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Utilization of Mesoporous Silica from Rice Husk to Reduce Copper Level in Water Using Adsorption Method

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ABSTRACT
Conducted research on the utilization of mesoporous silica derived from rice husks for copper reduction using adsorption methods. This work aims to evaluate the efficacy of copper adsorption with mesoporous silica derived from rice husk, calcined at a temperature of 900 °C. Mesoporous silica possesses a pore diameter ranging from 5 to 17 nm. The approach employed to decrease copper is the adsorption method. Identifying the optimal settings entails an adsorbent mass of approximately 0.2 g, 0.4 g, 0.6 g, 0.8 g, and 1.0 g an adsorbate concentration of 10 mg/l, and a contact duration of 60 minutes. The adsorption technique involves contacting mesoporous silica with a copper solution in an Erlenmeyer flask, followed by stirring with a magnetic stirrer utilizing varying masses of mesoporous silica. The results indicated that a substantial adsorption occurs with the utilization of 1.6 g of mesoporous silica, achieving a copper adsorption percentage of 99.73%. The quantity of adsorbed copper ions is determined by the difference in metal concentration before and after adsorption, evaluated using Atomic Absorption Spectroscopy (AAS).

Keyword : Adsorption, Mesoporous Silica, Rice Husk

ABSTRAK
Telah dilakukan penelitian mengenai pemanfaatan mesopori silika dari sekam padi untuk menurunkan kadar tembaga dengan metode adsorpsi. Penelitian ini bertujuan untuk menentukan efektivitas adsorpsi terhadap logam Cu dengan menggunakan mesopori silika dari sekam padi yang dikalsinasi pada suhu 900oC. Mesopori silika memiliki ukuran pori antara 5 sampai 17 nm. Metode yang digunakan untuk menurunkan kadar logam Cu adalah metode adsorpsi. Penentuan kondisi optimum meliputi variasi massa adsorben sebanyak 0,2 g, 0,4 g, 0,6 g, 0,8 g, dan 1,0 g konsentrasi adsorbat 10 mg/l dan waktu kontak 60 menit. Proses adsorpsi dilakukan dengan cara mesopori silika dikontakkan terhadap larutan Cu dalam erlenmeyer kemudian diaduk menggunakan magnetik stirer dengan berbagai variasi massa mesopori silika. Hasil penelitian menunjukkan adsorpsi yang paling baik terjadi pada pemakaian sekam padi sebanyak 1,6 g dengan persen adsorpsi logam Cu sebesar 99,73 %. Jumlah ion tembaga yang teradsorpsi dihitung secara kuantitatif berdasarkan selisih konsentrasi logam sebelum dan setelah adsorpsi yang dianalisis dengan Spektroskopi Serapan Atom (SSA).

Kata Kunci : Adsorpsi, Mesopori Silika, Sekam Padi

1 Introduction

Rapid economic development on one hand will improve the quality of human life by increasing people's income, but on the other hand, it will lead to a decline in health due to pollution from industrial and household waste [1]. One of the hazardous industrial waste chemicals when it enters aquatic environments is heavy metals. If the presence of these heavy metals exceeds the threshold limit, their presence in the ecological system becomes a dangerous pollutant for the environment, especially for aquatic environments. Some hazardous environmental pollutants are cadmium (Cd), lead (Pb), zinc (Zn), mercury (Hg), copper (Cu), and iron (Fe) [2].

Several methods have been developed to reduce heavy metal content in wastewater, such as coagulation, solvent extraction, ion exchange, and adsorption [3]. However, adsorption method has advantages compared to other techniques due to it is cheaper, non-toxic, and can be effectively adsorpted the metal at low concentrations [4]. Additionally, the types of adsorbents used are also numerous and varied. (El-Said et al., 2010). According to Malekmohammadi et al. (1982), the adsorbents commonly used in the adsorption process include activated carbon, alumina, silica, and zeolite [5].

Silica can be utilized to adsorpt the metal according to its properties and characteristics. This is because its purity, surface area, and pore size of silica. Silica from rice husk has various uses, such as for catalyst materials, ink additives, concrete hardeners, components in detergents and soaps, and as a hardening agent in brick making [6]. Meanwhile, mesoporous silica is often used as an adsorbent [7]. In this study, mesoporous silica was produced from rice husk, which is believed to contain silica material. Considering the significant potential availability of rice husk waste, which reaches 20% of the 649.7 million tons of rice produced annually, there is a need for the utilization of rice husk waste [8]. Andriaayani et al. (2023) conducted research on the synthesis and characterization of mesoporous silica from rice husk using the calcination method with temperature variations of 800°C, 850°C, and 900°C. The nitrogen adsorption-desorption isotherm results of the silica show that the obtained silica material is characteristic of mesoporous material [9].

Some researcher have reported about the utilization of rice husk based-mesopori silica to adsorp the metal derived from indrustry waste. Kukwa et al. (2020) conducted a study on the adsorption of Cu metal using silica from rice husk modified with amine. The Cu level reduced was 99.48% [10]. In addition, cadmium (Cd) metal had been successful adsorpted by rice husk ash that is used as an adsorbent was 73.96 as reported by Ye and Du (2010) [11]. Furthermore, Amaria (2012) has also utilized silica from rice husk modified with aminopropyl hybrid to absorb cyanide ions. The maximum percentage of cyanide ion adsorption is 51.11% [12]. Therefore, this study is trusted to adsorb the Cu metal derived from industrial waste using adsorption method.

2 Materials and Methods

2.1 Materials

The material used in this study were rice husk was obtained from Deli Serdang District, North Sumatera, Indonesia. Next, hydrochloric acid (HCl), sodium hydroxide (NaOH), distilled water, and $Cu(NO_3)_2$ were purchased from Sigma Aldrich. In contrast, the tools used were a set of glassware (Pyrex), furnace (Fisher), oven, measuring flask, Pyrex), analytical balance, magnetic stirrer (Termilyte), fourier transform-infrared (FT-IR-Shimadzu), scanning electron microscopy (SEM-JSM-35 C Shumandju), and Atomic Absorption Spectrophotometer (AAS).

2.2 Preparation of Mesoporous Silica from Rice Husk

Rice husk was washed with distilled water until clean and then dried. It was then calcined at 900 °C for 6 hours. The obtained calcinated rice husk was dispersed with 60 mL of distilled water and HCl is added until pH=1, then stirred for 2 hours and filtered. The obtained precipitate was washed with distilled water. Futhermore, NaOH 1 N was added and boiled while stirring for 2 hours, then filtered. The obtained precipitate was washed with distilled water. The washing filtrate was added with HCl 1N until pH=7 and left for 18 hours. The precipitate was washed several times using distilled water and then centrifuged. The obtained silica iwas then heated at 120°C for 2 hours. The mesopore silica obtained was characterised using FT-IR and SEM spectroscopy.

2.3 Adsoption Process of Copper Metal Using Rice Husk based- Mesoporous Silica

The adsorption of copper concentration in water was carried out by adding mesoporous silica with varying masses of 0.4 g, 0.8 g, 1.2 g, and 1.6 g with contact time of 60 minutes. Next, the filtrate obtained was analyzed using an AAS at λ= 324.8 nm to determine the Cu metal content before and after adsorption.

3 Results and Discussion

3.1 FT-IR Analysis

The obtained silica is then analyzed using FT-IR to determine the presence of functional groups bonded to the silica. Qualitative analysis using infrared spectroscopy was conducted in the wavenumber range of 4000-400 cm^{-1}. Observations were made to determine the changes in the microscopic structure that occur before and after the adsorption process of Cu (II) metal ions onto mesoporous silica derived from rice husk.

The FTIR spectrum of silica at a calcination temperature of 900°C (Figure 1) shows similarities in absorption peaks with the FT-IR spectrum of mesoporous silica before and after adsorption. Absorption bands are found at nearly the same wave numbers. Thus, the functional groups present in this silica mesopore are also siloxane and silanol groups, with the difference lying in the number of groups present. The absorption peak at 1073.08 cm^{-1} (strong) indicates the presence of asymmetric Si-O-Si groups, and the absorption peak at 799.60 cm^{-1} indicates the presence of Si-H groups. The spectrum at a wavelength of 3213.36 cm^{-1} indicates the presence of Si-OH (Silanol) groups [13].

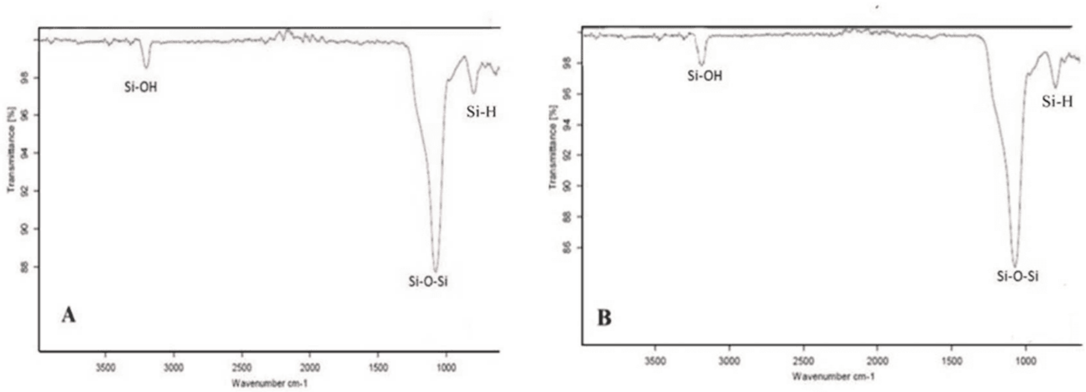

Figure 1. FT-IR spectra of mesoporous silica before adsorption (A) and mesoporous silica after adsorption (B)

3.2 SEM Analysis

The surface morphology of mesoporous silica can be observed using SEM at a magnification of 500x to observe the spatial morphology (Figure 2). Figure 2 shows that , there was a visible difference in surface area between the mesoporous silica before adsorption and the mesoporous silica after adsorption.

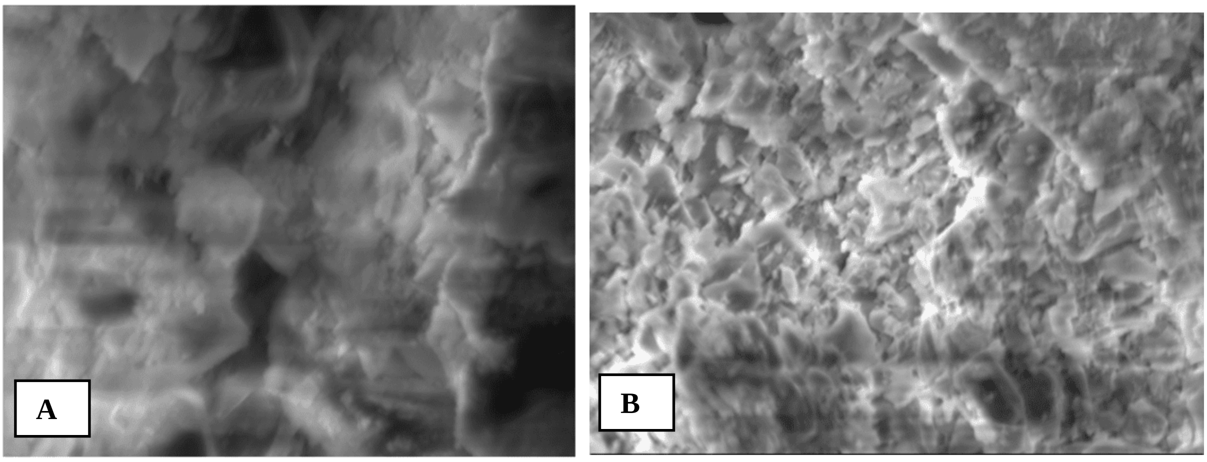

Figure 2. SEM images of mesoporous silica before adsorption (A) and mesoporous silica after adsorption (B)

Based on Figure 2A, the surface morphology of the mesoporous silica is shown before being used for copper metal adsorption.The morphology of its surface is viewed from the perspective of the inner space and the morphology of the mesoporous silica interior appears dispersed, neither compact nor loose (with many empty spaces). Meanwhile, Figure 2B showed that the interior appears to be cohesive. This indicates that the mesoporous silica have been able to bind Cu metal. It can be seen that the holes present in most of them have been filled with copper metal adhering to the surface of the silica mesopores. As a result, the surface morphology of the mesoporous silica appears more unified and the distance between the spaces is reduced. With the binding of Cu metal to the mesoporous silica, it shows that the mesoporous silica from rice husk have the potential to be used as an adsorbent [14].

3.3 Analysis of Cu Metal Adsorption Using Mesoporous Silica

The adsorption process was carried out using AAS equipment at room temperature of 20°C. This room temperature was chosen because the adsorption process at higher temperatures causes fewer heavy metal ions to be absorbed by the adsorbent. This happens because the higher the temperature during the adsorption process, the faster the movement of ions, resulting in a decrease in the number of heavy metal ions absorbed by the adsorbent [15]. The reduction percentage of Cu metal is displayed in Table 1 and its calibration curve is presented in Figure 3.

Table 1. Absorbance data of the standard Cu solution

Concentration (mg/L)	Average of Absorbance ($\bar{A}$)
0.2000	0.0286
0.4000	0.0591
0.6000	0.0921
0.8000	0.1225
1.0000	0.1526

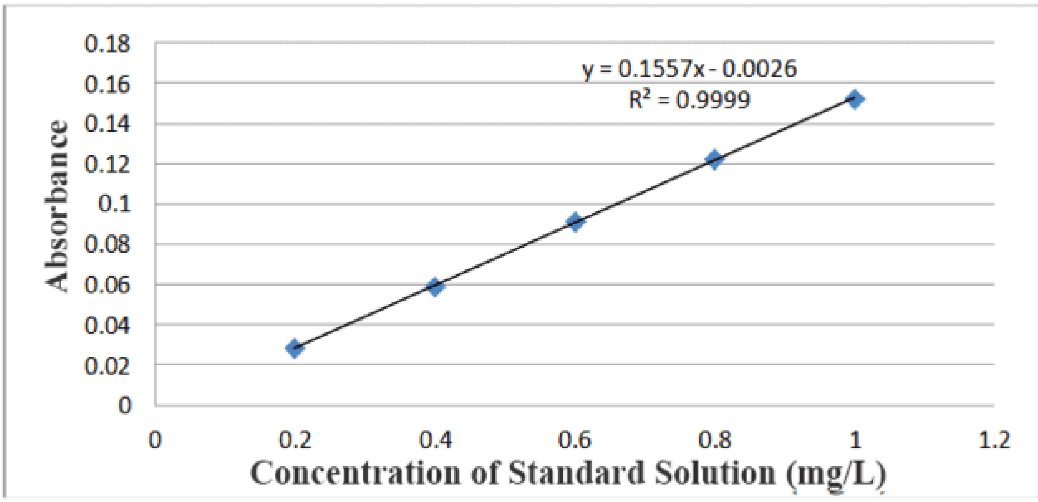

Figure 3. The graph of calibration curve of Cu Standard Solution

The surface of silica (SiO_2) has a high affinity for metal ions. The central silica ion (Si^{4+}) has a strong affinity for electrons. Oxygen atoms bonded with silica ions, which have low basicity properties, make the silica surface weakly acidic. Oxygen atoms on the surface of free silica react with water to form silanol groups (SiOH) [16]. This is confirmed by Figure 1, where the FTIR analysis spectrum of mesoporous silica shows the Si-OH (Silanol) group at an absorption band of 3213.36 cm^{-1}, according to the theory (Silverstein, 1986) Si-OH ranges from 3700-3200 cm^{-1}. After forming silanol (SiOH), the next mechanism is the adsorption of Cu (II) metal onto silanol. Electrostatic interactions occur between Cu^{2+} ions and the silanol groups and OH groups of silica, causing H^+ on the OH to be replaced by Cu^{2+}. The reaction mechanism is as follows:

$$Si(OH)_{4(s)} + 4\,Cu^{2+} \longrightarrow Si(OCu)_{4(s)} + 4H^{+}{}_{(aq)}$$

From the adsorption process between mesoporous silica and Cu^{2+} metal, it can be concluded that mesoporous silica from rice husk are capable of absorbing and reducing the concentration of Cu^{2+} metal ions, where the maximum absorption of copper metal ions occurs at a silica mesoporous mass of 1.6 g with an absorption efficiency of 99.73%.

4 Conclusion

The adsorption of copper metal occurs due to the electrostatic interaction between Cu^{2+} ions and the silanol groups (Si-OH) of silica, causing H^+ on OH to be replaced by Cu^{2+}. Next, by varying the mass of mesoporous silica from 0.2 g, 0.4 g, 0.8 g, and 1.0 g with a metal ion concentration of 10 mg/L and a contact time of 60 minutes, the best adsorption capacity was observed with the use of 1.0 g of mesoporous silica with 99.73% of Cu metal absorbed.

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6. Conflict of Interest

Authors declare no conflicts of interest.

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