       | 47.2                      |
3.3. Result of determining the adsorption capacity of cocoa pods husk in adsorption of Fe (III) and Cu (II) ions

Based on data analysis of Fe (III) metal ion adsorption model, the value of $b = 0.1796$ L/g, $a$ or $q_{\text{max}} = 11.074$ mg/g, and $R^2 = 0.9871$ for the Langmuir isotherm while for the Freundlich model, the value of $n = 5.767$ L/g, $k = 4.7829$ mg/g, and $R^2 = 0.9689$ (Figure 1). The adsorption capacity of the adsorbent for Fe (III) ions was 11.074 mg/g.

![Figure 1. Adsorption isotherms of (a) Langmuir and (b) Freundlich of Fe (III) ion by fruit skin of cocoa M45 (contact time = 90 min, the amount of adsorbent = 0.1 g, and pH = 6)](image1)

Based on the analysis of Cu (II) metal ion adsorption model, the value of $b = 0.0266$ L/g, $a$ or $q_{\text{max}} = 28.4091$ mg/g, and $R^2 = 0.9556$ for the Langmuir isothermal, while for the the Freundlich model, the value of $n = 1.8238$ L/g, $k = 1.7688$ mg/g, and $R^2 = 0.997$ (Figure 2). Adsorption capacity of adsorbent on Cu (II) ion was 28.4091 mg/g.

![Figure 2. Adsorption isotherms of (a) Langmuir and (b) Freundlich of Cu (II) ion by fruit skin of cocoa M45 (contact time = 90 min, the amount of adsorbent = 0.1 g, and pH = 6)](image2)
3.4. Results of determining the optimum flow rate and adsorbent height in a continuous process

The experimental results obtained an optimum flow rate of 6.166 mL/sec and an optimum adsorbent height of 15 cm (Table 3).

Table 3. The amount of Fe (III) and Cu (II) ions adsorbed in continuous system with the adsorbent height of 15 cm and in the batch system

| Treatment system | Q (mg/L) | qe Fe(III) (mg/g) | qe Cu (II) (mg/g) |
|------------------|---------|------------------|------------------|
| Continuous       | 4.18    | 0.0009           | 0.0003           |
|                  | 6.17    | 0.0055           | 0.0015           |
|                  | 10.73   | 0.0033           | 0.0003           |
|                  | 19.19   | 0.0004           | 0.0003           |

| Treatment system | m (g) | V (mL) | qe Fe (III) (mg/g) | qe Cu (II) (mg/g) |
|------------------|-------|--------|-------------------|------------------|
| Batch            | 0.107 | 20     | 0.8280            | 0.0512           |
|                  | 0.106 | 20     | 0.6906            | 0.0255           |

4. Discussion

This research shows that the adsorbent of cocoa fruit skin can reduce levels of heavy metals Fe (III) and Cu (II) in laboratory liquid waste. The amount of Fe (III) and Cu (II) metal ions adsorbed increased with increasing contact time between the adsorbent and the metal ions. Initially, at 30 minutes, biosorbent was able to bind metal Fe (III) ions as much as 10.74 mg/g and Cu (II) as much as 11.70 mg/g, and continued to increase until 90 minutes with the number of adsorbed metal ions increasing by 13.72 mg/g for Fe (III) metal ions and 12.70 mg/g for Cu (II) metal ions. In the 120th minute the amount of Fe (III) and Cu (II) adsorbed metal ions decreased ie 12.30 mg/g for Fe (III) metal ions and 12.66 mg/g for Cu (II) metal ions. This tendency is caused by saturation of the active site of the adsorbent and even desorption. According to research conducted by Wibowo et al. (2017)[16], the optimum contact time was obtained to absorb Fe and Cu metal ions in the 60th minute by using nanosilica adsorbents, while research using biosorbents of peanut shells to absorb Cu metal ions optimum conditions occurred at 100 minutes [17]. Factors that influence adsorption are types of adsorbent, type of adsorbate, the surface area of adsorbent, the concentration of adsorbed substance and temperature [18].

The pH value is one of the variables that influence the biosorption process in terms of the solubility aspect of metal ions and the total charge on the biosorbent surface so that protons can be adsorbed or released [19]. The amount of Fe (III) metal ion adsorbed by purple cocoa pods husk M45 (Theobroma cacao) at pH 2 was 1.80 mg/g for Fe (III) metal ion and 2.33 mg/g for Cu (II) metal ion. This amount rises with the increase in pH and the maximum amount adsorbed at pH 6 was 13.72 mg/g for the Fe (III) metal ion and 12.70 mg/g for the Cu (II) metal ion, and at pH 7 the amount decreased because at high pH both ions experienced a reduction of the charged ion [20].

Based on the Langmuir and Freundlich isotherm, the Fe (III) metal ion has the Langmuir isotherm equation, \( y = 0.0903x + 0.5028 \) (\( R^2 = 0.9871 \)), and the Freundlich isotherm equation, \( y = 0.1799x + 0.6664 \) (\( R^2 = 0.9689 \)). Based on the value of \( R^2 \), the adsorption of Fe (III) ion followed the Langmuir isotherm, so that the interaction that occurs is a chemical interaction. Langmuir illustrates that on the surface of the adsorbent, there are a certain number of active sides that are proportional to the surface area [21]. The Cu (II) ion has the Langmuir isotherm equation, \( y = 0.0352x + 1.3243 \) (\( R^2 = 0.9556 \)), and the Freundlich isotherm equation, \( y = 0.5483x + 0.2477 \) (\( R^2 = 0.997 \)). The values of \( R^2 \) (coefficient of determination) are almost the same, so the adsorption of Cu (II) follows the Freundlich and Langmuir isotherms but tends to be Freundlich. Adsorption of Cu (II) ion by adsorbent cocoa pods husk M45 tends to follow the Freundlich isotherm because the \( R^2 \) value using this isotherm is greater than that using the Langmuir isotherm. Therefore, it can be interpreted that the interactions that occur are physical and chemical interactions but are more likely to be physical interactions where the Cu (II) ion adheres to the cellulose surface of the cocoa pods husk M45. Based on the value of \( R^2 \geq 0.9 \) (close
to 1), then the Langmuir and Freundlich adsorption equation can be applied to the adsorption process [22]. The optimum flow rate occurred at a rate of 6.166 mL/sec with an adsorbent height of 15 cm. The optimum adsorption process is due to the chance of contact between the Fe (III) and Cu (II) metal ions with the optimum adsorbent active group so that the optimum amount of metal ions is absorbed [4].

Adsorption of Fe (III) and Cu (II) metal ions in laboratory wastewater by cocoa pods husk M45, with optimum adsorbent speed and height was 0.0055 and 0.0015 mg/g, respectively. The number of ions adsorbed in batch systems was 0.8280 and 0.052 mg/g for Fe (III) and Cu (II) ions, respectively. In accordance with Government Regulation No. 82 of 2001 concerning quality management and control of water pollution, a maximum Fe standard is 10 mg/L, and a maximum Cu is 3 mg/L. Preliminary analysis of laboratory waste showed that Fe concentrations generally exceeded the quality standard, and after passing through the adsorption column decreased but did not meet the quality standard. This finding is different from Cu; generally, laboratory waste is below the quality standard, and after passing through the adsorption column has decreased. Biosorption is an alternative treatment for liquid waste because it is cheap and easy to obtain raw materials [12].

5. Conclusion
The results showed that purple cocoa pods husk, M45 can be used as adsorbents for Fe (III) and Cu (II) ions with an optimum contact time of 90 minutes and a pH of 6. The adsorption capacity of purple cocoa pods husk, M45 to Fe (III) ion was 11.07 mg/g, and to Cu (II) ion was 28.41 mg/gm. The optimum flow rate in the continuous adsorption process was 6.166 mL/sec with an adsorbent height of 15 cm.

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