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Banana Peels And Stem (*Musa x paradisiaca* Linn.) As Biosorbent Of Copper In Textile Industry Wastewater

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ABSTRACT

An adsorbent were needed to reduce copper levels in textile industry wastewater. In this research the adsorbent from natural resource, commonly named as biosorbent was prepared from banana peels and banana stem (*Musa x paradisiaca* Linn.) to reduce the copper content in textile industry wastewater. Biosorbent was prepared by heating using direct sunlight and then activated with sodium hydroxide and formalin. The adsorption capability of the biosorbent was carried out in batch system, using variations of activator type, biosorbent particle size, pH and contact time. Copper content was measured by using atomic absorption spectrophotometry (AAS). The results indicated that biosorbent made from banana peels and stem have ability to adsorb copper metal. Optimum adsorption capacity and adsorption percentage for banana stem were 19.7 mg/g and 89.019%, respectively performed by banana stem which activated with formalin for 12 hours at pH and 30 mesh. Optimum adsorption capacity and adsorption percentage for banana peel were 13.235 mg/g and 59.806%, obtained by biosorbent activated with NaOH for 24 hours at pH 5 and 20 mesh of particle size.

Keywords: Banana peel, Banana stem, Biosorption, Copper metal

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INTRODUCTION

One of the dominant environmental issues today is wastewater from industry. Wastewater that was not managed will cause a tremendous impact on the water, especially water resources [1]. One of the issues dominating the liquid waste in Indonesia's is textile industry wastewater. The content in the wastewater of textile industry, especially heavy metals such as As, Cd, Cr, Pb, Cu, Zn; halogenated hydrocarbons (of the process of dressing and finishing); pigments, dyes and organic solvents; and surfactant. Heavy metals in the environment becomes an important concern due to the toxicity and the bad effects to human health and other living things [2].

In most of the textile finishing, dyes were adsorbed in textile materials and the rest will be brought together with textile industry wastewater.

Copper is one metal that is essential in a certain concentration (0.6 mg / day for women and 0.7 mg / day for men), but if excessive can cause intoxication and cause hepatitis, erythematous lesions, brain congestion and hemorrhage [3]. Several methods have been developed for the treatment of heavy metals in textile industry wastewater. These methods include chemical precipitation, membrane filtration, the electrolytic process, adsorption and biological sorption [4]. Adsorption techniques for handling waste has become popular in recent years because of its efficiency in removing pollutants, especially heavy metal ions, dyes, flavorings and organic pollutants [5]. Adsorption is usually done by using activated carbon. In addition to activated carbon, a variety of natural materials has been able to serve as sorbent with the process known as biosorption. Various products such as plants and microorganisms of wood ash, solid residue of olive mill products, straw, yeast, inactivated bacteria, fungi, algae, and seaweed have been used as an efficient biosorbent since a long time [6].

Materials that contain cellulose can be used to treat heavy metal waste and one of the biomaterial that proved to be as heavy metals sorbent was bagasse containing 36% cellulose [3]. Cellulose can be used as an adsorbent for the carboxyl and hydroxyl functional group which becomes the active binding site of the metal [7]. Other biomaterials containing cellulose is a banana peel and banana stem. Banana skins contain 31.7% crude fiber whose composition is 90% cellulose and cellulose-containing banana stem 39.12%, 72.71% holocellulose, klason 8.88% lignin and acid soluble lignin 1.90% [8,9].

Banana peels and banana stem is part of the banana plant that is generally discarded as waste. This research aims is to increase the utilization of banana and use it as a biosorbent of metallic copper (Cu) in the textile industry wastewater.



MATERIALS AND METHODS

Preparation of the Biosorbent

Banana peel and banana stems are cut into pieces and washed with tap water to remove dust and dirt. Furthermore, the peels of bananas and banana stem is dried under sunlight to obtain a water content below 10%. Once dried, the biosorbent is grinding using milling machine with a screen 2 and was sieved using a siever size of 20 mesh and 30 mesh to homogenize the particle size of the biosorbent.

Activation of the Biosorbent

Biosorbent which has subsequently prepared using two different activating agent which are sodium hydroxide and 0.1 M formaldehyde 1 N by using different activation methods based on research results of Karthika et.al 2010 and Vanessa et.al., 2010. The second method is used because it produces over 90% adsorption of Cu metal for different types of adsorbents. Each gram of the biosorbent was added by 20 mL of 0.1 M NaOH solution and the mixture was stirred for 2 hours and the supernatant discarded. Furthermore, the material was washed again with distilled water and dried at 55°C for 24 hours [3]. 50 g of another biosorbent was being add with formalin 500 ml of 1 N for 24 hours and placed in a waterbath (70 ° C) for 1.5 hours. Furthermore, biosorbent was cooled and neutralized with 250 ml NaOH [10].

Chemicals

Chemicals used in this study were distilled water (IKA PT Pharma), concentrated hydrochloric acid (HCl) (Merck), concentrated nitric acid (HNO₃) (Merck), formalin (Bratachem), sodium hydroxide (NaOH) (Bratachem), anhydrous sodium sulfite (Na₂SO₃) (Merck), copper nitrate trihydrate (Cu (NO₃)₂.3H₂O) (Merck).

Instrumentation

Moisture balance equipment (OHAUS, MB35), Electronic Scales (Mettler Toledo), Oven, Mechanical Agitator (IKA, HS260 Basic), pH Meter (Mettler Toledo), Grinding Machine with Screen 2 (Hammer Mill), and glass tools commonly used in laboratory analysis.

Materials

Plant material used is a banana peels from the nearly ripe bananas and banana stems derived from plants found in the banana plantations in the area Majalaya, Bandung regency, West Java, Indonesia. Textile industry wastewater samples obtained from a textile factory located in Majalaya area, West Java with a copper content of 0.8852 ppm.

Biosorbent activity assays

Activity of the biosorbent was performed in this study include the measurement of the initial copper content, applications of the biosorbent on copper adsorption by using the batch method, and measurement of copper content after adsorption process using Atomic Absorption Spectrophotometry technique (AAS).

A. Measurement of Levels of Copper in Textile Industry Wastewater Using AAS

1. Sample preparation : a total of 5 ml samples of textile industry wastewater was added with 1 ml of concentrated nitric acid. Furthermore, the sample was agitated for 24 hours and then filtered. Filtrate was put into 10 ml volumetric flask and add with distilled water until mark.
2. AAS Determination Tool Condition

Table 1 Conditions of AAS to Determine Copper Levels

Condition	Parameter
Wavelength	324,7 nm
Cathode lamp	Cu
Gas type	Udara- C ₂ H ₂
Flow rate	1,8 L/m
Current lamp	6 mA
Flame wide	0,5 nm
Flame height	7 mm

3. Standard curve

Standard curve is created by measuring solutions of various concentrations of Cu 0.1: 0.2: 0.4: 0.6 and 0.8 ppm using the SSA. The relationship of concentration (C) of Cu by absorbance (A) made in the linear regression equation. Preparation of standard curves produce a regression line equation $y = 0.096 x - 0.003$ with a correlation coefficient of 0.996. The regression equation then is use to determine the levels of copper in textile wastewater.

B. The adsorption capability of Biosorbent by using Batch Methods

Adsorbent capability of the the biosorbent testing on copper in the textile industry wastewater by batch method carried out using 150 ml glass bottles by varying the size of four parameters, namely:

1. biosorbent particle size: 20 mesh and 30 mesh
2. the activation process: activating with formalin 1 N and NaOH 0.1 M
3. pH adsorption: 4 and 5. pH was adjusted by adding hydrochloric acid
4. stirring time: 12 hours and 24 hours with a mechanical agitator speed 150/minutes

The fourth combination of the above parameters performed on two types of biosorbent namely banana stem and banana peel with a full factorial technique to obtain optimum conditions for adsorption on each biosorbent. Textile industry wastewater is used as much as 100 ml and weight of each biosorbent was 4 g. After testing and measurement of copper content remaining after the adsorption and adsorption capacity calculation and the percentage of adsorption with the following formula:

$$\text{Adsorption capacity (mg / g)} = \frac{(C_0 - C_{eq}) \times V}{M}$$

$$\text{The percentage adsorption (\%)} = \frac{C_0 - C_{eq}}{C_0} \times 100$$

Description:

C_0 = initial concentration of copper in the effluent (ppm)

C_{eq} = final concentration of copper after adsorption (ppm)

V = volume of waste solution (ml)

M = weight biosorbent used (g)

Instrumentation

Copper content was measure by using Atomic Absorption Spectrophotometer (Shimadzu, AA-6501S),

RESULTS AND DISCUSSION

Banana is taken from a banana plantation in Majalaya, West Java. Banana stem and fresh banana peel were washed and cut into pieces then dried under sunlight. The drying process carried out during 5-7 days until the moisture content of less than 10% and can be milled with a milling machine. After grinding, the material is sieved with mesh sizes 20 and 30 to homogenize the particle size. Loss on drying value was measured by using moisture balance.

Table 2 Loss on drying determination

Biosorbent	Loss on drying before activation	Activating agent	Particle Size	Loss on drying after activation (%)
Banana stem	8,43	NaOH	Mesh 20	17,99
			Mesh 30	17,42
		Formalin	Mesh 20	10,41
			Mesh 30	10,57
Banana peel	4,46	NaOH	Mesh 20	11,73
			Mesh 30	6,42
		Formalin	Mesh 20	8,7
			Mesh 30	8,93

Banana peel activating with NaOH has different loss on drying value between mesh 20 and mesh 30, this is assumed because of the higher cellulose content [8]. This condition makes the crystalline cellulose structure of the smaller particle size becomes bigger because of the NaOH treatment and makes it easier to dried [11].

Biosorbent activity assays

Final copper content in the textile industry wastewater, adsorption capacity and adsorption percentage of the biosorbent listed in Table 3.

Table 3 Copper content before and after adsorption, adsorption capacity and adsorption percentage of the biosorbent

Biosorbent	Activating agent	Particle size	pH	Contact time (jam)	Initial copper content (ppm)	Final copper content (ppm)	Adsorption capacity (mg/g)	Adsorption percentage (%)	
Banana Stem	NaOH	Mesh 20	4	12	0,8852	0,4302	11,375	51,401	
				24	0,8852	0,5523	8,323	37,607	
		5	12	0,8852	0,6815	5,093	23,012		
			24	0,8852	0,5460	8,480	38,319		
		Mesh 30	4	12	0,8852	0,4446	11,015	49,774	
				24	0,8852	0,4271	11,453	51,751	
	5		12	0,8852	0,6236	6,540	29,553		
			24	0,8852	0,4623	10,573	47,775		
	Formalin	Mesh 20	4	12	0,8852	0,2937	14,788	66,821	
				24	0,8852	0,2364	16,220	73,294	
		5	12	0,8852	0,4814	10,095	45,617		
			24	0,8852	0,3587	13,163	59,478		
		Mesh 30	4	12	0,8852	0,0972	19,700	89,019	
				24	0,8852	0,2865	14,968	67,634	
	5		12	0,8852	0,1570	18,205	82,264		
			24	0,8852	0,4724	10,320	46,634		
	Banana peel	NaOH	Mesh 20	4	12	0,8852	0,5480	8,430	38,093
					24	0,8852	0,4230	11,555	52,214
5			12	0,8852	0,5347	8,763	39,596		
			24	0,8852	0,3558	13,235	59,806		
Mesh 30			4	12	0,8852	0,6039	7,033	31,778	
				24	0,8852	0,5460	8,480	38,319	
		5	12	0,8852	0,5109	9,358	42,284		
			24	0,8852	0,6608	5,610	25,350		
Formalin		Mesh 20	4	12	0,8852	0,5255	8,993	40,635	
				24	0,8852	0,4202	11,625	52,531	
		5	12	0,8852	0,4420	11,080	50,068		
			24	0,8852	0,3709	12,858	58,100		
		Mesh 30	4	12	0,8852	0,4385	11,168	50,463	
				24	0,8852	0,5820	7,580	34,252	
5			12	0,8852	0,6350	6,255	28,265		
			24	0,8852	0,5632	8,050	36,376		

In Table 3, the optimum percentage adsorption for banana stem is 89.019%, obtained from biosorbent activated with formalin at pH 4, the particle size of 30 mesh, and the contact time of 12 hours. It is thought to occur because the surface structure of the weakly acidic biosorbent be activated with formalin and its improve the negative side so that the interaction of copper with biosorbent become easier [10]. Better adsorption of copper metal was obtained with formalin activator compared to NaOH, this is maybe because formalin that naturally produced a carboxylic group has a more acidic nature weaker than NaOH and make the negative side of the medium is slightly acidic, and the interaction of metal cations in solution becomes much easier [12]. pH 4 yields a better adsorption capacity than pH 5 due to a lower pH makes the sorbent surface is more surrounded by hydronium ions that increase the interaction with the copper ion due to an increase of traction [13].

The percentage adsorption optimum for banana peel obtained on biosorbent activated with NaOH at pH 5, the particle size of 20 mesh, and a contact time of 24 hours. This is presumably because the compound NaOH reacts with the silica present in the form of sodium silicate (Na_2SiO_3). Sodium silicate is water soluble and can disappear after washing with water to form holes in the outer epidermis which allows the metal ion adsorb in it [14]. In the banana peels silica content are of 0.36%, while in banana silica contained in much smaller quantities [15]. Activation by NaOH which is a strong base in comparison with formalin resulted in the possibility of metal cation interactions with the adsorbent is more difficult and required a longer contact time for better adsorption occurs, pH 5 produced a better adsorption than at pH 4 due to lower surface pH sorbent may be more surrounded by the hydronium ion is likely even more difficult due to the interaction of the acidity of the hydroxyl ions produced by different activators.

CONCLUSION

Based on the results, it can be concluded that the banana peel and stem were potential to be used as copper adsorbent in the textile industry wastewater. The adsorbent activity on metallic copper in the effluent of textile industry showed a capacity of 23-89% for banana stem and 25-59% for a banana peel. Optimum adsorption capacity and adsorption percentage obtained by biosorbent activated with formalin at pH 4, the particle size of 30 mesh, and a contact time of 12 hours, amounting to 19.7 mg / g and 89.019%.

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