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Binary Biosorption of Cu(II) and Cr(VI) by Sawdust

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Abstrak

Water pollution is one of many significant environmental problems. One of the sources of pollutants that become a problem in the aquatic environment is the heavy metals Cu(II) and Cr(VI), whose presence can harm living things, including humans. Therefore, a technology is needed to overcome Cu(II) and Cr(VI) pollution. Biosorption is one of the technologies offered to overcome these problems with several advantages, namely cost-effectiveness and environmentally friendly. This study investigated the biosorption of Cu(II) and Cr(VI) using sawdust. The use of sawdust was chosen because it is easy to find and the price is affordable. This study's results indicate that sawdust can adsorb Cu(II) and Cr(VI). The optimum contact time for biosorption in this study was 5 minutes. The biosorption characteristics shown in this study matched the Langmuir adsorption model. This study shows that the biosorption of Cu(II) and Cr(VI) by sawdust occurs through physicochemical reactions, ion exchange, and electrostatic interactions. Therefore, sawdust is one of the promising biosorption agents to overcome pollution in aquatic ecosystems, especially pollution caused by Cu(II) and Cr(VI).

Keywords: biosorption, aquatic ecology, cu(ii), cr(vi), sawdust, water pollution

INTRODUCTION

Industrial activities such as textile, paper, leather tanning, mining, and electroplating factories are increasing along with the increasing human needs in developing countries, including Indonesia [1]; [2]; [3]. However, this increase in activity is also followed by an increase in water pollution problems [4]; [5]; [6]. Often the industrial waste is dumped directly into the surrounding aquatic ecosystem, causing water pollution and degradation of aquatic ecosystems.

One of the most crucial pollution problems is pollution caused by waste from the tanning industry [7]; [3], electroplating, mining, and electronics [8]. In this case, Cu(II) and Cr(VI) are dangerous metals. Although these heavy metals are essential microelements for animal, plant, and human life, at specific concentrations, Cu(II) and Cr(VI) can be potentially toxic because they can accumulate in organisms and humans through the food chain, causing various health problems [9]; [10]; [11]. Therefore we need the right technology to overcome this water pollution.

Biosorption is one of the technologies that can be offered to overcome Cu(II) and Cr(VI) pollution by using living organisms or parts of organisms as biosorption agents [12]; [13]. Biosorption is a promising technology because it is practical, economical, and environmentally friendly [12]; [14]. Not only does this biosorption process require an effective biosorption agent, but it is also cheap and environmentally friendly. Sawdust is one of the suitable waste materials as an alternative biosorption agent.

Although sawdust is thought to be a promising biosorption agent, studies that focus on the use of these materials as biosorption agents in water pollution caused by Cu(II) and Cr(VI) are still rarely carried out [9]; [3]; [15]. Considering the abundance of sawdust and its potential as a biosorption agent, a study focused on using sawdust as a water pollutant biosorption agent is essential. This study analyzes the use of sawdust in biosorption and integrates its potential as a Cu(II) and biosorption agent. Cr(VI) to develop biosorption as an alternative technology to overcome water pollution.

MATERIALS AND METHOD

This research is conducted in two steps. The first step is the kinetic analysis of the adsorption of Cu(II) and Cr(VI) by sawdust and followed by an analysis of the characteristics of the adsorption isotherms of Cu(II) and Cr(VI) by sawdust.

Sawdust Sample Preparation

Sawdust comes from Sengon wood (*Paraserianthes falcataria*) collected from a

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sawmill in Kepanjen, Malang, Indonesia. A total of 100 grams of sawdust were cleaned with distilled water, dried in an oven at 80oC for 24 hours, and then sieved using a 100 mesh sieve.

Sawdust Delignification

Thirty grams of sawdust that passed the sieve was added to a glass beaker containing 600 ml of 0.5 M aq NaOH and then stirred for 2 hours on hot plate stirrers. The suspension was filtered using filter paper and washed with distilled water. The delignified sawdust is stored in a desiccator.

Cellulose Modification with Citric Acid Esterification

The delignified sawdust was dissolved in 20 ml of 1.2 M aq citric acid. Then stirred for 6 hours on hot plate stirrers (120 °C), then washed using distilled water until the pH of the remaining distilled water approached neutral pH (7.0-7.5). Then it is dried in the oven until the weight is constant.

Kinetics of Adsorption

Cu(II) and Cr(VI) solutions were prepared using aqueous reagent grade $CUSO_4$ and $K_2Cr_2O_7$ in distilled water. 1.5 grams of sawdust was added to a beaker glass containing 150 ml 50 mg/l CuCr. The suspension was homogenized on a hot plate stirrer. 4 ml of the solution was sampled after 5, 15, 30, 60, and 120 minutes. Cu(II) and Cr(VI) concentrations in the solution were measured using a UV-VIS. Spectrophotometer.

Adsorption Isotherm

Several sets of Cu(II) and Cr(VI) solutions of different concentrations were prepared. The concentrations are 5, 25, 50, 100 and 125 mg/l. Then 1.5 grams of sawdust was added to each Erlenmeyer containing 200 ml of Cu(II) and Cr(VI) solutions and homogenized on a hot plate stirrer for 60 minutes (that is, the optimum contact time for adsorption resulting from the kinetic adsorption step). . The concentrations of Cu(II) and Cr(VI) in solution were measured using a UV-VIS Spectrophotometer.

RESULTS AND DISCUSSION

Kinetics of Adsorption

Adsorption kinetic research was conducted to determine the optimum contact time of sawdust to adsorb Cu(II) and Cr(VI). After the optimum time is reached, the biosorption has reached a saturation phase where the sawdust can no longer adsorb Cu(II) and Cr(VI) (Kurniawan et al., 2012). The results of the Cu(II) and Cr(VI) adsorption kinetics are shown in **Figure 1**.

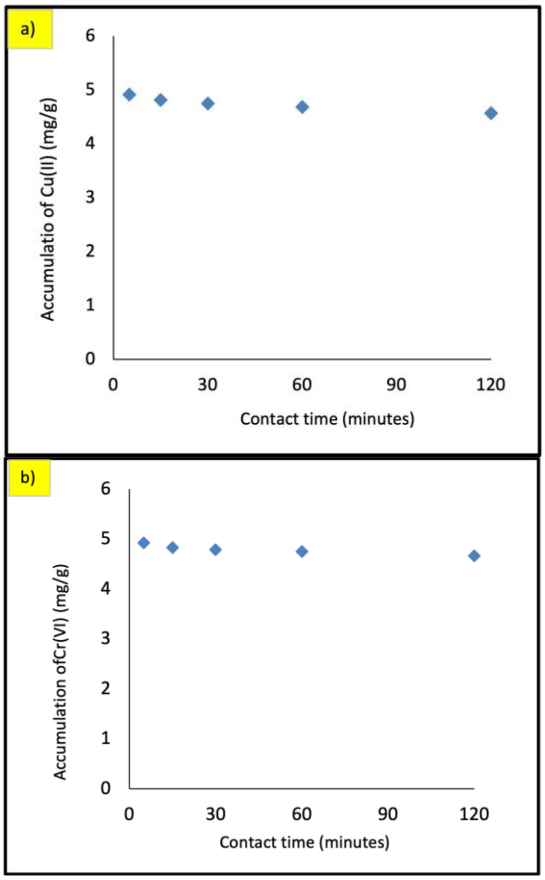

Figure 1. Time course of adsorption of Cu(II) (a) and Cr(VI) (b) by activated sawdust

In the 5 – 120 minutes range, the accumulation of Cu(II) and Cr(VI) by sawdust tends to be stable. This result is because the number of active adsorption sites of sawdust that binds Cu(II) and Cr(VI) has stabilized at 5 minutes. These results indicate that the equilibrium concentration of Cu(II) and Cr(VI) between sawdust and surrounding water has been reached. This result follows the opinion of Kurniawan et al., (2012), which revealed that in addition to the electrostatic interaction process, the adsorption process could also be caused by the ion exchange process. The ion exchange mechanism occurs when the ion adsorbed from the solution to the adsorbent replaces the charge of the desorbed ion (release of ions on the adsorbent) [16]. The adsorption process can take place very quickly, even in 1 minute. [8] also explained that the availability of a relatively larger surface area of sawdust could be easily entirely consumed by ions in a short time.

After 5 minutes, there was no significant change in the amount of absorption of Cu(II) and Cr(VI) ions because the absorption rate was controlled by the rate of transport from the outside into the active site on the surface area of the sawdust, thus obtaining equilibrium results.

The adsorption rate of Cu (II) and Cr (VI) reached equilibrium due to the active sites on the surface area of the sawdust, which could easily absorb metal ions. Based on these results, the optimum contact time used in this study was 5 minutes.

Adsorption Isotherm

The adsorption isotherm study was conducted to determine the biosorption characteristics of Cu(II) and Cr(VI) by sawdust, especially those related to the mechanism. In this experiment, we analyzed the correlation between the equilibrium concentration (solution concentration after biosorption in each treatment) and the amount of Cu(II) and Cr(VI) adsorption by sawdust (**Figure 2**).

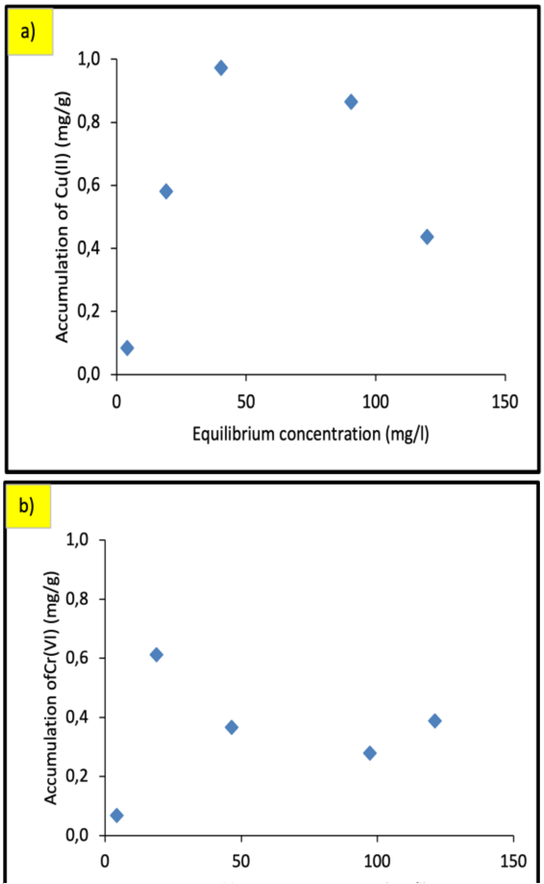

Figure 2. Adsorption Isotherm of Cu(II) (a) and Cr(VI) (b) by activated sawdust

The results shown in **Figure 2** indicate that the biosorption rate of Cu(II) and Cr(VI) increased in the low-concentration phase and then decreased in the high-concentration phase. It is suspected that the biosorption process occurs very effectively at low concentrations. The accumulation decreases after the saturated adsorption phase are reached, where there is no more increase in adsorption.

This type of adsorption can be classified as the Langmuir type of adsorption. The adsorption isotherm experimental results were further analyzed by plotting the biosorption results using the Langmuir adsorption equation model as described below [1]; [17]; [18]; [19]:

$$C/N = 1/(N_{max})b + C/N_{max}$$

Where C is the equilibrium concentration (mg/l), N is the amount of Cu(II) and Cr(VI) adsorption by sawdust (mg/g), Nmax is the maximum adsorption capacity of Cr(VI) by sawdust (mg/g), and b is the adsorption equilibrium constant. The results of this plotting are shown in **Figure 3**.

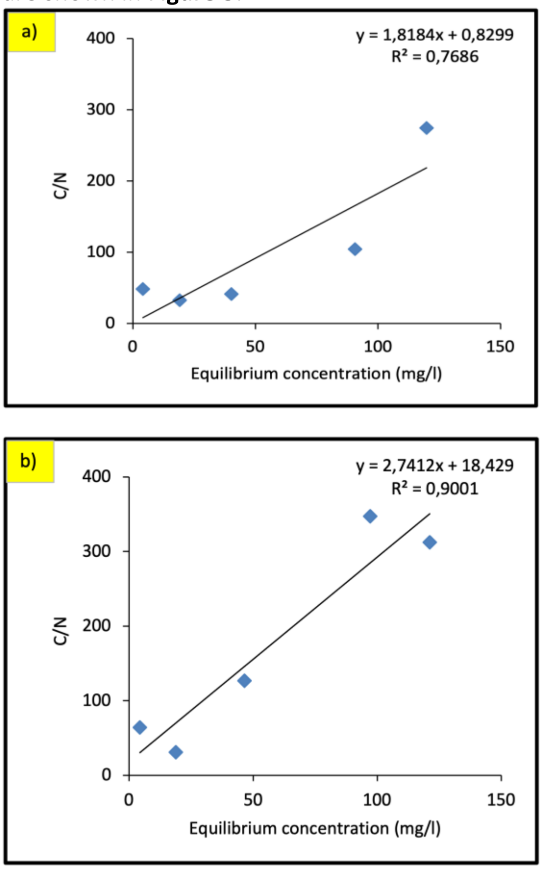

Figure 3. Regression Analysis of Cu(II) (a) and Cr(VI) (b) adsorption by Sawdust based on Langmuir Equation Model

The biosorption of Cu(II) and Cr(VI) by sawdust matched the Langmuir adsorption model (R=0,7686 and R=0,9001). The plot of C/N against C produces a straight line with a slope of 1/Nmax, and the y-axis intersects 1/(Nmax)b; thus, the value of Nmax can be calculated. The results showed that the Nmax of Cu(II) and Cr(VI) by sawdust were 0.54 and 0.36 mg/g, respectively.

The Langmuir adsorption model showed that the adsorbate [Cu(II) and Cr(VI)] would be bound to the adsorbent (sawdust), which had the same affinity for the adsorbate. In this case, adsorption occurs in the form of a monolayer, and the adsorbate cannot move freely from and to the active site of the adsorbent. If the adsorbate concentration increases while the amount of adsorbent remains, the adsorption will increase linearly in the initial phase (low concentration phase) and only increase slightly until the saturation point is reached. After this phase, the adsorption will become constant [1]; [20]; [21].

Biosorption Characteristics

Based on the results of this study, the mechanism of Cu(II) and Cr(VI) biosorption by sawdust is thought to be a passive uptake type. This type of adsorption is very likely to occur in the case of inactive biomaterials such as sawdust. In this process, an ion exchange mechanism can occur between Cu(II) and Cr(VI) ions with ions present in sawdust [18]. In addition, the biosorption mechanism can also occur through electrostatic interactions between the adsorbate and the oppositely charged sites on the surface of the adsorbent [12].

The results of this study strongly indicate that sawdust can be used as an alternative to Cu(II) and Cr(VI) biosorbents in overcoming the water pollution problem. Most adsorbents used in current water treatment technologies are not biological materials such as activated carbon, silica gel, zeolites, or ion exchange [22]; [23]; [24]; [25]. Although the adsorbent can absorb pollutants, the technology is relatively expensive and difficult to find. This study shows that sawdust can be used as an alternative biosorbent for the biosorption of heavy metals such as Cu(II) and Cr(VI).

CONCLUSION

In this study, the optimum contact time of Cu(II) and Cr(VI) by sawdust was 5 minutes. The optimum effectiveness of biosorption occurs at a low concentration phase, then decreases with increasing concentration. The type of accumulation of Cu(II) and Cr(VI) by sawdust is thought to be Langmuir adsorption, where adsorption occurs in the form of a monolayer. The biosorption mechanism is indicated as passive uptake that occurs through ion exchange and electrostatic interactions. Based on the results of this study, sawdust is a prospective biosorbent for the biosorption of water pollutants such as Cu(II) and Cr(VI).

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