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Equilibrium and kinetic studies of copper(II) removal by three species of dead fungal biomasses

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ABSTRACT

The batch experiments were conducted to study the copper(II) removal by formaldehyde inactivated *Cladosporium cladosporioides*, *Gliomastix murorum* and *Bjerkandera* sp., at conditions of agitation speed of 150 rpm, temperature of 25 °C, biosorbent dose of 2 g l^{-1} and contact time of 12 h. It was found that, for each biomass, the optimum pH was 6.0 and the equilibrium establishing time was about 2 h. Without acid or alkali treatment for improving adsorption properties, the experimental maximum copper(II) biosorptions were relatively high: 7.74 mg g^{-1} for *C. cladosporioides*, 9.01 mg g^{-1} for *G. murorum*, and 12.08 mg g^{-1} for *Bjerkandera* sp.. The biosorption data of all the dead fungal biomasses were quite fitted to Langmuir isotherm model and pseudo second-order kinetic model; first-order Lagergren kinetic model gave good adjustment to the data of *Bjerkandera* sp. but did not fit the data of *C. cladosporioides* and *G. murorum* very well. These fungal biomasses exhibited relatively high capacity for the removal of copper(II) from aqueous solutions.

1. Introduction

Environmental contamination by hazardous heavy metals (like copper, lead, zinc and cadmium) has become one serious environmental problem of worldwide concern [1]. There is no time to delay the removal of heavy metals from effluents. Since the 1990s, heavy metal removal by biomaterials has become more and more acceptable [2]. Fungal biomasses are considered to be good biosorbents for heavy metals because of their advantages such as low cost, environmental friendliness, regeneration, performing simplicity and short cycle [1–3]. Many fungi have been studied on their capacities for heavy metal biosorption, for example, *Pleurotus pulmonarius*, *Schizophyllum commune* [4], *Auricularia polytricha* [5], *Phanerochaete chrysosporium* [6], *Aspergillus* spp. [7–9], *Penicillium* spp. [10,11], *Rhizopus arrhizus* [10,12,13] and *Saccharomyces* spp. [14,15].

Researchers have suggested that the two main mechanisms of heavy metal biosorption are: (1) ion exchange reacting with the active chemical groups such as hydroxyl, carbonyl, carboxyl, sulfhydryl, sulfonate, thioether, amine, imine and phosphonate [16–18]; (2) physicochemical inorganic interactions directed by adsorption phenomena [16]. It is noticeable that the former is a critical mechanism [16] for removal of most of the heavy metals, but never for precious metals such as gold and silver [19]. These mechanisms determine the significance of control over the experimental parameters. Several crucial parameters can influence heavy metal biosorption, such as pH, pretreating methods, fungal species, metal species, contact time and initial metal concentration [20,21]. These parameters which provide information about effectiveness of metal-biosorbent system can be obtained from batch experiments.

The literatures [9,16,18] indicate that heavy metal biosorption by fungal biomass follows adsorption isotherm and kinetic equations. Adsorption isotherm models such as Langmuir [4], Freundlich [2], Temkin [23], Redlich–Peterson [24], and kinetic models such as first-order Lagergren [25] and pseudo second-order [26] have been used to simulate heavy metal biosorption processes.

For this biosorption study, filamentous fungi *Cladosporium cladosporioides*, *Gliomastix murorum* and *Bjerkandera* species were selected. The highly porous and meshes structure of the mycelia of filamentous fungi might provide ready access and large surface area for biosorption of metals [15]. Some different strains of melanin-producing *C. cladosporioides* have been confirmed as good biosorbents for removal of many heavy metals [19,27,28] including precious metals gold and silver [19]. In this work, a special strain of *C. cladosporioides* was isolated from an underground river in a gold mine. White-rot fungus *Bjerkandera* sp. has been well researched on its dye-decolorizing property and peroxidase [29,30]. Fewer investigations on filamentous fungus *G. murorum*

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are mostly about taxonomy and metabolites [31,32]. There is no report on heavy metal biosorption by *Bjerkandera* sp. and *G. murorum* as far as we know. The objective of this study was to measure the copper(II) biosorption capacities of these three species of dead fungal biomasses, to evaluate the optimum removal conditions, and to investigate the biosorption equilibrium and kinetics.

2. Materials and methods

2.1. Preparation of the biomasses

The fungal biosorbents used for this study were *C. cladosporioides*, *G. murorum*, and *Bjerkandera* sp.. *C. cladosporioides* and *G. murorum* were isolated from the underground river of Fushan Gold Mine, Zhaoyuan, China; *Bjerkandera* sp. was isolated from the bark of camphor tree (*Cinnamomum camphora*) in campus of Nanjing University, Nanjing, China. The fungi were cultivated in liquid medium composed of malt extract (20.0 g l^{-1}), peptone (1.0 g l^{-1}) and dextrose (20.0 g l^{-1}). The Erlenmeyer flasks (250 ml) containing 100 ml of culture medium were inoculated and incubated on a rotary shaker (150 rpm) at 25 °C. Fungal mycelium was harvested after 7-day incubation and washed several times with deionized water. After being inactivated by immersion into 1% formaldehyde and washed, the mycelium was dried at 60 °C for 24 h and finally ground into particles less than 0.5 mm in diameter. The particles were called dead biomass without acid or alkali treatment.

2.2. Copper(II) biosorption experiments

The copper(II) solutions were prepared by diluting copper(II) stock solution (1 g l^{-1}), which was obtained by dissolving $CuCl_2{\cdot}2H_2O$ (analytical reagent grade, Shanghai Zhenxin Chemical Reagent Factory, China) in deionized water.

For each treatment, 0.2 g dead fungal biomass was added into 100 ml of copper(II) solution in 250 ml Erlenmeyer flask. The flasks were agitated (150 rpm) at 25 °C for 12 h to reach adsorptive equilibrium. The biomasses then were separated by vacuum filtration through 0.45 μm Millipore membranes (Shanghai Xingya Purification Material Factory, China).

Experiments to evaluate the effect of pH on biosorption were conducted at pH 2.5, 3.0, 3.5, 4.0, 4.5, 5.0, 5.5, 6.0, 6.5 and 7.0 (at solution concentration of 100 mg l^{-1}). Experiments to evaluate the effect of initial copper(II) concentration were conducted at 5, 10, 25, 50, 75, 100, 200 and 300 mg l^{-1} (at optimum pH), which were also designed for biosorption isotherm studies (at 25 °C). Batch kinetic experiments were performed at optimum pH and copper(II) concentration of 100 mg l^{-1}, during which samples were harvested at 1/12, 1/6, 1/4, 1/2, 1, 2, 4, 8 and 12 h.

2.3. Measurements

The characteristics of three species of dead fungal biomasses were measured by a Nicolet Nexus 870 Fourier transform infrared (FTIR) spectrometer (Nicolet Instruments Co., USA). Solution pH was measured by pH meter (PHS-3C, Shanghai Hongyi Instrumentation Co., Ltd, China) and adjusted with 0.1 mol l^{-1} HCl and 0.1 mol l^{-1} NaOH. Copper(II) concentrations were analyzed by flame atomic absorption spectrophotometer (AA320CRT, Shanghai Analytical Instrument Overall Factory, China).

2.4. Models of copper(II) biosorption

2.4.1. Copper(II) biosorption isotherms

Langmuir and Freundlich isotherms were used for the simulation of the experimental biosorption data from the batch system.

The linear Langmuir isotherm Eq. (1) [4] and Freundlich isotherm Eq. (2) [22] are

$$\frac{1}{q_e} = \frac{1}{q_{max}} + \left(\frac{1}{q_{max}K_L}\right)\frac{1}{C_e}, \quad (1)$$

$$\ln\ q_e = \ln K_F + \frac{1}{n}\ln C_e, \quad (2)$$

where q_e is the amount of copper adsorbed on per gram of biomass (mg g^{-1}) at equilibrium, constant q_{max} is theoretical maximum amount of copper adsorbed on per gram of biomass (mg g^{-1}), C_e (mg l^{-1}) is the copper(II) concentration at equilibrium, K_L is the Langmuir adsorption constant (l mg^{-1}), K_F ($mg^{(n-1)/n}\ l^{1/n}\ g^{-1}$) and n is the Freundlich adsorption constants.

2.4.2. Kinetics of copper(II) biosorption

Kinetics of copper(II) biosorption was simulated by the linear first-order Lagergren Eq. (3) [25,33] and pseudo second-order Eq. (4) [26,34] shown below:

$$\ln(q_e - q_t) = \ln\ q_e - \frac{k_L}{2.3}t, \quad (3)$$

$$\frac{t}{q_t} = \left(\frac{1}{q_e}\right)t + \frac{1}{2k'q_e^2}, \quad (4)$$

where k_L (h^{-1}) and k' (g mg^{-1} h^{-1}) are the Lagergren and pseudo second-order rate constants for adsorption, respectively, q_e and q_t are the amount of copper adsorbed on per gram of biomass (mg g^{-1}) at equilibrium and time t (h), respectively.

3. Results and discussions

3.1. Effects of pH on copper(II) biosorption

At pH 6.5 and 7.0, precipitation of copper hydroxide resulted in inaccuracy of the experimental data. The results showed that the adsorptive capacity of all biomasses approximately increased with the raising of pH (from 2.5 to 6.0). As pH values increased, *Bjerkandera* sp. showed the most pH sensitivity with the data of copper(II) adsorbed increasing from 2.20 to 12.08 mg g^{-1}. The optimum pH value for the biomasses was 6.0 at which the amounts of copper(II) biosorption were 7.74 mg g^{-1} by *C. cladosporioides*, 9.01 mg g^{-1} by *G. murorum*, and 12.08 mg g^{-1} by

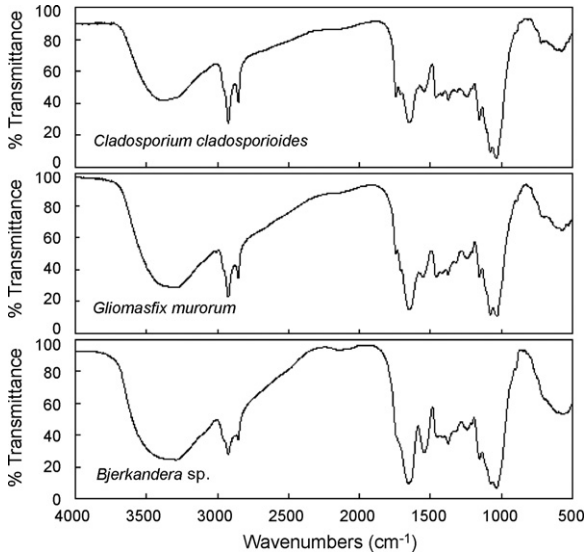

Fig. 1. FTIR spectra of three species of dead fungal biomasses.

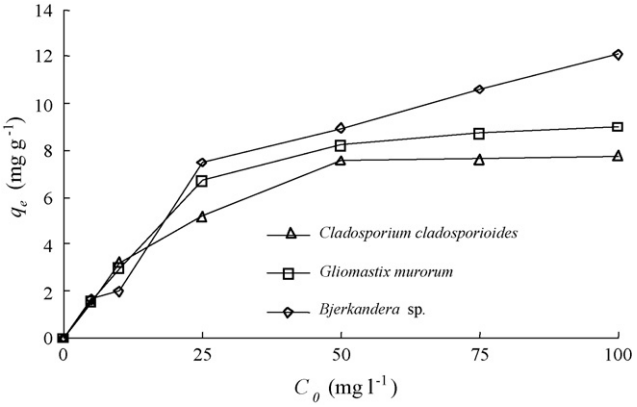

Fig. 2. The effect of initial copper(II) concentration on copper(II) biosorption by three species of dead fungal biomasses at optimum pH 6.0 for 12 h.

Bjerkandera sp.. Under the same conditions, the amount and category, as well as their interactions of binding groups on fungal biomass surfaces might be the crucial factors which caused different biosorption capacities in this study. Different cell wall compositions of the three species of fungi [35] provided different functional groups to the metal ions. FTIR spectra (Fig. 1) could help us to estimate that these functional groups might be amino (3500–3200 and 1549 cm^{-1}), hydroxyl (3500–3300 cm^{-1}), carbonyl (1653 and 1240 cm^{-1}), carboxyl (1458 cm^{-1}), phosphonate (1157 and 1080 cm^{-1}), etc. [15–18].

Many studies have proved that pH of solution is an important parameter for metal biosorption. This might be because that solution pH affects both chemical properties of biosorbates and surface characteristics of biosorbents [5,18,36–39]. At low pH 2.5 and 3.0, the amounts of copper(II) adsorbed by each species of fungal biomass were very low and almost kept unchanged. This phenomenon might be caused by protonation of the cell wall components [17]. With the increase of pH (3.5–6.0), protonation effect became minor, so that the amounts of copper(II) adsorbed by the biomasses all increased sharply. That was because the raise of negative charge density on the biomass surfaces offered more metal binding sites [7,17,40]. This work had the similar optimum pH value (6.0) with some other works for *P. chrysosporium* [17,38], *Aureobasidium pullulans* [27] and *Trametes versicolor* [41].

3.2. Effects of initial copper(II) concentration on biosorption

At pH 6.0, copper(II) precipitated at initial concentration higher than 200 mg l^{-1}. Therefore, concentrations from 5 to 100 mg l^{-1} were available. The effects of initial copper(II) concentration on biosorption by the dead fungal biomasses are presented in Fig. 2. The results showed that, for each fungal biomass, copper biosorption increased with the raise of initial copper(II) ion concentration

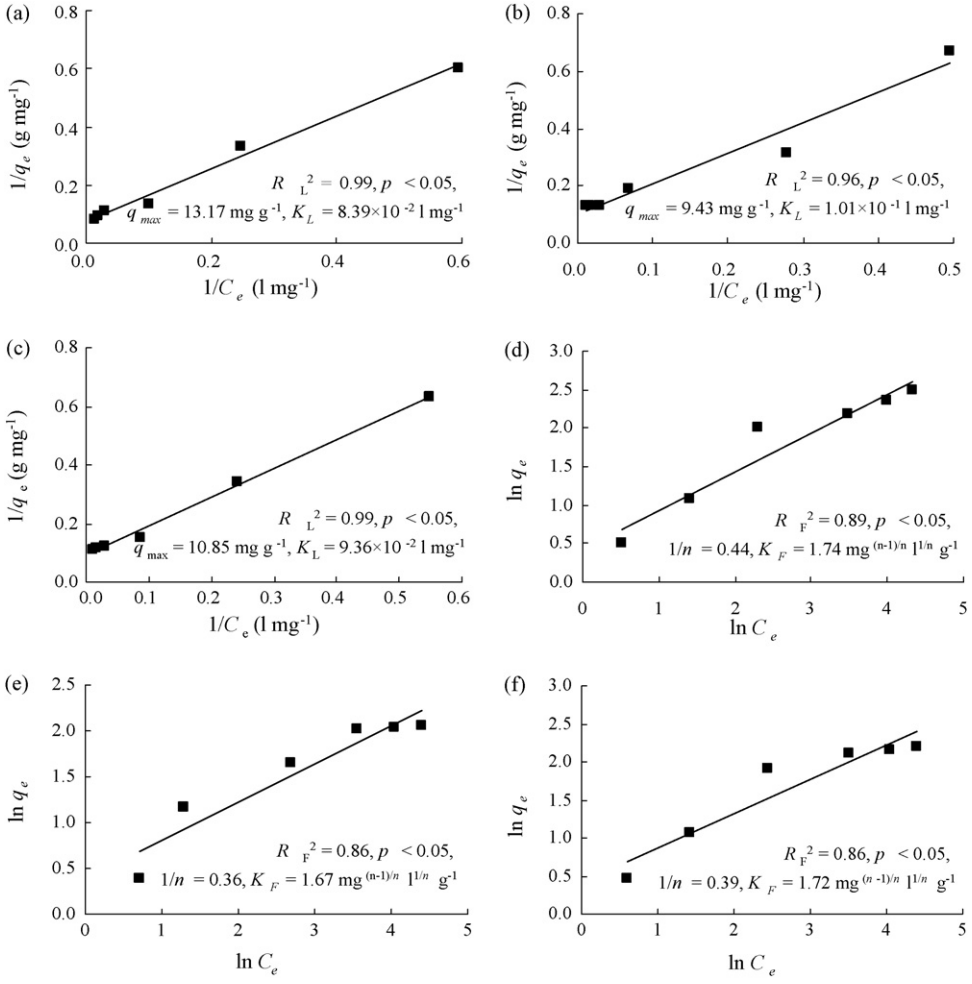

Fig. 3. Copper(II) biosorption isotherms by three species of dead fungal biomasses at optimum pH 6.0, 25 °C. (a–c) Langmuir model: (a) *Cladosporium cladosporioides*, (b) *Gliomastix murorum* and (c) *Bjerkandera* sp.; (d–f) Freundlich model: (d) *C. cladosporioides*, (e) *G. murorum* and (f) *Bjerkandera* sp..

at un-precipitable pH. At the initial copper(II) concentration of 100 mg l^{-1}, each of the biomasses exhibited the highest biosorption capacity. And the biosorption amounts were very close to those at the condition of pH 6.0 in the experiments for evaluating pH effects on biosorption. Copper biosorption by *C. cladosporioides* increased sharply from 1.49 to 7.58 mg g^{-1} while the initial concentration was from 5 to 50 mg l^{-1}. But this increase became minor when the initial concentration continued to be raised. Sharp increase (from 1.59 to 8.23 mg g^{-1}) of biosorption by *G. murorum* was observed at the same range of initial copper(II) concentration, but *Bjerkandera* sp. (from 1.66 to 12.08 mg g^{-1}) was at a range of 5–100 mg l^{-1}.

Under the same conditions, there are more copper(II) ions around the active sites of biomasses in the solution of higher concentration, where biomasses could adsorb copper(II) ions more sufficiently [42]. Once almost all active sites of biomass surface have combined with copper(II) ions, biosorption process reaches saturation. Therefore, copper(II) biosorption by most fungal biomasses keeps unchanged after increasing obviously with the increase of the initial concentration.

3.3. Biosorption isotherms

Langmuir model (Fig. 3a–c) presented the best adjustment for copper(II) removal by each fungus with high regression coefficient ($R_L^2 \geq 0.96$, $p < 0.05$), while Freundlich model did not give very good adjustments with R_F^2 values from 0.86 to 0.89 ($p < 0.05$) at 95% confidence level (Fig. 3d–f).

The Freundlich model is an empirical equation based on adsorption on a heterogeneous surface [22]. Prakasham et al. [43] proved that Freundlich isotherm was not corrected for variations in environmental conditions. Langmuir model assumes a monolayer adsorption whose energy is constant and that there is no migration of adsorbate molecules in the surface plane [15,16,44]. A lot of studies on heavy metal biosorption by fungi were better fitted by Langmuir model than Freundlich model [9,15,41,42,45].

Freundlich model had constants of 1.67, 1.72 and 1.74 $mg^{(n-1)/n}\, l^{1/n}\, g^{-1}$ separately for three K_F values and 2.80, 2.58 and 2.29 for n values. Langmuir model showed the theoretical maximum capacities (q_{max}) of adsorbing copper(II) were 9.43, 10.85 and 13.17 mg g^{-1} for *C. cladosporioides*, *G. murorum* and *Bjerkandera* sp., respectively. These theoretical values were somewhat higher than corresponding experimental ones (7.74, 9.01 and 12.08 mg g^{-1}).

The q_{max} of the Langmuir model was assumed to be the maximum amount of copper(II) ions which form a complete monolayer onto the surface of biosorbents. The values of q_{max} suggested that, on biosorption capacity, the arrangement of the dead fungal biomasses was *Bjerkandera* sp. > *G. murorum* > *C. cladosporioides*. There was the same conclusion while arranged according to Freundlich constants K_F or $1/n$, which related to the adsorptive capacity and intensity, respectively [4,22]. This suggested that there was a relationship between biosorption capacity and adsorptive intensity for the dead fungal biomasses in this work.

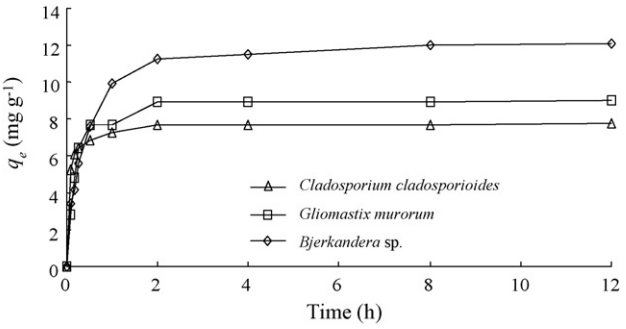

Fig. 4. The amount of copper(II) biosorption by three species of dead fungal biomasses at different conducted time (at initial concentration of 100 mg l^{-1} and optimum pH 6.0).

3.4. Comparison of biosorption capacity with other fungal adsorbents

The Langmuir constants (q_{max}) of some fungal biomasses are listed in Table 1. Pretreatments (like NaOH-boiling, immobilization) could avail copper(II) ions more functional groups to bind on, so that q_{max} of pretreated biomasses were higher than un-pretreated biomasses. Nevertheless, compared with other un-pretreated fungal biosorbents, the dead biomasses in this study presented high capacities of copper(II) biosorption. Therefore, *C. cladosporioides*, *G. murorum* and *Bjerkandera* sp. had potential as biosorbents for the removal of copper(II) from solutions.

3.5. Biosorption kinetics

The changes of copper(II) biosorption by the dead fungal biomasses with time are shown in Fig. 4. It was found that the adsorbed amount of copper(II) increased during the biosorption process. This process consisted of two phases: the rapid phase (the first 1 h) at which biosorption contributed significantly to adsorptive equilibrium, and the subsequent slower phase at which biosorption contributed relatively small. During the initial phase, copper(II) biosorption reached 93.79% (*C. cladosporioides*), 85.09% (*G. murorum*) and 81.96% (*Bjerkandera* sp.) of the equilibriums.

Table 1
Copper(II) biosorption by fungal biomasses: a selection of the Langmuir constant q_{max} and some parameters of various fungal biosorbents from the literatures.

Biosorbent	pH	C_0 (mg l^{-1})	q_{max} (mg g^{-1})	References
NaOH-treated *Aspergillus niger*	5.0	0–10.0	4.69	[9]
NaOH-treated *A. niger*	6.0	0–10.0	6.35	[9]
Hydrochloric acid-treated waste beer yeast	5.0	3.20–44.8	1.45	[42]
Immobilized *Phanerochaete chrysosporium*	6.0	10.0–500	99.9	[38]
NaOH-treated *Botrytis cinerea*	5.0	5.00–300	20.4	[46]
Dead *Botrytis cinerea* (heat inactivated)	5.0	5.00–300	9.23	[46]
Dead *Pleurotus pulmonarius* (HCHO inactivated)	4.0	5.00–200	6.20	[4]
Dead *Schizophyllum commune* (HCHO inactivated)	4.0	5.00–200	1.52	[4]
Cladosporium cladosporioides	–	–	19.5	[19]
Dead *C. cladosporioides* (HCHO inactivated)	6.0	5.00–100	9.43	This study
Dead *Gliomastix murorum* (HCHO inactivated)	6.0	5.00–100	10.9	This study
Dead *Bjerkandera* sp. (HCHO inactivated)	6.0	5.00–100	13.2	This study

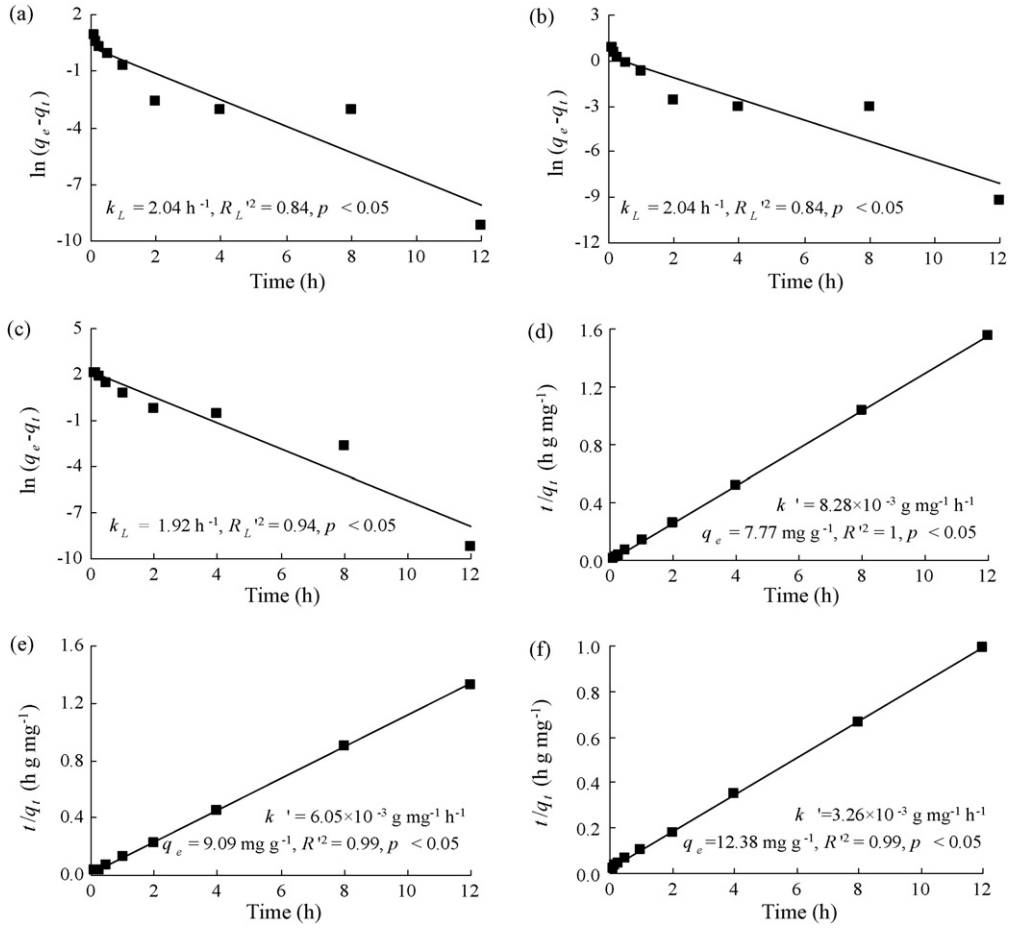

Fig. 5. Linear plot of the kinetic models for copper(II) biosorption by three species of dead fungal biomasses. (a–c) First-order Lagergren kinetic model: (a) *C. cladosporioides*, (b) *G. murorum* and (c) *Bjerkandera* sp.; (d–f) pseudo second-order kinetic model: (d) *C. cladosporioides*, (e) *G. murorum* and (f) *Bjerkandera* sp..

The time for each of the equilibriums was about 2 h. Most of the biosorption works [13,15,42] reported that the equilibrium time was very short (within 30 min). However, Sağ et al. [47] and Gabriel et al. [48] also reported that their equilibrium time was about 2 h.

To simulate the metal biosorption kinetics, first-order Lagergren and pseudo second-order models were most often used [9,26,49]. First-order Lagergren model relies on that the rate of occupation of adsorption sites is proportional to the number of unoccupied sites [50]. Literatures [49,51] indicated that, in most cases, this model was not applicable for all experimental data throughout the whole biosorption process. In this study, it fitted the kinetic data of *Bjerkandera* sp. (Fig. 5a) with regression coefficient (R'^2_L, 0.94) statistically significant ($p < 0.05$) at 95% confidence level, though it was only comparatively applicable during the initial 1/2 h as mentioned by Taty-Costodes et al. [51]. It did not fit the data of *C. cladosporioides* or *G. murorum* very well with R'^2_L of 0.88 and 0.84, respectively (Fig. 5b and c).

The pseudo second-order model relies on that biosorption capacity is proportional to the number of active sites occupied on the biosorbent, and that biosorption may be the rate-limiting step involving valence forces through sharing or exchanging electrons between biosorbent and adsorbate [34,49]. Being similar to the results of [26] and [52], this model fitted the kinetic data of the three fungi very well in this study (Fig. 5d–f). It presented good adjustment for copper(II) adsorption with regression coefficients (R'^2) higher than 0.99 ($p < 0.05$) at 95% confidence level. The constant q_e (7.77, 9.09 and 12.38 mg g^{-1} for *C. cladosporioides*, *G. murorum* and *Bjerkandera* sp., respectively) was very close to the experimental q_e correspondingly.

4. Conclusions

The present work showed that pH, contact time and initial copper(II) concentration influenced the copper(II) biosorption process of dead *Bjerkandera* sp., *G. murorum* and *C. cladosporioides* biomasses. The optimum pH was 6.0. The equilibrium established within the first 2 h. Without pretreatment for improving biosorption capacity, the experimental maximum amounts of copper(II) adsorbed by per gram biomass were relatively high: 7.74 mg g^{-1} for *C. cladosporioides*, 9.01 mg g^{-1} for *G. murorum*, and 12.08 mg g^{-1} for *Bjerkandera* sp.. The biosorption data of three fungi were quite fitted to Langmuir model but not very well to Freundlich model. The pseudo second-order model gave good adjustments for adsorptive kinetic data of the three fungi. First-order Lagergren model fitted the data of *Bjerkandera* sp., but did not quite fit those of *C. cladosporioides* or *G. murorum*. The three species of dead fungal biomasses had relatively high capacity for the removal of copper(II) from aqueous solutions.

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References

[1] A. Sánchez, A. Ballester, M.L. Blázquez, F. González, J. Muñoz, A. Hammaini, Biosorption of copper and zinc by *Cymodocea nodosa*, FEMS Microbiol. Rev. 23 (1999) 527–536.

[2] T. Pümpel, F. Schinner, Native fungal pellets as a biosorbent for heavy metals, FEMS Microbiol. Rev. 11 (1993) 159–164.

[3] R.H. Vierira, B. Volesky, Biosorption: a solution to pollution, Int. Microbiol. 3 (2000) 17–24.

[4] M.T. Veit, C.R.G. Tavares, S.M. Gomes-da-Costa, T.A. Guedes, Adsorption isotherms of copper(II) for two species of dead fungi biomass, Process Biochem. 40 (2005) 3303–3308.

[5] E. Galli, F.D. Mario, P. Rapanà, P. Lorenzoli, R. Angelini, Copper biosorption by *Auricularia polytricha*, Lett. Appl. Microbiol. 37 (2003) 133–137.

[6] J. Gabriel, J. Vosalo, P. Baldrian, Biosorption of cadmium to mycelial pellets of wood rotting fungi, Biotechnol. Techniques 10 (1996) 345–348.

[7] C.C. Townsley, I.S. Ross, Copper uptake in *Aspergillus niger* during batch growth and in non-growing mycelial suspension, Exp. Mycol. 10 (1986) 281–288.

[8] C. Huang, C.P. Huang, A.L. Morehart, Proton competition in Cu(II) adsorption by fungal mycelia, Water Res. 25 (1991) 1365–1375.

[9] A. Kapoor, T. Viraraghavan, D.R. Cullimore, Removal of heavy metals using the fungus *Aspergillus niger*, Bioresource Technol. 70 (1999) 95–104.

[10] L. de Rome, G.M. Gadd, Copper adsorption by *Rhizopus arrhizus*, *Cladosporium resinae* and *Penicillium italicum*, Appl. Microbiol. Biotechnol. 26 (1987) 84–90.

[11] Kh. Rostami, M.R. Joodaki, Some studies of cadmium adsorption using *Aspergillus niger*, *Penicillium austurianum*, employing an airlift fermenter, Chem. Eng. J. 89 (2002) 239–252.

[12] J.M. Tobin, D.G. Cooper, R.J. Neufeld, Uptake of metal ions by *Rhizopus arrhizus* biomass, Appl. Environ. Microbiol. 47 (1984) 821–824.

[13] T. Bahadir, G. Bakan, L. Altas, H. Buyukgungor, The investigation of lead removal by biosorption: an application at storage battery industry wastewaters, Enzyme Microb. Technol. 41 (2007) 98–102.

[14] B. Volesky, H.A. May-Phillips, Biosorption of heavy metals by *Saccharomyces cerevisiae*, Appl. Microbiol. Biotechnol. 42 (1995) 797–806.

[15] A. Çabuk, T. Akar, S. Tunali, S. Gedikli, Biosorption of Pb(II) by industrial strain of *Saccharomyces cerevisiae* immobilized on the biomatrix of cone biomass of *Pinus nigra*: equilibrium and mechanism analysis, Chem. Eng. J. 131 (2007) 293–300.

[16] A. Kapoor, T. Viraraghavan, Fungal biosorption—an alternative treatment option for heavy metal bearing wastewaters: a review, Bioresource Technol. 53 (1995) 195–206.

[17] R. Say, A. Denizli, M.Y. Arıca, Biosorption of cadmium(II), lead(II) and copper(II) with the filamentous fungus *Phanerochaete chrysosporium*, Bioresource Technol. 76 (2001) 67–70.

[18] B. Volesky, Biosorption and Me, Water Res. 41 (2007) 4017–4029.

[19] A.V. Pethkar, S.K. Kulkarni, K.M. Paknikar, Comparative studies on metal biosorption by two strains of *Cladosporium cladosporioides*, Bioresource Technol. 80 (2001) 211–215.

[20] M. Treen-Sears, B. Volesky, R.J. Neufeld, Ion exchange/complexation of the uranyl ion by *Rhizopus* biosorbent, Biotechnol. Bioeng. 26 (1984) 809–814.

[21] E. Fourest, J.C. Roux, Heavy metal biosorption by fungal mycelial by-products: mechanisms and influence of pH, Appl. Microbiol. Biotechnol. 37 (1992) 399–403.

[22] Y. Sağ, A. Kaya, T. Kutsal, The simultaneous biosorption of Cu(II) and Zn(II) on *Rhizopus arrhizus*: application of the adsorption models, Hydrometallurgy 50 (1998) 297–314.

[23] X. Wang, Y. Qin, Equilibrium sorption isotherms for of Cu^{2+} on rice bran, Process Biochem. 40 (2005) 677–680.

[24] O. Redlich, D.L. Peterson, A useful adsorption isotherm, J. Phys. Chem. 63 (1959) 1024.

[25] Y.S. Ho, D.A.J. Wase, C.F. Foster, Kinetic studies of competitive heavy metal adsorption by sphagnum peat, Environ. Technol. 17 (1996) 71–77.

[26] B. Benquella, H. Benaissa, Cadmium removal from aqueous solution by chitin: kinetic and equilibrium studies, Water Res. 36 (2002) 2463–2474.

[27] Y.B. Patil, K.M. Paknikar, Removal and recovery of metal cyanides using a combination of biosorption and biodegradation processes, Biotechnol. Lett. 21 (1999) 913–919.

[28] M. Fomina, G.M. Gadd, Metal sorption by biomass of melanin-producing fungi grown in clay-containing medium, J. Chem. Technol. Biotechnol. 78 (2002) 23–34.

[29] P.R. Moreira, E. Almeida-Vara, G. Sena-Martins, I. Polónia, F.X. Malcata, J.C. Duarte, Decolourisation of Remazol Brilliant Blue R via a novel *Bjerkandera* sp. strain, J. Biotechnol. 89 (2001) 107–111.

[30] M.T. Moreira, G. Feijoo, J.M. Lema, Manganese peroxidase production by *Bjerkandera* sp. BOS55, Bioprocess. Biosyst. Eng. 23 (2000) 657–661.

[31] T.M. Hammill, On *Gliomastix murorum* and *G. felina*, Mycologia 73 (1981) 229–237.

[32] S. Aritajat, K. Saenphet, C. Srikalayanukul, The toxicity of a crude enzyme extract from *Gliomastix murorum* in Swiss Albino mice, Southeast Asian, J. Trop. Med. Public Health 36 (2005) 242–245.

[33] K.K. Pandy, G. Prasad, V.N. Singh, Copper(II) removal from aqueous by fly ash, Water Res. 19 (1985) 869–873.

[34] Y.S. Ho, G. McKay, Pseudo-second order model for sorption processes, Process Biochem. 34 (1999) 451–465.

[35] S.S. Ahluwalia, D. Goyal, Microbial and plant derived biomass for removal of heavy metals from wastewater, Bioresource Technol. 98 (2007) 2243–2257.

[36] E. Luef, T. Prey, C.P. Kubicek, Biosorption of zinc by fungal mycelial wastes, Appl. Microbiol. Biotechnol. 34 (1991) 668–692.

[37] A. Özer, E. Özer, Comparative study of the biosorption of Pb(II), Ni(II) and Cr(VI) ions onto *S. cerevisiae*: determination of biosorption heats, J. Hazard. Mater. B 100 (2003) 219–229.

[38] M. Iqbal, R.G.J. Edyvan, Biosorption of lead, copper and zinc ions on loofa sponge immobilized biomass of *Phanerochaete chrysosporium*, Miner. Eng. 17 (2004) 217–223.

[39] N. Tewari, P. Vasudevan, B.K. Guha, Study on biosorption of Cr(VI) by *Mucor hiemalis*, Biochem. Eng. J. 23 (2005) 185–192.

[40] D. Brady, J.R. Duncan, Bioaccumulation of metal cations by *Saccharomyces cerevisiae*, Appl. Microbiol. Biotechnol. 41 (1994) 149–154.

[41] G. Bayramoğlu, S. Bektaş, M.Y. Arıca, Biosorption of heavy metal ions on immobilized white-rot fungus *Trametes versicolor*, J. Hazard. Mater. B 101 (2003) 285–300.

[42] R. Han, H. Li, Y. Li, J. Zhang, H. Xiao, J. Shi, Biosorption of copper and lead ions by waste beer yeast, J. Hazard. Mater. B 137 (2006) 1569–1576.

[43] R.S. Prakasham, J.S. Merrie, R. Sheela, N. Saswathi, S.V. Ramakrishna, Biosorption of chromium VI by free and immobilized *Rhizopus arrhizus*, Environ. Pollut. 104 (1999) 421–427.

[44] M.I. Kefala, A.I. Zouboulis, K.A. Matis, Biosorption of cadmium ions by *Actinomycetes* and separation by flotation, Environ. Pollut. 104 (1999) 283–293.

[45] M.Y. Arıca, A. Çigdem, A. Ergene, G. Bayramoğlu, Ö. Genç, Ca-alginate as a support for Pb(II) and Zn(II) biosorption with immobilized *Phanerochaete chrysosporium*, Carbohydr. Polym. 52 (2003) 167–174.

[46] T. Akar, S. Tunali, Biosorption performance of *Botrytis cinerea* fungal by-products for removal of Cd(II) and Cu(II) ions from aqueous solutions, Miner. Eng. 18 (2005) 1099–1109.

[47] Y. Sağ, A. Yalçuk, T. Kutsal, Mono and multi-component biosorption of heavy metal ions on *Rhizopus arrhizus* in a CFST, Process Biochem. 35 (2000) 787–799.

[48] J. Gabriel, P. Baldrian, K. Hladíková, M. Háková, Copper sorption by native and modified pellets of wood-rotting basidiomycetes, Lett. Appl. Microbiol. 32 (2001) 194–198.

[49] C. Yan, S. Wang, A. Zeng, X. Jin, Q. Xu, J. Zhao, Equilibrium and kinetics of copper(II) biosorption by *Myriophyllum spicatum* L., J. Environ. Sci.-China 17 (2005) 1025–1029.

[50] R. Rakhshaee, M. Khosravi, M.T. Ganji, Kinetic modeling and thermodynamic study to remove Pb(II), Cd(II), Ni(II) and Zn(II) from aqueous solution using dead and living *Azolla filiculoides*, J. Hazard. Mater. B 134 (2006) 120–129.

[51] V.C. Taty-Costodes, H. Fauduet, C. Porte, A. Delacroix, Removal of Cd(II) and Pb(II) ions from aqueous solutions by adsorption onto sawdust of *Pinus sylvestris*, J. Hazard. Mater. B 105 (2003) 121–142.

[52] A. Kapoor, Removal of heavy metals from aqueous solution by *Aspergillus niger*, Ph.D. Thesis, University of Regina, Sakstche-wan, Canada, 1998.