Glutamic acid-modified cellulose fibrous composite for adsorption of heavy metal ions from single and binary solutions

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1. Determination of COOH content

Figure S1. Electric conductivity titration ([NaOH]= 0.061mol·L⁻¹, \(V_{NaOH, equilibrium} = 5.95 \text{ mL}, m_{GMC} = 0.3 \text{ g}\). The COOH was calculated to be 1.2 mmol·g⁻¹.

2. FTIR spectra
Figure S2. FT-IR spectra of cellulose, TEMPO oxidised cellulose (1.2 mmol·g⁻¹ COOH), Glutamic modified cellulose and Cu(II)-loaded GMC, Hg(II)-loaded GMC.

3. Adsorption capacity comparison of unmodified cellulose and GMC
Figure S3. The adsorption capacity comparison of unmodified cellulose and GMC. Conditions: pH = 5, both unmodified cellulose and GMC dosage were 2.0 g L\(^{-1}\), and t = 30 mins, \([\text{Cu}^{2+}] = [\text{Hg}^{2+}] = 50\) ppm.

4. The pseudo-first-order kinetic model, the pseudo-second-order kinetic model
and intraparticle diffusion model curves fitted for Cu$^{2+}$ and Hg$^{2+}$ adsorption onto GMC

4.1 Pseudo-first-order kinetic model

\[
\ln(Q_e - Q) = \ln Q_e - kt
\]  

(1)

where \(Q_e\) and \(Q\) are the amount of solute adsorbed per unit adsorbent at equilibrium and time \(t\), respectively. \(k\) is the rate constant for the pseudo-first-order kinetics.

**Figure S4.** Pseudo-first order kinetic model for Cu$^{2+}$ adsorption

**Figure S5.** Pseudo-first order kinetic model for Hg$^{2+}$ adsorption

4.2 pseudo-second-order kinetic model
\[ \frac{t}{Q} = \frac{1}{k Q_e^2} + \frac{t}{Q_e} \]  

(2)

where \( Q_e \) and \( Q \) are the amount of solute adsorbed per unit adsorbent at equilibrium and time \( t \), respectively. \( k \) is the rate constant for the pseudo-second-order kinetics.

Figure S6. Pseudo-second order kinetic model for Cu\(^{2+}\) adsorption

Figure S7. Pseudo-second order kinetic model for Hg\(^{2+}\) adsorption

### 4.3 Intraparticle diffusion model

The rate constant of intraparticle diffusion (\( k_{\text{di}} \)) at the stage \( i \) was given by the
equation:

\[ Q_t = k_{d1} t^{1/2} + C_1 \]  \hspace{1cm} (3)

Where \( Q_t \) is the amount of \( \text{Cu}^{2+}/\text{Hg}^{2+} \) absorbed on bioadsorbent, \( t^{1/2} \) is the square root of adsorption time, and \( C_1 \) is the intercept at different stage.

Fig. S8  Intraparticle diffusion model for adsorption of \( \text{Cu}^{2+} \) and \( \text{Hg}^{2+} \) on GMC at pH=5 and 25 °C

<table>
<thead>
<tr>
<th>C_0/Metal</th>
<th>( k_{d1} ) ( \text{mg} \cdot \text{L}^{-1} )</th>
<th>( C_1 ) ( \text{mg} \cdot (\text{g} \cdot \text{t}^{1/2})^{-1} )</th>
<th>( k_{d2} ) ( \text{mg} \cdot (\text{g} \cdot \text{t}^{1/2})^{-1} )</th>
<th>( C_2 )</th>
<th>( (R^2) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>50- ( \text{Cu}^{2+} )</td>
<td>6.24</td>
<td>-3.46</td>
<td>0.84</td>
<td>0.16</td>
<td>22.25</td>
</tr>
<tr>
<td>50- ( \text{Hg}^{2+} )</td>
<td>12.93</td>
<td>-0.27</td>
<td>0.99</td>
<td>0.02</td>
<td>22.8</td>
</tr>
</tbody>
</table>

5. Langmuir isotherm model and Freundlich isotherm model curves of \( \text{Cu}^{2+} \) and
Hg$^{2+}$ adsorption onto GMC

5.1 Langmuir isotherm model

\[
\frac{c_e}{Q_e} = \frac{1}{Q_m \times b} + \frac{c_e}{Q_m}
\]

(4)

where $Q_m$ and $b$ are the Langmuir constants related to maximum adsorption capacity and equilibrium constant or energy of adsorption, respectively. $Q_e$ is the observed adsorption capacity (mg/g) and $C_e$ is the equilibrium concentration (mg/L).

![Figure S9. Langmuir adsorption isotherm of GMC for Cu$^{2+}$ adsorption](image)

![Figure S10. Langmuir adsorption isotherm of GMC for Hg$^{2+}$ adsorption](image)

5.2 Freundlich isotherm model
\[
\ln Q_e = \ln K_f + \frac{1}{n} \ln C_e
\]  
(5)

where \( n \) is adsorption strength, \( K_f \) is adsorption capacity, \( Q_e \) is the observed adsorption capacity (mg/g) and \( C_e \) is the equilibrium concentration (mg/L).

**Figure S11.** Freundlich adsorption isotherm of GMC for Cu\(^{2+}\) adsorption

**Figure S12.** Freundlich adsorption isotherm of GMC for Hg\(^{2+}\) adsorption