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# Biosorption of cadmium(II) and lead(II) from aqueous solutions by fruiting body waste of fungus *Flammulina velutipes*

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## ABSTRACT

The biosorption of $Cd^{2+}$ and $Pb^{2+}$ by fruiting body wastes of macrofungi *Flammulina velutipes* was studied. The factors affecting absorbtion including pH, initial metal concentration, biosorbent dosages and mutual competitive biosorption of both metal ions were focused. The sorption of $Cd^{2+}$ and $Pb^{2+}$ was increased with pH value from 2 to 6 and maximum biosorption was at pH 6. The quantity of $Cd^{2+}$ and $Pb^{2+}$ adsorbed increased with the initial concentration of metal ions and both metals removal gradually increased with the biosorbent dosage. There existed mutual competitive biosorption between $Cd^{2+}$ and $Pb^{2+}$ when they were in the same solution. The Langmuir isotherm model fitted both metal ions sorption data well in the experiment and the calculated maximum sorption capacity of $Cd^{2+}$ and $Pb^{2+}$ by *F. velutipes* was 8.4317 mg/g dry biomass with $R^2$ of 0.9228 and 18.3486 mg/g dry biomass with $R^2$ of 0.9280, respectively. Pseudo-first order equation fitted for adsorption data of $Cd^{2+}$ with $R^2$ of 0.9504, while pseudo-second order equation more fitted for adsorption data of $Pb^{2+}$ with $R^2$ of 0.9917.

*Keywords*: Biosorption; $Cd^{2+}$; $Pb^{2+}$; *Flammulina velutipes*; Langmuir isotherm; Pseudo-first and second-order equation

## 1. Introduction

High fungi *Flammulina velutipes* (donggu) is a kind of famous edible mushroom in China and Japan, which is popularly artificially cultivated in China and has been a delicacy. The fruiting body of *F. velutipes* contains donggu polysaccharide which has significant function against cancer. Experimental results indicated that the restraining rate of polysaccharide extracted from *F. velutipes* with water fighting against flesh tumor of petty-white mouse and Ehrlich carcinoma has reached 81–100% and 80% respectively [1].

Toxic heavy metals like copper, mercury, chromium, lead, nickel and cadmium cause serious impact on the aqueous environment, animals and humans [2]. In Japan, the inhabitants around the Jinstsu River suffered painful Itai-Itai after eating rice grown in contaminated soil irrigated by the river polluted with cadmium, lead and zinc [3]. Biosorption of various metals, especially heavy metals, by micro-organisms like fungi appears to be promising for clean-up of waters because of their ability to accumulate metals from their external environment,

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especially since conventional physical and chemical techniques of removing soluble metal waste (such as ion exchange, precipitation, electrochemical treatment, and evaporative recovery) are generally very expensive when the contaminant concentration are in the range of 10–100 mg/kg [4–7].

Fungi cell walls and their components have major role in the biosorption [8]. Fungus biomass can take up considerable quantities of heavy metals from aqueous solution by adsorption or a related process, even in the absence of physiological activity [9]. Many fungal species such as *Rhizopus arrhizu*s, *Penicilium spinulum*, *Aspergillus niger*, *Trametes versicolor*, *Mucor rouxii*, *Lentinus sajor-caju*, *Pleurotus ostreatu*s, *Polyporous versicolo*r and *Phanerochaete chrysosporium* etc. have been extensively studied for heavy metals biosorption and the process mechanism seems to be dependent upon species [10–13]. No study has been done with *F. velutipes* in detoxifying metal effluents. *F. velutipes* is one of the most principal cultivated mushroom in China and its annual output was around 1,179,627 T. The byproducts after *F. velutipes* being processed were quietly abundant and almost no cost for employment.

The purpose of the present study was to investigate the use of fruiting body wastes of *F. velutipes* in Cd(II) and Pb(II) removal and this study is directed towards determining possibility of using the fungus in industrial wastewater treatment. Metabolically inactive fruiting body wastes of *F. velutipes* were used to determine their effectiveness in sorbing Cd(II) and Pb(II). The effects of various operational parameters such as pH, initial heavy metal concentration, biomass concentration on biosorption were studied. The kinetics of biosorption was also analyzed.

## 2. Materials and methods

### 2.1. Preparation of biomass used as biosorbents

The fungal biosorbents used for this study were fruiting body wastes of *F. velutipes*, which came from a mushroom processing factory. The biomass employed as biosorbents was the brown down stalks after cutting the edible yellow up stalks. The stalks were dried at 60°C until balance weight and grinded into powder which was deposited in bottles for use.

### 2.2. Chemicals

Standard solution of 1000 mg/kg $Cd^{2+}$: dissolving 1.000 g pure Cd in HCl solution ( HCl:distilled water = 1:3) of 200 mL, cooling and transferred into flask of 1000 mL.

Standard solution of 1000 mg/kg $Pb^{2+}$: weighing 1.5990 g $Pb(NO_3)_2$ in distilled water containing 100 mL $HNO_3$ (density 1.42 g/cm$^3$), transferred into flask of 1000 mL.

The pH of the solutions was adjusted with 1 M/L $HNO_3$ or 1 M/L NaOH.

### 2.3. Experiments on factors affecting biosorption

#### 2.3.1. Initial pH experiments

100 mg of *F. velutipes* waste powder was added to 25 mL of 10 mg/L solution of $Cd^{2+}$ and $Pb^{2+}$ in pH range 2–7 and at temperature of 25°C.

#### 2.3.2. Initial metal ion and biomass concentration experiments

Different amounts of *F. velutipes* waste powder were added to 25 mL of $Cd^{2+}$ and $Pb^{2+}$ (30 mg/L) solutions and different biomass (100, 200, 300, 400, 500 mg of powders corresponding with biomass concentrations of 4, 8, 12, 16, 20 g/L respectively) were obtained. Different volumes of $Cd^{2+}$ and $Pb^{2+}$ solutions (1000 mg/L) were added to appropriate distilled water and the final solution volume was 25 mL, then different concentration solutions of $Cd^{2+}$ and $Pb^{2+}$ (10, 20, 40, 60, 80, 100 mg/L) were obtained. 100 g of mushroom waste powder was added into the solutions.

#### 2.3.3. Competitive biosorption experiment

Concentration of $Pb^{2+}$ was 10 mg/L, while concentrations of $Cd^{2+}$ were 0, 1, 5, 10, 30 mg/L respectively and concentration of $Cd^{2+}$ was 10 mg/L, while concentrations of $Pb^{2+}$ were 0, 1, 5, 10, 30 mg/L respectively for investigating their competitive biosorption.

In above experiment, the flask with $Cd^{2+}$ and $Pb^{2+}$ and powder was stirred at 100 rpm at 25°C for 30 min. The biomass was removed by filtration through Whatman No. 3 filter and the filtrates were analyzed for metal concentration by a Perkin Elmer Atomic Absorption Spectrophotometer, model 1100 B (AAS).

#### 2.3.4. Isotherm analysis

Adsorption experiment was conducted by varying the initial concentration of $Cd^{2+}$ and $Pb^{2+}$ from 1 to 60 mg/L. An amount of 100 mg of *F. velutipes* waste powder was added to flasks containing 25 mL of metal-bearing solution with pH adjusted to a value of 5. Flasks were shaken at 100 rpm at 25°C for 30 min. Samples were filtered and metal concentrations in filtrate were determined by AAS.

#### 2.3.5. The kinetic biosorption experiment

The experiment was carried out by sampling in different time intervals after shaking (0, 1, 3, 5, 10, 15, 20, 30, 60 min.). Other conditions were the same as in isotherm analysis.

The biosorption tests were replicated 3 times. The mean values were used.

## 3. Results and discussion

The adsorption of $Cd^{2+}$ and $Pb^{2+}$ biosorption was investigated as a function of initial pH, initial metal ion concentration and fungal biomass. The metal uptake value ($q_e$) and adsorption rate ($X$) were calculated from Eqs. (1) and (2):

$$q_e = \left(C_0 - C_e\right)V / m \tag{1}$$

$$X = \left(C_0 - C_e\right)/ C_0 \times 100\% \tag{2}$$

where $q_e$ (mg/g dry weight) is the metal uptake per unit biosorbent, $C_0$ (mg/L) is the initial concentration of metal in solution, $C_e$ (mg/L) is the metal concentration at adsorption equilibrium, $V$ (L) is the volume of metal solution, $m$ (g) is the fungal biomass, $X$ (%) is the biosorption rate of metal ion.

### 3.1. Effect of solution pH on biosorption of $Cd^{2+}$ and $Pb^{2+}$

The medium pH affected the solubility of metals and the ionization state of the functional groups (carboxylate, phosphate, and amino groups) of the fungal cell wall [13]. There was an increase in $Cd^{2+}$ and $Pb^{2+}$ adsorption with increasing pH from 2 to 6 and beyond which no real changes in $Cd^{2+}$ and $Pb^{2+}$ adsorption were observed. The observation of the present studies supported the idea that the initial pH of the metal solution plays a vital role in the metal adsorption in general and in particular in $Cd^{2+}$ and $Pb^{2+}$ biosorption by using macrofungi biomass as biosorbent.

Fig. 1 depicts the effect of pH on $Cd^{2+}$ and $Pb^{2+}$ biosorption. There is an increase in metal ions adsorption per unit weight of fungal biomass with increasing pH from 2 to 6, but it seems to level off at pH greater than 6. At acidic pH (pH = 2), protonation of the cell wall component adversely affected the biosorption capacity of the fungal biomass, but its effect became minor with increasing pH in the medium. With an increase in pH, the negative charge density on the cell surface increased due to the deprotonation of the metal binding sites and thus increased in biosorption. Some researchers had investigated the effect of pH on biosorption of heavy metals by using different kinds of fungi biomass. For example, biosorption of $Cd^{2+}$ and $Pb^{2+}$ by fungus *Phanerochaete chrysosporium* was pH-dependent and maximum biosorption was obtained in the pH 6 (13.24 mg Cd/g dry biomass and 45.25 mg Pb/g dry biomass) [13]. The results obtained in this study indicated that optimum pH range for adsorption of $Cd^{2+}$ and $Pb^{2+}$ in solution by *F. velutipes* waste was around pH 6. The amount of $Pb^{2+}$ (pH 2–7: 0.9311–1.9417 mg Pb/g dry biomass) absorbed by *F. velutipes* was higher than amount of $Cd^{2+}$ adsorbed (pH 2–7: 0.0732–1.3125 mg Cd/g dry biomass) under the same conditions.

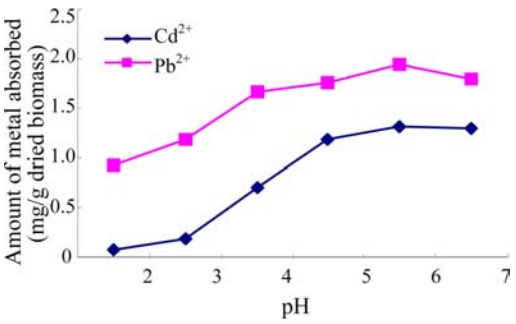

Fig. 1. The effect of pH on biosorption by *F. velutipes*.

### 3.2. Effect of $Cd^{2+}$ and $Pb^{2+}$ concentration on biosorption of $Cd^{2+}$ and $Pb^{2+}$

The amount of $Cd^{2+}$ and $Pb^{2+}$ ions adsorbed per unit mass of the biosorbent (i.e biosorption capacity) increased, as expected, with the initial concentration of metal ions. This may be explained by the possibility that increasing the Cd and Pb strength in solution, the free sites of fungi are occupied by metal ions much faster than when the solution is dilute. As seen from Fig. 2, the amount of $Cd^{2+}$ and $Pb^{2+}$ ions adsorbed at equilibrium on *F. velutipes* was 5. 5730 and 17.9128 mg/g dry biomass, respectively. Bayramoglu reported that the amount of $Pb^{2+}$ ions adsorbed at equilibrium on the plain CMC beads of macrofungi *Trametes versicolor* was 74.63 ± 2.90 mg/g dry beads [14]. Say et al. employed *Phanerochaete chrysosporium* as sorbent absorbing $Cd^{2+}$ and $Pb^{2+}$ in solution with the adsorption of 23.04 mg Cd/g dry biomass and 69.77 mg Pb/g dry biomass [13]. The biosorption capacity of the NaOH pretreated with *Aspergillus niger* was 7.24 mg Pb and 3.43 mg Cd/g dry biomass [15]. The biosorption capacity of dead *Fusariium flocciferum mycelium* was 19.20 mg $Cd^{2+}$/g dry biomass [16].

### 3.3. Effect of biosorbent dose on biosorption

The percentage removal of $Cd^{2+}$ and $Pb^{2+}$ was studied by varying the adsorbent dose between 4–20 g/L at a concentration $Cd^{2+}$ and $Pb^{2+}$ of 10 mg/L (Fig. 3). The data show that the increase in the biosorbent dose in the medium from 4 to 20 g/L led to a gradual increase in the percentage of both metals removal, and this was leveled at around 18 g/L biosorbent in the adsorption medium.

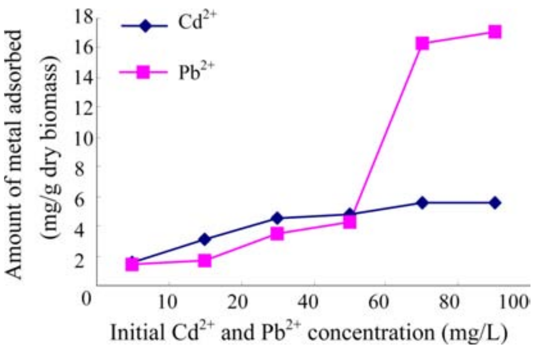

Fig. 2. The effect of $Cd^{2+}$ and $Pb^{2+}$ concentration on biosorption by *F. velutipes*.

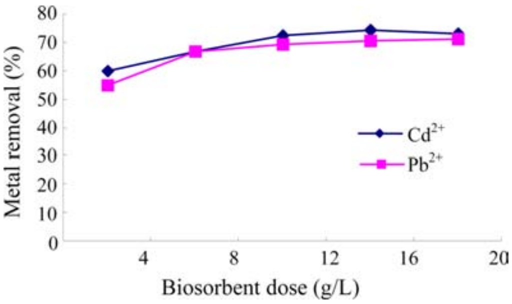

Fig. 3. Effect of biosorbent dosage on biosorption by *F. velutipes*.

The $Cd^{2+}$ and $Pb^{2+}$ removal efficiency was increased up to an optimum dosage beyond which the removal efficiency did not change. Some researchers reported that the increase in the percentage removal with the increase in the adsorbents dosage was due to the increase in the number of adsorption sites [17].

### 3.4. Competitive biosorption

Competitive biosorption of $Cd^{2+}$ and $Pb^{2+}$ was also studied. The medium contained 10 mg/L of $Pb^{2+}$ and 1, 5, 15, 30 mg/L of $Cd^{2+}$, from which series of solution with different concentration of $Cd^{2+}$ and the same concentration of $Pb^{2+}$ were composed. At the same time, the medium series of containing 10 mg/L of $Cd^{2+}$ and 1, 5, 15, 30 mg/L of $Pb^{2+}$ were also prepared for study of competitive biosorption between $Cd^{2+}$ and $Pb^{2+}$ in solution.

When the concentration of $Cd^{2+}$ was anchored to be 10 mg/L, the amount of biosorption for $Cd^{2+}$ decreased with increasing $Pb^{2+}$ concentration in the solution (from 1 to 30 mg/L), which means that the existence of $Pb^{2+}$ hinders the biosorption for $Cd^{2+}$. In a single-ion system, the maximum uptake obtained at the initial concentration of 10 mg $Cd^{2+}$/L, pH 5 and 25°C was found to be 2.2240 mg/g dry biomass (Table 1), while the uptake obtained in binary metal solutions at the same initial concentration of $Cd^{2+}$ and adsorption conditions was found to be 1.5379 and 1.3038 mg/g dry biomass when concentration of $Pb^{2+}$ was 5 and 30 mg/L, respectively. Under almost the same experimental conditions, there appeared to be an inhibition in the biosorption of $Cd^{2+}$ by the presence of $Pb^{2+}$. When the initial concentration of $Pb^{2+}$ increased from 0 to 30 mg/L, there was a sharp drop in the adsorbed quantity of $Cd^{2+}$, and the uptake of $Cd^{2+}$ decreased by about 76.67% as the initial concentration of $Cd^{2+}$ was 15 mg/L.

In Table 2 the equilibrium uptake of $Pb^{2+}$ by *F. velutipes* in the presence of varied concentration of $Cd^{2+}$ in the range of 1–30 mg/L is compared with the results in the single-ion system. The results show that the competitive adsorption data for $Pb^{2+}$ approached that in the binary-ion system at a higher concentration of competing metal ions (30 mg $Cd^{2+}$/L), while the equilibrium uptake decreased from 1.6332 to 1.5555 mg/g dry biomass with increasing the concentration of $Cd^{2+}$ from 1 to 15 mg/L.

In the single-ion system, the maximum uptake for $Pb^{2+}$ obtained at the initial concentration of 10 mg $Pb^{2+}$/L, pH 5 and 25°C was found to be 1.7742 mg/g dry biomass,

Table 1
Effect of $Pb^{2+}$ concentration on $Cd^{2+}$ biosorption

| Concentration of $Cd^{2+}$ (mg/L) | Concentration of $Pb^{2+}$ (mg/L) | $C_e$ (mg/L) | | $q_e$ (mg/g dry biomass) | | Sorption rate (%) | |
|---|---|---|---|---|---|---|---|
| | | $Cd^{2+}$ | $Pb^{2+}$ | $Cd^{2+}$ | $Pb^{2+}$ | $Cd^{2+}$ | $Pb^{2+}$ |
| 10 | 0 | 1.1030 | — | 2.2240 | — | 88.97 | — |
| 10 | 1 | 3.4810 | 0.2253 | 1.5398 | 0.1937 | 61.59 | 77.50 |
| 10 | 5 | 3.8483 | 1.2850 | 1.5379 | 0.9288 | 61.52 | 74.30 |
| 10 | 15 | 4.0897 | 3.4670 | 1.4776 | 2.8833 | 59.10 | 76.79 |
| 10 | 30 | 4.7850 | 3.6011 | 1.3038 | 6.5998 | 52.15 | 40.00 |

Table 2
Effect of $Cd^{2+}$ concentration on $Pb^{2+}$ biosorption

| Concentration of $Pb^{2+}$ (mg/L) | Concentration of $Cd^{2+}$ (mg/L) | $C_e$ (mg/L) | | $q_e$ (mg/g dry biomass) | | Sorption rate (%) | |
|---|---|---|---|---|---|---|---|
| | | $Cd^{2+}$ | $Pb^{2+}$ | $Cd^{2+}$ | $Pb^{2+}$ | $Cd^{2+}$ | $Pb^{2+}$ |
| 10 | 0 | — | 2.9030 | — | 1.7742 | — | 70.97 |
| 10 | 1 | 0.3127 | 3.4670 | 0.1718 | 1.6332 | 68.73 | 65.33 |
| 10 | 5 | 1.8223 | 3.6030 | 0.7944 | 1.5992 | 63.55 | 63.97 |
| 10 | 15 | 4.2567 | 3.7807 | 2.6858 | 1.5555 | 71.62 | 62.19 |
| 10 | 30 | 17.4550 | 2.9033 | 3.1362 | 1.7742 | 41.82 | 70.97 |

while the uptake obtained in the binary metal solutions at the same initial concentration of $Pb^{2+}$ and biosorption conditions was found to be 1.6332 and 1.5555 mg/g dry biomass, when the initial concentration of $Cd^{2+}$ was 1 and 15 mg/L, respectively.

The comparison between Table 1 and Table 2 shows that the difference is distinct between the competitive biosorption of $Cd^{2+}$ and $Pb^{2+}$. As the initial concentration of $Cd^{2+}$ increased from 1 to 15 mg/L, there was no significant drop in $Pb^{2+}$ biosorption with $Pb^{2+}$ absorbed decreasing by about 4.76%. When the initial concentration of $Cd^{2+}$ was 30 mg/L, $Pb^{2+}$ (1.7742 mg/g) absorbed became the same as in the single-ion system. This proves that the biosorption of $Pb^{2+}$ by the biomass of *F. velutipes* is preferential to that of $Cd^{2+}$. Because both electro-negativity and ionic radii of $Pb^{2+}$ were larger than those of $Cd^{2+}$, there might be a stronger chemical and physical affinity for $Pb^{2+}$ on *F. velutipes* [18].

### *3.5. Isotherm biosorption analysis*

The adsorption process is a mass transfer operation that can be described mathematically by an equilibrium process and a rate process. The equilibrium is established between the concentration of the metal ions dissolved in the aqueous phase and that bound to the biosorbent. The isotherm was used to characterize the interaction of each metal species with the adsorbent. This provides a relationship between the concentration of $Cd^{2+}$ and $Pb^{2+}$ in the adsorption medium and the amount of $Cd^{2+}$ and $Pb^{2+}$ adsorbed on the solid phase when the two phases are at equilibrium. Among the several isotherm equations, two isotherms (Langmuir and Freundlich adsorption isotherms) were investigated, which are widely used to analyze data for water and wastewater treatment application. The Langmuir adsorption isotherm was used to describe the equilibrium process in this study. The Langmuir model was based on the assumption of surface homogeneity such as equally available adsorption sites, monolayer surface coverage, and no interaction between adsorbed species. The mathematical description of this model is as follows:

$$q_e = \frac{q_{\max} b C_e}{1 + b C_e} \tag{3}$$

where $q_{\max}$ (mg/g dry biomass) is the maximum metal uptake value corresponding to sites saturation and $b$ (L/mg) is a constant on affinity of metal and connection sites.

The adsorption equilibrium curves of $Cd^{2+}$ and $Pb^{2+}$ biosorption were obtained by plotting $q_e$ against $C_e$ at the time of adsorption equilibrium (Figs. 4 and 5), showing a lineal tendency among the observed and predicted values.

For quantitatively analyzing the thermodynamic process of heavy metal biosorption by *F. velutipes*, according to Pan, the Langmuir equation was deformed into Eq. (4):

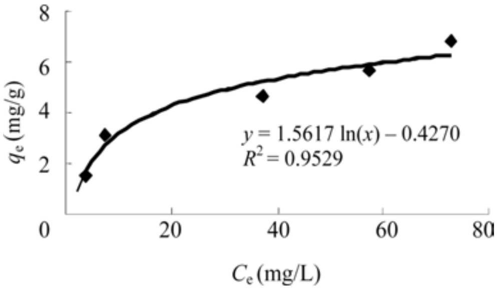

Fig. 4. Equilibrium of $Cd^{2+}$ by *F. velutipes* biomass.

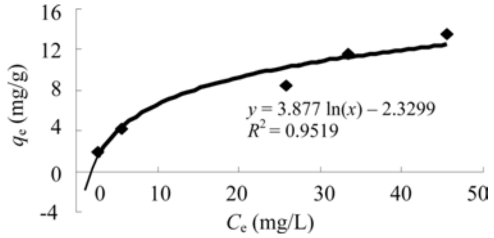

Fig. 5. Equilibrium of $Pb^{2+}$ by *F. velutipes* biomass.

$$C_e / q_e = C_e / q_{\max} + 1 / q_{mzx} b \tag{4}$$

The Langmuir isotherm model was able to fit $Cd^{2+}$ and $Pb^{2+}$ sorption data well in this experiment and indicated that the experimental data was adjusted to the model. By the equation, the maximum sorption capacity of $Cd^{2+}$ and $Pb^{2+}$ by *F. velutipes* was calculated, which was 8.4317 mg/g dry biomass for $Cd^{2+}$ and 18.3486 mg/g dry biomass for $Pb^{2+}$ respectively (Figs. 4 and 5).

The Langmuir isotherm plot for the biosorption of $Cd^{2+}$ and $Pb^{2+}$ on the biosorbent was obtained by plotting $C_e$ against $C_e/q_e$ (Fig. 6). At the adsorption equilibrium, the practical metal concentration in solution $C_e$ and $C_e/q_e$ was an obvious linear relationship with the correlation coefficient $R^2$ of 0.9228 for $Cd^{2+}$ and 0.9280 for $Pb^{2+}$, respectively. The thermodynamic saturation sorption capacity $q_{\max}$ and sorption/desorption constant b in the Langmuir equation can be obtained by $q_{\max} = 1/k$, $b = k/c$ ($k$ and $c$ are slope and intercept of line, respectively).

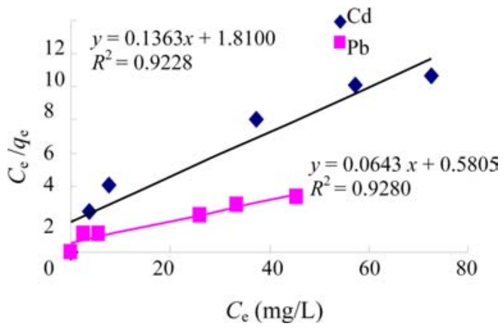

Fig. 6. Langmuir adsorption isotherm of $Cd^{2+}$ and $Pb^{2+}$ biosorption.

The difference between the capacity of metal adsorption could be caused by the specific superficial properties of biomass. According to Volesky and Holan [18], some biosorbent types showed the capacity to remove several types of heavy metals, while others could be specific for certain types of metals. This indicates that the fungal biomass used in this work could present a greater removal capacity for other types of heavy metals. Some also attributed metal sorption capacity to the influence of culture broth composition used in the biomass production [19].

The adsorption capacities of biomass studied in this work had similar removal values to those reported in literature [11,18,20,21]. However, a direct comparison of the data is not possible, because the types of fungal biosorbents and the operation conditions used in each work are different.

### 3.6. Biosorption kinetics studies

In order to examine the controlling mechanisms of the biosorption process, such as mass transfer and chemical reaction, kinetic models were used to test the experimental data. A large number and different chemical groups on the cell was constitute of the fungal mycelia (e.g. –COOH, –NH$_2$, =NH, –SH, –OH) implying that there were many types of fungal mycelia-metal ion interactions [22]. The kinetic models including the pseudo-first order and pseudo-second order equations could be used in this case assuming that measured concentrations were equal to cell surface concentrations. The first-order rate equation of the Lagergren is one of the most widely used for the sorption of a solute from a liquid solution. It might be represented as Eq. (5):

$$dq_t / dt = k_1 \left( q_e - q_t \right) \tag{5}$$

where $q_t$ (mg/g) denotes the amounts of biosorption at time $t$, $k_1$ (g/mg.min) is the rate constant of pseudo-first order biosorption. If applying boundary condition $t = 0$, $q = 0$, Eq. (6) can be obtained:

$$\log\left( q_e - q_t \right) = \log q_e - \left( k_1 / 2.303 \right) t \tag{6}$$

If the absorption process could be expressed by pseudo-first order equation, the relation between log ($q_e - q_t$) and $t$ should be linear.

A pseudo-second order equation based on adsorption equilibrium capacity might be expressed in Eq. (1):

$$dq_t / dt = k_2 \left( q_e - q_t \right)^2 \tag{7}$$

where $k_2$ (g/mg.min) is the rate constant of pseudo-second order. If applying boundary condition $t = 0$, $q_t = 0$, Eq. (8) is obtained:

$$t / q_t = 1 / k_2 q_e^2 + t / q_e \tag{8}$$

The rate constant ($k_2$) could be obtained from the intercept and slope. If the pseudo-second order equation are fitted for the adsorption data, $t/q_t$ ant $t$ should be linear relation.

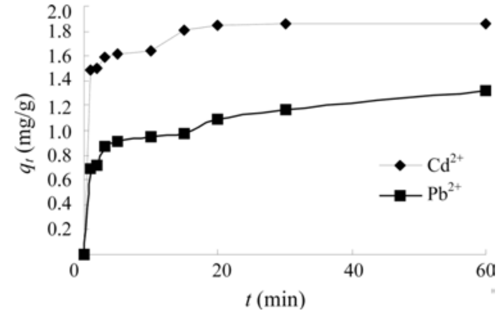

Fig. 7. Plot for the intra-particle diffusion.

The relationship between $q$ and $t$ was not linear over the whole time range (Fig. 7) and this indicated that there were several processes affecting the adsorption.

Fig. 8 is the plot of log ($q_e - q_t$) for Cd$^{2+}$ biosorption, from which a linear regression relationship with $R^2$ of 0.9504 was obtained. This confirmed that intra-particle diffusion was the rate-determining step for Cd$^{2+}$ adsorption by *F. velutipes*. While the intra-particle diffusion for Pb$^{2+}$ adsorption by *F. velutipes* was not the only rate-determining step with a nonlinear relationship of $R^2$ of 0.6745 (Fig. 9).

Fig. 10 depicts the plots of $t/q_t$ vs. time t according to the pseudo-second order equation for Pb$^{2+}$ biosorption with the correlation coefficient $R^2 = 0.9917$. The theoreti-

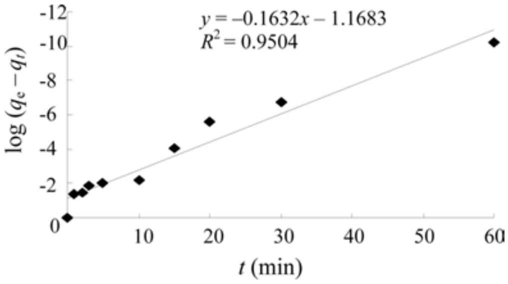

Fig. 8. Plot of log ($q_e - q_t$) vs. time for Cd$^{2+}$.

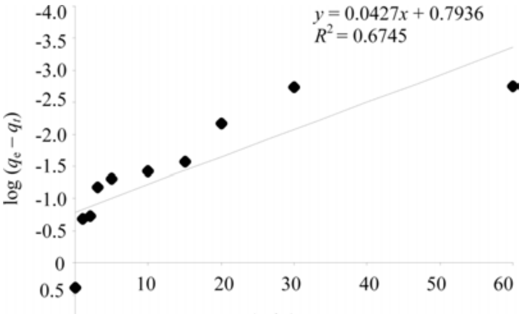

Fig. 9. Plot of log ($q_e - q_t$) vs. time for Pb$^{2+}$.

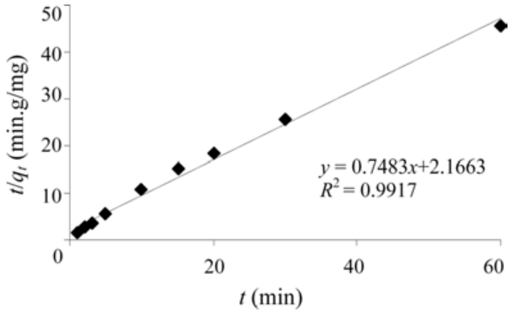

Fig. 10. Plots of $t/q_t$ vs. time $t$ for $Pb^{2+}$ biosorption.

cal values for the tested biosorbent systems were very close to the experimental values in the case of pseudo-second order kinetics, based on the assumption that the rate-limiting step might be biosorption involving valence forces through sharing or exchanging electrons between biosorbent and sorbate, and provided the best correlation of the data [23,24]. By linear regression of $t/q_t$ vs. $t$, $q_e$ and $k_2$ could be obtained [25–29] which was 13.0400 mg $Pb^{2+}$/g dry biomass and 2.1660 $Pb^{2+}$ g/mg.min, respectively.

## 4. Conclusion

The media pH plays a very important role in $Cd^{2+}$ and $Pb^{2+}$ biosorption by *F. velutipes* waste. With an increase in pH from 2 to 6, there was an increase in $Cd^{2+}$ and $Pb^{2+}$ adsorption with maximum amount of adsorbed of 1.9417 mg Pb/g dry biomass and 1.3125 mg Cd/g dry biomass at pH 6 respectively. The amount of $Cd^{2+}$ and $Pb^{2+}$ adsorbed increased with increasing the initial concentration of metal ions. The biosorbent dosage also affected the biosorption efficiency. In the experimental range, the percentage of metal removal firstly gradually increased, then leveled. There was competition between $Cd^{2+}$ and $Pb^{2+}$ biosorption. The affinity of $Pb^{2+}$ in competitive conditions was bigger than $Cd^{2+}$. The Langmuir model analysis indicated a linear tendency among the observed and predicted values with $R^2$ of 0.9529 for $Cd^{2+}$ and $R^2$ of 0.9519 for $Pb^{2+}$ biosorption by F. velutipes waste and maximum sorption capacity of 8.4317 mg $Cd^{2+}$/g dry biomass and 18.3486 mg $Pb^{2+}$/g dry biomass were obtained. Using the kinetic models, both metal biosorption was described and it indicated that the pseudo-first order equation could fit $Cd^{2+}$ biosorption well with $R^2$ of 0.9504, while the pseudo-second order equation could fit $Pb^{2+}$ biosorption well with $R^2$ of 0.9917. The biosorption mechanisms still needs further research such as electron microscope and FTIR spectrum and so on, so that the more accurate explanation can be obtained.

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