Characterization of the Adsorption of Cu (II) from Aqueous Solutions onto Pyrolytic Sludge-Derived Adsorbents

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Abstract: The adsorption of Cu (II) onto two typical types of pyrolytic sludge was investigated in this study. The examined conditions include pH, adsorption time, and temperature, as well as the dosage of adsorbents. Results show that the adsorbents removed the Cu (II) effectively. The adsorbent made from pyrolyzed paper mill sludge (CuMS) exhibited exceptional performance, with a removal efficiency of around 100%. Moreover, the adsorption of Cu (II) onto CuMS was not affected by pH in the range of 3–9. The kinetic data showed better conformation with the pseudo-second-order kinetic model, and the adsorption processes of the CuMS fit well to the Langmuir isotherm model. The adsorption capacity reached 4.90 mg·g⁻¹ under appropriate conditions. Microscopic analysis and FT-IR analysis revealed that the adsorbent with porous structure and high monosilicate content was beneficial to Cu (II) adsorption. Thus, the CuMS is a potentially promising candidate for retaining Cu (II) in aqueous environments.

Keywords: pyrolytic sewage sludge; adsorbent; Cu (II) adsorption characterizations

1. Introduction

There is steady concern about the pervasive detection of heavy metals in aquatic environments, as heavy metals are increasingly discharged into the drainage systems by the electroplating, metallurgical, paper manufacturing, and tannery industries. These elements are generally known to exhibit acute toxicity and inflict permanent damage on living organisms even at extremely low concentrations [1–3]. Hence, their sufficient removal and reclamation is pressing. Treatment technologies for water remediation, such as physical–chemical precipitation, membrane filtration, ion exchange, nanotechnology, and adsorption, have been well developed to eliminate the pollutants over the years [4]. Among these techniques, adsorption has been extensively used due to its unique properties, such as efficient performance, operational simplicity and economic feasibility [5,6]. In detail, the developed adsorbents have a relatively extraordinary capacity and large surface area, such that they can decrease the heavy metal concentrations to an acceptable level [7,8]. In view of the intended applications, the fabrication of adsorbent materials involves severe technological requirement limitations with respect to cost effectiveness, available precursors, applicable functions, and corrosion resistance. Therefore, the feasibility of this work has to be taken into account [9–11]. Sewage sludge,
generated as a by-product of the wastewater treatment process, can be converted to an attractive adsorbent [12]. The general adsorption performances of pyrolytic sludge are definitely far from meeting the needs of commercial applications. Pyrolytic sludge usually suffers from slow adsorption or limited adsorption capacity, probably due to the high ash content, which is inevitably produced during the pyrolytic process. However, resource utilization for sewage sludge will be a preferred and attractive application option in coming years [9]. In other words, it is imperative to redefine a sustainable destination for these engineered materials [6,13,14]. As confirmed in the literature, through oxygen-limited pyrolysis and chemical treatment, sewage sludge can be converted into cost-effective and eco-friendly adsorbents [15,16]. Compared to untreated sewage sludge, the leaching efficiency and mobility of heavy metals present in the pyrolytic sludge were dramatically reduced [17]. These innovative and promising adsorbent materials, featuring double benefits of favorable adsorption properties and renewable sources, were used as substitutes for activated carbon. Indeed, their particular properties are superior to those of activated carbon [18].

Herein, the straightforward objective of the present study was to describe the adsorption characteristics of pyrolytic sludge-based adsorbents with respect to Cu (II)-containing aqueous solutions. For comparison, two typical low-cost adsorbents derived from excess domestic sewage sludge (SS) and paper mill sludge (MS) were prepared by pyrolysis technology under laboratory conditions, and their underlying discrepancies in adsorption characterizations were fully revealed. To this end, simulated batch experiments at environmentally relevant concentrations were conducted to symmetrically investigate the effects of variable conditions on their removal efficiency and adsorption performance. Subsequently, the dominant mechanism for the adsorption was elucidated in detail based on the gathered results with high accuracy and reliability. Similar to qualitative indications reported previously, this study documents a favorable strategy bridging the gap between undesired waste utilization and intractable environmental repercussions.

2. Materials and Methods

2.1. Sludge Collection and Preparation

The original types of sewage sludge used in the carbonaceous absorbent preparation were respectively collected from a sewage treatment plant and a paper mill sewage treatment plant located in Guangzhou, South China. Sludge was immediately stored in a refrigerator (4 °C) before use. The sludge was air-dried at room temperature, ground into powder, and then sieved with the desired particle diameter ranging from 0.15 mm to 0.25 mm. The sludge was transported to porcelain crucibles and then pyrolyzed using a muffle furnace at 800 °C for 3 h (heating rate of 10 °C/min) under an inert atmosphere. Afterwards, the pyrolyzed sludge was naturally cooled to room temperature. The obtained samples were abbreviated as CuSS and CuMS, respectively, for sludge collected from the sewage treatment plant and the paper mill sewage treatment plant. After conversion, samples were repeatedly washed with distilled water to remove chemical residues remaining in the resultant product.

2.2. Batch Adsorption Experiments

The Cu (II) standard stock solutions were freshly prepared using CuCl₂, and the working solutions were obtained by successively diluting the stock solutions with distilled water. Simulated batch absorption experiments were performed in 250 mL Erlenmeyer flasks with stoppers. The pH of Cu (II)-bearing solutions was adjusted by adding 0.1 mol L⁻¹ HCl or NaOH solutions. A specific amount of the solid adsorbents was initially dispersed into 100 mL of a simulated solution of Cu (II) at defined concentrations. The homogeneous mixtures were then intensively shaken in the reciprocating water-bath oscillator operated at 220 rpm and three controlled temperatures (20, 30, and 40 °C). The suspension solution was collected for analysis at prescribed time intervals. Samples were centrifuged at 4000 rpm for 20 min, and then filtered with 0.45-μm membranes before analysis. The percentage removal efficiency (RE) of the experiments was estimated according to Equation (I).
In addition, the amount of Cu (II) adsorbed per unit mass of adsorbent ($q_t$, mg·g$^{-1}$) at time $t$ (min) was calculated using Equation (2).

$$RE(\%) = \frac{C_i - C_t}{C_i} \times 100\%$$  \hspace{1cm} (1)

$$q_t = \frac{(C_i - C_t) \times V}{M}$$  \hspace{1cm} (2)

where $C_i$ (mg·L$^{-1}$) and $C_t$ (mg·L$^{-1}$) are the initial concentration and the residual concentration of Cu (II), respectively; $V$ (L) is the volume of Cu (II) solution; and $M$ (g) represents the mass weight of adsorbents.

2.3. Analytical Methods and Characterization

Concentrations of metals were determined by flame atomic absorption spectrometry (AAS, ZA-3000, Hitachi, Toyota, Japan). The metal-leaching characteristics were obtained according to the Chinese standard method (HJ/T299-2007). The chemical composition was determined by X-ray fluorescence spectroscopy (XRF1800, Shimadzu, Kyoto, Japan). All solution pH values were monitored using a digital pH meter (pH-3C, Leici, Shanghai, China). The surface morphology was examined by scanning electron microscopy (SEM, S-4800, Hitachi, Toyota, Japan). The surface area and porosity were measured using an ASAP 2020 Surface Area and Porosity Analyzer (Micromeritics, Washington, WA, USA). Fourier Transform infrared spectroscopy (FT-IR) was obtained using a Bruker VERTEX 70 Fourier transform infrared spectrometer (Bruker, Billerica, German) with the KBr pressed pellet method.

3. Results and Analysis

3.1. Physical and Chemical Properties and Leaching Toxicity Characteristics of Adsorbents

The chemical compositions were summarized in Table 1. The chemical compositions in CuSS were mainly Al$_2$O$_3$, P$_2$O$_5$ and SiO$_2$, while the major chemical constituents in CuMS were Al$_2$O$_3$, CaO, and SiO$_2$.

Table 1. Chemical composition of the CuSS and CuMS used in the present study. CuSS: the adsorbent made from the sewage sludge; CuMS, the adsorbent made from pyrolyzed paper mill sludge.

| Chemical Composition | Al$_2$O$_3$ | CaO | Fe$_2$O$_3$ | K$_2$O | MgO | MnO | Na$_2$O | P$_2$O$_5$ | SiO$_2$ | TiO$_2$
|---------------------|------------|-----|-------------|-------|-----|-----|--------|----------|--------|-----
| CuSS (wt %)         | 18.41      | 3.59| 7.97        | 3.93  | 2.72| 0.06| 0.78   | 10.42    | 51.22  | 0.92|
| CuMS (wt %)         | 15.95      | 50.34| 0.84        | 0.35  | 2.17| 0.03| 0.42   | 0.96     | 28.41  | 1.03|

The total and leaching concentrations of heavy metals in CuSS and CuMS are presented in Table 2. In this study, the threshold values in the standards (GB4284-84 and GB5085.3-2007) promulgated by the Chinese Ministry of Ecology and Environment (CMEE) were adopted. The total and leaching metal concentrations were lower than the permissible limits. Accordingly, CuSS and CuMS could be further applied for the treatment of waste water.

Table 2. Total and leaching concentrations of heavy metals in CuSS and CuMS.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Cr (mg kg$^{-1}$)</th>
<th>Ni (mg kg$^{-1}$)</th>
<th>Cu (mg kg$^{-1}$)</th>
<th>Pb (mg kg$^{-1}$)</th>
<th>Mn (mg kg$^{-1}$)</th>
<th>Zn (mg kg$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuSS</td>
<td>8.19</td>
<td>5.69</td>
<td>ND</td>
<td>82.4</td>
<td>214</td>
<td>909</td>
</tr>
<tr>
<td>CuMS</td>
<td>1.32</td>
<td>6.41</td>
<td>ND</td>
<td>175</td>
<td>ND</td>
<td>717</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Materials</th>
<th>Cr (mg L$^{-1}$)</th>
<th>Ni (mg L$^{-1}$)</th>
<th>Cu (mg L$^{-1}$)</th>
<th>Pb (mg L$^{-1}$)</th>
<th>Mn (mg L$^{-1}$)</th>
<th>Zn (mg L$^{-1}$)</th>
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<tbody>
<tr>
<td>CuSS</td>
<td>49.6</td>
<td>74.0</td>
<td>190</td>
<td>82.4</td>
<td>214</td>
<td>909</td>
</tr>
<tr>
<td>CuMS</td>
<td>19.4</td>
<td>103</td>
<td>175</td>
<td>ND</td>
<td>161</td>
<td>717</td>
</tr>
</tbody>
</table>

The total and leaching concentrations of heavy metals in CuSS and CuMS are presented in Table 2. In this study, the threshold values in the standards (GB4284-84 and GB5085.3-2007) promulgated by the Chinese Ministry of Ecology and Environment (CMEE) were adopted. The total and leaching metal concentrations were lower than the permissible limits. Accordingly, CuSS and CuMS could be further applied for the treatment of waste water.
The reason behind this pattern was that the hydrolysis of Cu (II) varied dramatically from weak to vacant binding sites in Cu affected by pH, and its RE and drastically increased from 52.84% to 73.60%. It can be concluded that Cu (II) competed with H+ for depending on their adsorption capacity.

In the present study, the pH of a solution plays an important role in the adsorption process and can radically change the existing speciation of an adsorbate and surface charge of an adsorbent [19]. In the present study, the effect of pH was tested under a temperature of 25 °C, an initial Cu(II) concentration of 25 mg·L−1, a reaction time of 360 min, and dosages of Cu SS and Cu MS of 20 g·L−1 respectively. Interestingly, when the pH initial increased from 6 to 7, the RE was ≥96.81% and 4.84 mg·g−1 respectively. Interestingly, when the pH initial increased from 6 to 7, the RE was drastically increased from 52.84% to 73.60%. It can be concluded that Cu (II) competed with H+ for the vacant binding sites in Cu SS under acidic conditions. In contrast, Cu (II) adsorption of Cu MS was less affected by pH, and its RE and qe values were greater than 96.81% and 4.84 mg·g−1 respectively.

According to Figure 1, by increasing the pH initial from 3 to 7, the RE of Cu SS sharply increased from 21.56 to 73.60%. When the pH initial was 8, the RE and qe reached the maximum values of 77.12% and 0.964 mg·g−1, respectively. Interestingly, when the pH initial increased from 6 to 7, the RE was drastically increased from 52.84% to 73.60%. It can be concluded that Cu (II) competed with H+ for the vacant binding sites in Cu SS under acidic conditions. In contrast, Cu (II) adsorption of Cu MS was less affected by pH, and its RE and qe values were greater than 96.81% and 4.84 mg·g−1 respectively.

Table 2. Total and leaching concentrations of heavy metals in CuSS and CuMS.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Heavy Metals</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cr</td>
</tr>
<tr>
<td>Threshold values for pH ≥ 6.5 (mg kg−1)</td>
<td>1000</td>
</tr>
<tr>
<td>pH &lt; 6.5 (mg kg−1)</td>
<td>600</td>
</tr>
<tr>
<td>Permissible limits for leaching toxicity (mg kg−1)</td>
<td>15.0</td>
</tr>
</tbody>
</table>

1 Not detected; 2 The threshold values of the Chinese control standards for pollutants in sludge from agricultural use (GB4284-84); 3 The permissible limits of the Chinese control standards for identification standard of hazardous wastes-identification of extraction toxicity (GB5085.3-2007).

3.2. Effect of pH on Adsorption

The pH of a solution plays an important role in the adsorption process and can radically change the existing speciation of an adsorbate and surface charge of an adsorbent [19]. In the present study, the effect of pH was tested under a temperature of 25 °C, an initial Cu(II) concentration of 25 mg·L−1, a reaction time of 360 min, and dosages of Cu SS and Cu MS of 20 g·L−1 and 5 g·L−1 respectively, depending on their adsorption capacity.

According to Figure 1, by increasing the pH initial from 3 to 7, the RE of Cu SS sharply increased from 21.56 to 73.60%. When the pH initial was 8, the RE and qe reached the maximum values of 77.12% and 0.964 mg·g−1, respectively. Interestingly, when the pH initial increased from 6 to 7, the RE was drastically increased from 52.84% to 73.60%. It can be concluded that Cu (II) competed with H+ for the vacant binding sites in Cu SS under acidic conditions. In contrast, Cu (II) adsorption of Cu MS was less affected by pH, and its RE and qe values were greater than 96.81% and 4.84 mg·g−1 respectively.

As shown in Figure 1, the solution pHfinal in mixtures with CuSS increased from 5.14 to 8.30. The reason behind this pattern was that the hydrolysis of Cu (II) varied dramatically from weak to
strong with the solution pH ranging from acidic to alkaline conditions. Additionally, compared with CuSS, CuSS had notably stronger buffering ability by releasing reactive OH groups into mixtures, with the adsorption of Cu (II) by CuMS.

3.3. Effect of Constant Temperature on Adsorption

The effect of the temperature was also investigated, under conditions of pH = 7, Cu(II) concentration of 25 mg·L\(^{-1}\), and dosages of CuSS and CuMS of 20 g·L\(^{-1}\) and 5 g·L\(^{-1}\), respectively. According to Figure 2, when the temperature increased from 20 to 40 °C, the RE and adsorption capacity of CuSS considerably increased. This implied that the adsorption behavior was an endothermic process in nature, showing an enhanced adsorption capacity at higher temperatures. And the higher the temperature, the faster the equilibrium of adsorption reached. However, the adsorption process of CuMS was not affected by the temperature, especially when the temperature reached 30 °C.

![Figure 2](image)

**Figure 2.** Effect of temperatures and time on Cu(II) adsorption by CuSS and CuMS.

3.4. Effect of Adsorption Dosage on Adsorption

As shown in Figure 3, when the dosages increased from 1 to 20 g·L\(^{-1}\), the RE of CuSS almost reached a balance, increasing from 44.82 to 73.60%. The \(q_t\) decreased with the ascending dosage of the CuSS, and it was affected by the reaction time. The maximum \(q_t\) for CuSS was 2.02 mg·g\(^{-1}\) when the dosage was 5 g·L\(^{-1}\) after the 480-min adsorption process.

When the dosages of CuMS ranged from 1 to 5 g·L\(^{-1}\), the RE of CuMS reached a balance, and it reached approximately 100%. Interestingly, the reaction time had little effect on RE and the \(q_t\) value. These results indicated that, in comparison with CuSS, CuMS showed a lower dosage and a higher adsorption capacity.

A pseudo-second-order model is commonly employed for the adsorption mechanism, where the main interaction involved in adsorption was adsorbent-adsorbate affinities in an aqueous
solution. In an attempt to discriminate the adsorption behavior, the kinetics data were fitted to a pseudo-second-order model, as empirically expressed mathematically in Equation (3) [3,20,21].

$$\frac{t}{q_t} = \frac{1}{k_2 \times q_e^2} + \frac{t}{q_e} = \frac{1}{h_0} + \frac{t}{q_e} \tag{3}$$

where $k_2$ is the second-order rate constants for the adsorption process, g·mg⁻¹·min⁻¹; $t$ is the reaction time, min; $q_e$ is the equilibrium adsorption capacity amount of the adsorbent, mg·g⁻¹; and $h_0$ represents the initial adsorption rate, mg·g⁻¹·min⁻¹.

![Figure 3](image1.png)

**Figure 3.** The effect of dosage on the Cu (II) adsorption (temperature is 25 °C, Cu(II) is 25 mg·L⁻¹; pH is 7).

The fitted curves of the pseudo-second-order kinetic model for Cu (II) onto CuSS and CuMS at different doses and constant temperatures are depicted in Figure 4. Obviously, the model for the modified adsorbents at different doses were well fitted, the $R^2$ were higher than 0.99.

![Figure 4](image2.png)

**Figure 4.** The pseudo-second-order model for the adsorption process.
The slope \( (1/q_t) \) and intercept \( (h_0, 1/(k_2 \times q_e^2)) \), referring to the fitting values of the corresponding parameters, were determined by the linear plots \( t/q_t \) against \( t \) for the experimental data (Table 3). The second-order rate constants \( (k_2) \) and the initial adsorption rate \( (h_0) \) increased with increased adsorbent dosages. At the given experimental conditions, CuMS required less time to reach equilibrium than CuSS, likely because the \( q_e \) for CuMS was 2.5 times that for CuSS.

**Table 3. Adsorption kinetics parameters for Cu (II) adsorption at different dosages.**

<table>
<thead>
<tr>
<th>Dosage</th>
<th>Temperature</th>
<th>Pseudo-Second-Order Model</th>
<th>( R^2 )</th>
<th>( 1/q_e )</th>
<th>( q_e )</th>
<th>( 1/(k_2 \times q_e^2) )</th>
<th>( k_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 g.L(^{-1})</td>
<td>30 °C</td>
<td>( y = 0.6267x + 4.2587 )</td>
<td>0.9964</td>
<td>0.6032</td>
<td>1.6578</td>
<td>2.4939</td>
<td>0.1459</td>
</tr>
<tr>
<td>2.5 g.L(^{-1})</td>
<td>30 °C</td>
<td>( y = 0.6032x + 2.4939 )</td>
<td>0.9992</td>
<td>0.6032</td>
<td>1.6578</td>
<td>2.4939</td>
<td>0.1459</td>
</tr>
<tr>
<td>5 g.L(^{-1})</td>
<td>30 °C</td>
<td>( y = 0.4787x + 11.448 )</td>
<td>0.9929</td>
<td>0.4787</td>
<td>2.0890</td>
<td>11.4480</td>
<td>0.0200</td>
</tr>
<tr>
<td>10 g.L(^{-1})</td>
<td>30 °C</td>
<td>( y = 1.0694x + 14.01 )</td>
<td>0.9968</td>
<td>1.0694</td>
<td>0.9351</td>
<td>14.0100</td>
<td>0.0816</td>
</tr>
<tr>
<td>20 g.L(^{-1})</td>
<td>30 °C</td>
<td>( y = 1.6519x + 3.6656 )</td>
<td>1.0000</td>
<td>1.6519</td>
<td>0.6054</td>
<td>3.6656</td>
<td>0.7444</td>
</tr>
<tr>
<td>CuSS</td>
<td>1 g.L(^{-1})</td>
<td>30 °C</td>
<td>( y = 0.2054x + 0.6007 )</td>
<td>0.9999</td>
<td>0.2054</td>
<td>4.8685</td>
<td>0.6007</td>
</tr>
<tr>
<td>2.5 g.L(^{-1})</td>
<td>30 °C</td>
<td>( y = 0.1973x + 0.4399 )</td>
<td>1.0000</td>
<td>0.1973</td>
<td>5.0684</td>
<td>0.4399</td>
<td>0.0885</td>
</tr>
<tr>
<td>5 g.L(^{-1})</td>
<td>30 °C</td>
<td>( y = 0.2021x + 0.0228 )</td>
<td>1.0000</td>
<td>0.2021</td>
<td>4.9480</td>
<td>0.0228</td>
<td>1.7914</td>
</tr>
<tr>
<td>10 g.L(^{-1})</td>
<td>30 °C</td>
<td>( y = 0.4016x + 0.0116 )</td>
<td>1.0000</td>
<td>0.4016</td>
<td>2.4900</td>
<td>0.0116</td>
<td>13.9037</td>
</tr>
<tr>
<td>20 g.L(^{-1})</td>
<td>30 °C</td>
<td>( y = 0.7999x + 0.0403 )</td>
<td>1.0000</td>
<td>0.7999</td>
<td>1.2502</td>
<td>0.0403</td>
<td>15.8769</td>
</tr>
</tbody>
</table>

The Langmuir and Freundlich isotherm models were used to analyze the adsorption isotherms according to the data from Figure 3. The Langmuir isotherm model is expressed as Equation (4), and its linear form is expressed as Equation (5) [12].

\[
q_t = \frac{K_L \times q_{\text{max}} \times C_e}{1 + K_L \times C_e}
\]  

(4)

\[
\frac{C_e}{q_t} = \frac{1}{K_L \times q_{\text{max}}} + \frac{C_e}{q_{\text{max}}}
\]  

(5)

where \( K_L \) is the Langmuir adsorption constant related to adsorption energy and the affinity of binding sites; \( C_e \) is the equilibrium concentration in the solution, mg L\(^{-1}\); and \( q_{\text{max}} \) is the maximum adsorption capacity of MS, mg g\(^{-1}\).

The Freundlich isotherm model assumes that all adsorption sites in the MS are heterogeneous and that the adsorption mechanism is multilayer adsorption. The Freundlich isotherm model is expressed as Equation (6):

\[
q_t = K_F \times C_e^{1/n}
\]  

(6)

where \( n \) is the heterogeneity factor and \( K_F \) is the Freundlich constant (mg g\(^{-1}\)). The linear form of the Freundlich equation is expressed as Equation (7):

\[
\ln q_t = \ln K_F + \frac{1}{n} \ln C_e
\]  

(7)

The \( n \) is related to the adsorption intensity or surface heterogeneity. A lower value of \( n \) indicates a lesser heterogeneity. All of the thermodynamic parameters for the Langmuir model and Freundlich model are shown in Table 4. The adsorption of CuMS fitted well with the Langmuir isotherm model. The correlation coefficient values (\( R^2 \)) for the Langmuir model were greater than 0.99. However, the adsorption of CuSS fitted badly both with the Langmuir isotherm model and the Freundlich model. The maximum adsorption capacity (\( q_{\text{max}} \)) of CuMS was 4.90 mg g\(^{-1}\), and \( K_L \) for CuMS was 111.93 L g\(^{-1}\), indicating that the CuMS had a strong adsorption capacity.
Table 4. Thermodynamic parameters for the Langmuir and Freundlich models.

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>Langmuir Model</th>
<th>Freundlich Model</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>$R^2$</td>
<td>$q_{\text{max}}$</td>
</tr>
<tr>
<td>CuSS</td>
<td>0.4796</td>
<td>3.179</td>
</tr>
<tr>
<td>CuMS</td>
<td>0.9994</td>
<td>4.901</td>
</tr>
</tbody>
</table>

4. Discussion

As the adsorption tests and the analysis show, the pseudo-second-order kinetic model for Cu(II) onto the two adsorbents at different doses and temperatures were well fitted, the $R^2$ were higher than 0.99. However, CuMS required less time to reach equilibrium compared to CuSS, and the $q_e$ for CuMS was about 2.5 times that for CuSS. Furthermore, the adsorption of CuMS was fitted well by the Langmuir isotherm model. The maximum adsorption capacity ($q_{\text{max}}$) of CuMS was 4.90 mg g$^{-1}$. The value was competitive with some similar low-cost adsorbents, including sawdust [22], coal [23], and also modified waste [24], their adsorption capacity was between 1.62 and 2.10 mg g$^{-1}$.

The micro-structural properties of CuSS and CuMS are illustrated in Figure 5. Both CuSS and CuMS exhibited irregular particles. More specifically, CuSS bears clearly large irregular agglomerates (Figure 5), whereas CuMS showed porous surface features, which could be beneficial for increasing its specific surface area and providing available active adsorption sites.

![Representative SEM images of CuSS and CuMS.](image)

With the characterization of surface area and porosity, it can be found that the BET-specific surface area of CuMS reached 386.22 m$^2$·g$^{-1}$, which was approximately 2 times greater than that of CuSS (115.31 m$^2$·g$^{-1}$). Furthermore, the micro-pore volume of CuMS reached 0.6893 cm$^3$·g$^{-1}$, which was approximately 2 times higher than that of CuSS (0.2653 cm$^3$·g$^{-1}$).

Additionally, compared with CuSS, CuMS had notably stronger buffering ability. With the chemical compositions analysis, we found that the major chemical constituents in CuSS were Al$_2$O$_3$, P$_2$O$_5$, and SiO$_2$, while the major chemical constituents in CuMS were Al$_2$O$_3$, CaO, and SiO$_2$. Thus, the mechanism for the adsorbents must be different.

FT-IR analysis of adsorbents after Cu(II) adsorption was conducted (Figure 6). The broad absorption band at 3423 cm$^{-1}$ present in CuSS is ascribed to the $–$OH stretching vibrations [25]. The absorption band at 1051 cm$^{-1}$ is ascribed to the stretching vibration of O-H. It can be deduced that the adsorption of Cu(II) on CuSS occurred and the H-bond and electrostatic interactions played an important role.
The absorption bands at 1090 and 1500 cm$^{-1}$ are related to the Si–O–Si stretching vibrations, while the absorption band at 468 cm$^{-1}$ is related to the Si–O bending vibrations [25], which is related to the disordering of SiO$_4$ [26], that is, a monosilicate is produced. The disordering of silicate in CuMS causes the overlap of the different absorption bands, which broaden the absorption band. Furthermore, the adsorption of the Cu would promote by the monosilicate [27].

5. Conclusions

Two types of pyrolytic sludge were studied for Cu(II) removal in this paper. Cu(II) adsorption by CuMS was not affected in the pH range of 3–9, whereas the pH values were narrow for CuSS adsorption of Cu(II). The adsorption residence time exerted insignificant impacts on the adsorption of CuMS, which was closely related to the dosage added. The maximum adsorption capacity of CuMS reached 4.90 mg/g. Moreover, the adsorption of the CuMS fitted well with the Langmuir isotherm model, and the pseudo-second-order kinetic model for Cu(II) onto the two adsorbents at different doses was also well fitted. Combining the surface area and porosity analysis and the FT-IR analysis, the higher adsorption capacity and the wider range of pH adaptation were due to its porous structure and higher monosilicate contents.

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