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Metal Adsorption in Batik Liquid Waste Using Adsorbents from Duck Eggshell and Durian Skin Waste

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ABSTRACT

If industrial factory waste is directly disposed of into the surrounding environment, it can cause pollution, damaging the areas affected by the waste. Therefore, it is necessary to process the waste to reduce the harmful substances contained in the waste. This study conducted an experiment to reduce the metal content in batik liquid waste (Cu and Cd) using duck egg shells and durian peels as adsorbents. Before the production of activated charcoal, the duck egg shells and durian skins were washed and then sun-dried. Next, the duck egg shells are crushed into small granules, and the durian skins are cut into small pieces to facilitate carbonization. The carbonization process is carried out using a device called a furnace at a temperature of 600 °C for 2 hours for duck egg shells, and 300 °C for 1 hour for durian peels. Then, the obtained charcoal is ground and sieved using a 140 mesh sieve, followed by activation using a 4 N H_3PO_4 solution for 24 hours. The adsorption process is differentiated based on variations in contact time of 30, 90, and 180 minutes as the independent variable in the study, with adsorbent weight and stirring speed as the constant variables. After being analyzed using atomic absorption spectrophotometry, a reduction in Cu metal content by 27% and Cd metal content by 19% was obtained. The pH decreased from 13 to 10.

1. Introduction

In this era of globalization, Indonesian society must produce high-value products of the best quality to balance its production with the increasing amount of imported goods circulating in our country. One of the products that can generate a high selling value with good creativity and not too much capital is the processing of waste in our environment. Besides reducing environmental pollution, eggshell waste can also produce high-value and environmentally friendly products that can be sustainably maintained. Waste is the byproduct or residue generated from an industrial or domestic process or activity.

In the production of batik from start to finish, chemicals containing metals and dyes are used, so the batik liquid waste includes heavy metals that are directly discharged into the environment, exceeding the set raw materials. This disposal causes environmental degradation and damage to ecosystems. Therefore, it is necessary to implement batik liquid waste treatment to reduce the effects of waste disposal. Liquid metal waste from batik is still commonly found, including cadmium (Cd) and lead (Pb) [1].

Adsorption is a separation in which components from a fluid phase move to the surface of an adsorbing solid. The adsorption process can occur due to the surface pores within the adsorbent [2] [3]. Another kind of process to treat the wastewater is membrane technology [4] [5], coagulation using tawas and PAC [6], and AOP Fenton, which can be used for the detoxification of distillery wastewater [7]. The specific surface area significantly affects the capacity of the adsorbent. In our research, we used duck egg shell waste, which has good absorption capacity and is easily obtained from industrial and domestic waste [8].

Duck eggs are widely utilized by the community, resulting in a large amount of duck egg shell waste being discarded without any use. The utilization of duck eggs generates waste in the form of their shells, which are considered waste from both industrial and domestic sources. Duck egg shells are one of the solid wastes that have the potential to be utilized as an economical alternative adsorbent. Each eggshell has 10,000-20,000 pores and contains calcium carbonate ($CaCO_3$). The calcite compound (CaO) produced from $CaCO_3$ can adsorb heavy metals [9]. This study used duck egg shells as adsorbents.

Durian is one of the native plants of Indonesia, and in Indonesia, durian is very popular, even being dubbed the king of fruits. The part of the durian fruit that can be consumed is only about 20.52%. That means about 79.48% of the parts cannot be consumed. That part consists of the skin and seeds of the durian. The durian skin proportionally contains a high amount of carboxymethylcellulose, around 50-60%, a lignin content of 5%, and low starch content [10].

Table 1. Mineral and vitamin content of durian skin

Value: 100 g from the edible part	Mineral	Vitamin
Water 64.990 g	Kalsium 6 mg	Vitamin C 19.7 mg
Energy 147 kcal	Besi 0.430 mg	Tiamin 0.374 mg
Energy 615 kJ	Magnesium 30 mg	Riboflavin 0.2 mg
Protein 1.47 g	Fosfor 38 mg	Niasin 1.074 mg
Total fat 5.33 g	Kalium 436 mg	*Pantothenic acid* 0.23 mg
Carbohydrates 27.09 g	Natrium 1 mg Zinc 0.28 mg	Vitamin B6 0.316 mg Vitamin A 45.000 IU
Fiber 3.8 g	Tembaga 0.207 mg Mangan 0.324 mg	

Batik liquid waste is a combination or mixture of water and pollutants carried by batik water in a dissolved or suspended state, which is disposed of from domestic sources. The liquid waste from the batik industry originates from fabric treatment, dyeing, and bleaching. The fabric processing and dyeing processes produce liquid waste containing chemicals that can potentially increase the Chemical Oxygen Demand (COD) value and the color of the wastewater. Meanwhile, in the scouring process, the liquid waste produced contributes to increased Biological Oxygen Demand (BOD) of the wastewater. In batik production, chemicals containing heavy metals are also used, so the resulting waste still contains heavy metals. In general, batik liquid waste is alkaline and has a high organic content [11].

In the production process of batik, liquid waste is generated, amounting to approximately 80% of the total water used in the batik-making process. Several previous studies have reported that batik waste contains Total Chromium (Cr) at < 0.0231 mg/l for the Cap and Printing batik production methods, Iron (Fe) at 2.0587 mg/l, Cadmium (Cd) at 0.0063 mg/l, Chromium (Cr) at 0.1385 mg/l, Copper (Cu) at 0.2696 mg/l, Zinc (Zn) at 54.7175 mg/l, and Lead (Pb) at 0.2349 mg/l. The metal content in batik liquid waste can reduce water quality and kill the biodiversity present in the water [12].

Adsorption is a separation process that occurs in a fluid phase where specific components move towards the surface of an adsorbent. The adsorption process occurs on the surface or pores of the adsorbent [13]. Adsorption is one of the most commonly used methods for metal adsorption and removing colorants from textile industry wastewater [1]. Adsorbents used in adsorption are derived from organic materials or potent metal-binding agents. Several factors influence the adsorption capacity of an adsorbent, including the following [14]: Surface Area of the Adsorbent (particle size), Characteristics of the Adsorbent, Characteristics of the Adsorbate, Acidity Level, Temperature, Contact Time, and Stirring.

2. Research Methodology

2.1. Materials

Materials used in the research are batik liquid waste, obtained from the Giriloyo Wukirsari batik village; Durian skins, obtained from durian sellers around RSUD Wirosaban; Duck eggshells, obtained from the martabak seller; Aquades, obtained from Tekun Jaya store; H_3PO_4 4 N, obtained from Tekun Jaya store.

2.2. Procedures

2.2.1 Sample Collection

The samples used were duck egg shells, obtained from several martabak vendors in the Condongcatur and Minomartani villages, Sleman Regency. Durian skins were obtained from durian sellers near Campus 4, Ahmad Dahlan University. And the batik liquid waste samples were obtained from the Giriloyo batik village, Imogiri district, Bantul regency. The batik liquid waste that was collected is naphthol waste.

2.2.2 Production of Activated Carbon

a. Dehydration Process

Duck egg shells and durian skins are washed thoroughly. For duck eggshells, the membrane is removed to prevent any unpleasant odor. Then it is dried using sunlight and baked in an oven at 100 °C for 30 minutes.

b. Carbonization Process

Duck egg shells: Duck eggshells are weighed and then crushed to make them easier to place into the porcelain dish. Then it is placed in the furnace and heated for 2 hours at 600 °C. After being placed in the furnace and allowed to cool, the charcoal is ground and sieved using a 140 mesh sieve.

Durian Skin: The durian skin is weighed and then cut into small pieces to fit into the porcelain dish. Then it is placed in the furnace and heated at 300 °C for 1 hour. After being placed in the furnace and allowed to cool, the charcoal is ground and sieved using a 140 mesh sieve. Another kind of process that can be used to produce carbon from organic waste are pyrolysis [15] and gasification [16]–[22].

2.2.3 The Activation Process of Charcoal

Duck egg shell charcoal and durian skin that have been sifted are mixed, then placed into a beaker and activated by adding 4 N H_3PO_4 into the beaker and letting it sit for 24 hours. Then the filtration process is carried out. The activated charcoal is then washed until it reaches a neutral pH and heated in an oven for 1 hour at 100 °C. Then the activated charcoal is stored and ready for adsorbent characterization.

a. Moisture Content

The watch glass was constant in weight, then the watch glass containing the sample was oven-dried at 100 °C for 1 hour, and its weight was recorded. The ovening process is carried out until a constant weight is obtained. Then calculate the moisture content using the formula:

$$Moisture\ content = \frac{W_{before\ heating}(g) - W_{after\ heating}(g)}{W_{before\ heating}(g)} \quad (1)$$

b. Yield

The equation used to determine the amount of yield obtained is:

$$Yield = \frac{W_{after\ heating}(g)}{W_{before\ heating}(g)} \times 100\% \quad (2)$$

c. Ash Content

The activated charcoal that has been obtained is taken as a 2-gram sample, then furnace-treated at a temperature of 600 °C for 2 hours, allowed to cool, and then weighed. Do this until a constant sample weight is obtained. Then calculate the ash content using the formula:

$$Ash\ content = \frac{W_{total\ of\ ash}(g)}{W_{sample}(g)} \times 100\% \quad (3)$$

2.2.4 Data Analysis Based on Time-Adsorbent Contact and Batik Liquid Waste

Activated charcoal is sieved using a 140 mesh sieve. Then, it weighed 10 grams and was placed into a beaker, followed by adding 200 ml of batik liquid waste, and then stirred using a magnetic stirrer at a speed of 300 rpm for 30 minutes. Then, filtration and the resulting filtrate will be analyzed for Cu and Cd metal content using AAS spectrophotometry. Repeating the same steps with variations in stirring time of 90 and 180 minutes.

3. Results and Discussion

3.1. Production and Characterization of Charcoal

The first step was to clean the duck eggshells and durian peels using clean water, then dry them in the sun until they were dry. Next, the duck eggshells are crushed, and the durian peels are cut into small pieces to facilitate carbonization.

The second stage is carbonization. Carbonization is a method used to obtain charcoal by burning/heating at a temperature of 400-600 °C [23]. The carbonization process uses a furnace. For duck egg shells, the furnace is operated at a temperature of 600 °C for 2 hours. Meanwhile, a temperature of 300 °C is used for 1 hour for durian skin.

The charcoal produced from the carbonization process has low absorbency. Therefore, activation is necessary to increase the size of the pores in the charcoal, which will also enhance its absorbency.

The activation process is the process of activating charcoal by adding certain chemicals aimed at reducing the water content still present on the surface of the charcoal, which will cause the pores of the charcoal to open more and increase its absorption capacity [24]. This study carried out the charcoal activation process for 24 hours using a 4 N H_3PO_4 solution. Then, the activated charcoal is neutralized by washing it with water and drying it in an oven. Then, the activated charcoal is sieved using a 140 mesh sieve. The result of the activated charcoal that has been sieved can be seen in Fig. 1.

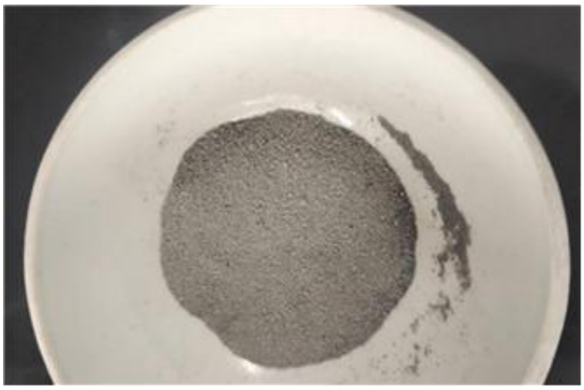

Fig. 1 Activated charcoal that has been sifted

Table 2 is results were obtained from the production and activation of the charcoal that was carried out.

Table 2. Results of the activated carbon characterization test

Type of Requirement	Result	Quality Standard SNI 06–3730-1995
Water Content	11.3%	Maximum 15%
Ash Content	3.5%	Maximum 10%
Yield	59.165%	-

3.2. The levels of Cu and Cd metals

The batik liquid waste sample used in this study is naphthol, a substance used in batik dyeing. Next, 200 ml of batik liquid waste was treated with 10 grams of activated charcoal and stirred using a magnetic stirrer at 300 rpm. Then, filtration was tested using an AAS Spectrophotometer. The testing was conducted at the Ministry of Industry of the Republic of Indonesia, Human Resource Development Agency for Industry, SMK SMTI Yogyakarta. The results of the tests that have been conducted can be seen in Table 3.

Table 3. Metal content and pH of the adsorbed sample

Sample	Metal content (mg/L)		pH
	Cu	Cd	
Original sample (naphthol)	0.063	0.021	13
A (30’)	0.061	0.021	10
B (90’)	0.049	0.019	10
C (180’)	0.046	0.017	10

Table 3 presents the metal content and pH of wastewater samples subjected to varying adsorption times. At 30 minutes, copper (Cu) concentration showed a minimal reduction from 0.063 mg/L to 0.061 mg/L (approximately 3.2%), while cadmium (Cd) levels remained unchanged at 0.021 mg/L. Extending the adsorption to 90 minutes resulted in a 22% decrease in Cu and a 10% decrease in Cd, reaching concentrations of 0.049 mg/L and 0.019 mg/L, respectively. The most significant reductions occurred at 180 minutes, with Cu reduced by 27% (to 0.046 mg/L) and Cd by 19% (to 0.017 mg/L). These trends suggest that longer contact times enhance metal removal, likely due to increased surface interaction between metal ions and the adsorbent material as equilibrium approaches.

Additionally, pH levels decreased from 13 in the original sample to 10 post-adsorption, which may have influenced metal solubility and adsorption efficiency. High pH can promote the precipitation or reduced mobility of metal ions, contributing to improved removal performance.

Importantly, the final concentrations of both Cu and Cd fall well within the limits set by DIY Regional Regulation No. 7 of 2016, which caps industrial wastewater concentrations at 2 mg/L for Cu and 0.05 mg/L for Cd. This demonstrates the potential of the adsorption process to meet environmental safety standards.

Compared to other studies, such as those utilizing activated carbon or modified biowaste materials, where Cu and Cd removals often exceed 70%, the current system shows modest but promising results. Further optimization of contact time, pH control, and adsorbent characteristics could significantly enhance performance.

3.3. Appearance of adsorption results

The maximum result is obtained in the adsorption process with an adsorption time of 180 minutes. At that time, the amount of metal content decreased significantly. After experimenting, it can be observed that the longer the time used for the adsorption process, the more the color of the batik liquid waste (naphthol) will fade. This can be seen in Fig. 4.

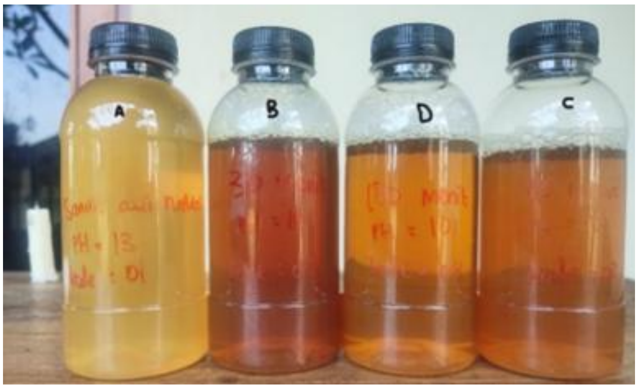

Fig. 2 The difference in color before and after adsorption, a) original batik liquid waste, b) after adsorption for 30 minutes, c) after adsorption for 90 minutes, d) after adsorption for 180 minutes.

4. Conclusion

The use of activated duck egg shell and durian peel adsorbents can reduce the content of Cu and Cd metals. The longer the stirring time between the adsorbent and the batik liquid waste, the lower the metal concentration. The concentrations of Cu and Cd metals decreased by 0.017 mg/l and 0.004 mg/l, respectively, with an adsorption time of 180 minutes. After the adsorption process, the color of the waste changed from yellow to brownish yellow. Factors influencing adsorption include particle size, adsorbent characteristics, adsorbate characteristics, acidity level, temperature, contact time, and stirring.

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