SUPPORTING INFORMATION

Acrylic acid grafted and acrylic acid/sodium humate grafted bamboo cellulose nanofibers for Cu$^{2+}$ adsorption

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Characterization

The graft yield, based on the weight change, was calculated using the following equation:

\[
\text{graft yield (wt\%) = \frac{W_2 - W_1}{W_1} \times 100\%}
\]

where \( W_1 \) is the weight of BCN before grafting and \( W_2 \) is the total weight after grafting PAA onto the BCN.

The carboxyl content on PAA-grafted BCN was calculated according to literature.¹ The purified PAA-grafted BCN (0.5 g) was treated with 0.01 M HCl for 1 h, followed by thorough washing with deionized water. Then the sample was suspended in 50 ml of a 2% (w/w) calcium acetate solution followed by ultrasonic treatment for 30 min. The mixture was titrated with 0.1 M standardized sodium hydroxide using phenolphthalein.
as an indicator. The volume of NaOH solution consumed was corrected for the blank. The carboxyl content in the sample was calculated as follows:

$$\text{carboxyl content (\%w/w)} = \frac{0.1 M \times V_{\text{NaOH}} \times MW_{\text{COOH}}}{m \times (1 - w/100)} \times 100\%$$

Where 0.1 M is the normality concentration of NaOH, $V_{\text{NaOH}}$ is the volume (ml) of NaOH solution used in titration after correcting for the blank, $m$ is the weight of sample fibers, and $w$ is the moisture content of the fibers (%).

Nitrogen physisorption measurements were performed by Quantachrome NovaWin instrument (USA) at 77K. The Brunauer-Emmett-Teller (BET) analysis from the amount of $N_2$ adsorbed at various relative vapor pressures (five points $0.01 < P/P_0 < 0.3$, nitrogen molecular cross-sectional area = 0.162 nm$^2$) was used to determine the surface area.

EDS spectrum was acquired in order to confirm the Cu$^{2+}$ ions on the surface of modified BCN. Adsorption experiments were carried out by adding 40 mg BCN-g-PAA/SH to 20 mL of 40 mmol/L CuSO$_4$ aqueous solution. The pH of the CuSO$_4$ solution was adjusted to 4.5 using 0.1M H$_2$SO$_4$. During the adsorption, the solutions were constantly stirred for 2h using a shaking table (KS, Aohua, China) at 20 $^\circ$C/180 rpm.

After reaching the adsorption equilibrium, the Cu$^{2+}$-adsorbed BCN suspension was used for SEM observation coupled with EDS.

**Result and discussion**
The graft yield of PAA on the BCN was calculated to be 10.73%, and the corresponding carboxyl content of PAA-grafted BCN was calculated to be 8.01%, which was higher than some reported similar materials.\(^2\)

Nitrogen adsorption was used to estimate the specific surface area of BCN, which was free-dried into aerogels. The BCN aerogel has a specific surface area of 79 m\(^2\)g\(^{-1}\), much higher than that of the bamboo fibers (0.80 m\(^2\)g\(^{-1}\)). The high specific surface area of the BCN was very beneficial for the adsorption of heavy ions in water purification.

The SEM-EDS Cu-mapping photograph and the EDS spectrum were presented in Figure S1A and B, respectively. The element analysis was shown in Table S1. In Figure S1A, the nanofibers seemed to agglomerate to form condense structure after the adsorption of Cu\(^{2+}\). In the EDS spectrum, the characteristic Cu peaks were clearly identified. The content of Cu was as high as 68.17%, suggesting the Cu\(^{2+}\) ions could be effectively adsorbed by the modified BCN.
Table S1. The element content on the surface of BCN-g-PAA/SH after Cu\textsuperscript{2+} adsorption.

<table>
<thead>
<tr>
<th>Element</th>
<th>C</th>
<th>O</th>
<th>S</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight Ratio</td>
<td>14.79</td>
<td>8.18</td>
<td>8.87</td>
<td>68.17</td>
</tr>
<tr>
<td>Atomic Ratio</td>
<td>39.82</td>
<td>16.53</td>
<td>8.94</td>
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</tr>
</tbody>
</table>

Fig S1. SEM image (A) and EDS spectrum (B) of BCN-g-PAA/SH after Cu\textsuperscript{2+} adsorption.

References