The Decreasing of Copper (Cu) and Lead (Pb) Concentration in Electroplationg Liquid Waste with Coconut Coir Adsorbent

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ABSTRACT
The study about determining the characteristics, optimize of mass and adsorption efficiency of Cu and Pb metal ions in electroplating waste on each coconut coir adsorbent have been done as an alternative to commercial activated charcoal. The adsorption process is carried out by the batch method. Analysis of metal content was carried out using AAS instrument and SEM-EDX to determine the morphology and components of coconut coir adsorbent. The results of the characteristics of the coconut coir adsorbent meet SNI 06-3730-1995 for volatile substances and carbon subtances, meanwhile the commercial activated charcoal have not meet SNI 06-3730-1995 for the content of volatile substances, ash content, carbon subtances and absorption capacity of I2 . The characteristics with the morphology of the surface of the coconut coir adsorbent before and after adsorption has less uniform particle size and has a round pore with a large cavity like a honeycomb. The optimize mass of coconut coir adsorbent for adsorption of Cu and Pb metal ions is 0.9 grams. The efficiency and capacity adsorption of Cu and Pb metal ions using coconut coir adsorbent on 50 mL electroplating waste were 8.39% and 34.38%, respectively also has 11 mg/g and 0.026667 mg/g. The surface component of coconut coir adsorbent before adsorption contain Pb metal had a mass% of 0.4%, while after adsorption there was a metal content of Cu which had a mass% of 0.9% and Pb metal had a mass% of 4.5%.

Keyword: *coconut coir adsorbent, characteristics, optimize mass, the efficiency of adsorption*

1. INTRODUCTION

One of the quite large electroplating industry centers is the handicraft industry center in Kota Gede, Yogyakarta. This industrial center produces various accessories such as bracelets, necklaces, earrings, brooches and various home decorations such as decorative lights, drinking water baskets and so on. The industrial center performs coating of products with metals such as chrome, nickel, gold, copper, silver and other metals through the electroplating process (Marwati, et al., 2008: 2). Most of the electroplating craftsmen in Kota Gede are home-based industry with no adequate waste treatment units. They usually discharged the waste directly to the environment without prior treatment.

The components in the electroplating industrial wastewater contain various heavy metals with fairly high concentrations such as Mg2+, Al3+, Fe2+, Cr3+, Zn2+, Cu2+, Ni2+ and Cd2+ (Bai, et al., 2016).

The presence of heavy metals in nature is persistent or difficult to decompose and bio-accumulates if the heavy metals accumulate in the bodies of living things (Madukasi, 2009 and Ram S, 2011). Metals that are often found in electroplating wastewater are Cu and Pb. Cu metal in doses exceeding 3.5 mg/BW can cause kidney disease, anemia, cramps and even death. Meanwhile, Pb in doses exceeding 0.05 mg/BW can cause anorexia, vomiting, anemia and even damage to the nervous and digestive systems. (Widowati, et. al., 2008).

The adsorption method is an easy and inexpensive method to reduce the concentration of heavy metals in the electroplating industrial wastewater (Endarwati, 2008). The adsorption method uses adsorbents as a medium for heavy metal adsorption in wastewater (Lempang, 2014). An adsorbent is a material that has a high adsorption capacity to anions, cations or molecules, both organic and inorganic compounds. Coconut husk as a raw material for the manufacture of adsorbents because of the high lignin and cellulose content so that it will produce charcoal with a high carbon content. Therefore, this study aims to determine the characteristics, optimum mass and efficiency of Cu and Pb adsorption in electroplating waste on each adsorbent of coconut coir and commercial activated charcoal. In addition, knowing the morphology and components of coconut coir adsorbent before and after adsorption.

2. RESEARCH METHOD

2.1. Materials

Materials used in this research are wastewater of electroplating industry, commercial activated charcoal, coconut coir (*Cocos nucifera Linn.*), aquadest, HCl, $Na_2S_2O_3$; Iodine (I_2), amylum indicator; $Cu(NO_3)_2$, $Pb(NO_3)_2$ and HNO_3

2.2. Procedure

The coconut husks are washed with running water. The coconut husks were cut and then dried in the oven at 100°C for 30 minutes. The coir was carbonized at a temperature of 800°C for 1 hour with a furnace. The coconut coir charcoal was mashed and sieved using an 80 mesh sieve. Activated charcoal was chemically activated using 100 mL 2M HCl solution with a magnetic stirrer at 60 rpm for 1 hour and allowed to stand for 24 hours. Charcoal is neutralized using distilled water. The adsorbent was dried using an oven at 100°C for approximately 3 hours.

Characterization of coco coir adsorbent and commercial activated charcoal according to SNI 06-3730-1995 includes determination of water content, volatile matter content, ash content, carbon content and absorption of iodine.

Determination of the optimum mass of each adsorbent of coconut coir and commercial activated charcoal. Commercial activated charcoal and coconut coir adsorbent were weighed according to variations, namely 0.15; 0.4; 0.65 and 0.9 grams. Charcoal or adsorbent is put into each solution of Cu^{2+} and Pb^{2+} electroplating as much as 50 mL. Commercial activated charcoal and coconut coir adsorbent were contacted using a magnetic stirrer for 24 hours with a stirring speed of 150 rpm. After the adsorption process, the absorbance was filtered and measured using AAS with a wavelength of 217 nm for Pb and 324.7 nm for Cu.

The real electroplating waste solution was taken as much as 50 mL and put into an tube. Commercial activated charcoal and coconut coir adsorbent were weighed according to their optimum mass. The commercial activated charcoal or coconut fiber adsorbent was contacted into each electroplating real waste solution and stirred using a magnetic stirrer for 24 hours with a stirring speed of 150 rpm. Commercial activated charcoal or coconut coir adsorbent was filtered and the absorbance measured using AAS.

Morphological characterization and composition of coco coir adsorbent before and after adsorption of electroplating real waste were analyzed using Scanning Electro Microscope (SEM-EDX). Qualitative analysis using SEM-EDX to determine the morphology and metal composition of Pb and Cu on the surface of the coconut coir adsorbent before and after the adsorption process. Quantitative analysis using AAS was used to determine the concentration of Cu and Pb metals in simulated waste and electroplating real waste before and after adsorption by coconut coir adsorbents and commercial activated charcoal

3. RESULTS AND DISCUSSION

The characterization data of coconut coir adsorbent and activated carbon according to SNI No. 06-3730-1995 were listed in Table 1, which indicated that the water content of both sample is fulfilling the standard requirements. Determination of water content aims to determine the hygroscopic nature of charcoal (Hendaway, 2003). Analysis of the ash content on the adsorbent of coconut coir and commercial activated charcoal has met the SNI standard. Determination of ash content aims to determine the content of metal oxides in charcoal or adsorbents (Pari, 2004). The high ash content is caused by the presence of metal oxides consisting of minerals (Na, Ca, Mg and K) in the charcoal which cannot evaporate during carbonization and further combustion in the carbonization process because the charcoal interacts with oxygen in the air causing it to become ash (Scroder, 2006).

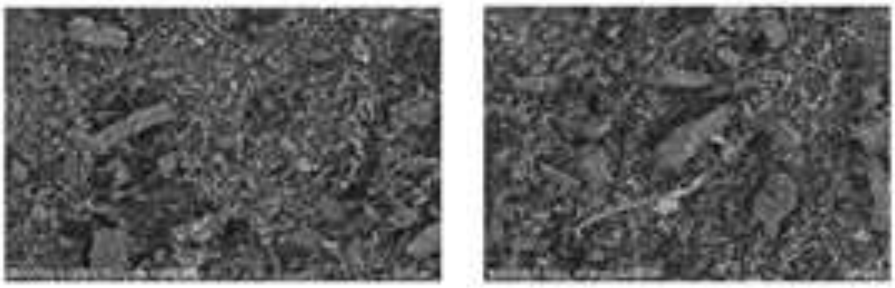
Table 1. Characterization data according SNI No. 06-3730-1995

	Water content	Ash content	Volatile content	C content	Adsorption toward I_2 (mg/g)
Standard	Max 15	Max 10	Max 25	Min 65	Min 750
Commercial activated carbon	7.38	10.6	26	55.8882	609.12
Coconut coir adsorbent	10.578	7.4	32	49.4673	1015.2

Analysis of volatile substances in coconut coir adsorbents and commercial activated charcoal did not meet SNI standards. This is due to imperfections in the carbonization process where there may be compounds that have not evaporated in the carbonization process but evaporated at a temperature of 950°C (Sudradjat, et al.¸2005). Analysis of carbon content in coco coir adsorbents and commercial activated charcoal did not meet SNI standards. This is due to the high levels of volatile substances and water content in coconut coir adsorbents, while commercial activated charcoal is caused by high levels of ash and volatile substances.

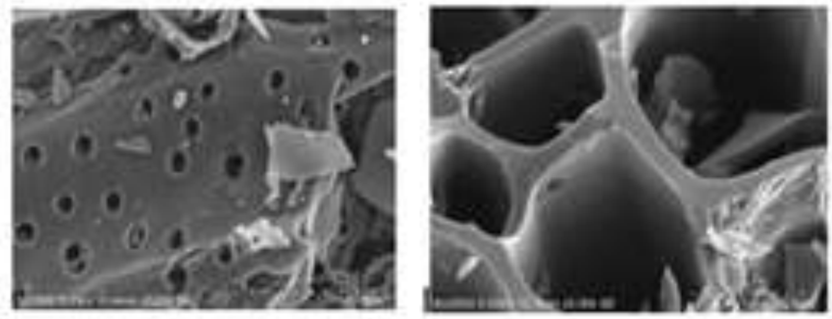
The absorption of iodine shows the ability of activated charcoal to absorb substances with a molecular size smaller than 10 (Irmanto and Suyata, 2010). Coconut coir adsorbent has met SNI standards while commercial activated charcoal does not meet SNI standards. The low absorption of iodine in commercial activated charcoal is possible because of the increasing number of impurities contained in the pores and covering the pores of commercial activated charcoal so that it will reduce the ability of commercial activated charcoal pores to be able to absorb the desired adsorbate, namely iodine (Jamilatun and Setyawan, 2014). This is supported by high ash content data.

Characterization based on the morphology of the surface of the coconut coir adsorbent showed that coco coir adsorbent has less uniform size, can be seen in Figure 1a and b. Morphologically, it can be seen that there are pores of coconut coir adsorbent having a round shape with a large cavity like a honeycomb (Figure 2).



(a) (b)

Figure 1. The morphology of coconut coir adsorbent before (a) and (b) after adsorption with magnificent 100x



(a) (b)

Figure 2. The pore morphology of coconut coir adsorbent before (a) and (b) after adsorption with magnificent 500x

The efficiency data of coconut coir adsorbent and commercial activated carbon toward Cu metal were listed in Table 2, which indicated that both adsorbents with same variation have efficiency value in accordance with the increase of mass (Wijayanti, 2009).

Table 2. Adsorption efficiency of Cu toward coconut coir adsorbent and commercial activated carbon

Nama Sampel	Massa (gram)	C awal (mg/L)	Volume Larutan (mL)	Efisiensi Adsorpsi ASK (%)	Efisiensi Adsorpsi AAK (%)
Sampel 1	0,15225	23,3	50	51,8566	76,2556
Sampel 2	0,4005	23,3	50	96,4889	92,9183
Sampel 3	0,6514	23,3	50	83,3968	**94,7036**
Sampel 4	0,9008	23,3	50	**98,2742**	94,1085

The optimum mass of coconut coir adsorbent is 0.9 grams with an adsorption efficiency of 98.3742% while the optimum mass of commercial activated charcoal has a mass of 0.651 grams with an adsorption efficiency price of 94.7036%. of 0.65 grams can be caused by the coagulation of some of the coco coir adsorbent particles so that it interferes with the contact between the coco coir adsorbent particles and Cu metal ions in the Cu^{2+} solution. The movement of coco coir adsorbent particles is slightly inhibited resulting in low Cu metal ion sorption. The deviation in sample 4 using commercial activated charcoal can be caused by the occurrence of desorption events because the surface of the commercial activated charcoal has reached a saturated condition. The surface of commercial activated charcoal is in a saturated state which simultaneously re-releases the adsorbed Cu metal ions out into the simulated waste fluid flow until it reaches a constant state (Refilda, et al., 2001; Sulistyawati, 2008 and Tabak, et al., 2010).

The adsorption capacity of coconut coir adsorbent and commercial activated carbon toward Cu^{2+} solution are listed in Table 3, which showed that as the mass of adsorbent or commercial activated charcoal increases, the adsorption capacity of Cu metal ions decreases. This is because the increasing mass of the adsorbent of coconut coir or commercial activated charcoal is not proportional to the concentration of adsorbed Cu metal ions. There are still many pores of the coconut coir adsorbent and commercial activated charcoal which are still empty and do not have the opportunity to interact with Cu metal ions because most of the Cu metal ions in the Cu^{2+} solution have been adsorbed.

Table 3. The adsorption capacity of coconut coir adsorbent and commercial activated carbon toward Cu^{2+} solution

Nama Sampel	Massa (gram)	C awal (mg/L)	Volume Larutan (mL)	Kapasitas Adsorpsi ASK(mg/g)	Kapasitas Adsorpsi AAK (mg/g)
Sampel 1	0,15225	23,3	50	4,006161996	5,779946025
Sampel 2	0,4005	23,3	50	2,808133777	2,701518876
Sampel 3	0,6514	23,3	50	1,490598925	**1,694773091**
Sampel 4	0,9008	23,3	50	**1,271963782**	1,21615574

Table 4. Adsorption efficiency of Pb toward coconut coir adsorbent and commercial activated carbon

Massa ASK (gram)	C Awal (mg/L)	Volume larutan (mL)	Efisiensi Adsorpsi ASK (%)	Efisiensi Adsorpsi AAK(%)
0,1516	40	50	50	100,6271953
0,4017	40	50	96,864	**103,13598**
0,6501	40	50	99,3728	90,5920725
0,9007	40	50	**99,3728**	89,33768189

The efficiency data of coconut coir adsorbent and commercial activated carbon toward Pb metal were listed in Table 4, which indicated that there is an adsorption process of Pb metal ions with coconut coir and commercial activated charcoal as adsorbent according to the theory. The optimum mass of coconut coir adsorbent is 0.9 g with an adsorption efficiency price of 99.3728% while the optimum mass of commercial activated charcoal is 0.4 g with an adsorption efficiency price of 103.1359%. The adsorption process with a coir adsorbent mass of 0.9 grams reached an equilibrium state. This balance is achieved because the pores of the coconut coir adsorbent which have adsorbed Pb metal ions are comparable to the empty coconut coir adsorbent pores so that the surface of the inner coconut coir adsorbent has a van der Waals force equilibrium on the surface of the coconut coir adsorbent. The mass of commercial activated charcoal of 0.65 and 0.9 grams decreased the value of Pb metal adsorption efficiency. This is because there has been a desorption event. This desorption event occurs because the surface of commercial activated charcoal reaches a saturated condition.

The adsorption capacity of coconut coir adsorbent and commercial activated carbon toward Pb^{2+} solution are presented in Table 5, which showed that on the adsorbent capacity of coconut coir when compared with the adsorption capacity of commercial activated charcoal, it can be seen that an increase in the mass of the adsorbent of coconut coir or commercial activated charcoal will decrease the adsorption capacity of Pb metal ions. This is because the increasing mass of the adsorbent of coconut coir or commercial activated charcoal is not proportional to the concentration of adsorbed Pb metal ions.

Table 5. The adsorption capacity of coconut coir adsorbent and commercial activated carbon toward Cu^{2+} solution

Nama Sampel	Massa ASK (gram)	C Awal (mg/L)	Volume larutan (mL)	Kapasitas Adsorpsi ASK (mg/g)	Kapasitas Adsorpsi AAK (mg/g)
Sampel 1	0,1516	40	50	6,596306	13,34578186
Sampel 2	0,4017	40	50	4,822705	**5,147790167**
Sampel 3	0,6501	40	50	3,443061	2,781030622
Sampel 4	0,9007	40	50	**2,206568**	1,983959181

Adsorption of Cu and Pb Metals in Electroplating Wastewater

The optimum mass of each adsorbent of coconut coir and commercial activated charcoal was adsorption on the real electroplating waste so that the value of adsorption efficiency and adsorption capacity of Cu metal ions is shown in Table 6. The adsorption of Cu metal ions in Cu^{2+} solution was 98.2742%. The value of the adsorption efficiency of Cu metal ions in Cu^{2+} solution is greater than in the adsorption of real electroplating waste. This is because the adsorption process of the real electroplating waste takes place simultaneously or simultaneously and there is competition between metal ions in the real electroplating waste, the absorption of Cu metal ions will be low.

Table 6. The comparation between adsorption efficiency and adsorption capacity of Cu toward of coconut coir and commercial activated charcoal

Nama Sampel	Absorbansi	C akhir (mg/L)	C awal (mg/L)	C teradsorpsi (mg/L)	Ea (%)	Qm (mg/gram)
ASK4	0,0801	2160	2358	198	8,396947	11
AAK3	0,0964	2618	2358	-260	-11,026	-20

Based on Table 6, the adsorption capacity of Cu metal ions in electroplating real waste is 11 mg/g while the adsorption capacity of Cu metal ions in Cu^{2+} solution is 1.2719 mg/g. The value of the adsorption capacity of Cu metal ions on the adsorption of Cu^{2+} solution is smaller than the adsorption on the real electroplating waste. The adsorption capacity of Cu metal ions is influenced by the adsorption competition between metal ions in the real electroplating waste based on the initial amount of Cu metal ions in the real electroplating waste or Cu^{2+} solution. The adsorption process with commercial activated charcoal did not absorb Cu metal ions. The adsorption capacity with a mass of 0.65 gram commercial activated charcoal has a negative value because commercial activated charcoal adsorption of Cu metal ions using electroplating real waste tends to experience desorption events rather than adsorption events.

Table 7. The comparation between adsorption efficiency and adsorption capacity of Pb toward of coconut coir and commercial activated charcoal

Nama Sampel	Absorbansi	C akhir (mg/L)	C awal (mg/L)	C teradsorpsi (mg/L)	Ea (%)	Qm (mg/gram)
ASK4	0,016	0,92	1,4	0,48	34,2857	0,026667
AAK2	0,0092	0,52	1,4	0,88	62,8571	0,11

The optimum mass of each adsorbent of coconut coir and commercial activated charcoal was adsorption on the real electroplating waste so that the value of adsorption efficiency and adsorption capacity of Pb metal ions is shown in Table 7, which showed that The value of the metal ion adsorption efficiency of Pb in the real electropalting waste adsorption was 34.287% while the Pb^{2+} solution adsorption was 99.372%. The value of the efficiency of Pb metal ion adsorption on the electroplating real waste adsorption is smaller than the value of the Pb metal ion adsorption efficiency on the adsorption of Pb^{2+} solution. This is because the adsorption process of the real electroplating waste takes place simultaneously or simultaneously and there is competition between metal ions in the real electroplating waste, the absorption of Cu metal ions will be low.

The adsorption capacity of coconut coir adsorbent in electroplating real waste is 0.026667 mg/g while the adsorption capacity of Pb2+ solution is 2.2065 mg/g, so the adsorption capacity of Pb metal ions in electroplating real waste is smaller than the adsorption capacity of Pb metal ions in Pb2+ solution. . The adsorption capacity of Pb metal with coconut coir and commercial activated charcoal as adsorbent is relatively low, this may be due to the influence of adsorption competition between metal ions based on the number of initial Pb metal ions in the electroplating real waste and the Pb metal ion radius. The initial amount of Pb metal ions in the electroplating real waste was 1.4 mg/L. The smaller the initial amount of Pb metal ions, the smaller the interaction between the pores and the Pb metal ions, so that fewer Pb metal ions are adsorbed on the pores of the coconut coir adsorbent or commercial activated charcoal (Tanindya and Dina, 2014). The relatively large radius of Pb metal ions causes Pb metal ions to take longer to be adsorbed on the surface of coconut coir adsorbents or commercial activated charcoal (Tanindya and Dina, 2014). Commercial activated charcoal in the adsorption of real electroplating waste has an efficiency and adsorption capacity of Pb metal ions of 62.857% and 0.11 mg/gram, respectively.

The results of the SEM-EDX analysis obtained data in the form of tables and graphs regarding the components of the coconut coir adsorbent before and after adsorption on the electroplating real waste which can be seen in Table 8. The material components contained in the coconut coir adsorbent before the adsorption process according to Table 16. It can be seen that the components the materials contained in the coco coir adsorbent before the adsorption process were C, O, Pb and Cr metals. The metal content of Pb and Cr is probably derived from the coconut coir adsorbent as the basic material for making activated carbon, not only containing carbon compounds but also containing some minerals that have been partially lost during carbonization and activation, some are estimated to still be left in activated carbon (Suhendarwati, 2013).

Table 8. The composition of coconat choir

Element	Sebelum		Setelah	
	Weight %	Atomic %	Weight %	Atomic %
C K	82,2	86,4	69,1	79,8
O K	17,1	13,5	20	17,3
Cu L	0	0	0,9	0,2
Si K	0	0	0	0
S K	0	0	2,7	1,3
Cr K	0,3	0,1	1,6	0,7
Pb M	0,4	0	4,5	0,3
Cr K	0,3	0,1	1,2	0,3

Based on the data in Table 8, it can be seen that the material components contained in the coconut coir adsorbent after adsorption are C, O, Si, S, Cu metal, Cr metal and Pb metal. The presence of Cu and Pb metals indicates that Cu and Pb metal ions are adsorbed in the coconut coir adsorbent during the adsorption process. The components of Si and S elements are also adsorbed, possibly due to the presence of external contaminants contained in the real electroplating waste or from the coconut fiber itself. Several metals are also adsorbed on the coir adsorbent after the adsorption process, namely Pb metal, Cr metal and Cu metal. These metals are naturally present in real electroplating waste, according to Marwati, et al., (2008) which states that heavy metals in electroplating liquid waste.

4. CONCLUSION

Coconut coir adsorbent has the characteristics of volatile content and carbon content that does not meet SNI 06-3730-1995. Commercial activated charcoal has the characteristics of ash content, volatile content, carbon content and absorption capacity of (I2) that do not meet SNI 06-3730-1995. The characteristics of coco coir adsorbents before and after adsorption have particles of less uniform size, rounded pores and large cavities like honeycomb. The optimum mass of coco coir adsorbent on Cu and metal adsorption was 0.9 grams, while the optimum mass of commercial activated charcoal for Cu metal adsorption was 0.65 grams and Pb adsorption was 0.4 grams. The adsorption efficiency (%) of Cu metal ions on coco coir adsorbent (*Cocos nucifera Linn.*) was 8.39% and commercial activated charcoal was -11.026% while the adsorption efficiency (%) of Pb metal ions on coco coir adsorbent (Cocos nucifera Linn.) of 34.28% and 62.85% for commercial activated charcoal. The surface component of the coconut coir adsorbent before adsorption contained no Cu metal and there was Pb metal having a mass % of 0.4 while after adsorption there was a Cu metal content having a mass % of 0.9 and Pb metal having a mass % of 4.5.

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