The Effectiveness of Corncob Activated Carbon in Reducing Chromium (Cr), Cadmium (Cd), Copper (Cu), and Zinc (Zn) Levels in Electroplating Wastewater

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Abstract. The heavy metal from industrial electroplating wastewater can directly affect the environment even at very low concentration. The application of agricultural waste as low-cost adsorbents of removing heavy metal has been developed. This study aimed to determine the effectiveness of corncob activated carbon in reducing levels of Cu, Zn, Cr, and Cd in electroplating wastewater. The adsorbent from corncob dried in the sun, carbonized for 24 hours until carbon was formed. Then it was activated by HCl 9% for 24 hours, dried, crushed, and sieved with 80 mesh size sifter. The variation of the discharge are 15 ml/min, 20 ml/min, and 25 ml/min, the sample was taken at 0, 5, 10, 15, and 20 minutes. The results show that the highest reduction of Cr, Cd, Cu, and Zn occurred at 15 ml/minute discharge in the 5th minute with the total removal efficiency of Cr, Cd, Cu, and Zn were 25.75%, 43.42%, 50.39%, and 53.97%. Furthermore, it indicates that corncob activated carbon was found to be most effective in reducing of Zinc (Zn).

1. Introduction
The development of the Indonesian economy is characterized by various industries like electroplating industry. Their activities not only providing benefits, but also has a negative impact due to the discharge of heavy metal contaminated wastewater, such as Cd, Cr, Zn Cu, Ni, As, Ag, and Pb. These include electroplating, coating, cleaning, electroless deposition, etc. All of these metals are discharged into the environment directly or indirectly, reaching the water, air, and land. Then these metals can be absorbed by living organism and accumulated in the vital organ on the human being, plants, and another living organism. Besides, these can lead to various health disorder [1-2]. It is necessary to treat metal-contaminated wastewater as well as reduction the environment effect.

Recently, numerous researches have been studied for the cheaper and effective technologies for the dissolved and suspended heavy metals from wastewater. These include ion exchange, adsorption, electrochemical treatment technologies, chemical precipitation, membrane filtration, electro dialysis, photocatalysis [3-10]. Adsorption is one of the alternative treatments that has intensified increase. Many adsorbents may be used from agricultural raw materials and residues, such as corncob, nutshells, rice husks, fruit pits, soybean, rice straw, sugarcane bagasse [11],[12]. The choice of those adsorbents based on the low-cost adsorbents, easy operating conditions, having a wide pH range, and high metal binding capacities [13].

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Lampung province is the 3rd largest corn-producing after Jawa Timur and Jawa Tengah [14]. Its followed by a large amount of corncob waste with the estimate of waste 18 kg per 100 kg of corn grain production[15]. The utilization of corncob as the activated carbon being economical and eco-friendly because of their high adsorptive capacities based on pore volume, porosity, and surface area. Due to the activation process, all of that’s developed and increase the absorption. Furthermore, temperature, pH, and contact time also affect carbon absorption. The process of activated carbon divided two types, the chemical and physical activation. The chemical activation method involves the co-carbonization of feedstock with a chemical, such as zinc chloride (ZnCl2), phosphoric acid (H3PO4), and potassium hydroxide/carbonate. The physical activation method involves carbonization of the raw material and subsequent activation in high temperature in carbon dioxide or steam.

Several studies on the various method have been done. The preparation of activated carbons from corncob with chemical activation with ZnCl2, H2SO4, and HCl [16-18]. But it can be pointed out that ZnCl2 and H3PO4 are the most widely used as chemical agents. Hence, the objective of the present study was to analyze the effectiveness of corncob activated carbon by chemical activation (HCl) with discharge and contact time variation for Chromium (Cr), Cadmium (Cd), Copper (Cu), and Zinc (Zn) contaminants wastewater.

2. Methods

2.1. Materials

Industrial electroplating wastewater was obtained from CV Bintang Chroom and the corncob was obtained from the farmer in East Lampung.

2.2. Sample Preparation

Ten kilograms corncob washed, cleaned, and dried in the sun for 3 days until completely dry. Subsequently, air-dried corncob was carbonized in artificial furnace from stacked bricks for 24 hours. In this process, the rice husk sprinkled as the bottom layer the furnace and on the corncob mound to make the combustion process easier.

2.3. Sample Activation

After the carbon is formed, then the activation is carried out by soaking the carbon into HCl with a concentration of 9% in a 1000 ml beaker glass for 24 hours. The separating carbon then dried in an oven at 100°C for 2 hours. The carbon was inserted to desiccator so that the carbon temperature was stable and washed with distilled water to release the acid. The carbon then dried with aerating it with the wind. Finally, the activated carbon is finely ground and it sieved with 80 mesh size sifter.

2.4. Filtration Process

A schematic diagram of the experimental for the sample filtration as shown in Figure 1.
A is an industrial electroplating wastewater container, wastewater from A then pumped to B which is a feeder container that serves to keep the discharge stable. C is a reactor tube with corn cob activated carbon. Treated wastewater then collected in the bottle sample (D) for further laboratory testing.

3. Results and Discussion

3.1. The Concentration of Adsorption Cr, Cd, Cu, and Zn with discharge 15 ml/minute, 20 ml/minute, and 25 ml/minute

The concentration of corn cob activated carbon adsorption can be seen in the Table 1, 2, and 3.

Table 1. The Concentration of Adsorption Cr, Cd, Cu, and Zn with discharge 15 ml/min

| No | Minutes | Cr (mg/l) (Before) | Cr (mg/l) (After) | Cd (mg/l) (Before) | Cd (mg/l) (After) | Cu (mg/l) (Before) | Cu (mg/l) (After) | Zn (mg/l) (Before) | Zn (mg/l) (After) |
|----|---------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|
| 1  | 0       | 171.56            | 25.24             | 20.54             | 7.17              |
| 2  | 5       | 161.43            | 17.66             | 12.40             | 4.02              |
| 3  | 10      | 145.10            | 16.51             | 11.42             | 3.89              |
| 4  | 15      | 127.39            | 14.28             | 10.19             | 3.30              |
| 5  | 20      | 136.96            | 16.06             | 11.01             | 3.70              |
| 6  | 25      | 157.53            | 17.88             | 11.30             | 3.79              |

Table 2. The Concentration of Adsorption Cr, Cd, Cu, and Zn with discharge 20 ml/min

| No | Minutes | Cr (mg/l) (Before) | Cr (mg/l) (After) | Cd (mg/l) (Before) | Cd (mg/l) (After) | Cu (mg/l) (Before) | Cu (mg/l) (After) | Zn (mg/l) (Before) | Zn (mg/l) (After) |
|----|---------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|
| 1  | 0       | 171.56            | 25.24             | 20.54             | 7.17              |
| 2  | 5       | 163.30            | 18.20             | 13.52             | 4.35              |
| 3  | 10      | 147.07            | 17.16             | 12.59             | 4.12              |
| 4  | 15      | 130.63            | 15.53             | 11.80             | 3.78              |
| 5  | 20      | 138.92            | 17.77             | 12.53             | 4.00              |
| 6  | 25      | 159.89            | 17.88             | 12.36             | 4.08              |

Table 3. The Concentration of Adsorption Cr, Cd, Cu, and Zn with discharge 25 ml/min

| No | Minutes | Cr (mg/l) (Before) | Cr (mg/l) (After) | Cd (mg/l) (Before) | Cd (mg/l) (After) | Cu (mg/l) (Before) | Cu (mg/l) (After) | Zn (mg/l) (Before) | Zn (mg/l) (After) |
|----|---------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|
| 1  | 0       | 171.56            | 25.24             | 20.54             | 7.17              |
| 2  | 5       | 165.90            | 19.18             | 15.05             | 5.04              |
| 3  | 10      | 149.79            | 18.77             | 14.55             | 4.70              |
| 4  | 15      | 133.23            | 16.06             | 13.78             | 4.12              |
| 5  | 20      | 141.52            | 18.50             | 13.99             | 4.32              |
| 6  | 25      | 162.77            | 18.98             | 14.20             | 4.70              |

Table 1, 2, and 3 showed the concentration of Cr, Cd, Cu, and Zn have changed. Generally, all of the heavy metals concentration decrease at the same time 0, 5, 10 minutes, and have a turning point at 15, 20, 25 minutes. At 0, 5, 10 minutes 5th minute the adsorption process was occurred. It happened because the absorption of Cr, Cd, Cu, and Zn occurred in the surface layer or between phases where ions/molecules of Cr, Cd, Cu, and Zn are fill the cavity and collected in corn activated carbon. Then, at
the 15th to 25th minutes, the concentration of Cr, Cd, Cu, and Zn gradually increased because the process of releasing back the ions/molecules Cr, Cd, Cu, and Zn that have bonded with the corn activated carbon.

The ability of corncob activated carbon in 4 heavy metals process is most effective at 5th minute because the cavity of corncob can absorb well and there is a balance between adsorption to desorption in the 15th minute.

3.2. The Effectiveness of Adsorption
The effectiveness measurement of adsorption in this study were all carried out using discharge 15 ml/minute. That's based on the experiment results from the variation of discharge, the highest velocity of adsorption occurred at 15 ml/minute. The effectiveness of corncob activated carbon adsorption can be seen in Figure 2.

Based on the data, it can be concluded the total removal efficiency of Cr, Cd, Cu, and Zn were 25.75%, 43.42%, 50.39%, and 53.97%. Furthermore, it indicates that corncob activated carbon was found to be most effective in reducing of Zinc (Zn).

4. Conclusion
The most significant finding showed that the corncob activated carbon was most effective in reducing Zn (53.97%) than Cr (25.75%), Cd (43.42%), Cu (50.39%) at 15 ml/min of discharge.

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