Preparation of bio-adsorbents by modifying licorice residue via chemical methods and removal of copper ions from wastewater

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ABSTRACT

In this paper, a series of bio-adsorbents (LR-NaOH, LR-Na\textsubscript{2}CO\textsubscript{3} and LR-CA) were successfully prepared by modifying Licorice Residue (LR) with NaOH, Na\textsubscript{2}CO\textsubscript{3} and citric acid, and were used as the adsorbents to remove Cu\textsuperscript{2+} from wastewater. The morphology and structure of bio-adsorbents were characterized by Fourier Transform Infrared, scanning electron microscopy (SEM), thermogravimetry (TG) and X-ray diffraction (XRD). Using static adsorption experiments, the effects of the adsorbent dosage, the solution pH, the adsorption time, and the initial Cu\textsuperscript{2+} concentration on the adsorption performance of the adsorbents were investigated. The results showed that the adsorption process of Cu\textsuperscript{2+} by the bio-adsorbents can be described by pseudo-second-order kinetic model and the Langmuir model. The surface structure of the LR-NaOH, LR-Na\textsubscript{2}CO\textsubscript{3} and LR-CA changed obviously, and the surface-active groups increased. The adsorption capacity of raw LR was 21.56 mg/g, while LR-NaOH and LR-Na\textsubscript{2}CO\textsubscript{3} significantly enhanced this value up to 43.65 mg/g and 43.55 mg/g, respectively. After four adsorption–desorption processes, the adsorption capacity of LR-NaOH also maintained about 73%. Therefore, LR-NaOH would be a promising adsorbent for removing Cu\textsuperscript{2+} from wastewater, and the simple strategy towards preparation of adsorbent from the waste residue can be a potential approach for use in the water treatment.

Key words: adsorbent, Cu\textsuperscript{2+}, licorice residue, modification, wastewater

HIGHLIGHTS

- Licorice Residue-based biological adsorbents with the ability to remove heavy metal ions were fabricated.
- The Cu\textsuperscript{2+} ions in the water were easily removed using the bio-adsorbents which were made by this study.
- The adsorption capacity of Licorice Residue which was modified by NaOH maintained above 73% after four cycles.
INTRODUCTION

With the acceleration of urbanization process and the increase in industrialization, heavy metal pollution of water bodies has gradually become a big issue which troubles many countries around the globe (Li et al. 2019). Heavy metals are seriously harmful to human health and eco-system due to their stable and lasting existence in the environment, and accumulating in human beings’ body through food chain (Afonne & Ifediba 2020; Wu et al. 2020). Thereby, removing heavy metal from water is significant for human beings and eco-system.

At present, the main methods of removing heavy metals from wastewater include ion exchange (Wang et al. 2019a, 2019b), chemical precipitation (Nepel et al. 2019; Niu et al. 2020) and membrane filtration (Liu et al. 2018), etc. But the widespread use of these methods in commercial applications is limited by high cost and low reusability. Conversely, biosorption has drawn growing attention in heavy metal removal due to its operability and low cost (Kumar & Sharma 2019). And, bio-adsorbents have extensive resources and easy accessibility, such as coir pith (Swarnalatha & Ayoob 2016), algae residues (Li et al. 2020a), herb residue (Hu et al. 2019; Shi et al. 2020), etc.

Herb residue, a kind of waste of pharmaceutical industry, is rich in lignocellulose (cellulose, lignin and hemicellulose) which contains functional groups such as hydroxyl, carboxyl and amino groups (Nagarajan & Venkatanarasimhan 2020). According to relevant studies, Astragalus residues (Feng et al. 2018), Turmeric residues and other herb residues have the ability to adsorb heavy metals. Licorice, as a genuine medicinal material in Gansu Province, with anti-tumor, anti-inflammatory effects and other pharmacological effects, was used widely in China (Wang et al. 2020). The Licorice from which the active ingredients have been extracted still contains a lot of residue—Liquorice Residue (LR), which can be used as a heavy metal adsorbent (Ma et al. 2015; Wang et al. 2019a, 2019b). But, it has a barrier for the direct use of LR as an adsorbent because the adsorption capacity of LR is relatively low. The probable reasons are as follows: firstly, encapsulating of the highly crystalline structure of cellulose, lignin and hemicellulose reduces the availability of cellulose (Xing et al. 2019); secondly, lignin, the most abundant aromatic bio-based polymer in nature, has the characteristics of being difficult to degrade (Pérez et al. 2002). Therefore, exploring effective modification methods and conditions plays important roles in expanding the application of herb residue in the field of bio-adsorption (Karmakar et al. 2019).

At present, the common treatment methods are physical, chemical and biological methods (Kwak et al. 2019). Among them, the chemical modification (Anghel et al. 2019) is the most common measure because of its simplicity and low energy consumption. The principle of chemical modification (Liu et al. 2010; Abdel-Halim & Al-Deyab 2014) is that different
components of lignocellulose have different stability to different chemical reagents. In addition, this modification method can also introduce some functional groups into the surface of herb residues to enhance the adsorption capacity to heavy metal ions.

In this study, LR was chemically modified to prepare the bio-adsorbents which were used to remove Cu$^{2+}$ from wastewater. Firstly, LR was pretreated with methanol ahead to remove pigments and other bioactive ingredients remaining in the LR after extracting, then it was modified with NaOH, Na$_2$CO$_3$ and citric acid, obtaining a series of LR-based bio-adsorbents. The static adsorption test was used to study the adsorption capacity of the adsorbents, and the effect of factors including pH of solution, adsorption time, adsorbent dosage, and initial concentration of Cu$^{2+}$ was tested. The adsorption kinetics and adsorption isothermal were analyzed with the kinetic model and the isothermal model.

**EXPERIMENT**

**Materials**

LR (Licorice Residue) was purchased from Huirentang pharmacy (Lanzhou, China), and washed repeatedly to remove the residual organic components. Then LR was dried in the oven at 80 °C until it achieved constant weight and was pulverized. The particle size of LR used in the further chemical treatment was in the 40–60 mesh. Analytical grade of methanol, hydrochloric acid, sodium hydroxide and copper nitrate all were obtained from Sinopharm group chemical reagent Co., Ltd. All the solutions used in the adsorption experiment were prepared with distilled water.

**Preparation of bio-adsorbents**

**Pretreatment of LR**

Firstly, 0.5 g, 1 g and 1.5 g LR with the particle size of 40–60 mesh were added into 50 mL methanol, continuously stirred for 24 h to remove further bioactive ingredients and pigments of the medicine residue, and then they were dried to constant weight at 70 °C. Through decolorization effect comparison, 1 g LR in 50 mL methanol can make LR decolorized effect better than 1.5 g LR in 50 mL, and in this ratio, decolorization meets the experimental needs, so in the following study, 1 g LR in 50 mL methanol was used as an optimal ratio to pretreat LR.

**LR was modified by NaOH and Na$_2$CO$_3$**

1 g decolored LR was added into 10 mL, 20 mL, 30 mL of NaOH or Na$_2$CO$_3$ solution (1 mol/L), vibrated at rotation speed of 120 r/min at room temperature for 4 h, respectively. Comparing their adsorbability, LR treated with 20 and 30 mL of NaOH or Na$_2$CO$_3$ solution showed similar adsorption performance, while better than that of LR treated with 10 mL of NaOH or Na$_2$CO$_3$ solution. So, 1 g LR was treated with 20 mL NaOH or Na$_2$CO$_3$ as the optimal ratio to prepare bio-adsorbents. The treated LR was washed to neutrality with deionized water. And after drying, it was named LR-NaOH or LR-Na$_2$CO$_3$.

**LR was modified by citric acid**

The bio-adsorbent prepared from the citric acid treatment was conducted firstly to treat decolored LR with 0.1 mol/L NaOH for 30 minutes, then immersed into 0.6 mol/L citric acid solution with a ratio of 10: 1, and vibrated at rotating speed of 120 r/min at room temperature for 4 h. The product was washed with distilled water to neutrality and dried in the oven at 60 °C, and named LR-CA.

**Characterization**

The structure of LR, LR-NaOH, LR-Na$_2$CO$_3$ and LR-CA was characterized with Fourier Transform Infrared spectrometer (FTIR, Nicolet Nexus, USA) in the region 4,000–400 cm using KBr pellets. The surface morphologies of bio-adsorbents were scanned with scanning electron microscopy (SEM; JSM-6701F, JEOL, Japan) after the samples were covered with gold film. The thermal stability of samples was analyzed in oxygen atmosphere, by Perkin Elmer TGA-7 thermogravimetric instruments (Perkin-Elmer Cetus Instruments, Norwalk, CT) at a heating rate of 10 °C/min and in 30–800 °C range. The composition of material, the structure and morphology of internal atoms or molecules were observed by X-ray diffraction (XRD) (JEOL, JDX-3530, 2 kW, Tokyo, Japan) at a scan rate of 12°/min from 3° to 50°.

**Adsorption experiments**

An amount of LR, LR-NaOH, LR-Na$_2$CO$_3$ and LR-CA was respectively added into 10 mL Cu$^{2+}$ solution (concentration range from 20 mg/L to 150 mg/L) and shaken at 30 °C (as the room temperature to mimic practical application) at 120 r/min for 2 h.
After that, the liquid supernatant was filtered and the Cu\textsuperscript{2+} concentration was determined by atomic absorption spectrophotometer (PerkinElmer, PinAAcle 900 T, USA). The adsorption capacity \( (q, \text{mg/g}) \) was calculated with the following equations (1):

\[
q = \frac{(C_0 - C_e) \times V}{m}
\]

(1)

where, \( C_0 \) and \( C_e \) were the concentrations of metal ions (mg/L) before and after adsorption, respectively, \( V \) the solution volume of Cu\textsuperscript{2+} (mL), \( m \) the mass of adsorbent (mg).

The kinetics study was performed with 100 mg/L Cu\textsuperscript{2+} solutions by varying the adsorption time from 10 to 120 min. The adsorption kinetics was evaluated based on the pseudo-first-order equation and the pseudo-second-order equation. The adsorption isotherms for Cu\textsuperscript{2+} were obtained in the 20–150 mg/L concentration range. In order to evaluate the control factors of the adsorption process, the Langmuir and Freundlich isotherm models were used. The effect of pH on the adsorption capacity was evaluated in the pH 1–6 range, and the initial pH of the Cu\textsuperscript{2+} solutions was adjusted by the addition of NaOH or HCl solution.

The reusability of bio-adsorbents

After the adsorption process, LR-NaOH was filtered and washed with distilled water repeatedly, and then desorbed with 25 mL HCl (0.5 mol/L) for 3 h. Later the bio-adsorbent was washed with distilled water for several times with the purpose of removing the acid and the metal ions, and then used in the next adsorption process. The adsorption–desorption experiment was performed four times.

RESULTS AND DISCUSSION

Fourier transform infrared analysis

The changing information of functional groups of LR, LR-NaOH, LR-Na\textsubscript{2}CO\textsubscript{3} and LR-CA is shown in Figure 1. The LR displayed a number of adsorption peaks at 3,413 cm\textsuperscript{-1} (stretching vibration of hydroxyl group in the structure of cellulose and lignin), 2,927 cm\textsuperscript{-1} (vibration of -CH\textsubscript{3} and -CH\textsubscript{2} in lignin), peak near 1,731 cm\textsuperscript{-1} (stretching vibration of C=O in glycyrrhizic acid ester), 1,639 cm\textsuperscript{-1} and 1,246 cm\textsuperscript{-1} (stretching vibration of C=O and the stretching vibration of -CN in the protein amide bond, respectively), 1,373 cm\textsuperscript{-1} (stretching vibration of the -CO- bond in the benzene hydroxyl group in lignin), 1,249 cm\textsuperscript{-1} and 1,157 cm\textsuperscript{-1} (stretching vibration of C=O in the ester group in cellulose), and 1,050 cm\textsuperscript{-1} (the bending vibration of hydroxyl group).

Comparing the infrared spectra of LR, LR-NaOH and LR-Na\textsubscript{2}CO\textsubscript{3}, the main change was that 1,157 cm\textsuperscript{-1} disappeared in the infrared spectra of LR-NaOH and LR-Na\textsubscript{2}CO\textsubscript{3}. The ester bonds in the lignin-polycarbonate composite (LCC) (the bond between lignin and hemicellulose in lignin-carbohydrate complex) were broken by NaOH and Na\textsubscript{2}CO\textsubscript{3}. The other absorption

![Figure 1](image-url)  

Figure 1 | Fourier Transform Infrared spectra of LR, LR-Na\textsubscript{2}CO\textsubscript{3}, LR-CA and LR-NaOH.
peaks were significantly weakened in the infrared spectra of LR-NaOH and LR-Na$_2$CO$_3$, indicating that NaOH and Na$_2$CO$_3$ could remove lignin and part of the hemicellulose to a great extent.

Comparing the infrared spectrum of LR and LR-CA, the main change was that the absorption peak at 1,157 cm$^{-1}$ in the infrared spectrum of LR significantly weakens or even disappears in the infrared spectrum of LR-CA; this indicated that part of the cellulose could be removed by citric acid treatment.

**SEM analysis**
The surface morphologies of LR, LR-NaOH, LR-Na$_2$CO$_3$ and LR-CA are shown in Figure 2. It can be seen from Figure 2 that the structure of LR was relatively dense. Compared with LR, LR-NaOH, LR-Na$_2$CO$_3$ and LR-CA, the adsorbents had more surface pores, which might derive from the damage of the lignocellulose structure by the reagents, indicating that the structure of LR-NaOH, LR-Na$_2$CO$_3$ and LR-CA was relatively loose. The possible reason was that alkali could effectively destroy the connection between lignin and hemicellulose in the LCC, especially breaking the ether bonds and ester bonds in the LCC structure, as well as dissolving lignin and hemicellulose to some extent. Besides, acid improved the accessibility of cellulose in chemical reaction (Ikramullah et al. 2018). In addition, an internal substitution between two adjacent atoms in its molecule (a 5-molecular ring) was formed by citric acid treatment, and then it reacted with a hydroxyl group to form an ester bond, so that the amorphous area of cellulose swelled and improved the accessibility of cellulose in chemical reactions (Anuar et al. 2019). That is, the modified LR(LR-NaOH, LR-Na$_2$CO$_3$ and LR-CA) were easier removed Cu$^{2+}$ in wastewater more easily.

**TG analysis**
The thermal stability of LR, LR-NaOH, LR-Na$_2$CO$_3$ and LR-CA is shown in Figure 3. The thermal degradation of cellulose can be divided into three stages. (1) The weight loss started in the region of 40–180 °C for LR-NaOH, LR-Na$_2$CO$_3$, LR-CA and LR. The possible cause was mainly due to the evaporation of water of the samples, low molecular weight components and hemicellulose. Generally, the thermal degradation of hemicellulose occurs before the degradation of cellulose and lignin (Saelee et al. 2016). (2) The second stage of the weight loss was observed in the region of 180–400 °C for LR and LR-CA, and 180–480 °C for LR-NaOH and LR-Na$_2$CO$_3$, respectively. The main possible reason was the decomposition of the cellulose molecular skeleton (Belyi et al. 2015). The thermal stability of LR and LR-CA was much higher than that of LR-NaOH and LR-Na$_2$CO$_3$ after modification with the same degradation onset temperature of 180 °C, and degradation peak temperature of 480 °C vs 400 °C. (3) The third stage was from 400 °C to 800 °C, the residual of bio-adsorbents was more than 20%, probably due to the leftover sodium element that was introduced in the chemical modification process (Li et al. 2020b).
XRD analysis

The crystallinity of LR, LR-NaOH, LR-Na$_2$CO$_3$ and LR-CA is shown in Figure 4. Lignocellulose (including cellulose, lignin and hemicellulose) plays an important role in the adsorption process, while cellulose was usually in crystalline state, and both lignin and hemicellulose were in amorphous state. Therefore, after removing lignin and hemicellulose to some degree, the crystallinity of LR-NaOH increased, and the structure of the LR-NaOH became loose. The results showed that the degree of looseness of the three bio-adsorbents was as follows: LR-NaOH > LR-Na$_2$CO$_3$ > LR-CA. Compared to LR, the crystallinity index of LR-CA, LR-Na$_2$CO$_3$ and LR-NaOH increased from 48.77% to 65.11%, 79.24% and 85.85%, respectively. The possible reason was the reduction of lignin and hemicellulose (Phitsuwan et al. 2016).

The adsorption performance of bio-adsorbents

Effect of adsorbent dosage

Figure 5 shows the influence of bio-adsorbent dosage on the adsorption capacity of Cu$^{2+}$. It can be seen that, firstly, the adsorption capacity decreased with the increase of the dosage of the four bio-adsorbents. That is, after adsorption, the adsorption capacity of bio-adsorbents decreased significantly. This may be because, at the beginning of adsorption, there are many sites on the surface of the bio-adsorbent that can be used to adsorb Cu$^{2+}$, so a large amount of Cu$^{2+}$ was adsorbed, but as the reaction progresses, Cu$^{2+}$ gradually was bound totally with these surface-active sites, the adsorption tends to equilibrium, and therefore the adsorption capacity of bio-adsorbents decreased.
Secondly, when the amount of the adsorbents increased to 0.010 g, the highest adsorption capacity was achieved. After modification, the adsorbent capacity of bio-adsorbents was different. The maximum adsorption capacities of LR, LR-NaOH, LR-Na2CO3 and LR-CA were 21.56, 43.65, 43.55 and 27.56 mg/g, respectively. Besides, the adsorption capacity of LR-NaOH, LR-Na2CO3 and LR-CA was higher than that of LR, and the order was as follows: LR-NaOH > LR-Na2CO3 > LR-CA. The possible reason was that the hydrogen bond between cellulose and hemicellulose was broken through the action of NaOH, Na2CO3 and citric acid. And hemicellulose and lignin were saponified at the same time, so that the amorphous region of cellulose swelled, and the accessibility of cellulose in chemical reactions was improved. Therefore, the adsorption capacity of LR-NaOH, LR-Na2CO3 and LR-CA was higher than that of the LR.

**Effect of pH on adsorption effect**

The pH value of the solution is an important factor affecting the main morphology of metal ions in the solution and the surface charge distribution of bio-adsorbents. Figure 6 shows the influence of pH on the adsorption capacity for Cu2⁺; the adsorption capacity gradually increased with the increasing of pH at room temperature. This trend could be explained by changes in surface active sites. Here, the hydroxyl was the main adsorption site. When solution pH was in the range of 1–3, the adsorption capacity for Cu²⁺ was all under 14 mg/g, while the adsorption capacity of the bio-adsorbents increased rapidly when pH increased in the range of 3–6. It was mainly because when pH ≤ 3, hydrogen ions and metal ions competitively bound adsorbing sites on the surface of the adsorbents. Also, the hydroxyl groups were protonated by hydrogen ions, reducing the number of active sites available for metal ion uptake. With the increase of pH, the concentration of hydrogen ions gradually decreased, the competition effects with metal ions gradually weakened, and the adsorption capacity gradually increased. When pH reached 6, the adsorption capacity of the bio-adsorbents to Cu²⁺ reached the maximum.
adsorption capacities of LR, LR-NaOH, LR-Na₂CO₃ and LR-CA were 21.56, 43.65, 43.55 and 27.56 mg/g, respectively. Because the Cu²⁺ forms hydroxide precipitation at a pH value greater than 6.0, the pH effect of this study was tested in the range of 1–6.

**Effect of adsorption time**

Adsorption time also was an important factor for affecting the adsorption to reach the equilibrium. Figure 7 shows the effect of contact time on the adsorption capacity for Cu²⁺ in the wastewater. The adsorption capacity gradually increased with the increase of the contact time, until the adsorption reached adsorption equilibrium. The removal of Cu²⁺ was mainly carried out in the first stage, when the adsorption sites were completely bound with the metal ions, which may gather near the active sites, that is, the adsorption saturation state of the bio-adsorbents. The order of equilibrium adsorption time of four bio-adsorbents was as follows: LR-NaOH(75 min) > LR-Na₂CO₃(60 min) > LR(40 min) > LR-CA(30 min). The adsorption capacity of LR-CA and LR-Na₂CO₃ was higher than that of LR. The adsorption capacity of LR-NaOH was lower than that of LR within the first 60 minutes, higher than that of LR from 60 minutes to 75 minutes, and basically equilibrated after 75 min. This may be because in the adsorption process of LR-NaOH, swelling and adsorption might proceed at the same time, when the surface active groups were occupied, so the adsorption capacity of LR-NaOH might arise.

**Effect of initial concentration of metal ions**

The initial concentration of metal ions effecting on the adsorption capacity of bio-adsorbents is shown in Figure 8. The adsorption capacity increased with the increase of the initial concentration, and when it reached a certain initial
concentration, the adsorption capacity remained constant. This was because when the initial concentration was low, the active sites of adsorption were not saturated. As the concentration increased, the driving force for adsorption increased, which led to an increase in adsorption capacity. When the initial concentration increased further, the adsorbed active sites tended to be saturated (Chen et al. 2020). The order of adsorption concentrations of the three bio-adsorbents was as follows: LR-NaOH (100 mg/L) > LR-Na2CO3 (80 mg/L) > LR-CA (60 mg/L).

Based on the XRD characterization, the treatment of LR with NaOH showed significant modification efficiency, indicating that alkaline treatment not only improved the surface active groups but also destroyed the structure of lignin. Comparing the infrared spectra of LR, LR-NaOH and LR-Na2CO3, the ester bonds in the LCC (the bond between lignin and hemicellulose in the LCC) were broken by NaOH and Na2CO3. The other absorption peaks were significantly weakened in the infrared spectra of LR-NaOH and LR-Na2CO3. Comparing the SEM of LR, LR-NaOH, LR-Na2CO3 and LR-CA, the adsorbents had more surface pores, which might derive from the damage of the lignocellulose structure by the reagents, indicating that the structure of LR-NaOH, LR-Na2CO3 and LR-CA was relatively looser. Therefore, the performance of modification bio-adsorbents had improved.

Adsorption kinetics
In order to better understand the adsorption mechanism, the adsorption process was evaluated using pseudo-first-order model (Equation (2)) and pseudo-second-order model (Equation (3)).

The pseudo-first-order mode:

\[
\log \left( \frac{q_e}{q_t} \right) = \log \left( \frac{q_e}{k_1 C_0} \right) - \frac{k_1}{2.303} t
\]

The pseudo-second-order model:

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

where \( q_t \) and \( q_e \) were the \( Cu^{2+} \) adsorption capacity (mg/g) of the bio-adsorbents at the time of \( t \) and the equilibrium state, and \( k_1 \) and \( k_2 \) the Rate constant (min\(^{-1}\)) of pseudo-first-order model and pseudo-second-order model, respectively. The data fitting results are shown in Table 1.

In Table 1, the linear correlation coefficient \( R_1^2 \) obtained from the pseudo-first-order model of four bio-adsorbents was relatively low, while the linear correlation coefficient \( R_2^2 \) of pseudo-second-order model was higher (\( R > 0.990 \)), indicating that the pseudo-second-order model could describe the adsorption data of bio-adsorbents, consistent with other reports (Tan et al. 2020; Xue et al. 2020). This also showed that chemical adsorption played a dominant role in the adsorption process of heavy metal \( Cu^{2+} \) on LR-NaOH, LR-Na2CO3 and LR-CA.

Adsorption isotherm
In order to clear the adsorption mechanism, Langmuir (Equation (4)) and Freundlich (Equation (5)) isotherm adsorption model was used to analyze experimental data, and its linear equation was shown in the formula:

### Table 1 | Pseudo-first-order and pseudo-second-order parameters

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>( q_{e,exp} ) (mg/g)</th>
<th>( q_{e,cal} ) (mg/g)</th>
<th>( k_1 ) (min(^{-1}))</th>
<th>( R_1^2 )</th>
<th>( q_{e,exp} ) (mg/g)</th>
<th>( k_2 ) (g/mg·min(^{-1}))</th>
<th>( R_2^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>LR</td>
<td>21.7</td>
<td>11.83</td>
<td>5.77 × 10(^{-2})</td>
<td>0.909</td>
<td>23.01</td>
<td>7.16 × 10(^{-3})</td>
<td>0.997</td>
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<tr>
<td>LR-NaOH</td>
<td>43.65</td>
<td>12.78</td>
<td>2.47 × 10(^{-2})</td>
<td>0.527</td>
<td>44.34</td>
<td>3.98 × 10(^{-3})</td>
<td>0.992</td>
</tr>
<tr>
<td>LR-Na2CO3</td>
<td>43.49</td>
<td>9.25</td>
<td>3.21 × 10(^{-2})</td>
<td>0.648</td>
<td>45.49</td>
<td>4.37 × 10(^{-3})</td>
<td>0.995</td>
</tr>
<tr>
<td>LR-CA</td>
<td>33.55</td>
<td>4.64</td>
<td>2.55 × 10(^{-2})</td>
<td>0.564</td>
<td>28.46</td>
<td>1.07 × 10(^{-2})</td>
<td>0.991</td>
</tr>
</tbody>
</table>
Langmuir isothermal model:

\[
\frac{C_e}{q_e} = \frac{C_e}{Q_m} + \frac{1}{Q_m K_L}
\]

(4)

Freundlich isothermal model:

\[
\log q_e = \log K_F + \frac{1}{n} \log C_e
\]

(5)

where, \( C_e \) (mg/L) and \( q_e \) (mg/g) are the equilibrium adsorption concentration and equilibrium adsorption amount, respectively. \( Q_m \) (mg/g) referred to the maximum adsorption capacity, \( K_L \) and \( K_F \) the isothermal constants of the Langmuir isotherm and Freundlich isotherm, respectively, and \( n \) (no dimension) the constant for describing the adsorption strength. The results are shown in Table 2.

The fitting constant obtained by the Langmuir isothermal model was closer to 1, so the Langmuir isothermal model could better describe the adsorption data. This showed that the adsorption of heavy metal ions on the adsorbent was a single-layer adsorption, and that this adsorption process was a chemical adsorption process. According to the Langmuir adsorption isotherm, the saturated adsorption capacities of LR, LR-NaOH, LR-Na2CO3 and LR-CA for \( \text{Cu}^{2+} \) were 24.41, 59.38, 53.82 and 33.89 mg/g, respectively, showing the sodium hydroxide modified licorice residue has the best adsorption effect on \( \text{Cu}^{2+} \) in wastewater.

A comparison among the \( q_{\text{max}} \) values obtained in the present study with various celluloses as bio-adsorbents for removal of \( \text{Cu}^{2+} \) reported in the literature is illustrated in Table 3. The results showed that the adsorption capacity of LR-NaOH and LR-Na2CO3 was higher than for other bio-adsorbents (such as modified sawdust cellulose, and activated carbon fibers).

A possible reason for better performance of LR is that the alkali might severely destroy the LR structure, which made the structure of LR-NaOH, LR-Na2CO3 looser, and the adsorption sites of cellulose were increased, so the performance of modified LR had improved.

### Table 2 | Isotherm parameters for two isotherm models

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Langmuir model</th>
<th>Freundlich model</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>( q_{\text{max}} ) (mg/g)</td>
<td>( K_L ) (L/mg)</td>
</tr>
<tr>
<td>LR</td>
<td>24.41</td>
<td>6.49 \times 10^{-2}</td>
</tr>
<tr>
<td>LR-NaOH</td>
<td>59.38</td>
<td>2.02 \times 10^{-2}</td>
</tr>
<tr>
<td>LR-Na2CO3</td>
<td>53.82</td>
<td>3.15 \times 10^{-2}</td>
</tr>
<tr>
<td>LR-CA</td>
<td>33.89</td>
<td>3.87 \times 10^{-2}</td>
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</table>

### Table 3 | Comparison of Cu(II) adsorption for various bio-adsorbents

<table>
<thead>
<tr>
<th>Biosorbent</th>
<th>Iron</th>
<th>( q_{\text{max}} ) (mg/g)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>LR-NaOH</td>
<td>Cu(II)</td>
<td>43.65</td>
<td>present study</td>
</tr>
<tr>
<td>Coffee residues</td>
<td></td>
<td>9.91</td>
<td>Wu et al. (2015)</td>
</tr>
<tr>
<td>Modified Sawdust Cellulose</td>
<td></td>
<td>4.33</td>
<td>Ulfa et al. (2019)</td>
</tr>
<tr>
<td>Activated carbon fibers</td>
<td></td>
<td>25.51</td>
<td>Yu et al. (2019)</td>
</tr>
<tr>
<td>LR-Na2CO3</td>
<td></td>
<td>43.55</td>
<td>present study</td>
</tr>
</tbody>
</table>
The reusability of bio-adsorbents

LR-NaOH, the best bio-adsorbent for Cu\(^{2+}\) in our experiment, was selected to study the adsorption and desorption conditions. The regeneration and reusability of LR-NaOH for the heavy metal Cu\(^{2+}\) were evaluated by five consecutive adsorption–desorption cycles (Figure 9). It showed that LR-NaOH has good reusability for Cu\(^{2+}\); the adsorbability remained higher than 74% after five consecutive adsorption–desorption cycles, consistent with other reports (Shi et al. 2020; Tan et al. 2020; Maaloul et al. 2021), which indicated that the LR-NaOH is a suitable potential adsorbent for the removal of the heavy metal ion Cu\(^{2+}\) from water.

CONCLUSION

In this paper, the bio-adsorbents were prepared by chemical modification from the Licorice Residue, and the performance of bio-adsorbents for removal of Cu\(^{2+}\) from aqueous solution was improved. By comparing the adsorption capacity of a series of bio-adsorbents, the results were as follows: LR-NaOH > LR-Na\(_2\)CO\(_3\) > LR-CA. The adsorption process of Cu\(^{2+}\) by the adsorbent complies with the pseudo-second-order model and Langmuir model. The best bio-adsorbent was LR-NaOH and its adsorption capacity dramatically reached up to 43.65 mg/g. The adsorption equilibrium for Cu\(^{2+}\) was reached in 75 min. After four consecutive adsorption–desorption cycles, the bio-adsorbent remained stable at about 73% of its original adsorption capacity. In conclusion, the preparation of adsorbent modified by NaOH with Licorice Residue can not only improve the adsorption performance, but also alleviate the environmental pollution caused by the unreasonable utilization of the residue, and improve the resource utilization of the Licorice Residue.

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DATA AVAILABILITY STATEMENT

All relevant data are available from an online repository or repositories: https://doi.org/10.2166/wst.2021.463.

REFERENCES


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