TREATMENT OF COPPER-CONTAINED JEWELLERY WASTEWATER BY PRECIPITATION AND ADSORPTION USING RICE HUSK CHARCOAL

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ABSTRACT
The wastewater from the jewellery industry generally contains a large amount of metal. Metal removal can be done with many techniques, including precipitation and adsorption. Precipitation is done to convert the metal content from the dissolved phase to a solid that is easily precipitated. Generally, precipitation is unable to separate one hundred percent of metal content, so further processing is needed, i.e. adsorption. This research was done by using rice husk charcoal which is an agricultural waste in Indonesia. The rice husk charcoal was burnt to charcoal, then activated with acid. A SEM-EDX analysis was conducted to obtain a surface description of rice husk charcoal before and after use in the adsorption process. The results showed that the copper content in the jewellery wastewater can be adsorbed with a 40–50 mesh rice husk charcoal and the adsorption process follows the Freundlich isotherm model with R² value of 0.9625.

Keywords: adsorption, copper, jewelry industry, rice husk charcoal.
Several studies were conducted to remove the heavy metal content with rice husk, by [Alexander et al., 2017; El–Moselhy et al., 2017; Hanum et al., 2017; Hsu et al., 2009; Ye et al., 2012]. Rice husk was washed, dried with oven at 70°C for 24 hours and then homogenized to uniform particle size [El-Moselhy et al., 2017]. This rice husk is used to remove cadmium and copper. The optimum conditions were obtained at pH 6, the adsorbent mass 0.2 g, contact time 120 minutes, initial concentration 10 mg/L, and temperature 30°C. [Hanum et al., 2017] used carbonized rice husk at 500°C for 150 minutes, immersed in HCl 5% with carbon-acid ratio 1:10 (b/v) for 24 hours, to adsorb lead. [Mullich et al., 2017] compared commercial adsorbents and rice husk to remove chromium (VI) in artificial waste at contact time of 300 minutes. The result of adsorption capacity with commercial adsorbent was 43.79 mg/g, while with rice husk the adsorption capacity of 34.85 mg/g was obtained. [El-Shafey, 2010] studied husk charcoal that was activated with 13 M sulfuric acid to remove zinc and mercury. The optimum conditions were obtained at pH 6, the concentration of adsorbate 50 mg/L, and the adsorbent mass of 0.1 g.

Several factors that influence the adsorption processes include the properties of adsorbent, adsorbate concentration, adsorption properties, temperature, pH, and contact time. In addition, there is an activation process of adsorbent which is an adsorbent modification to increase the capacity and efficiency of adsorption. Activation can be performed by chemical treatments as reacted with acids or bases and physical treatments such as heating and washing [Marshall and Johns, 1996].

The most widely used adsorption models in the analysis of experimental adsorption data are Freundlich isotherm and Langmuir isotherm [El-Moselhy et al., 2017; Banerjee et al., 2016; Bhatti et al., 2015]. The Freundlich isotherm model is widely used in the study of adsorption kinetics is pseudo first order kinetics and pseudo-second order kinetics. The pseudo-first order kinetics equation is expressed by equation (3) and the pseudo-second order adsorption kinetics is expressed by equation (4) [Fang et al., 2018].

\[
\log(qe - qt) = qe - \frac{K_1}{2.303} t \tag{3}
\]

\[
\frac{t}{qt} = \frac{1}{K_1 qe^2} + \frac{1}{qe} t \tag{4}
\]

where: \( x/m \) is mass of adsorbate per mass of adsorbent (is called adsorption capacity, expressed in mg/g), \( K \) and \( n \) are Freundlich constant (dimensionless), and \( Ce \) is the adsorbate concentration at equilibrium in mg/L.

The Langmuir isotherm model assumes that the amount of surface site which adsorb the adsorbent is fixed, in accordance with the surface area of the adsorbent and is reversible. Equilibrium is achieved when the adsorption speed of the molecule to the surface of the adsorbent is equal to the speed of molecular desorption of the adsorbent surface. The Langmuir isotherm model is expressed as the follow equation:

\[
\frac{x}{m} = \frac{qm b Ce}{1 + b Ce} \tag{2}
\]

where: \( qm \) and \( b \) are Langmuir constant (dimensionless), and \( Ce \) is adsorbate concentration at equilibrium in mg/l.

The adsorption process can take place quickly or slowly, depending on many factors. The speed of the adsorption process is assessed in terms of the adsorption kinetics. According to [Hammed and Ahmad, 2010], a model widely used in the study of adsorption kinetics is pseudo first order kinetics and pseudo-second order kinetics. The pseudo-first order kinetics equation is expressed by equation (3) and the pseudo-second order adsorption kinetics is expressed by equation (4) [Fang et al., 2018].

\[
\log(qe - qt) = qe - \frac{K_1}{2.303} t \tag{3}
\]

\[
\frac{t}{qt} = \frac{1}{K_1 qe^2} + \frac{1}{qe} t \tag{4}
\]

where: \( qe \) is the metal ion adsorption capacity at equilibrium (mg/g), \( qt \) is the amount of ion absorbed at time t (mg/g), \( K_1 \) is the pseudo-first order kinetics constant (min\(^{-1}\)), and \( K_2 \) is the pseudo-second order kinetics constant (mg/g min\(^{-1}\)).
MATERIALS AND METHODS

Preparation of Rice Husk Adsorbent

The production of rice husk adsorbents begins with washing to remove impurities, then drying in an oven for 3 hours at 110°C to reduce the water content [Hsu et al., 2009]. After drying, the rice husk is then burned in the furnace for 2 hours at a temperature of 400°C until it becomes charcoal. In this process the combustion is maintained so that no air enters so the rice husk does not burn to ash. The next process is activation by immersion of 5% HCl (v/v) on the carbon to acid ratio of 1:10 (w/v) for 24 hours [Hanum et al., 2017]. The adsorbent of the husk is sieved to obtain the size according to the variation of media size used, i.e. 2.0–0.841 mm (10–20 mesh) and 0.4–0.29 mm (40–50 mesh).

Adsorbent Characterization with SEM-EDX

Prior to use in the adsorption process, the adsorbent was characterized by Scanning Electron Microscopy-Energy Dispersive X-ray (SEM-EDX). The characterization of the adsorbent aims at finding out the content of the adsorbent material and the grain surface image as well as the pore distribution of the adsorbent based on particle size and the type of adsorbent.

Precipitation Experiment

The precipitation process was carried out by adjusting the pH. The pH variations are 7, 8, 9, and 10 (as the minimum metal solubility). The chemical used to raise the pH was NaOH 50%. During precipitation, stirring was done at 120 rpm for one minute to obtain the homogeneous mixture. Then, it was followed by slow stirring at 45 rpm for 20 minutes. After the slow stirring was complete, the waste sample was clarified for 5 hours to obtain the most precipitation. The supernatant was filtered, and filtrate was measured by AAS (Atomic Absorption Spectrometry) method according to the American Public Health Association (APHA).

Isotherm Adsorption Experiment

The adsorption isotherm experiments were conducted in batch with variations of adsorbent size. The added adsorbent mass was 0.5 g, 1.0 g, 1.5 g, 2.0 g [Alexander et al., 2017]. The experiment was carried out by putting 100 ml of sample into the flask and then adsorbent was added according to the specified variation. Then, the mixture of the sample and adsorbent was stirred at 150 rpm [Alexander et al., 2017] for 3 hours and the sample was subsequently filtered with filter paper. The filtered sample was analyzed for each metal concentration by AAS method.

RESULTS AND DISCUSSION

Wastewater Characteristics

The wastewater samples used in the experiments included the jewellery industry wastewater from Surabaya, Indonesia. The wastewater characteristics can be seen in Table 1. The large concentration of Cu is caused by the use of acid solutions in the process of producing gold jewellery.

Adsorbent Profile of Rice Husk Charcoal with SEM-EDX

Before being used as adsorbent, the rice husk charcoal was analyzed with SEM-EDX method to know the surface description and composition of adsorbent. The characteristic of rice husk before being used as adsorbent can be seen in Figures 1 to 7. The rice husk charcoal before activation (Figure 2) shows that some of the pores present in the carbon are still covered by hydrocarbons and other organic compounds. These carbon components include bonded carbon, ash, water and nitrogen. The activation process results in a larger carbon surface area due to the breaking of hydrocarbon bonds or the oxidation process of the surface molecules that clog pores. The activation process also increases the silica content. The EDX spectra result of rice husk charcoal characterization before and after activation showed a significant difference. The percentage of silica before activation is 8.45%, while after activation, it increased to 19.41%. The rice husk adsorbent with particle size of 10–20 mesh and 40–50 mesh

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Unit</th>
<th>Value</th>
<th>Standard*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>mg/L</td>
<td>3,227</td>
<td>2</td>
</tr>
<tr>
<td>pH</td>
<td>-</td>
<td>0.6–0.7</td>
<td>6–9</td>
</tr>
</tbody>
</table>

*) Effluent standard according to the local governmental regulation
Figure 1. Photo of rice husk charcoal: a) particle size 10–20 mesh; b) particle size 40–50 mesh

Figure 2. SEM micrograph of rice husk charcoal before activation at 5000x magnification

Figure 3. EDX spectra of rice husk charcoal before activation
Figure 4. SEM micrograph of rice husk charcoal of 10–20 mesh after activation at 5000x

Figure 5. EDX spectra of rice husk charcoal of 10–20 mesh after activation

Figure 6. SEM micrograph of rice husk charcoal of 40–50 mesh after activation at 5000x
show pore or empty hollow and arranged regularly. This pore will become the adsorption site in the adsorption process.

**Preliminary Experiment**

Before the adsorption experiments were performed, the wastewater samples were precipitated by the addition of sodium hydroxide to increase the pH value and followed by precipitate formation. The process of precipitation of the waste sample was carried out as a preliminary study to reduce the metal content by adding NaOH as a precipitating agent. In this case, it is expected to form a lot of hydroxide metal solids that can be physically separated. Precipitation was performed at pH 7, 8, 9 and 10 variations. The addition of NaOH to the waste sample was proportional to the increase in pH of wastewater due to the presence of OH ions derived from the addition of NaOH. This ion reacts with the metal cations in the waste sample to form a precipitate of the hydroxide metal as the reaction follows.

\[
\text{NaOH} \rightarrow \text{Na}^+ + \text{OH}^- \\
2\text{OH}^- + \text{Cu}^{2+} \leftrightarrow \text{Cu(OH)}_{2(s)}
\]

In this study, the process of precipitate formation after the addition of NaOH was very rapid. In the precipitation process, there was a separation between the supernatant and the precipitate. The copper metal content of the supernatant was measured. The result of measurement data with AAS related to the effect of pH on copper metal concentration can be seen in Figure 8.

At pH 9, the precipitation process is most optimal and can reduce the copper content by 99%. This corresponds to the metal solubility curve, i.e. pH 9 is the minimum solubility point for the copper metal. A perfect precipitation process occurs at pH 9, but it requires a lot of NaOH solution in the formation of a hydroxide metal solid. The
precipitation process at pH 7 (neutral condition) is considered capable of significantly decreasing the copper metal content by 99.86%. The result of waste precipitation at pH 7 indicates that the copper content still does not meet the quality standard (max 2 mg/L). Therefore, further treatment is required with the adsorption process to reduce the copper content.

**Adsorption Experiment**

The adsorption process of the precipitated sample was carried out using the physically-activated rice husk charcoal. The particle size variation of adsorbent was 10–20 mesh and 40–50 mesh. The batch adsorption process was done by varying the adsorbent mass and contact time.

**Effect of Adsorbent Size and Mass**

The adsorption of copper metal was carried out at an initial copper concentration of 1.9 mg/L. The rice husk charcoal as used adsorbent had two kinds of grain size, which is 10–20 mesh and 40–50 mesh. The adsorbent mass was varied with 0.5, 1.0, 1.5, and 2.0 grams. After contact between the wastewater with the adsorbent in a certain time, the sample was filtered, and the filtrate was analyzed with AAS. The concentration of copper in the sample can be seen in Table 2.

Table 2 shows that two grams mass of adsorbent mass obtained the largest adsorbate (copper) mass compared to the others. Meanwhile, the 10–20 mesh adsorbent size adsorbs much more copper than the 40–50 mesh adsorbent. In general, the magnitude of the adsorption capacity increases with the amount of adsorbent mass. The ability to absorb metal ions also increases along with the initial concentration of metal ions.

Observing the results of this experiment, the adsorption is relatively low. This is because the initial concentration of copper is low as well. The greater the concentration is, the higher the number of molecules in the solution; thus, the interaction between adsorbate molecules and adsorbents is increased. In addition, this low absorption rate was due to the presence of noncarbon compounds such as ash, water and other metals attached to the surface of activated carbon, which covered the pores [Sathasivam and Haris, 2010].

**Influence of Contact Time**

The adsorption process by varying the contact time was carried out to test the effect of contact time or the chance of interaction between the adsorbate and the adsorbent. After the specified time (0.5, 1, 2, and 4 hours), the sample was filtered, and the filtrate was analyzed by AAS. The concentration of copper in the sample can be seen in Table 3.

Table 3 shows that the removal of copper metal by rice husk charcoal increases along with the contact time. This indicates that with the increase of contact time, the chance of interaction between adsorbate and adsorbent is longer, so that the adsorption process increases and the remaining metal content in the solution becomes reduced. The optimum contact time in copper metal removal is 4 hours (240 minutes). This result similar to the one reported by [El-Moselhy et al., 2017], i.e. the highest removal of copper and cadmium metals in a solution with rice husk adsorbents also occurred at the longest contact time of 120 minutes.

**Adsorption Model**

Laboratory experimental data were analyzed by the Freundlich and Langmuir isotherm adsorption model as expressed in equation (1) and equation (2). The data analysis obtained Freundlich and Langmuir constants, as can be seen in Table 4.

An adsorption experiment with variation of adsorbent size showed that 40–50 mesh adsorbent size resulted in a larger adsorption capacity than adsorption with 10–20 mesh adsorbent. Thus, the copper metal adsorption process with 40–50 mesh rice husk adsorbents tends to follow Freundlich isotherm model with R² value of 0.9625. This explains that the process of adsorption of copper with rice husks is multilayer and

<table>
<thead>
<tr>
<th>Adsorbent size (mesh)</th>
<th>Mass of Adsorbent (g)</th>
<th>Concentration of Cu (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10–20</td>
<td>0.5</td>
<td>1.82</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>1.74</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>1.68</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>1.58</td>
</tr>
<tr>
<td>40–50</td>
<td>0.5</td>
<td>1.87</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
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<tr>
<td></td>
<td>1.5</td>
<td>1.76</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>1.58</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Adsorbent size (mesh)</th>
<th>Contact Time (hours)</th>
<th>Concentration of Cu (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10–20</td>
<td>0.5</td>
<td>1.15</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>0.81</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.63</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>0.44</td>
</tr>
<tr>
<td>40–50</td>
<td>0.5</td>
<td>0.92</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>0.72</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.45</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>0.32</td>
</tr>
</tbody>
</table>
rather ignores the effect of surface area, where the 10–20 mesh adsorbent should theoretically result in a larger adsorption capacity.

**SEM-EDX Analysis of Adsorbent after Adsorption**

The SEM-EDX analysis after the adsorption process was performed to characterize the surface features of the rice husk charcoal and prove the metal attachment on the surface of the adsorbent. The result of characterization with SEM-EDX can be seen in Figures 9 and 10.

<table>
<thead>
<tr>
<th>Adsorbent size (mesh)</th>
<th>Freundlich</th>
<th>Langmuir</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>n</td>
<td>K</td>
</tr>
<tr>
<td>10–20</td>
<td>4.2955</td>
<td>0.0138</td>
</tr>
<tr>
<td>40–50</td>
<td>-0.1574</td>
<td>0.3035</td>
</tr>
</tbody>
</table>

Table 4. Results of Copper Adsorption Isotherms using Rice Husk Charcoal

![Figure 9. SEM micrograph of rice husk charcoal of 40–50 mesh after adsorption process](image)

![Figure 10. EDX spectra of rice husk charcoal after used in adsorption process](image)

There is the adsorbate membrane attached on the surface of adsorbent that was used in the process of metal adsorption, so the pores of the adsorbent become slightly closed. At 5.000× magnification, it appears that the pores of the adsorbent are already covered by adsorbate adsorbed on the surface of adsorbent. The existence of these pores explains that the adsorption process that occurs in this research is multilayer adsorption. Figure 10 shows that the rice husk charcoal used in the adsorption process...
absorbed the copper metal. It can be seen from the EDX data that contained elements of copper (Cu). The chemical content composition of the adsorbent used is shown in Table 5. After the adsorption process, there were Cu elements of 1.07%. This shows that the adsorbent of rice husk absorbed Cu.

### CONCLUSIONS

The treatment of jewellery waste water with a very high copper metal content begins with precipitation process. By adjusting the pH to alkaline conditions, the copper is easily precipitated. After the copper concentration reaches a lower value, the next process is adsorption with rice husk. The copper content in the jewellery wastewater can be adsorbed with a 40–50 mesh rice husk charcoal and the adsorption process follows the Freundlich isotherm model with R² value of 0.9625.

### Acknowledgements

Acknowledgements and appreciations are given to LPDP (Institute of Education Fund Management), Ministry of Finance of the Republic of Indonesia which has provided education and research funds, so this research can be well done.

### REFERENCES

12. Karniba, M., Kabbanib, A., Holaila, H. and Ola-

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon (C)</td>
<td>28.01</td>
</tr>
<tr>
<td>Oxygen (O)</td>
<td>48.18</td>
</tr>
<tr>
<td>Natrium (Na)</td>
<td>3.54</td>
</tr>
<tr>
<td>Chlor (Cl)</td>
<td>2.16</td>
</tr>
<tr>
<td>Copper (Cu)</td>
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</tr>
<tr>
<td>Potassium (K)</td>
<td>0.11</td>
</tr>
<tr>
<td>Magnesium (Mg)</td>
<td>0.07</td>
</tr>
<tr>
<td>Iron (Fe)</td>
<td>0.23</td>
</tr>
<tr>
<td>Silicon (Si)</td>
<td>16.40</td>
</tr>
</tbody>
</table>

Table 5. Composition of rice husk charcoal
103


