Utilization of charcoal rambutan (Nephelium Sp.) adsorbent to remove dissolved copper (II) by natural batch operation

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Abstract. The adsorption ability of rambutan charcoal with the size 100/200 mesh in absorbing dissolved 70 ppm copper metal ions (Cu(II)) at pH 4.5 have evaluated. The adsorption kinetics of rambutan charcoal carried out by natural batch operation. The optimum contact time was 120 minutes with the best removal percentage was obtained 43.84%. The adsorption interaction of copper metal ions on the rambutan charcoal surface has analysed by using SEM-EDX. The kinetic model of the pseudo second-order was applied with interaction with $R^2 = 0.9816$. The result was identified that adsorption occurred chemically. The diffusion kinetic model has indicated the diffusion down to the inter-particle surface of the adsorbent with the value of $R^2 = 0.8863$.

1. Introduction

Heavy metals as industrial waste cause serious problems to the environment. Besides being toxic, heavy metals are also non degradable. [1]. Wastes that contain the heaviest metals generally come from industrial waste such as mining, coating, dyeing, electrochemical metal processing, and battery storage [2]. Therefore, this dangerous heavy metal can disturb the life of organisms in the environment if its existence exceeds the threshold [3]. Heavy metal refers to metallic elements that have comparatively high density ranging from 3.5-7g/cm$^3$ which have toxic and hazardous properties [4]. Metals that are toxic to humans and the ecological environment [5].

Adsorption is a method that is commonly used because it has a simpler and more economical concept. Recently, an adsorption method has been developed using plant biomass known as phytofiltration and has used as biodesorbtent in many research [6]. The several types of natural materials as biodesorbents have been used in many applications and beneficial to the environment [7]. Rambutan (Nephelium Sp.) is a horticultural plant in the form of a tree with wood has a brown colour and has corrugated fibres [8].

The following is research on bio-desorbtent and the utilization of charcoal as an adsorbet in absorbing ions. Researchers Shivakumar et al. [9] conducted a study using balsamodendron wood waste as an adsorbet where the carbonization process was carried out at a temperature of 800°C for 60 minutes, used with a pH of 6.4-9.52. The use of biomass as an adsorbet is good at micro size [10] with a minimum amount of adsorbet as much as 1 gram [11]. In absorbing chromium metal ions, the maximum pH that is good to use is 4 with a contact time of 60 minutes [12] while for absorbing cadmium and copper metals, the maximum pH is 4.5 [13]. In controlling the pH, a solution of sodium hydroxide and hydrochloric acid can be used as a pH regulator [11].
The research conducted was to utilize rambutan wood biomass charcoal which is a lot as rambutan plant remains on the public. Performed without activation so that the application is simpler and suitable for the public society and industrial wastewater purification and does not pollute the environment.

2. Materials and methods

This research has conducted at the Unit Operations Laboratory and the Surfactants and Applications Laboratory at the Chemical Engineering Department, University of Sumatra Utara, Medan. The local material charcoal rod rambutan have used in this study as an adsorbent. Copper (II) sulfate (CuSO4.5H2O) was used as a source of copper (Cu (II)). Hydrochloric acid (HCl) and sodium hydroxide (NaOH) were used as a pH regulator, and distilled water (H2O) was used as a solvent. All chemicals were purchased from chemical distributor CV. Rudang Jaya Medan. The Atomic Absorption Spectroscopy (AAS) (iCE 3300, Thermo Scientific, USA) was applied to analyse the removal concentration of Cu (II). The Scanning Electron Microscope (SEM) and Energy Dispersive X-Ray (EDX) (Phenom ProX Dekstop SEM, Thermo Scientific, USA) was used to confirm the presence of Copper ions as contaminant on absorbent surface.

Rambutan charcoal is washed using pure water until it reaches a constant pH condition and removes impurities that are still attached to rambutan wood charcoal such as dust, soil, and other organic and inorganic substances. Then the charcoal is mashed using a ball mill to the size of a powder. Then the rambutan wood charcoal which has been separated according to their respective sizes using a sieve. Then dried in an oven with operating conditions at 60°C and weighed every 20 minutes until the mass of rambutan wood charcoal does not change anymore.

Copper (II) 70 ppm solution was provided about 2,5 L at pH 4.5 [10]. NaOH (0.1 M) and HCL (0.1 M) solutions each one were prepared 100 mL [11]. Erlenmeyer flask was used for the adsorption operation. Into erlenmeyer was then added 100 ml of Cu (II) 70 ppm and as much as 1 gram of rambutan charcoal adsorbent with size 70/100 mesh. Adsorption was carried out in a natural batch at 27°C [14]. Samples were taken 2 mL at a certain interval operation time and analysed for copper (II) by AAS. The adsorption capacity was calculated by using equation 1 [15].

$$q_t = \frac{(C_0-C_e) \cdot V}{W}$$

where $q_t$ is the amount of metal adsorbed per unit mass of adsorbent at time t; $C_0$ is the initial metal concentration; $C_e$ is the liquid-phase metal concentrations at equilibrium; V is the volume of the solution and W is the mass of adsorbent used.

The adsorption kinetic with increasing time was calculated by using equation 2 [15]:

$$\%R = \frac{(C_0-C_t)}{C_0} \times 100$$

Which R% is the percentage removal of adsorbed metal ion, $C_0$ is the initial metal ion concentration (mg/L), $C_t$ is the removed copper concentrations in solution on increasing time (mg/L). The SEM and EDX was applied to analyse the surface and composition of wood charcoal after used as adsorbent.

3. Results and discussion

3.1 Determination of the optimal contact time and adsorption kinetics

Figure 1 shows that metal removal increases with increasing contact time and will be constant at a certain time. The adsorption equilibrium occurs when the solution is in contact with the solid adsorbent and the molecules of the adsorbate move from the solution to the solid in an equilibrium [16]. The increase in the concentration of adsorbed Cu (II) reached its optimum point at 120 minutes with a metal removal percentage in the natural batch of 43.8%. This can be seen in Figure 1.
absorption capacity of the adsorbent increases with increasing stirring speed because the concentration of ions to be absorbed will be higher around the surface of the adsorbent [17]. In this study, the operation was naturally without a stirring effect.

**Figure 1.** Adsorption kinetics of Cu(II) ions

In this study, the data of the adsorption rate have used to predict the interaction on the adsorbent surface with the adsorbate. It was evaluated using the first-order pseudo model (equation (3)) [18] and the pseudo second-order (equation (4)) [17].

\[
\frac{1}{q_t} = \frac{k_1}{q_e} \frac{1}{t} + \frac{1}{q_e}
\]  

(3)

\[
\frac{1}{q_t} = \frac{1}{q_e} + \frac{1}{k_2 q_e^2}
\]  

(4)

The first-order equation has $R^2$ value of 0.6788 and the second-order equation has $R^2$ value of 0.9816 which were shown in figure 2 and figure 3. From the results were obtained that the adsorptions on the surface have dominant chemical interactions (chemisorption) compared to the physical interaction. Evidenced by the $R^2$ value of the Pseudo second-order model was closer to 1.

**Figure 2.** Pseudo first-order model  
**Figure 3.** Pseudo second-order model
3.2 Determination of pore diffusion

Internal and external diffusion equations models have been used to evaluate the adsorption diffusional type of copper (II) on rambutan charcoal adsorbent. The diffusion model was investigated by using Equation 5 for the internal diffusion kinetics model and equation (6) for the external diffusion kinetics model [19].

\[ q_t = k_{id}t^{1/2} \]  
\[ \ln \frac{C_t}{C_0} = -k_f \left( \frac{V}{A} \right) t \]  

The diffusion kinetics models are shown in figures 4 and 5. The internal diffusion kinetics model has a value of \( R^2 = 0.8863 \) and external has a value of \( R^2 = 0.7642 \). Based on the value of the correlation coefficient \( R^2 \), internal diffusion has a higher value compared to external diffusion. If the diffusion of the ion occurs on the inner surface and the pore area of the adsorbent that the process is called internal diffusion [19]. From the \( R^2 \) value in this study, the adsorption kinetic model has an internal diffusion tendency. This shows that in the adsorbent there are inter-particle surface areas of rambutan charcoal that experience internal diffusion between pore particles.

**Figure 4.** Internal diffusion kinetic  
**Figure 5.** External diffusion kinetic

3.3 Analysis rambutan charcoal using SEM-EDX

SEM/EDX analysis has been applied to confirm the surface characteristics and chemical compound of the adsorbent. Figure 6A shows the surface characteristics of rambutan charcoal with 5000 times magnification after adsorption. SEM result shows the shape surface of wood charcoal. The EDX analysis result as shown in Figures 6B, there is the composition of the adsorbent after adsorption. It was confirmed the presence of additional chemical component of copper ions after adsorption. Copper metal ions have adsorbed by rambutan wood charcoal.
4. Conclusions

The copper (II) percentage increases with increasing contact time and will be constant at a certain time. The increase in adsorbed Cu\(^{2+}\) concentration reached its optimum point at 120 minutes with a metal removal percentage of 43.8%. The adsorption kinetics model was obtained a second-order correlation coefficient closer to 1, which indicates that the type of Cu\(^{2+}\) ion interaction on the adsorbent surface occurs chemically dominant. Adsorption kinetics model shows the tendency of internal diffusion, which shows that the adsorbent contains inter-particle surface areas of the rambutan stem charcoal which experience internal diffusion between pore particles. The EDX analysis result shows the copper metal ions on the adsorbent surface that has been adsorbed on rambutan wood charcoal.

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