Biosorption of Cu(II) from Aqueous Solutions by a Macrofungus (Ganoderma lobatum) Biomass and its Biochar

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ABSTRACT
The sorption capacities of the macrofungus viz. Ganoderma lobatum (C0) and its biochar (C400) were evaluated for the biosorption of Cu(II) from aqueous solution under different conditions, including adsorbent doses, pH of the solution, contact time and initial Cu(II) concentration. The results showed that Ganoderma lobatum could be used as an efficient biosorbent for the removal of Cu(II) ions from an aqueous solution. The desired biosorbent dose in the case of C0 and C400 for Cu(II) adsorption was 4 g/L, and the optimal pH value for biosorption was 8 for Cu(II). The Freundlich isotherm model fitted the absorption data of Cu(II) for both C0 and C400 better than the Langmuir isotherm model, and the adsorption capacity of C0 was better than C400. Our results indicate that C0 has a higher removal efficiency than C400 in adsorbing Cu(II) ions from aqueous solution. Biosorption kinetics were also studied using pseudo-first-order and pseudo-second-order models, which showed that the biosorption processes of Cu(II) ions based on C0 and C400 were in accordance with the pseudo-second-order kinetics.

INTRODUCTION
Water pollution by heavy metals at low concentrations is a worldwide environmental problem. Many methods have been widely used to remove these toxic substances (Fomina & Gadd 2014). However, these methods have become less effective because of low metal concentrations (Wang & Chen 2009). Therefore, as an excellent alternative to conventional techniques, biosorption has emerged as the most promising process for treating pollutants in the aquatic environment, especially the removal of low concentrations of heavy metals in the aqueous environment, because of its high efficiency, low cost, and non-hazardous nature (Javaid et al. 2011, Kapoor & Viraraghavan 1995). In recent years, macrofungi have attracted attention as biosorbents. Many studies have confirmed that copper ions in aqueous solutions are effectively adsorbed by the fruit bodies of macrofungi such as Pycnoporus sanguineus (Zulfadhly et al. 2001), Agaricus macrosporus (Melgar et al. 2007), Pleurotus ostreatus (Javaid et al. 2011), Auricularia polytricha (Xinyu et al. 2010), and Auricularia polytricha (Yū et al. 2010). Moreover, macrofungi grow prolifically and are found in many parts of the world (Vimala et al. 2011). They are visible in size, tough in texture, and have other physical characteristics that are conducive to their development as biosorbents without the need for immobilization or deployment of a sophisticated reactor configuration, as in the case of microorganisms (Muraleedharan et al. 1994). The adsorption capacity of macrofungi clearly depends on the species (Nagy et al. 2014). To our knowledge, no reports in the literature have examined the biosorption of heavy metal using the macrofungus Ganoderma lobatum. It is a species of wood-decaying fungi in the family Ganodermataceae (order Polyporales), widely distributed in China, America and Mexico, growing alone or gregariously on decaying logs and stumps of various hardwoods. The cap is flat and up to 20 cm wide, and the flesh of the cap is dark brown to cinnamon-brown, woody.

The aim of the present work was to investigate the biosorption potential of the fruit body of Ganoderma lobatum and its biochar for the removal of Cu(II) from an aqueous solution. Optimum biosorption conditions were determined as a function of the biomass dose, pH, contact time, and initial metal concentration. The Langmuir and Freundlich models were employed to describe equilibrium isotherms. Biosorption mechanisms of Cu(II) onto Ganoderma lobatum and its biochar were also evaluated in terms of kinetics.

MATERIALS AND METHODS
Biosorbent Preparation
The macrofungus Ganoderma lobatum was collected from Mojiang County, Yunnan Province, China. Fruit bodies were
washed 3 times using distilled water, sun-dried for 3 days, and then dried in an oven at 80°C for 48 h. The dried fruit bodies were ground and then filtered through a 2-mm nylon sieve. The dried samples were placed in clean polyethylene sample bags, labelled C0 for future use, and a portion of the dried samples was pyrolyzed in an electrical muffle furnace at 400°C for 4 h under oxygen-limited conditions. After cooling to room temperature, they were filtered through a 2-mm nylon sieve and stored in clean polyethylene sample bags labelled C400 for future experiments.

**Reagents and Equipment**

All chemicals used in this study were of analytical grade, and deionized water was used for all dilutions. A pH meter (Leici, ZD-2) was used to measure pH values in the aqueous phase. Cu(II) concentrations in the aqueous phase were determined by ICP-OES (VISFA-MPX). Fourier Transform Infrared (FT-IR) spectra of C0 and C400 prepared as KBr pellets were recorded in the 400-4000 cm\(^{-1}\) region using a Varian FT-IR 640 spectrometer.

A stock Cu(II) solution of 1000 mg/L was prepared by dissolving 3.8019 g Cu(NO\(_3\))\(_2\)·3H\(_2\)O in 1000 mL of deionized water. The Cu(NO\(_3\))\(_2\)·3H\(_2\)O used in this work was analytical grade and was supplied by Sinopharm Chemical Reagent Co., Ltd. (China). Stock solutions were used to prepare diluted solutions of different working concentrations. HCl (0.1 M) and NaOH (0.1 M) volumetric solutions were used to adjust the solution pH.

**Batch Biosorption Experiments**

The batch biosorption experiments for C0 and C400 were carried out in 150-mL stoppered conical flasks containing 0.2 g of the biosorbent in 50 mL of the Cu(II) solutions (10 mg/L) separately at room temperature on a rotary shaker at 100 rpm. For optimization of the experimental conditions, batch studies were performed for different metal concentrations (10-200 mg/L), pH (3-10), biosorbent doses (0.4-8 g/L), and contact times (10-1440 min). The contents of the flask were filtered, and the residual metal concentration in the filtrates was determined by ICP-OES (VISFA-MPX). Each sample was evaluated three times, and the results are presented as average values.

To evaluate the adsorption capacity of Cu(II) onto C0 and C400, the amount of Cu(II) adsorbed per unit mass of C0 and C400 was calculated using the following equation:

\[
Q_e = \frac{V(C_0 - C_e)}{M}
\]

Where \(Q_e\) (mg/g) is the amount of Cu(II) biosorbed onto the biosorbent at equilibrium, \(C_0\) and \(C_e\) respectively are the initial and equilibrium concentration (mg/L) of Cu(II), \(V\) (L) is the volume of the solution and \(M\) (g) is the biosorbent dose, \(Q_t\) (mg/g) is the amount of Cu(II) biosorbed onto biosorbent at time t (min), and \(C_t\) (mg/L) is the concentration of Cu(II) at time t (min).

\[
R_e = \frac{(C_0 - C_e)}{C_0} \times 100\% \tag{2}
\]

Where \(R_e\) is the ratio between Cu(II) biosorbed at equilibrium and the initial Cu(II) concentration (mg/L).

**RESULTS AND DISCUSSION**

**FT-IR Analysis**

Functional groups, such as carbonyl, carboxyl, and hydroxyl groups, have been identified as potential adsorption sites responsible for binding metallic ions to the adsorbent. The FT-IR spectra of C0 and C400 in the range from 400-4000 cm\(^{-1}\) were determined and are presented in Fig. 1. For the biomass material C0, the broad and strong absorption peaks were observed at 3200-3600 cm\(^{-1}\) and 1600 cm\(^{-1}\), which are attributed to the vibrations of hydroxyl (OH) and carboxyl (C=O) groups, respectively. The peak observed at 2925 cm\(^{-1}\) was attributed to the vibrations of C-H groups. These functional groups were mainly derived from the cellulose, hemicellulose, and lignin of the fungal cell wall, as well as some other kinds of organic components (Dashtban et al. 2009, Pérez et al. 2010, Sağ & & Kutsal 1996).

The effect of the adsorbent dose on the Cu(II) ion removal efficiency is presented in Fig. 2. The adsorbent dose results in aggregates of adsorbent due to interference between binding sites at a higher adsorbent dose or insufficient metal ions in the solution with respect to available binding sites. The removal efficiency increased with an increase in the adsorbent dose up to 4 g/L, after which it remained nearly constant. However, beyond this dose, the increase in removal efficiencies of C0 and C400 were marginal and became nearly constant. Similar results were observed by Fomina & Gadd (2014), who reported that an increase in adsorbent dose results in aggregates of adsorbent due to interference between binding sites at a higher adsorbent dose or insufficient metal ions in the solution with respect to available binding sites.
band at approximately 3200-3600 cm\(^{-1}\) could be attributed to stretching vibrations of hydroxyl groups (−OH). The peak observed at 2925 cm\(^{-1}\) was due to C–H stretching of CH\(_2\) groups. The band at 1639 cm\(^{-1}\) indicated a fingerprint region of C=O, C–O, and O–H groups that exist as functional groups (Wang & Chen 2009). The bands observed at 1074 cm\(^{-1}\) were assigned to C–O stretching of alcohols and carboxylic acids (Fig. 1a) (Fomina & Gadd 2014). For the calcined C400, the absorption bands of various functional groups disappeared, indicating that the organic structure of the fungal biomass had been decomposed at a high temperature (Fig. 1b). As shown in Fig. 1b, the weak bands at approximately 1620 and 849 cm\(^{-1}\) were attributed to the vibrations of C=C and C–C, respectively. FT-IR studies revealed that several functional groups, which can bind transition metal ions including Cu(II), were present in C0. These functional groups were mainly derived from the cellulose, hemicellulose, and lignin of the fungal cell wall, as well as some other kinds of organic components (Dashban et al. 2009, Pérez et al. 2002).

**Effect of the Adsorbent Dose**

The effect of the adsorbent dose on the Cu(II) ion removal efficiency is presented in Fig. 2. The removal efficiencies (%) were found to increase steeply with increasing concentrations of C0 and C400 up to a dose of 4 g/L. The maximum removal efficiencies of C0 and C400 respectively were 97.80% and 96.89% at the adsorbent dose of 4 g/L. However, beyond this dose, the increase in removal efficiencies of C0 and C400 were marginal and became nearly constant. Similar results have been reported for metal ion biosorption in an aqueous solution by oyster mushroom (Pleurotus platypus) (Vimala & Das 2009). Therefore, the optimum adsorbent dose was considered to be 4 g/L for further experiments. The above results can be explained by the finding that the biosorption sites remain unsaturated during the biosorption reaction, whereas the number of sites available for biosorption site increases by increasing the biosorbent dose (Sar & Tuzen 2009b). However, a high adsorbent dose results in aggregates of adsorbent due to interference between binding sites at a higher adsorbent dose or insufficient metal ions in the solution with respect to available binding sites (Rome & Gadd 1987). Moreover, protons might combine with metal ions for ligands and thereby decrease the interaction of metal ions with cell components (Ghorbani et al. 2008, Sağ & Kutsal 1996).

**Effect of pH**

The effect of initial pH on the removal efficiencies of Cu(II) ions onto adsorbent were investigated from pH 3-10 for the initial metal concentration of 10 mg/L Cu(II) solution. The results for the pH effect on the removal efficiencies of Cu(II) are shown in Fig. 3. The removal efficiencies of C0 and C400 for Cu(II) ions increased from 90% to 97% and from 93% to 97%, respectively, as the pH was increased from 3 to 8. The maximum removal efficiencies of 97 % were found at pH 8 for the two adsorbents. Therefore, all the biosorption experiments were carried out at pH 8. Previous researchers have indicated that pH is one of the most important factors affecting the adsorption of heavy metal ions from aqueous solution. This parameter is directly related to the competition ability of hydrogen ions with metal ions for active sites on the biosorbent surface (Senthilkumar et al. 2011, Tsai et al. 2007). Generally, metal biosorption involves complex mechanisms of ion-exchange, chelation, adsorption by physical forces, and ion entrapment in inter and intrafibrillar capillaries and spaces of the cell structural network of a biosorbent (Chojnacka et al. 2005). At low pH values, protons occupy most of the biosorption sites on the biosorbent surface, and fewer copper ions can be absorbed because of the electric repulsion with protons on the biosorbent. When the pH values increase, biosorbent surfaces are more negatively charged, and the biosorption of metal ions (positive charge) increases and reaches equilibrium at pH 8. Decreases in biosorption at higher pH values (> 8) are due to the formation of soluble hydroxylated complexes of the metal ions and their competition with the active sites, resulting in a repeated decrease in retention (Anayurt et al. 2009, Sar & Tuzen 2009a).

The FT-IR spectroscopic analysis showed that the macrofungus (C0) had various functional groups, and these groups were involved in almost all potential binding mechanisms. Moreover, depending on the pH value of the aqueous solution, these functional groups participate in metal ion binding (Sar & Tuzen 2009a).

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**Fig. 2: Effect of the biosorbent dose on Cu(II) removal efficiencies by the macrofungus (Ganoderma lobatum) and its biochar.**
Effect of Contact Time

The effect of contact time on the removal efficiencies of Cu(II) was investigated. The removal efficiencies of Cu(II) by the two biosorbents as a function of time are depicted in Fig. 4. In the case of Cu(II) removal efficiencies by C0 and C400, the removal efficiency reached equilibrium at 480 min, which was chosen as contact time for further experiments. In the initial stages, the removal efficiencies of Cu(II) by C0 and C400 increased rapidly due to the abundant availability of active binding sites on the biosorbents, and with gradual occupancy of these sites, the sorption became less efficient at later stages (Costa & Leite 1991).

The initial concentration of the metal in the solution dramatically influenced the equilibrium uptake of Cu(II). It was noted that the initial concentration increased the sorption of Cu(II), which was generally expected due to the equilibrium process (Fig. 5). This increase in uptake capacity of the biosorbents (C0 and C400) with the increase in initial metal concentrations was due to the higher availability of metal ions (copper) for sorption. Moreover, the higher initial concentration provided increased driving force to overcome all the mass transfer resistance of metal ions between the aqueous and solid phase, resulting in a higher probability of collision between metal ions and sorbents. This phenomenon also results in higher metal uptake (Tewari et al. 2005, Vimala & Das 2009).

Biosorption Isotherm Models

Sorption models are often used to predict the maximum adsorption capacity of the adsorbent. The Langmuir and Freundlich models are the most widely used models for the adsorption of metal ions with biomaterials (Febrianto et al. 2009, Langmuir 1918). The equilibrium adsorption data were analysed according to the Langmuir and Freundlich adsorption isotherm models. The Langmuir model suggests that monolayer sorption on a homogeneous surface occurs without interactions between absorbed molecules. In addition, the model assumes uniform energies of sorption onto the surface and no transmigration of the sorbate (Vimala & Das 2009). The Langmuir model can be written in linear form.

\[
\frac{C_e}{Q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \quad \cdots (3)
\]

Where \( q_m \) (mg/g) is the monolayer biosorption capacity of the adsorbent, and \( K_L \) (L/mg) is the Langmuir sorption
constant related to the free energy of biosorption.

The Freundlich model assumes a heterogeneous sorption surface. The Freundlich model is

\[ \ln Q_e = \frac{1}{n} \ln C_e + \ln K_f \]  \hspace{1cm} (4)

Where, \( K_f \) (mg/g) is a constant relating the biosorption capacity, and \( n \) is an empirical parameter relating to the biosorption intensity, which varies with the heterogeneity of the material.

The linear plots of the Langmuir and Freundlich isotherm models for the sorption of Cu(II) on C0 and C400 are presented in Fig. 6. The linear regression coefficient values (\( R^2 \)) were presented in Table 1, which indicated that the Langmuir model was not able to adequately describe the relationship between the amounts of Cu(II) adsorbed by the adsorbent and its equilibrium concentration in solution. However, the Freundlich isotherm model exhibited a better fit to the sorption data of Cu(II) for both C0 and C400 than the Langmuir isotherm model, since it provided higher \( R^2 \) values. Moreover, the \( n \) and \( K_f \) of C0 for Cu(II) biosorption were higher than for C400. This result indicated that C0 had greater removal efficiencies for Cu(II) than C400. It is likely that the functional groups of C400 were destroyed during the carbonization process. A comparison of the adsorption capacity of this biosorbent with those of different biosorbents reported by other researchers is provided in Table 2, and it can be concluded that the macrofungus as an effective biosorbent may play an important role in the removal of heavy metals from an aqueous environment.

### Biosorption Kinetics

To clarify the biosorption kinetics of Cu(II) ions onto C0 and C400, two kinetic models, the pseudo-first-order and pseudo-second-order model were applied to the experimental data. The linear form of the pseudo-first-order rate equation is given as follows (Senthilkumar et al. 2011):

\[ \ln(\frac{Q_e - Q}{Q_e}) = \ln Q_e - K_1 t, \quad \frac{t}{Q} = \frac{1}{K_1 Q_e^2} + \frac{t}{Q_e} \]  \hspace{1cm} (5)

### Table 1: Isotherm equations and parameters for Cu(II) biosorption by the macrofungus (Ganoderma lobatum) and its biochar.

<table>
<thead>
<tr>
<th>Biosorbent</th>
<th>Langmuir Equation</th>
<th>( q_m )</th>
<th>( K_L )</th>
<th>( R^2 )</th>
<th>Freundlich Equation</th>
<th>( n )</th>
<th>( K_F )</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>C0</td>
<td>( y = 0.0544x + 0.7947 )</td>
<td>18.38</td>
<td>0.0684</td>
<td>0.9697</td>
<td>( y = 0.3345x + 1.2132 )</td>
<td>2.989</td>
<td>3.364</td>
<td>0.9956</td>
</tr>
<tr>
<td>C400</td>
<td>( y = 0.0609x + 1.2912 )</td>
<td>16.42</td>
<td>0.0471</td>
<td>0.9408</td>
<td>( y = 0.3822x + 0.8368 )</td>
<td>2.616</td>
<td>2.308</td>
<td>0.993</td>
</tr>
</tbody>
</table>

### Table 2: Sorption capacity of Cu(II) on different macrofungi.

<table>
<thead>
<tr>
<th>Biosorbent</th>
<th>Adsorption capacity (mg/g)</th>
<th>pH</th>
<th>Metal concentration (mg/L)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ganoderma lobatum</td>
<td>18.38</td>
<td>8</td>
<td>10-160</td>
<td>Present study</td>
</tr>
<tr>
<td>Auricularia polytricha</td>
<td>8.36</td>
<td>5</td>
<td>0-250</td>
<td>(Xinyu et al. 2010)</td>
</tr>
<tr>
<td>Auricularia polytricha</td>
<td>18.69</td>
<td>6.03-6.56</td>
<td>10-100</td>
<td>(Yu et al. 2010)</td>
</tr>
<tr>
<td>Tremella fuciformis</td>
<td>20.15</td>
<td>6.03-6.56</td>
<td>10-100</td>
<td>(Yu et al. 2010)</td>
</tr>
<tr>
<td>Pleurotus ostreatus</td>
<td>8.06</td>
<td>4.5</td>
<td>20-100</td>
<td>(Javaid et al. 2011)</td>
</tr>
</tbody>
</table>

Fig. 6: Linear fitting of the Langmuir (A) and Freundlich (B) isotherms for Cu(II) biosorption of the macrofungus (Ganoderma lobatum) and its biochar.
Table 3: The equations and parameters of pseudo-first and second-order kinetics for Cu(II) biosorption by the macrofungus (Ganoderma lobatum) and its biochar.

<table>
<thead>
<tr>
<th>Biosorbent</th>
<th>First-order kinetics</th>
<th></th>
<th>Second-order kinetics</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Equation</td>
<td>$K_1$</td>
<td>$Q_e$</td>
<td>$R^2$</td>
</tr>
<tr>
<td>C0</td>
<td>$y = -0.0017x + 0.6457$</td>
<td>0.0017</td>
<td>0.5242</td>
<td>0.9398</td>
</tr>
<tr>
<td>C400</td>
<td>$y = -0.0025x + 0.2494$</td>
<td>0.0025</td>
<td>1.2832</td>
<td>0.9641</td>
</tr>
</tbody>
</table>

Where $K_1$ and $K_2$ are the rate constant of the first-order equation (min$^{-1}$) and second-order equation (g/mg min), respectively (Cheung et al. 2001).

The values of the rate constants and correlation coefficients for the two models are shown in Table 3. The biosorption mechanisms of Cu(II) ions onto the C0 and C400 biomass does follow the pseudo-second-order kinetic model (Fig. 7). The $K_2$ value of C0 was significantly higher than C400. This result indicated that the sorption rate of C0 for Cu(II) was greater than C400.

CONCLUSION

The macrofungus as an effective biosorbent of Cu(II) was confirmed. The effects of the biosorbent dose, pH, contact time, and initial copper ion concentration on the removal efficiencies were evaluated. The present results showed that the desired biosorbent dose in the case of Ganoderma lobatum and its biochar for Cu(II) adsorption was 4 g/L, and the pH value for biosorption was found to be 8 for Cu(II). The Freundlich isotherm model exhibited a better fit to the sorption data of Cu(II) for both C0 and C400 than the Langmuir isotherm model. The results indicated that C0 had greater removal efficiencies for Cu(II) than C400. This finding can be interpreted as due to the decomposition of the functional groups of C400 during the carbonization process. Equilibrium data showed that the biosorption of Cu(II) ions onto C0 and C400 effectively followed the pseudo-second-order kinetic model. Further research is in progress to explore the mechanism underlying the biosorption process.

ACKNOWLEDGEMENTS

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REFERENCES


The biosorption mechanisms of Cu(II) ions onto C0 and C400 biomass does follow the pseudo-first-order rate equation. The value of the rate constant of the first-order equation for Cu(II) was greater for C0 than for C400. The values of the rate constants and correlation coefficients for the two models are shown in Table 3. The selective biosorption of Chromium(VI) and Copper(II) ions from binary metal mixtures by R. arrhizus. Process Biochemistry, 31: 561-572.


