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STUDY OF ACTIVATED CARBON FROM COCONUT SHELL WASTE TO ADSORB Cu AND Mn METALS IN ACID MINE DRAINAGE

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***Abstract**. The purpose of this research is to make activated carbon from coconut shell carbon and examine its use in adsorbing metals in acid mine drainage; to study the types of activators; to determine the optimum mass for the efficiency of reducing the concentration of Cu^{2+} metal and Mn^{2+} metal (percent removal) using the activated carbon from coconut shell carbon; and to determine the adsorption of isothermal model. Based on the results of the study, it is concluded that activated carbon could be made from coconut shell carbon with 20% H_3PO_4 chemical activation. Before being activated, it was made by heating at a temperature of 300°C for 2 hours. The best activated carbon in terms of metals adsorption in acid mine drainage was in a mass of 4 grams with each percent removal of 57.62% for Cu metal and 91.37% for Mn metal. Data analysis of the effect of concentration on adsorption capacity used the Langmuir and Freundlich isotherm equations. The Langmuir equation for the adsorption of Mn metal obtained the maximum adsorption capacity (q_{max}) of 15.16 mg/g; K_L=73.09 mol/L and R^2=0.9568. Meanwhile, the adsorption of Cu metal obtained the maximum adsorption capacity (q_{max})=4.73 mg/g; K_L=73.14 mol/L and R^2= 0.9304. In Freundlich's equation, on the adsorption of Mn metal, the resulting K_F=15.14 mol/L; R^2=0.9129, while on the adsorption of Cu metal, the resulting K_F=.72 mol/L; R^2= 0.9092. Based on the data, the adsorption isotherm curve more closely follows the Langmuir isotherm model (adsorption takes place in one layer (monolayer).*

Keywords: Acid Mine Drainage; Coconut Shell Carbon; Activation; Adsorption; Metal Contents

1. Introduction

Acid mine waste water from the mining industry generally contains Cu and Mn metals Copper metal toxicity that occurs in humans, especially in children, is usually related to the presence of copper sulfate. Some of the symptoms of copper poisoning are abdominal pain, nausea, vomiting, diarrhea and some severe cases that can cause kidney failure and death [1]. Meanwhile, a lack of manganese causes testicular atrophy and an excess of manganese in plants and animals causes poisoning [2]. The toxic effects of heavy metals are able to block the work of enzymes so that they interfere with body metabolism and cause allergies. They are mutagens, teratogens, or carcinogens

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for humans and animals [3]. Several techniques have been developed in the treatment of waste containing heavy metals, but the adsorption process is the most desirable because it is economical, efficient, effective and inexpensive [4]. Adsorption is a process in which one or more constituents of a fluid solution are more concentrated on the surface of a particular solid (adsorbent). The adsorbent commonly used for metal ion waste treatment is activated carbon. Activated carbon can be made from carbon-containing materials, such as coconut shells.

Coconut shell carbon has been used for a long time and has become a subject of research. Coconut shell has a chemical composition of 74.3% C; 21.9%O; 0.2% Si; 1.4% K; 0.5% S; 1.7% P [5] making it a potential source of fuel and activated carbon. The formation and utilization of activated carbon from coconut shell carbon provide two advantages. First, the activated carbon can adsorb metals and colors in water. Second, the use can be a solution to the problem of environmental waste because the main source of raw material is coconut shell waste [6], [7].

In this study, activated carbon was focused on the mining industry, especially on waste from the mining industry, namely the extraction of Cu and Mn metals in acid mine drainage through an adsorption process with adsorbent raw materials from agricultural waste such as activated coconut shell (*cocos nucifera L.*). The media used is agricultural waste which is an economical and environmentally friendly biosorbent. The reuse of this waste will be useful not only for reducing waste, but also for treating acid mine drainage in the mining industry.

2. Material and Methods

2.1. Material

Agricultural waste was used as a raw material for the manufacture of coconut shell activated carbon. The chemicals used as activators include: H_3PO_4 and NH_4OH solutions with a concentration of 20%.

The equipment used in this research includes: Crusher, Oven dryer (Memmeth DIN 12880-KI), furnace (SX-2.8-12 Boc Huanghua Faitful Instrument Co.Ltd), analytical balance (Shimadzu AW-220), Screening (sieve tray size 850 micron) and other required tools, detailed according to the implementation stage. The stages in which the tools used are as follows:

1. Carbon Manufacturing Equipment

   Carbon manufacturing process of coconut shell waste used a furnace with the brand SX-2.8-12 Boc Huanghua Faitful Instrument Co.Ltd.

2. Equipment for Carbon Characterization

   Equipment for carbon Characterization: Brand SEM-EDX JEOL JSM-6360LA, analytical balances, ovens, porcelain dishes, desiccators, furnaces, and glassware commonly available in laboratories.

The research was carried out in two phases. The first phase includes the process of carbon manufacturing, making activated carbon, and analyzing the quality of the resulting product. The second phase is the application of activated carbon from coconut shell waste to adsorb Cu and Mn metal waste from acid mine drainage.

2.2. Methods

A. Carbon manufacturing Process

The coconut shells waste was cleaned first from the impurities present, then cut into pieces, crushed with a crusher with a size of about 1-2 cm and dried in an oven at 105^{o}C for 24 hours. Then, the waste was put into the furnace. Burning was carried out at 300^{o}C for 2 hours.

B. Chemical Activation

1. Activation with H_3PO_4 Solution

   70 grams of carbon were weighed each and immersed in a 20% H_3PO_4 solution for 24 hours. Subsequently, it was dried in an oven for 60 minutes at 105˚C, and the experiment was repeated twice for each.

2. Activation with NH_4OH Solution

   70 grams of carbon were weighed each and immersed in a 20% NH_4OH solution for 24 hours. Subsequently, it was dried in an oven for 60 minutes at 105˚C, and the experiment was repeated twice for each.

C. Application of Activated Carbon for Acid Mine Drainage Treatment and Determination of Adsorption Isotherms

Activated carbon which fulfilled the standard from the treatment results was applied as an adsorbent in the treatment of acid mine wastewater (artificial Cu and Mn) by mixing each activated carbon obtained from agricultural waste to form liquid waste. This treatment was carried out by adding 2g, 3g, 4g, 5g, 6g, and 7g of activated carbon into the wastewater sample (the mother liquor sample contains 58.52 ppm MnO_2 and 64.30 ppm $CuSO_4$) with a volume of 100 mL in each erlenmayer. Furthermore, the mixture was stirred using a rotary shaker at a speed of 50 rpm for 60 minutes and filtered with Whatman 42 paper. The liquid obtained from the separation was analyzed for its metal ion content by using atomic absorption spectrophotometry. The initial metal ion solution was also analyzed in the same way. Based on the calculation results, the amount of metal ions adsorbed was expressed in mg/g. These data can be used to determine the adsorption isotherm model. The spectrophotometric test utilized SNI 6989.5:2009 and SNI 6989.6:2009 for the total determination of Mn and Cu respectively. Data analysis was carried out by determining the final concentrations of MnO_2 and $CuSO_4$ after experiencing the adsorption process from the adsorbate concentration to the adsorption capacity. The results were entered into the Langmuir and

Freundlich isotherm equations to determine the adsorption isotherm model on the adsorbent.

The Langmuir isotherm model equation calculated using equation 1 [8]:

$$q = q_{max} \left(K_L \frac{C_e}{1 + K_L\, C_e} \right) \tag{1}$$

where q (mg/g) is the amount of heavy metal ions adsorbed into the unit mass of the polymeric beads, K_L is the Langmuir equilibrium constant which is related to the affinity of binding sites and q_{max} is the maximum adsorption capacity (theoretical monolayer saturation capacity) [8].

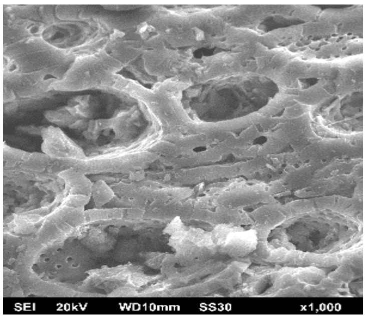
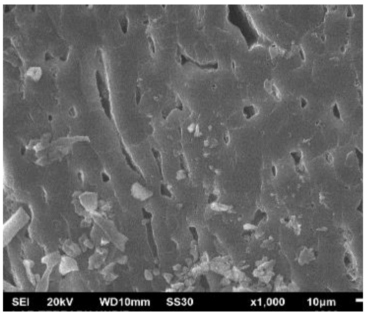
The Freundlich isotherm model was based on the adsorption on a heterogeneous surface, equation calculated using equation 2 [9]

$$q_e = K C_e^{1/n} \tag{2}$$

where q_e is the adsorption (mg/g), Ce is the concentration of adsorbate in the solution (mg/L), K and n are empirical constants that are characteristics of the system, indicating the adsorption capacity and intensity, respectively.

3. Results and Discussion

Table 1. SEM-EDX Test Results Carbon soaked with H_3PO_4 and NH_4OH

Scale	Solution	Coconut Shell
1000X	H_3PO_4	
	NH_4OH	

According to Table 1, where the carbon was activated using either acid or base, there were bigger and cleaner pores than the unactivated carbon. However, the pore formation was larger and cleaner in carbon activated with H_3PO_4 than in NH_4OH. The formation of several pores was also caused by the evaporation of volatile substances from the raw material due to the pyrolysis process.

Consequently, this caused the raw material components to degrade into gas (CO, CO_2, H_2, CH_4), liquid (liquid smoke, tar, hydrocarbons, and water), and solid products (carbon) [10]. The porosity of an adsorbent can affect the adsorption power. Therefore, those with a large number of pores and surface area can adsorb organic and inorganic compounds in wastewater [11], [12].

Table 2. AAS Test Results of Coconut Shell Activated Carbon (Mn Metal Parameter)

Parameter	Activated Carbon Mass (gram)	Results (mg/L)	Removal (%)	Method Specification
Mn	Preliminary Solution	37.00	0	SNI 6989.4:2009
	2	6.73	81.82	
	3	6.14	83.41	
	4	3.19	91.37	
	5	3.05	91.74	
	6	2.80	92.43	
	7	2.79	92.46	

Based on the AAS test results for Mn metal, a graph can be made as shown in Figure 1 below:

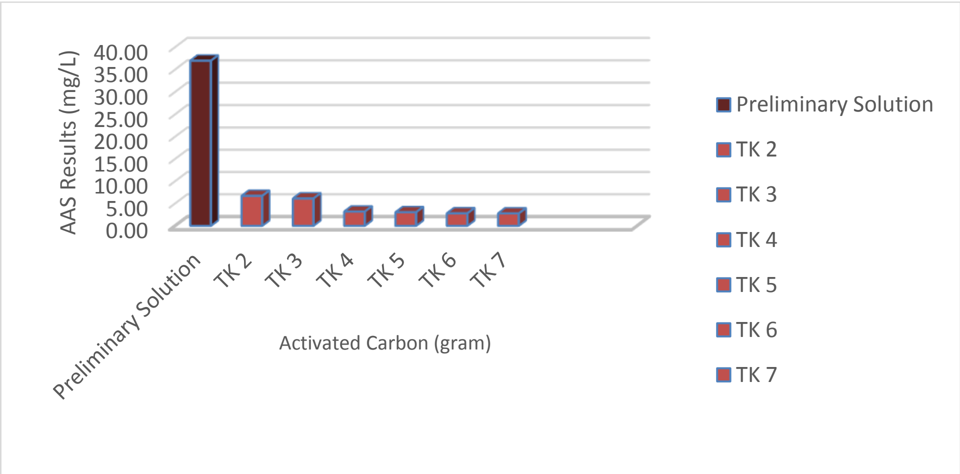


Figure 1. Graph of AAS Test Results for Coconut Shell Activated Carbon in Acid Mine Drainage (Mn Metal Adsorption)

Table 3. AAS Test Results of Coconut Shell Activated Carbon (Cu Metal Parameter)

Parameter	Activated Carbon Mass (gram)	Results (mg/L)	Removal (%)	Method Specification
Cu	Preliminary Solution	25.60	0	SNI 6989.4:2009
	2	16.15	36.91	
	3	12.03	53.02	
	4	10.85	57.62	
	5	10.67	58.34	
	6	10.12	60.45	

	7	10.02	60.85

Based on the AAS test results for Mn metal, a graph can be made as shown in Figure 2 below:

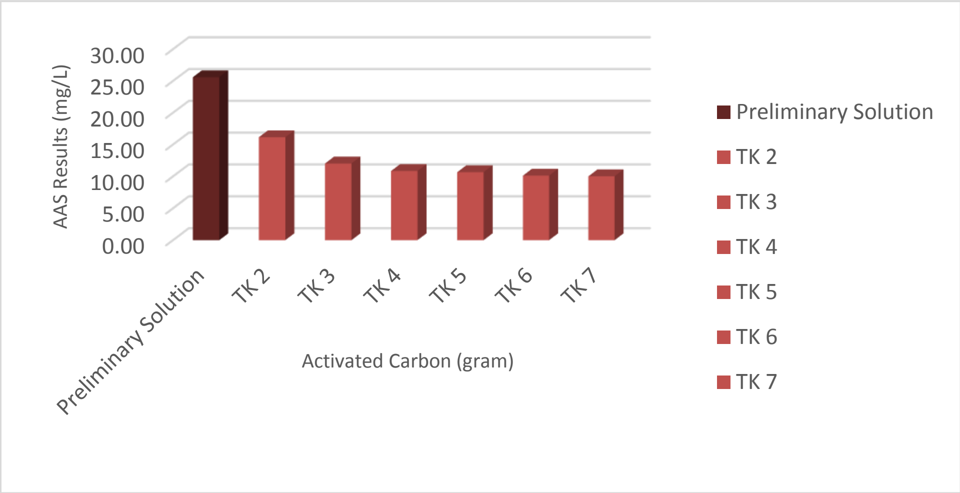


Figure 2. Graph of AAS Test Results for Coconut Shell Activated Carbon in Acid Mine Drainage (Cu Metal Adsorption)

The content of both types of metals decreased in the activated carbon application (Tables 2 and 3). This indicates that the activated carbon pores were able to adsorb Cu and Mn. The magnitude of the active adsorption for the metals illustrated that the pores were increasingly open. This is in accordance with [13] which stated that the internal mass transfer between the water and the adsorbate allowed the penetration of water into the adsorbent's pores due to the molecule size.

Tables 2 and 3, as well as Figures 1 and 2, show the ability of the pores to adsorb, the smaller concentration of waste, and the fewer pores covered by Cu and Mn. The pores can close at high concentration of these metals. The activated carbon pores were covered with more Cu and Mn, and a saturation state was also reached. Therefore, the carbon was unable to adsorb the metals (carbon pores bind both metals at optimum concentrations). With this increasing concentration, the percent removal of the metals also decreased and the highest was obtained at the adsorbent mass of 4 grams.

The calculation results of the Langmuir and Freundlich isothermal adsorption equations for Mn are shown in Table 4 as follows:

Table 4. Langmuir and Freundlich equations for Mn in the adsorption process

Metal	Langmuir Isotherm			Freundlich Isotherm		
	q_{max} (mg/g)	K_L (mol/L)	R^2	K_F (mol/L)	1/n	R^2
Mn	15.1648	73.0951	0.9568	15.1364	0.000001	0.9129

The calculation results of the Langmuir and Freundlich isothermal adsorption equations for Cu are shown in Table 5 as follows:

Table 5. Langmuir and Freundlich equations for Cu in the adsorption process

Metal	Langmuir Isotherm			Freundlich Isotherm		
	q_{max} (mg/g)	K_L (mol/L)	R^2	K_F (mol/L)	1/n	R^2
Cu	4.7269	73.1447	0.9304	4.7238	0.000001	0.9092

Based on the Langmuir adsorption model and the value of q_{max} (in Tables 4 and 5), activated carbon from the waste of coconut shell on Mn adsorption reached a maximum capacity of 15. 1648 mg/g. Meanwhile, the adsorption of Cu reached a maximum of 4.7269 mg/g. This follows the order: Mn>Cu. The value of adsorption capacity can be influenced by the outer layer of activated carbon when saturated. Hence, the adsorbent may not adsorb other metal molecules. The higher the concentration of the waste solution containing metals, the more molecules will collide and interact with the adsorbent to increase the adsorption ability. Based on the Freundlich parameters, it turns out that all activated carbon from the agricultural waste on Mn and Cu adsorption had a value of 1/n which was lower than 1. This indicates that the adsorption process under these conditions was favorable. This is in accordance with [14], when the value is $0 < 1/n < 1$ that the adsorption is favorable and indicates cooperative adsorption.

4. Conclusions

Carbon from coconut shell wastes activated using H3PO4 had larger, cleaner, and more pore formation than NH4OH activated carbon. The best activated carbon in absorbing metals in acid mine drainage was in a mass of 4 grams with each percent removal, namely 91.37% Mn and 57.62% Cu metal. Based on the data, the adsorption isotherm curve closely corresponded with the Langmuir isotherm model (adsorption occurred on one layer (monolayer). This is because R^2 in the Langmuir equation is closer to 1 than the Freundlich equation.

The media used is agricultural waste which is an economical and environmentally friendly biosorbent. The reuse of this waste will be useful not only for reducing waste, but also for treating acid mine drainage in the mining industry.

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