Removal of heavy metal ions from aqueous solution using biotransformed lignite as a low-cost adsorbent

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Abstract

Heavy metal pollution caused by industrial wastewater such as mining and metallurgical wastewater is a major global concern. Therefore, this study used modified lignite as a low-cost adsorbent for heavy metal ions. Pingzhuang lignite was dissolved and modified using *Fusarium lignite* B3 to prepare a biotransformed-lignite adsorbent (BLA). The O, H, and N contents of the BLA increased after transformation, and the specific surface area increased from 1.81 to 5.66 m$^2$·g$^{-1}$. Various adsorption properties were investigated using an aqueous solution of Cu(II). The kinetic and isothermal data were well fitted by pseudo-second-order and Langmuir models, respectively. The Langmuir model showed that the theoretical Cu(II) adsorption capacity was 71.47 mg·g$^{-1}$. Moreover, large particles and a neutral pH were favorable for the adsorption of heavy metal ions. The adsorption capacities of raw lignite and BLA were compared for various ions. Microbial transformation greatly improved the adsorption capacity, and the BLA had good adsorption and passivation effects with Cu(II), Mn(II), Cd(II), and Hg(II). Investigation of the structural properties showed that the porosity and specific surface area increased after biotransformation, and there were more active groups such as $-\text{COOH}$, $\text{Ar}–\text{OH}$, and $\text{R}–\text{OH}$, which were involved in the adsorption performance.

1. Introduction

Industrialization is accompanied by activities such as refining, mining, smelting, and agriculture that can contaminate the surrounding soil and water with heavy metals (Wang et al. 2019; Charvalas et al. 2021). In China, there are approximately 12 000 mine tailings that store wastewater and residue from industrial processes, and they can easily pollute the surrounding environment (Mohan et al. 2006; Ali et al. 2017; Munir et al. 2021). Moreover, unlike organic pollutants, heavy metals are not degraded by microorganisms, and they accumulate step by step in organisms along the food chain (Ezeokonkwo et al. 2008). Therefore, it is necessary to remove low concentrations of heavy metals from wastewater before it is discharged to satisfy discharge standards (Jochova et al. 2004). If wastewater is insufficiently treated or discharged without treatment, then it poses a significant threat to our living environment and health.

Conventional heavy metal wastewater treatment technologies include ion exchange, reverse osmosis, adsorption, chemical precipitation, membrane filtration, and electrodialysis (Doskoil et al. 2012; Ruan et al. 2022; Ramrakhiani et al. 2022). However, these methods have disadvantages such as high processing costs and technical complexity, and there is a risk of secondary pollution. Therefore, new methods have been developed for the treatment of wastewater polluted by heavy metals. Among these methods, modified lignite is considered to be a simple, effective, and economic approach, hence this technology has attracted considerable research attention (Pentari et al. 2019).

Lignite is the youngest type of coal and the degree of coalification is between that of peat and bituminous coal. It is brownish black in appearance and has strong reactivity (Pehlivan et al. 2006). Moreover, it contains many active groups, such as carboxyl ($-\text{COOH}$), alcoholic ($-\text{OH}$), hydroxy-phenolic ($\text{Ar}–\text{OH}$), aldehyde ($-\text{CHO}$), and carbonyl ($=\text{C}–\text{O}$) groups (Murakami et al. 2001; Jochova et al. 2004;
Yuliani et al. 2012; Havelcova et al. 2019), has a large cation exchange capacity, large specific surface area, and high chemical and biological stability. Thus, it can effectively reduce the migration and bioavailability of heavy metals in soil and industrial wastewater (Allen et al. 1995).

In recent years, various studies have investigated the mechanisms by which lignite adsorbs metal ions and a variety of theories have been proposed including complex chelation, covalent adsorption, ion-exchange, surface adsorption, and chemisorption (Pehlivan et al. 2007; Munir et al. 2020; Ruan et al. 2022). In particular, chelation and ion exchange are most widely accepted. The adsorption capacity of raw lignite for heavy metal ions is weaker than that of synthetic ion-exchange materials, which greatly limits its application in water treatment and soil remediation. However, the use of lignite for the adsorption of heavy metal ions remains of interest owing to its low cost (Karabulut et al. 2000; Uçurum et al. 2009; Milicevic et al. 2012). In recent years, various treatment technologies have been used to modify lignite to improve its porosity, active functional group content, and stability (Miao et al. 2021; Sakthivel et al. 2021; Liu et al. 2022). Thus, modified lignite has proven to be valuable in pollution control processes such as the removal of heavy metal ions and organic pollutants (Doskoil et al. 2012; Zhang et al. 2019; Bekisssa et al. 2021).

Existing literature shows that the adsorption capacity of raw lignite is very low. Therefore, this work aims to improve the ability of lignite to adsorb heavy metals via microbial depolymerization. This is achieved by converting low-cost Pingzhuang lignite from Inner Mongolia into a lignite-based adsorbent with greater adsorption capacity, higher porosity, and more active groups. Then the modified lignite is used to adsorb and remove a mixture of heavy metal ions such as Cu(II), Mn(II), Cd(II), and Hg(II) from an aqueous solution. This shows that the treated lignite is an excellent adsorbent for heavy metal ions.

2. Materials And Methods

2.1. Material, chemicals, and equipment

Pingzhuang lignite was mined from Yuanbaoshan Mining area, Chifeng City, Inner Mongolia, China. The lignite was dried at 80°C in a vacuum oven for 24 h, crushed, then shaken through a 60-mesh screen to obtain a lignite sample with a grain size of less than 0.5 mm. The lignite sample was packed in a flask and sterilized at 121°C for 20 min and then left to stand. The chemicals CuSO$_4$·5H$_2$O, HgCl$_2$, MnCl$_2$·4H$_2$O, and Cd(NO$_3$)$_2$·4H$_2$O were purchased from Merck & Co., Germany. All the solutions were prepared with double distilled water and different concentrations were prepared according to the adsorption experiments. All other chemicals were of analytical grade and were used as received. Solution pH was adjusted using 1 mol·L$^{-1}$ HCl or NaOH.

The fungus strain used in this study was isolated from Inner Mongolian lignite in our laboratory. The DNA was extracted and amplified with the primers ITS1 (50- TCCGTAGGTGAACCTGCGG-30) and ITS4 (50- TCCTCCTTATTGATATGC-30). The polymerase chain reaction (PCR) product was analyzed using the advanced 3730XL analysis system and the strain was genetically identified by Meiji Biological Co., Ltd.
(Shanghai, China). The GenBank® accession number was KJ767072.1 and according to the identification report it belonged to the species *Fusarium proliferatum* and the strain was *Fusarium lignite* B3. Notably, it showed an outstanding ability to degrade lignite. The *Fusarium lignite* B3 was preserved in glycerol medium at -20°C in a refrigerator. Before the lignite biosolubilization experiments, it was reactivated and purified in potato dextrose agar (PDA) media (obtained by washing, peeling, and chopping 200 g of potatoes, adding 1L of deionized water, boiling for 30 min, filtering through gauze, and adding 20 g of glucose and 15 g of agar; the natural pH was used) at 28°C three times (Akimbekov et al. 2020; Sezen et al. 2020; Kang et al. 2021).

The equipment included a pH meter (EL-20, Mettler Toledo), elemental analyzer (2400, Perkin Elmer), fourier-transform infrared spectrometer (FTIR; Spectrum 3, Perkin Elmer), atomic absorption spectrometer (AAnalyst 800, Perkin Elmer), scanning electron microscope (SEM; GAIA3, Tescan), surface area apparatus (ASAP-2460, Micromeritics), high-speed centrifuge (Multifuge X1R, Thermo), ventilated stirring fermentation system (GS8000-5L/A, Guangshi), constant temperature oscillator, electronic weighing balance, and vacuum drying oven.

### 2.2. Preparation of biotransformed-lignite adsorbents (BLAs)

Lignite biomodification was conducted under aerobic conditions using a liquid PDA medium and *Fusarium lignite* B3. To amplify the *Fusarium lignite* B3 culture, it was used to inoculate a 5.0 L ventilated stirring fermenter containing 3.5 L of PDA media without agar. A temperature of 28°C, sterile-air ventilation flow rate of 150 mL·min$^{-1}$, and stirring rate of 200 rpm were maintained for 48 h. Then, 100 g of lignite was added to the fermenter under aseptic conditions, and the fermentation state was maintained for an additional 10 d. The dissolved products and BLA were separated by centrifugation at 4500 rpm for 20 min. The BLA was washed with deionized water three times, then dried at 80°C. The surface of the dried BLA was characterized to investigate the heavy metal ion adsorption capacity of lignite. It should be noted that the dissolved products can be used to separate useful chemicals; however, this is not described in this work.

### 2.3. Adsorption experiments

All the adsorption experiments of heavy metal ions by lignite were carried out using a batch technique at ambient temperature in an aqueous solution. Three parallel experiments were performed for each adsorption experiment.

The main experimental methods used in this study were as follows. First, 0.5 g of BLA and 100 mL of heavy metal liquid with a known concentration were added to a 250 mL glass flask. Then, the adsorption experiment was conducted in a constant temperature oscillator with an oscillation frequency of 180–200 rpm to keep the lignite particles suspended in solution. Once the adsorption was complete, the solid-liquid separation was carried out with a 0.45 µm cellulose acetate filter. The residual heavy metal ions in the solution was determined by via atomic absorption spectrometry. The adsorptions of different heavy
metal ions in solution were recorded at different emission wavelengths using suitable hollow cathode lamps. The characteristic absorption wavelengths were 324.8, 279.5, 253.7, and 228.8 nm for Cu(II), Mn(II), Hg(II), and Cd(II), respectively. The adsorption of heavy metal ions by the lignite samples was measured according to the change in the content of heavy metal ions in the solution before and after equilibrium adsorption (Pehlivan et al. 2007; Havelcova et al. 2009; Jellali et al. 2021).

The effects of different experimental conditions on the adsorption performance were analyzed. (I) The performance of raw lignite and BLA were compared. (II) The effect of particle size was investigated using BLA ground to < 850, 850–425, 425–250, 250–150, and > 150 µm. (III) Contact times between 0 and 180 min were tested. (IV) The effect of heavy metal ions concentration was determined by varying the concentration of the initial solution from 50 to 1000 mg·L$^{-1}$. (V) Finally, the effect of the pH of the initial aqueous solution was tested over the range 2.0–6.0 using 0.1 mol·L$^{-1}$ HCl and 0.1 mol·L$^{-1}$ NaOH (Pehlivan et al. 2007; Ezeokonkwo et al. 2008; Jellali et al. 2021).

2.4. Adsorption kinetics and isotherm model

2.4.1 Determination of the adsorption kinetics

To evaluate the adsorption kinetics of BLA for heavy metal ions, the first-order reaction kinetic and pseudo-second-order reaction-rate models were used to fit the adsorption data over time (Ho. 2004; Hameed et al. 2008; Du et al. 2009; Bekissa et al. 2021). In recent years, the first-order reaction kinetic model has frequently been used to evaluate the adsorption of pollutants in wastewater. It is given by the equation

$$\frac{dq_t}{dt} = k_1(q_e - q_t)$$

1

where $q_e$ (mg·g$^{-1}$) is the adsorption amount of heavy metals at equilibrium, $q_t$ (mg·g$^{-1}$) is the adsorption amount of heavy metals at any time $t$ (min), $K_1$ (min$^{-1}$) is the equilibrium rate constant for the kinetic model.

Integrating Eq. (1) with the boundary conditions of $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_e$ yields the Eq. (2) (Beksissa et al. 2021):

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t$$

2
The pseudo-second-order kinetics can be described as:

\[ \frac{dq_t}{dt} = k_2(q_e - q_t)^2 \]

In the pseudo-second-order reaction-rate model, the kinetics process of the adsorption reaction is fitted by the amount of heavy metal ion adsorbate on the surface of the adsorbent at time \( t \) and equilibrium, and the adsorption rate is proportional to the number of active centers and porosity on the surface of the adsorbent (Hameed et al. 2008; Beksissa et al. 2021). Integrating Eq. (3) for the boundary conditions adsorption time \( t \) from 0 to \( t \) and adsorption amount \( q_t \) from 0 to \( q_t \). Final Eq. (3) can be rearranged to get:

\[ \frac{t}{q_t} = \frac{1}{q_e} t + \frac{1}{k_2q_e^2} \]

where \( q_t \) (mg·g\(^{-1}\)) is the amount of adsorbate on the adsorbent at any time \( t \) (min) and \( q_e \) (mg·g\(^{-1}\)) is the equilibrium adsorption capacity. \( k_2 \) (g·mg\(^{-1}\)·min\(^{-1}\)) is the rate constant of adsorption, which can be determined from the slope and intercept of a plot of \( t/q_t \) against \( t \) in experimental data (Hameed et al. 2008).

### 2.4.2 Determination of the adsorption isotherm

The adsorption isotherm was usually used to study some adsorption characteristics of adsorbents, such as adsorption specific surface area, pore volume and pore size distribution. It also provided information about the interaction mechanisms between the bimodified lignite adsorbent and heavy metal ions in the adsorption equilibrium process. In this part, the Langmuir and Freundlich isothermal models were used to describe the experimental results for the adsorption characteristics of Cu(II) by the BLA (Oguz et al. 2005; Ho. 2006; Hameed et al. 2008; Beksissa et al. 2021). The Langmuir model assumes that the adsorption groups are uniformly distributed on the surface of the adsorbent, that only one layer of solute molecules is adsorbed on the surface of the adsorbent, and that the adsorption is irreversible. Moreover, the maximum adsorption capacity occurs when the monolayer is saturated. In this study, the Langmuir model reflected that the adsorption of monolayer Cu(II) occurred on the homogeneous surface of the BLA sample and that the mixed heavy metal ions did not interact with each other during adsorption (Hameed et al. 2008). The Langmuir model is described linearly as Eq. (5)

\[ \frac{C_e}{Q_e} = \frac{1}{Q_mK_L} + \frac{C_e}{Q_m} \]
where $Q_m$ and $K_L$ denote the Langmuir constants, that is, the saturated monolayer adsorption capacity and the adsorption equilibrium constant, respectively. Moreover, $Q_e$ is the amount of Cu(II) adsorbed at equilibrium and $C_e$ is the concentration of Cu(II) adsorption equilibrium solution (Beksissa et al. 2021; Ho. 2004).

The characteristics of the Langmuir constants can also be used to express the affinity between the solutes (Cu(II)) and adsorbent (BLA) in terms of a dimensionless separation factor of equilibrium $R_L$. This is given by

$$R_L = \frac{1}{1 + K_L C_0}$$

where $C_0$ is the initial concentration of solute Cu(II). The $R_L$ criteria are listed in Table 1.

<table>
<thead>
<tr>
<th>Separation factor $R_L$</th>
<th>Adsorption characteristics of adsorbent</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_L &gt; 1$</td>
<td>Unfavorable adsorption</td>
</tr>
<tr>
<td>$R_L = 1$</td>
<td>Linear adsorption</td>
</tr>
<tr>
<td>$0 &lt; R_L &lt; 1$</td>
<td>Favorable adsorption</td>
</tr>
<tr>
<td>$R_L = 0$</td>
<td>Irreversible adsorption</td>
</tr>
</tbody>
</table>

The Freundlich isotherm model is an empirical model based on the assumption that adsorption occurs on heterogeneous surfaces and that the active adsorption sites have heterogeneous surface energy (Beksissa et al. 2021; Ho. 2006). Moreover, it assumes that the adsorption capacity is related to the concentration of Cu(II) at equilibrium. The model is expressed linearly as

$$\ln q_e = \ln K + \frac{1}{n} \ln C_e$$

where $K$ is an approximate indicator of the adsorption capacity and $1/n$ is the adsorption intensity.

**2.5. Characterization techniques**
FTIR spectroscopy (Perkin Elmer Spectrum 3, Perkin-Elmer Company, USA) was used to assess the functional groups present in raw lignite and BLA before and after adsorption. After drying, the lignite samples and KBr were ground into powders (diameter < 2 µm). The lignite power and KBr were mixed with a ratio of 1:200 (w:w) and then pressed into sheets using a tableting machine. Finally, the pressed sheets were scanned using light with wavelengths of $4000–550 \text{ cm}^{-1}$ and a resolution of $1 \text{ cm}^{-1}$. Each sample was scanned 32 times (Shi et al. 2016; Li et al. 2018; Li et al. 2020).

The differences in the surface morphology of the BLA before and after microbial modification and the adsorption of heavy metal ions were investigated via SEM/EDS. The samples were washed with anhydrous ethanol and dispersed, fixed on a conductive adhesive surface, naturally air-dried, and then characterized using field-emission SEM/EDS (FE-SEM; Tescan GAIA3, Tescan company, USA) (Niu et al. 2018). The elemental composition of the lignite samples was investigated using an element analyzer (PE PerkinElmer 2400; Perkin-Elmer Company, USA).

3. Results And Discussion

3.1. Evaluation of proximate analysis result of lignite samples

Table 2 shows that the chemical composition of the BLA was significantly different from that of raw lignite. After microbial treatment, the oxygen, hydrogen, and nitrogen contents increased from 20.43%, 4.87%, and 1.46–25.74%, 6.23%, and 1.97%, respectively. The oxygen, hydrogen, and nitrogen contents of the BLA are important factors in its ability to adsorb heavy metal ions. By contrast, after microbial treatment, the carbon and sulfur contents decreased. Moreover, the volatile matter and moisture contents decreased significantly, which improved the stability of the adsorbent (Beksissa et al. 2021). The Brunauer–Emmett–Teller (BET) surface area ($\text{m}^2 \cdot \text{g}^{-1}$) increased by a factor of more than three after treatment, from 1.81 to 5.66 $\text{m}^2 \cdot \text{g}^{-1}$, and a higher BET surface area is associated with a greater number of active groups that can react with heavy metal ions.
### Table 2
Basic characteristic of the lignite samples.

<table>
<thead>
<tr>
<th>Chemical properties</th>
<th>Experimental results</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Raw lignite</td>
</tr>
<tr>
<td>C (%)&lt;sub&gt;a&lt;/sub&gt;</td>
<td>72.32 ± 1.36</td>
</tr>
<tr>
<td>H (%)&lt;sub&gt;a&lt;/sub&gt;</td>
<td>4.87 ± 0.46</td>
</tr>
<tr>
<td>O *(%)&lt;sub&gt;a&lt;/sub&gt;</td>
<td>20.43 ± 0.32</td>
</tr>
<tr>
<td>N (%)&lt;sub&gt;a&lt;/sub&gt;</td>
<td>1.46 ± 0.15</td>
</tr>
<tr>
<td>S (%)&lt;sub&gt;a&lt;/sub&gt;</td>
<td>0.92 ± 0.08</td>
</tr>
<tr>
<td>M&lt;sub&gt;ad&lt;/sub&gt; (%)</td>
<td>11.63 ± 0.93</td>
</tr>
<tr>
<td>A&lt;sub&gt;ad&lt;/sub&gt; (%)</td>
<td>15.41 ± 0.54</td>
</tr>
<tr>
<td>V&lt;sub&gt;ad&lt;/sub&gt; (%)</td>
<td>38.77 ± 1.27</td>
</tr>
<tr>
<td>FC&lt;sub&gt;ad&lt;/sub&gt;* (%)</td>
<td>34.19 ± 0.69</td>
</tr>
<tr>
<td>BET(m&lt;sup&gt;2&lt;/sup&gt;·g&lt;sup&gt;-1&lt;/sup&gt;)</td>
<td>1.81 ± 0.32</td>
</tr>
</tbody>
</table>

<sup>a</sup> Water- and ash-free (900°C)

*FCad% = 100% - Mad% - Ad% - Vad%

*O% = 100% - C% - H% - N% - S%

## 3.2. Adsorption kinetics of BLA with Cu(II)

### 3.2.1. Adsorption kinetics

To explore the adsorption properties of BLA for heavy metal ions, the removal capacity was investigated for initial Cu(II) concentrations between 50 and 800 mg·L<sup>-1</sup> at pH 6.0, T = 24 ± 1°C. The results are shown in Fig. 1. Then, the first-order reaction kinetic and pseudo-second-order reaction-rate models were used to simulate the adsorption process. The dynamic simulation results are shown in Fig. 2(a, b).

When the initial Cu(II) concentration was 50 mg·L<sup>-1</sup>, the adsorption of Cu(II) by the BLA was complete and reached equilibrium within 120 min. Moreover, the removal rate was 97.1%. When the initial Cu(II) concentration was 150 mg·L<sup>-1</sup>, it took 240 min to reach equilibrium. At initial Cu(II) concentrations of 150, 300, 500, and 800 mg/L, the removal rates after 240 min were 96.1%, 82.3%, 59.0%, and 41.2%, respectively. When the adsorption dose of lignite was constant, the removal rate decreased as the Cu(II) concentration increased. The Cu(II) adsorption rate in the initial 30 min was fast, owing to the availability
of active centers on the BLA that quickly captured the heavy metal ions. The maximum Cu(II) adsorption capacity at equilibrium was approximately 65.0 mg·g\(^{-1}\). The Cu(II) adsorption capacity of the BLA was much higher than that of raw lignite. The maximum adsorption capacity was three times greater than that reported by Jellali et al. for Cd(II) and Cu(II) using raw lignite from the Cap Bon region (northeastern Tunisia) (Jellali et al. 2021). Moreover, it was approximately sixteen times greater than that reported by Milicevic for Cu(II) using low-cost adsorbent Kolubara lignite (Milicevic et al. 2012). However, it was lower than the value reported by Havelcova for Cu(II) using raw lignite (Pehlivan et al. 2007).

The adsorption kinetics were investigated to understand the relationship between the rate at which heavy metal ions were captured and the adsorption capacity of the adsorbent. Furthermore, the microporous diffusion coefficient and adsorption process were analyzed using fitting kinetics (Pentari et al. 2009; Vavouraki et al. 2020). In this study, pseudo-first-order and pseudo-second-order kinetic modeling were used to estimate the rate-determining step during the adsorption of Cu(II) ions by the BLA. Figure 2 shows the evolution of the adsorption capacity over time, and the corresponding fitting-rate constants for each model are listed in Table 3.

The results show that the pseudo-second-order model was most consistent with the experimental data. The \(R^2\) values of the adsorption capacity curves for all the concentrations were between 0.976 and 0.992. The equilibrium adsorption capacities \(Q_e\) of the pseudo-second-order model were 11.5, 27.5, 56.0, 64.4, and 66.3 mg·g\(^{-1}\), which were much closer to the experimental results of 11.48, 27.5, 56.1, 64.5, and 65.0 mg·g\(^{-1}\), respectively, than those obtained from the other model. Thus, the BLA removed heavy metal ions via chemisorption, and the absorption capacity rate depended on diffusion in the adsorbent particles (Kocaoba et al. 2007; Beksisa et al. 2021).

Table 3
Fitting parameters for pseudo-first-order and pseudo-second-order adsorption kinetics for Cu(II) with the BLA.

<table>
<thead>
<tr>
<th>Concentration (mg·L(^{-1}))</th>
<th>(Q_{e\text{exp}}) (mg·g(^{-1}))</th>
<th>(k_1) (min(^{-1}))</th>
<th>(Q_e) (mg·g(^{-1}))</th>
<th>(R_1^2)</th>
<th>(k_2) (g·mg(^{-1})·min(^{-1}))</th>
<th>(Q_e) (mg·g(^{-1}))</th>
<th>(R_2^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>11.48</td>
<td>0.107</td>
<td>11.3</td>
<td>0.950</td>
<td>0.181</td>
<td>11.5</td>
<td>0.991</td>
</tr>
<tr>
<td>150</td>
<td>27.5</td>
<td>0.037</td>
<td>28.2</td>
<td>0.932</td>
<td>0.032</td>
<td>27.5</td>
<td>0.976</td>
</tr>
<tr>
<td>300</td>
<td>56.1</td>
<td>0.033</td>
<td>56.4</td>
<td>0.927</td>
<td>0.013</td>
<td>56.0</td>
<td>0.977</td>
</tr>
<tr>
<td>500</td>
<td>64.5</td>
<td>0.042</td>
<td>61.7</td>
<td>0.981</td>
<td>0.0092</td>
<td>64.4</td>
<td>0.992</td>
</tr>
<tr>
<td>800</td>
<td>65.0</td>
<td>0.025</td>
<td>68.4</td>
<td>0.911</td>
<td>0.0097</td>
<td>66.3</td>
<td>0.982</td>
</tr>
</tbody>
</table>

3.2.2. Adsorption isotherms
To study the thermodynamic adsorption characteristics of the BLA, adsorption isotherm studies were conducted for Cu(II) with ion concentrations range from 20 to 1000 mg·L$^{-1}$. The other conditions were the same as those used to investigate the adsorption kinetics. For these tests, the contact adsorption equilibrium time was set to 240 min, because it was sufficient for the heavy metal ions to reach equilibrium in the kinetics experiments.

The Langmuir and Freundlich isotherm models were used to fit the experimental data of Cu(II) adsorption by the BLA. The results are shown in Fig. 3 and the fitting parameters and fitness of the models are given in Table 4. The determination coefficient $R^2$ of the Langmuir model was 0.95, which was much higher than that of the Freundlich model, which was 0.91. The $R_L$ values of the Langmuir model were between 0.10 and 0.88 ($0 < R_L < 1$). This indicated that monolayer adsorption occurred through chemical bonding, and the adsorption of Cu(II) on the BLA was positive (Hameed et al. 2008; Dada et al. 2012; Jin et al. 2022). Fitted by Langmuir model, the maximum equilibrium adsorption capacity $Q_m$ of Cu(II) was 71.47 mg/g, but the experimental result was 65.0 mg·g$^{-1}$. The $Q_m$ deviation between the experimental result and Langmuir model was 9.9%. In addition, the Freundlich constant $1/n$ for Cu(II) was 0.433, which is between 0 and 1, and the $K$ value was 3.25, which put it in the range of 1–10. This indicates that the adsorption of Cu(II) by the BLA was a favorable process (Dada et al. 2012).

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>Langmuir isotherm</th>
<th>Freundlich isotherm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$Q_m$ (mg·g$^{-1}$)</td>
<td>$K_L$ (L·mg$^{-1}$)</td>
</tr>
<tr>
<td>Cu(II)</td>
<td>71.47</td>
<td>0.00649</td>
</tr>
</tbody>
</table>

### 3.3. Factors affecting adsorption

#### 3.3.1. Effect of particle size distribution on adsorption

It is well known that adsorption is a surface phenomenon of solid adsorbents to surrounding molecules and ions and the particle size distribution of the adsorbent has a substantial effect on the adsorption properties. The effect of the size fraction on the Cu(II) adsorption was investigated under the following experimental conditions: initial Cu(II) concentration 500 mg·L$^{-1}$, pH 6.0, 0.5 g of BLA, 240 min contact adsorption time, and room temperature (24 ± 1°C). Figure 4 shows the relationship between the amount of Cu(II) adsorbed by the BLA and the particle size distribution. As the particle size decreased, the Cu(II) adsorption capacity first decreased and then increased. The greatest adsorption (71.0 mg·g$^{-1}$) was observed at the greatest granulometry (1000 > $\Phi$ > 825 µm). When the particle size distribution was between 150 and 250 µm, the adsorption capacity was lowest (52.6 mg·L$^{-1}$). Furthermore, when the
particle size was less than 150 µm, the adsorption capacity was 65.4 mg·g\(^{-1}\). This may be because after microbial dissolution and transformation the lignite with larger particles had more adsorption pores and a greater pore volume. If the particle size is large, then the pore solution and pore distribution dominate the adsorption process; however, if the particle size is small, then more active sites are exposed and the specific surface area dominates the adsorption process.

### 3.3.2. Effect of pH

Lignite has a high oxygen content there are many hydroxyl and carboxyl groups in its skeleton structure. These groups are the main active groups involved in the adsorption of metal ions onto lignite-derived adsorbents. Changes in the pH of the system will affect the solubility and state of the heavy metal ions, and the surface charge and other chemical properties of the adsorbents (Demirbas et al. 2009; Uçurum et al. 2009; Qi et al. 2011).

Metal cations in aqueous solution form different hydrolysis products, and the cations exist in different forms depending on the solution pH. When the pH is low, copper ions exist as Cu(II), and when the pH is high they exist as Cu(OH)\(^+\) and Cu(OH)\(_2\)\(^{\text{(s)}}\). Therefore, the pH of the experimental solution system was kept between 2 and 6 for this part of the study. In addition, the experiment was conducted with an initial Cu(II) concentration of 500 mg·L\(^{-1}\), 0.5 g of BLA, particle size of < 150 µm, contact time of 240 min, and at room temperature (24 ± 1°C).

The effect of pH on the adsorption efficiency of Cu(II) onto the BLA is shown in Fig. 5. With the increase of pH, the adsorption capacity of Cu(II) increased gradually and reached the maximum at pH of 6. This can be explained by the dissociation degree of surface active groups of the BLA. As the pH value increased, it became easier for Cu(II) to replace the hydrogen ions in the active groups of the BLA, hence the adsorption capacity increased. Similar results have been reported by other authors (Pehlivan et al. 2007; Doskoil et al. 2012; Milicevic et al. 2012).

### 3.4. Adsorption of four heavy metal ions

It is important to understand the adsorption characteristics of transformed lignite adsorbents with different heavy metal ions. Therefore, mixed ionic solutions of Cu(II), Mn(II), Hg(II), and Cd(II) with different concentrations (50 and 150 mg·L\(^{-1}\)) were used to investigate the selective adsorption characteristics of raw lignite and the BLA. The solutions were prepared and left to reach equilibrium for 24 h. Then, 100 mL of the mixed ionic liquid was transferred to a 250 mL glass flask for the adsorption test. A contact time of 120 min was selected, the pH was 6.0, and samples were taken at different times to determine the concentration of the residual heavy metal ions in the solution. The experimental results are shown in Fig. 6.

Comparing the results showed that the adsorption capacity of the BLA was much higher than that of raw lignite. When the raw lignite was used to adsorb a mixture of heavy metal ions from a solution with an
initial concentration of 50 mg·L$^{-1}$, the residual concentrations of Cu(II), Mn(II), Hg(II), and Cd(II) once the solution reached equilibrium were 44.2, 42.2, 43.3, and 46.8 mg·L$^{-1}$, respectively. In comparison, when the BLA was used the residual concentrations were 0.9, 4.0, 2.1, and 6.7 mg·L$^{-1}$, respectively. The average removal rate of the four heavy metal ions achieved using the BLA was 93.4%, which was six times higher than that achieved by raw lignite (15.5%).

When the initial concentration of the mixed heavy metal ions was 150 mg·L$^{-1}$, the maximum adsorption capacity was achieved with a contact reaction time of 240 min. The maximum adsorption capacities of the BLA for Cu(II), Mn(II), Hg(II), and Cd(II) in the mixed solution were 24.4, 16.1, 20.6, and 13.22 mg·g$^{-1}$, respectively. However, the adsorption capacity of raw lignite was less than 5 mg·g$^{-1}$. Thus, the heavy metal ion adsorption capacity and removal ability of lignite was greatly improved by microbial transformation. Furthermore, the experimental results showed that the adsorption capacity of the BLA for the four heavy metal ions followed the order Cu(II) > Hg(II) > Mn(II) > Cd(II). This phenomenon may be related to the electron absorption ability and atomic mass of the different metal cations.

### 3.5. Morphology and composition of the BLA

To explore the mechanisms by which lignite adsorbs heavy metal ions, SEM and energy dispersive X-ray spectroscopy (EDS) were used to characterize the lignite before and after microbial treatment. The surface morphologies of the lignite samples were observed at 700×, 2500×, and 20 000× magnification. The morphologies of raw lignite and the BLA are shown in Fig. 7. The surface of the raw lignite was smooth with few pores and cracks (Fig. 7a₁, a₂, a₃). In contrast, the surface of the BLA was rough with many dissolved pores and attached microbial cells (Fig. 7b₁, b₂, b₃). This explains the increase in the specific surface area. Thus, it may be concluded that during treatment part of the lignite structure is degraded and dissolved by the microorganisms, which forms pores on the surface, increases the specific surface area, and exposes active adsorption groups. This was confirmed by the EDS results, as shown in Fig. 8. The carbon, oxygen, and sulfur contents of raw lignite were 70.23%, 13.25%, and 1.61%, respectively. After microbial treatment, these values were 55.54%, 31.89%, and 0.73%, respectively. Thus, the microbial action reduced the carbon and sulfur content substantially and increased the oxygen content. This increase in the degree of oxidation may increase the number of oxygen-containing active groups, such as carboxyl, hydroxy–phenolic, and carbonyl groups, on the surface, thus increasing the heavy metal ion adsorption capacity and ion exchange ability.

### 3.6. FTIR analysis

To investigate the mechanism by which the BLA adsorbed heavy metal ions, FTIR analysis was conducted before and after Cu(II) adsorption. To facilitate an understanding of the effect that microbial transformation had on the adsorption of heavy metal ions, raw lignite was also analyzed. All the FTIR results are shown in Fig. 9.
Hydroxyl and carboxyl groups constitute important active centers for adsorption in lignite. Comparing the FTIR spectrums of raw lignite and the BLA shows that the absorption peaks of the active functional groups changed substantially. The sharp peaks at 3680 and 3627 cm\(^{-1}\) were associated with phenols or alcohols and O-H stretching vibrations. The wide absorption peak at 3240 cm\(^{-1}\) and the sharp peaks at 1583, 1550, 1440, and 1360 cm\(^{-1}\) were associated with carboxylic groups, O-H, and C=O stretching vibrations (Ezeokonkwo et al. 2008; Shi et al. 2016). There were also absorption peaks at 1270, 1160, 1090, and 1030 cm\(^{-1}\) in the lignite, which can be attributed to the presence of C–O, ester of alcohols, carboxylic acid groups, and carboxylic acids (Samsuri et al. 2014; Dong et al. 2020). The absorption peaks at 1000–650 cm\(^{-1}\) were associated with C–H bending vibrations of the ortho- and meta-substituted aromatics (Ezeokonkwo et al. 2008). After microbial transformation, the intensity of the absorption peaks associated with carboxylic groups, alcohols, and phenolic hydroxyl groups (Ar-OH and R-OH) increased significantly. Moreover, the absorption peaks of the functional groups moved to lower wavenumbers. Thus, after microbial treatment, more active adsorption sites were exposed and more intermolecular hydrogen bonds were formed, which was favorable for the adsorption of metal ions. Analyses of the FTIR spectra of BLA + Cu(II) revealed sharp peaks between 1600 and 1000 cm\(^{-1}\), and the wide absorption peak at 3240 cm\(^{-1}\) decreased considerably compared to the peak before adsorption. This may be because the functional groups were involved in the adsorption of heavy metal ions. This indicates that heavy metal ions were chemically adsorbed by the BLA (Yang et al. 2018; Wang et al. 2021).

4. Conclusion

Biotransformed lignite was investigated as a potential adsorption passivator for the removal of heavy metal ions from an aqueous solution. Raw lignite was modified using *Fusarium lignite* B3, which successfully improved its physical and chemical properties, and its ability to adsorb heavy metal ions. This was attributed to increases in the pore size, specific surface area, and the number of active adsorption groups, such as carboxyl and phenolic hydroxyl groups. A heavy metal adsorption experiment proved that the BLA had good adsorption effects with Cu(II), Hg(II), Mn(II), and Cd(II), and the adsorption capacity was Cu(II) > Hg(II) > Mn(II) > Cd(II). The adsorption equilibrium time was 120 min and the maximum adsorption capacity for Cu(II) was 65 mg·g\(^{-1}\). The adsorption kinetics and FTIR analysis demonstrated that chemisorption occurred between the BLA and heavy metal ions. The adsorption data were better fitted by the Freundlich model adsorption isotherm than the Langmuir isotherm model. The second-order kinetic models provided the best fit for the rate of Cu(II) adsorption onto the BLA. This work proposed an innovative method of fabricating low-cost adsorbents from lignite, and the microbiological method requires mild conditions that are relatively green compared to other techniques.

**Declarations**

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Data availability Data will be made available on request.

References


Figures
Figure 1

Adsorption effect of BLA for Cu(II) with different initial concentrations. The experiments were conducted with BLA = 0.5 g, pH = 6.0 ± 0.2, and T = 24 ± 1 °C.
Figure 2

Kinetics of Cu(II) removal by the BLA. Fitting with (a) the first-order reaction kinetic model and (b) the pseudo-second-order reaction-rate model.
Figure 3

Adsorption isotherms for the Langmuir and Freundlich adsorption models. The fitted models are shown in comparison to the experimental data.
Figure 4

Effect of BLA particle size on Cu(II) removal efficiency. The experiments were conducted with $C_0 = 500$ mg/L, BLA = 0.5 g, $t = 240$ min, pH = 6 and $T = 24 \pm 2$ °C.
Figure 5

Effect of solution pH on Cu(II) adsorption using BLA. The experiments were conducted with $C_0 = 500$ mg/L, BLA = 0.5 g; $t = 240$ min, $T = 24 \pm 2$ °C, and particle size < 150 μm.
Figure 6

Comparison of heavy metal adsorption characteristics of raw lignite and the BLA. Adsorption with an initial concentration of 50 mg·L\(^{-1}\) for (a) raw lignite and (b) the BLA. Adsorption with an initial concentration of 150 mg·L\(^{-1}\) for (c) raw lignite and (d) the BLA.
Figure 7

SEM images of raw lignite and the BLA. SEM images of (a₁, a₂, a₃) raw lignite and (b₁, b₂, b₃) the BLA.
Figure 8

**EDS characterization before and after microbial treatment.** EDS results for (a) raw lignite and (b) the BLA.
Figure 9

**FTIR spectrums of various samples.** FTIR spectrums of raw lignite, the BLA, and the BLA after adsorption of Cu(II).

**Supplementary Files**

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