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Adsorption of Cu(II) in Aqueous Solution by Modified Sawdust Cellulose

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Abstract. The utilization of modified sawdust cellulose and the adsorption capacity for Cu(II) removal in aqueous solution is reported. The modification of cellulose was conducted by delignification using NaOH followed by esterification using citric acid. Delignification sawdust (DLSD) using NaOH 0.5 M gave the increasing cellulose content to 22.38%. Then, the esterification of cellulose using 1.2 M of citric acid successfully increasing the hydroxyl and carboxyl group from the analysis of FTIR. The modified sawdust (MDSD) showed the increasing intensity of $\text{-OH}$ stretching in in 3348 cm$^{-1}$ in concomitant with the emergence of a new peak at 1717 cm $^{-1}$ identified as C=O, either from carboxyl and/or carbonyl moieties. Adsorption capacities of DSLD and MDSD for Cu(II) are evaluated in constant pH 6. The maximum adsorption of MDSD is achieved within 2 h and adsorbed 78.3% of Cu(II). The adsorption of Cu(II) is fitted well with the Langmuir model suggesting the physical interaction between $\text{-OH}$ and/or $\text{COO}^-$ with the metal cation. The adsorption capacity of Cu(II) by MDSD is 4.33 mg/g higher than DSLD which is 2.61 mg/g. Based on this result, modification of sawdust cellulose increased the adsorption capacity of Cu(II) in aqueous solution.

1. Introduction
Pollution caused by heavy metal in wastewater has been increasingly serious along with the development of industries such as mining, electroplating, and electronics. One of the heavy metals largely discharged into the environment is copper. Although copper is notified as essential microelements for animals, plants and human life, at specific concentrations, it can be potentially toxic as it can be accumulated in the organisms and human through food chains resulting in various health problems. Hence, the removal of copper from wastewater have been studied intensively since the environment problem becomes an important issue to be resolved [1], [2].

Several methods were studied for the removal of heavy metal for example by precipitation, flocculation, membrane filtration, ion-exchange, evaporation, and electrolysis. Among these technologies, adsorption is the most promising approach to remove heavy metal compared to conventional precipitation because of its low cost, high adsorption capacity for low concentration metal ions and very dilute effluents [3]. Then, the selection of efficient adsorbent become a crucial task as it has an essential role in the adsorption process.

Recent research has indicated that biomass is prospective material as an adsorbent to absorb heavy metals from wastewater, such as red pine sawdust [4], pulp [3] and sugarcane bagasse [5]. The use of
sawdust for removing heavy metals has attracted much attention because it is an abundant material which can be accessed easily and economically. The adsorption capacity of native sawdust towards heavy metals was reported can be enhanced by modifying the functional groups on its surface. Cellulose as the main compound in sawdust can be modified by treatment with NaOH solution and followed by esterification to increase the hydroxyl and carboxyl group as a potential anionic functional group which promptly interact with the cationic metal ions. The modification was performed by a hydrotreatment using citric acid or tartaric acid [4], [6]. The carboxyl groups were added to the sawdust surface by esterification reaction, and thus, increasing the number of active sites to interact with cations [7]. The adsorption of metal ions usually carried out using the batch method in which the binding of these metal ions is strongly influenced by the pH conditions and its kinetics [8], [9].

Here we reported the adsorption capacity of modified sawdust cellulose towards Cu(II) from aqueous solutions. The optimum conditions of Cu(II) adsorption to modified sawdust was determined based on different parameters on copper uptake (i.e., pH of the solution, various sorption time, and copper concentrations). Characterization process was carried out to analyze the specific functional group on materials using Fourier Transform Infrared (FT-IR) and observe the surface morphology of the adsorbent using a Scanning Electron Microscope (SEM). The amount of Cu(II) adsorbed by the modified biomass was performed by quantitative analysis using Atomic Absorption Spectrophotometer (SSA). The Langmuir isotherm models were used for analyzing the biosorption characteristics.

2. Experimental

2.1. Preparation sawdust
The sawdust is collected from a wood craftsman in Batu, Malang, Indonesia. 70 g of sawdust washed with deionized water in the beaker glass, filtered and dried for a night at 80°C until all constant weight. The dry sawdust is ground to a powder and sieved in 100 mesh then kept in airtight container for the next experiment.

2.2. Modification of sawdust

2.2.1. Delignification. The delignification is conducted to reduce lignin content in the sawdust. The procedure is referred to Gode et al. with modification [8], [9]. The sawdust (6 g) is dissolved in 120 mL of NaOH 0.1 M at ambient and stirred at 180 rpm for 2 h. The remaining solid removed by filtration and washed with deionized water until pH 7, then dried at 50°C for 24 h. Similar procedures were repeated by using NaOH in 0.3 M and 0.5 M. The delignification sawdust material obtained in this process is designated as DLSD-1 (delignification using 0.1 M NaOH), DLSD-2 (delignification using 0.3 M NaOH), and DLSD-3 (delignification using 0.5 M NaOH). All these materials were analyzed for the cellulose contain by modification of Chesson method [10].

2.2.2. Esterification. The method is adapted from Thanh et al. by replacing tartaric acid with citric acid [11]. The DLSD-3 (2 g) was mixed with 40 ml citric acid 1.2 M in the batch reactor and heated at 120°C for 6 h. After the reaction, the slurry washed with warm deionized water until neutral, then filtered and dried at 50°C for a night. The modified sawdust is labeled as MDSD-3.

2.2.3. Characterization. The characterization of DLSD and MDSD is mainly carried out by Infra-Red Spectrophotometry (FT-IR) Shimadzu 8400S (Shimadzu Corporation, Japan) and the spectrum was recorded from 4000–400 cm⁻¹. The FT-IR analysis is used for analyzing the functional group on modified cellulose which responsible for the adsorption process. Surface morphology is analyzed by Scanning Electron Microscope (SEM) FEI Type Inspect S50.

2.2.4. Adsorbate solution. The stock solution (1000 mg/L) of Cu(II) was prepared by dissolving the Cu(SO₄)₂·5H₂O salt in deionized water. The solution was then diluted into 0.5–40 ppm for further
adsorption experiment. All the reagents used in this procedure is supplied from Merck Singapore in analytical grade. The deionized water was obtained from Hydrobat (Indonesia).

2.3. Adsorption Cu(II)
The adsorption experiment is according to Gode et al. with modification of the adsorbent used [4]. The 0.05 g of DLSD-3 and MDSD-3 is used for each batch adsorption process. The adsorbent was added to 10 mL Cu(II) 20 ppm and then stirred using a magnetic stirrer at 125 rpm. The contact times evaluated for 60, 90, 120, and 360 minutes at room temperature. The pH is adjusted to 6 by added with NaOH or HCl 0.1 M. After each contact time, the adsorbent is centrifuged for 30 min. The remaining Cu(II) in the supernatant was measured by using Atomic Absorption Spectroscopy Shimadzu AA-6800 (Shimadzu Corporation, Japan). Each adsorption is repeated twice. The adsorption amounts of Cu(II) were calculated from the concentration differences between concentrations of Cu(II) in the supernatant and the control (the same aqueous solution without contacted with adsorbent).

The experiment for adsorption capacity is carried out based on the optimum contact time. The Cu(II) solution series (10, 20, 30, and 40 ppm) was prepared and the Cu(II) adsorption is carried out at 120 minutes using a similar procedure with previous. The adsorption capacity is calculated based on the Langmuir equation [1], [4], [12].

3. Result and Discussion

3.1. The characterization of modified sawdust cellulose
The modification of sawdust was carried out by a delignification process using NaOH followed by esterification using citric acid. The delignification using 0.1–0.5 M of NaOH resulted in the pale-brown sawdust cellulose and the cellulose content is tabulated in Table 1. The higher the NaOH concentration resulting in the increasing of cellulose content up to 22.38% compared with native sawdust. Kim et al. reported that delignification process is an important step to break down the lignin structure, increase the surface area, and reduced the crystallinity of cellulose. By this way, further treatment is easy to perform since the –OH group on the cellulose surface is free from others matrix [13].

| Parameter   | Sawdust | DLSD-1 | DLSD-2 | DLSD-3 |
|-------------|---------|--------|--------|--------|
| Cellulose (%) | 20.08   | 20.83  | 22.22  | 22.38  |

The esterification reaction is carried out using citric acid 1.2 M. This reaction is proposed to increase the –OH and COO\(^-\) moieties which are active for metal ion adsorption [4], [14]. The plausible mechanism reaction for the crosslink formation between cellulose and citric acid is depicted in Scheme 1, which is adapted from [14]. The physical properties of the sawdust cellulose after esterification did not show any differences, except the color changes into dark brown compared with previous.

The functional group identification for delignification-cellulose (DLSD-3) and modified-cellulose (MDSD-3) is performed by FT-IR analysis. It is observed that there is an increasing absorbance from –OH and COO\(^-\) vibration after treatment with citric acid (Figure 1). The region corresponding to –OH stretching vibration surface is identified at 3400 cm\(^{-1}\). The specific vibration of carboxylic acid groups incorporated into the cellulose chains after esterification is assigned at 1742 cm\(^{-1}\). The vibration at 1061 cm\(^{-1}\) can be elucidated for the stretching of C–O–C and O–H of polysaccharides. The carboxyl group was determined by the spectral band at 1512 cm\(^{-1}\) for asymmetric COO\(^-\) stretching and bending vibration of aliphatic groups. All the analysis data is supported by a similar report from Gode et al. [4].
Scheme 1. Plausible esterification reaction of cellulose with citric acid

Chemical modification with citric acid also influences the morphological structure of modified sawdust. The SEM analysis of the samples is shown in Figure 2. The DLSD-3 showed the smoother surface compared with MDSD-3 which was treated with citric acid. Rojas et al. reported a similar phenomenon when treated cotton fibers with acid [14].

Figure 1. FT-IR analysis of DLSD-3 (red) and MDSD-3 (black)
Figure 2. SEM micrograph of (a) DLSD-3 and (b) MDSD-3 (magnification 5000x)

3.2. The effect of contact time

The preliminary kinetic parameter of the adsorption of Cu(II) using MDSD-3 was evaluated to determine the contact time to achieve the equilibrium process. The result is depicted in Figure 3. The significant adsorption of the Cu(II) was observed after 120 min with the removal of Cu(II) until 80%. After 120 min, there is no significant change in Cu(II) adsorption amount. It seems that the availability of the active sites in modified cellulose might be all consumed by the metal ion. Rafatullah et al. reported that after equilibrium is achieved, the main driving force for the interaction of metal and adsorbent is physical transport from the exterior into the interior sites of the adsorbent [12]. Compare with the initial adsorption process which the active site was still vacant, the rate of adsorption of Cu(II) is previously high and by the time it is become slower and achieve the equilibrium. A similar result is reported by Gode et al. that the maximum contact time for modified red pine cellulose is achieved after 120 min [4]. Based on this result, in all experiment sequence, the contact time was maintained at 120 min.

Figure 3. Effect of contact time on Cu(II) adsorption

3.3. The adsorption capacity

The adsorption capacity of MDSD-3 and DSLD-3 was simulated based on the Langmuir model as shown in equation 1, where $C_e$ is the equilibrium concentration of metal ions in solution (mg/L), $q_e$ is the
adsorbed value of metal ions at equilibrium concentration (mg/g), $b$ is Langmuir constants/affinity parameter (L/mg), and $q_m$ is the maximum adsorption capacity (mg/g). The use of the Langmuir model is based on Rafatullah et al. which was compared with various adsorption models using sawdust as an adsorbent [12].

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{1}{q_m} C_e$$

(equation 1)

The isotherm data have linearized and depicted in Figure 4. The values of the correlation coefficient ($R^2$) of both MDSD-3 and DSLD-3 is 0.962 and 0.997, respectively. These results suggested that the adsorption of Cu(II) using MDSD-3 and DSLD-3 is fitted well with the Langmuir adsorption type. It is also confirmed that the Cu(II) adsorption occurred at specific homogeneous sites on to sawdust surface [1], [4], [12]. The adsorption of the Cu(II) to both biosorbents occurs due to the interaction between the adsorbate with the biosorbent where the biosorbent has the same affinity to each of the adsorbate.

The maximum adsorption capacity ($q_m$) can be determined by the slope values ($1/q_m$) of each equation on MDSD-3 and DSLD-3, resulting in the adsorption capacity of 4.33 mg/g and 2.61 mg/g, respectively. The adsorption capacities of the modified cellulose are higher than the non-modified cellulose. It indicates the increase of some active sites such as C=O ester and a carboxyl group to sawdust during modification using citric acid can improve the performance of biosorbent to bind more metal ions in the water [6]. The results suggested that the modification of the sawdust cellulose can increase the adsorption capacity to adsorb heavy metals pollutant such as Cu(II) metal ion.

![Figure 4. Langmuir equation plots for adsorption of Cu(II) at 30°C](image)

4. Conclusion
This research is demonstrated that modified sawdust cellulose is a prospective material for Cu(II) adsorption in aqueous solution compare with the native sawdust. The adsorption capacity is increased in twice after the treatment. The kinetic equilibrium of Cu(II) adsorption by modified sawdust is reached within 2 h with the kinetic adsorption followed the Langmuir equation.

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