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The biosorption of Pb^{2+}, Cd^{2+} and Cu^{2+} from aqueous solution by fruiting bodies and spores of *Oudemansiella radicata*

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ABSTRACT

In this study, sorption capacity of fruiting bodies and spores of *Oudemansiella radicata* were evaluated on biosorption of heavy metals, viz. lead, cadmium and copper from aqueous solutions. The optimum sorption conditions for each metal were analysed separately. Evaluation of the experimental data in terms of biosorption dynamics showed that the biosorption of three metals followed the pseudo-second-order kinetics model well. The fitness of the biosorption data for Langmuir and Freundlich adsorption models were investigated. It was found that the biosorption process for all three heavy metals fitted with Freundlich adsorption isotherm models. The different size of the adsorbent particles was found to have an irregular influence on the adsorption. Scanning electron microscope and energy dispersive spectrometry analysis confirmed the obvious change of the surface morphology and the presence of metal on the biosorbent after biosorption. The fourier transform infrared spectra analysis indicated that the chemical interactions as ion-exchange were mainly involved in the biosorption.

Keywords: Biosorption; Fruiting bodies; Spores; Mushrooms; Heavy metals

1. Introduction

Heavy metal pollution in the aqueous environment has become a serious problem due to the industrial process such as battery manufacturing, printing, mining and smelting. The heavy metal ions are non-degradable, and then they could be enriched through the food chain, posing health hazards on human beings. Among the heavy metals, lead, cadmium and copper are the most toxic ones. Lead could harm the hemopoietic system, leading to anaemia and brain damage. Cadmium could cause renal disturbance, bone lesions and hypertension. Copper also has the reproductive and developmental toxicity. The removal and recovery of heavy metals from wastewater is significant in the protection of the environment and human health [1].

Many conventional methods have been applied to treat the heavy metal polluted water, such as ion-exchange [2], electrocoagulation [3] and membrane process [4]. However, these methods are too expensive or ineffective in treating low concentration (<100 mg/L) metal polluted waste water. Some methods, such as chemical precipitation, also produce

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sludge which is difficult to dispose. It is necessary to find a new method to remove heavy metals from the water cost-efficiently. Biosorption is considered as an ideal alternative method in treating metal polluted water. The materials used in biosorption are usually widely available and cheap biomaterials. As reported by many studies, various materials have been investigated as biosorbent such as algae [5,6], bacteria [7,8], yeast [9], wool [10] and agricultural waste [11–13]. And some types of mushroom biomass have been successfully employed in recent years.

Particle size of the biosorbent influences the adsorption behaviour of metal ions in aqueous solutions. Spores of the mushroom have a small size which indicated that it could be an excellent biomaterial for the removal of heavy metals. This study chose the mushroom *Oudemansiella radicata*, which produces abundant spores as the biosorbent, to investigate the biosorption capacity of the powder of the fruiting bodies and the spores, aiming to find a new biosorbent which could be used in future applications of large-scale heavy metal polluted water treatment.

2. Materials and methods

2.1. *The collection of the spores of* O. radicata

Hyphae of *O. radicata* were purchased from fungi research centre in Sichuan Province. At proper temperature conditions, mushroom was cultivated in greenhouses on the ground. When it grew up, fruiting bodies were collected timely, and then removed the mud on the surface. Caps were cut-off and were placed on a transparent plastic film to collect the spores. The spores collected were labelled as powder S, also dried with the fruiting bodies. The collection of the spores is shown in Fig. 1.

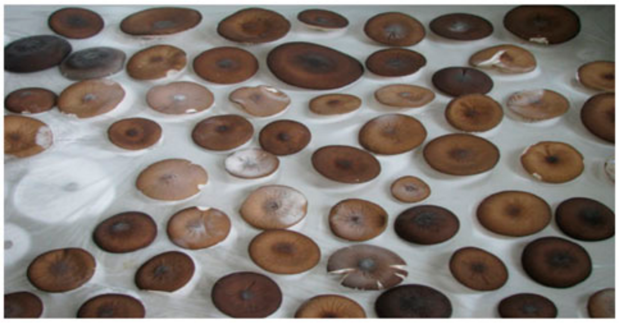

Fig. 1. The collection of the spores of *O. radicata*.

2.2. O. radicata *powder as adsorbent*

Mushrooms were washed with deionised water to remove the dirt and impurities and later dried in an oven at 60℃ for 24 h. The dried fruit bodies were pulverised in a grinding mill. Then, it was passed through 20, 40, 60, 80, 100 and 200 mesh (<75 μm) sieve and labelled as powder A, B, C, D, E and F, respectively, for further use.

2.3. *Preparation of metal stock solution*

The aqueous solutions used in this study were lead $Pb(NO_3)_2$, copper ($Cu(NO_3)_2\cdot 3H_2O$)and cadmium Cd $(NO_3)_2\cdot 4H_2O$ which were analytical grades. About 1,000 mg/L of stock solutions were prepared by dissolving the above-mentioned metal-salts in 1% of HNO_3 solution. The required working solutions for the adsorption experiments were obtained by diluting each stock solution. All vessels in contact with the metal solution were soaked with 10% HNO_3 solution for 12 h before use, then washed with deionized water and dried.

2.4. *Adsorption experiment*

To study some important parameters like pH, adsorption time, adsorbent dosage, initial concentration and the adsorbed liquid adsorption process, batch experiments were performed in 150 ml flasks containing a definite volume (50 mL in each flask) at 25℃ on a constant temperature breeding shaker with a shaking of 150 rpm filtered and residual metal ion concentration in the filtrates were analysed. The effect of pH on biosorption rate was investigated in a pH range of 2.0–6.0. The pH was adjusted by the addition of buffered solutions of HCl or NaOH (0.10 M). The effect of biosorbent dose was studied by varying the dosage in the range of 1–20 g/L. The samples were taken at definite time intervals for analysing the residual metal ion concentration. The effect of initial concentration of lead was conducted with the metal concentration varied from 50 to 2,000 mg/L; the metal concentration for cadmium and copper are ranged from 20 to 500 mg/L. The effect of particle size on metal removal was conducted by adding different particle size adsorbent into 50 ml and 100 mg/L metal solution.

Each experiment was repeated three times and the results are given as averages.

2.5. *Scanning electron microscopy (SEM) and energy dispersive spectrometry (EDS) analysis*

In order to examine the surface morphology and analyse the elemental constitute of fruiting bodies and spores of *O. radicata* before and after Pb bisorption (pH 4, sorbent mass 5 g/L, contact time 3 h and initial lead(II) concentration 100 mg/L), as well as to further confirm the identity of Pb onto the powders, scanning electron microscopy (SEM) (Inspect F, FET) and energy dispersive spectrometry (EDS) (INCAPenta-FET-x3, Oxford)were employed in this study. The samples were coated under vacuum with a thin layer of gold before being examined by SEM and EDS.

2.6. Fourier transform infrared spectra (FT-IR) analysis of biosorbent

Fourier transform infrared spectra (FT-IR) of the fruiting bodies and spores of *O. radicata* samples were obtained. The samples were mixed with KBr and pressed into a tablet form, and then spectrum was recorded.

2.7. Measurement of heavy metal concentration

Flame atomic absorption spectrometry was used to determine the concentrations of the solutions after adsorption, equipped with a deuterium lamp background. The standard solution was purchased from the National Centre for Iron and Steel Research Institute.

3. Results and discussion

3.1. Influence of pH

As described in the previous studies, hydrogen ion concentration in the adsorption is considered as an important parameter that influences the adsorption behaviour. Fig. 2 shows that for the two biosorbents, metals adsorption increased along with the increase of pH of the adsorbate solution. It can be seen the biosorption of metal ions reached equilibrium at pH 5. In the low pH conditions, for the two biosorbents metals adsorption are very low. At low pH value (pH 2), less ions could be sorbed. With the increase in solution pH, the two biosorbents metals adsorption increased and closed to the maximum rate at pH 4 for cadmium and copper. For the three heavy metals, both biosorbents showed maximum absorption when the pH is 5.

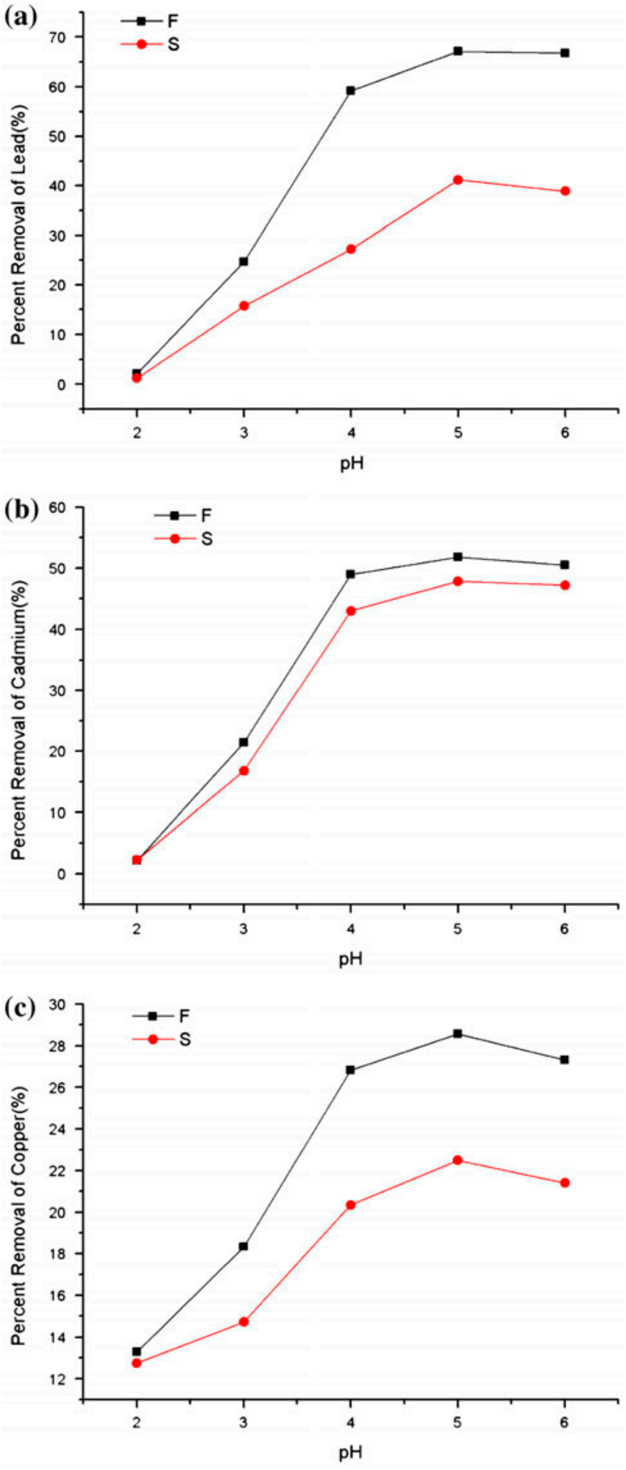

Fig. 2. Effect of pH on sorption of (a) Pb(II), (b) Cd(II) and (c) Cu(II) by fruiting bodies and spores of *O. radicata* (initial metal concentration = 100 mg/L, biosorbent dosage = 1 g/L and contact time = 3 h).

For all three heavy metal ions, fruiting bodies powder (powder F) adsorption rates are better than spore powder (powder S); although powder S has a smaller particle size (about 10 μm), at low pH conditions, both sorbed less metal ions because hydrogen ions occupy most of the biosorption sites on the biosorbent surface. With the increase of solution pH, powder F gradually shows its advantage in the adsorption. For all three heavy metal ions, the proportion in the absorption is maximum, Powder F's performance are better than Powder S and only in the adsorption of cadmium ions, Powder S powder adsorption ratio is closer to F. This suggests that as the germ cells, the surface of spores of *O. radicata* has special protection structures, making it less susceptible to the impact of heavy metal ions in the environment. On the other hand, powder F is made from dried fruiting bodies of mushrooms after the *O. radicata* gets crushed; crushing will break some of the cell wall structure, making the surface as spores that have the full protection of the structure, and may expose some of the active groups which could promote the adsorption. This is why powder F showed higher metal uptake capacity compared to spores.

The effect of single factor pH to the experimental results shows that, in the same adsorbent mass, the fruiting bodies powder of *O. radicata* has the greatest adsorption capacity for all three heavy metals, which followed the order: Pb>Cd>Cu. Similar results have been reported before [14].

3.2. *Influence of sorbent dosage*

The amount of adsorbent is important, which is related to the actual future costs of sewage treatment. The number of available sites and exchanging ions for adsorption depends upon the amount of adsorbent in biosorption. The effect of adsorbent concentration on the metal removal efficiency is presented in Fig. 3.

From the figures, we can see: when lesser sorbent mass was used, the adsorption percentage of powder F is better than powder S, which is similar to the result obtained in pH experiments. But in the case of high sorbent mass (20 g/L), spores adsorption percentage for all three heavy metals are very close to the adsorption rate of the powder F, especially in the lead ion, the maximum adsorption rates in case of lead ion for powder S and power F was 85.89 and 87.73%, respectively. That means spores of *O. radicata* as a biosorbent still has the prospect, although the highest absorption percentage needs more biosorbent. This means that if furtherly modified, the ability for the spores to adsorb heavy metal ions can still be improved. Adsorption rate of cadmium by the two biosorbents showed small difference. The maximum adsorption rates in case of power F for lead, cadmium and copper ions was 87.73, 63.20 and 52.75%, respectively, whereas in case of spores, it was 85.89, 61.12 and 48.92%, respectively. To the optimal sorbent mass, powder F and spores for lead ions were 2 and 10 g/L, respectively, for cadmium and copper ions adsorption, it is estimated that are to 5 g/L is more appropriate.

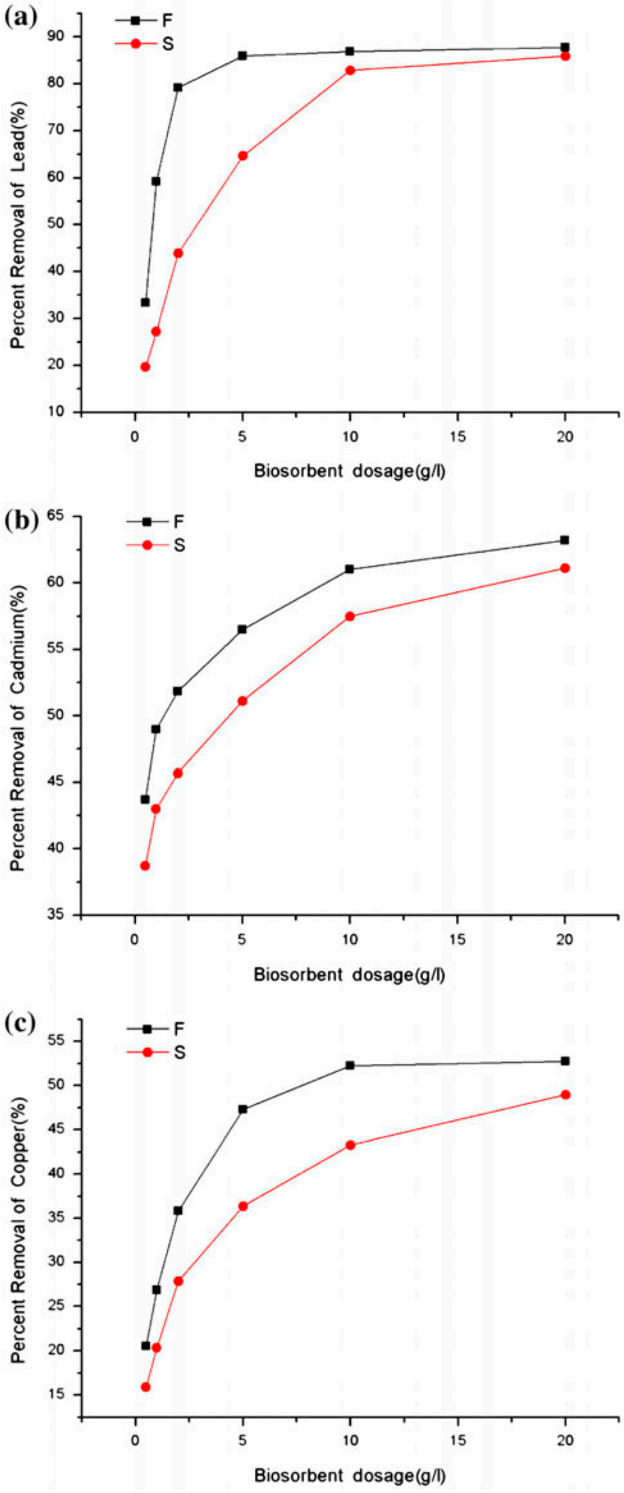

Fig. 3. Effect of biosorbent dosage on sorption of (a) Pb(II), (b) Cd(II) and (c) Cu(II) by fruiting bodies and spores of *O. radicata* (initial metal concentration = 100 mg/L, pH 4.0 and contact time = 3 h).

3.3. Influence of contact time and dynamic isotherm

Adsorbent adsorption rate reflects the rate of heavy metal ions biosorption in water. The biosorption percentage trend by the increase of time can reflect the adsorption rate. The influence of contact time on metal ions biosorption was examined by varying the contact time of suspensions from 1 to 180 min, the interval in the initial is short, because in the initial stages the removal efficiencies increased rapidly and the sorption became less efficient in the later stages [15,16]. Fig. 4 shows the trend of the adsorption percentage by powder F and spores for the three metals over time. It can be seen from the figure that a two-stage adsorption characteristics of three metals by both powder and spores are very obvious. For cadmium and copper adsorption by the two bisorbents, the removal efficiency reached equilibrium at 30 min. The removal efficiency of lead reached equilibrium at 60 min by the two bisorbents. The kinetic parameters are listed in Table 1.

It can be seen from Figs. 5 and 6 that pseudo-second-order kinetic model exhibited better fit to the sorption data of all metals for the two biosorbents than the pseudo-first-order kinetic model, and its linear regression coefficient reached 0.99. Most of the adsorption of biological processes is consistent with pseudo-second-order kinetic model [17].

3.4. Influence of initial heavy metal concentration and adsorption isotherm

Biosorption of metal ions onto two biosorbents was studied by changing the initial concentration of heavy metals in the test solution. For this experiment, the initial concentration of lead ion gradient is set to 50–2,000 mg/L, while the concentration of cadmium

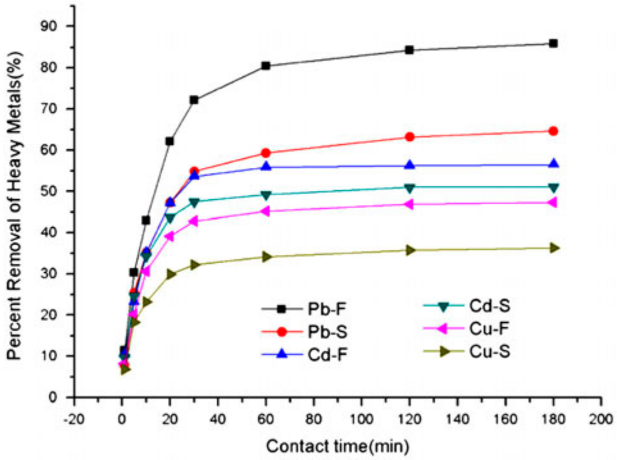

Fig. 4. Effect of contact time on sorption of Pb(II), Cd(II) and Cu(II) by fruiting bodies and spores of *O. radicata* (initial metal concentration = 100 mg/L, biomass dosage = 5 g/L and pH 4.0).

Table 1
Kinetic parameters obtained from pseudo-first-order and pseudo-second-order

Biosorbents material	Metal	Pseudo-first-order (R^2)	Pseudo-second-order (R^2)
Fruiting bodies	Pb	0.96532	0.99944
	Cd	0.92157	0.99914
	Cu	0.96371	0.99979
Spores	Pb	0.94941	0.99987
	Cd	0.96571	0.9998
	Cu	0.96135	0.99993

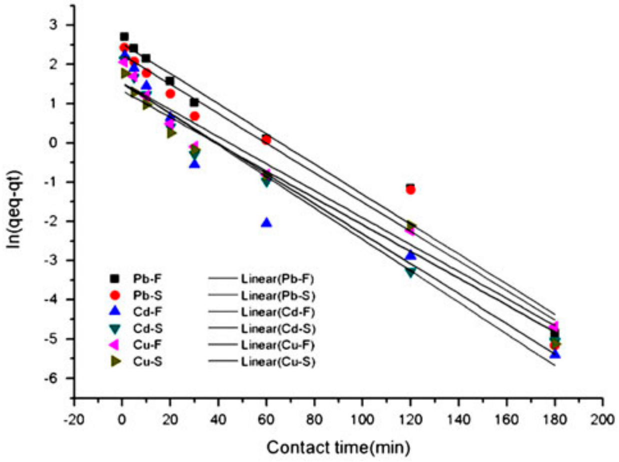

Fig. 5. Pseudo-first-order plots for uptake of Pb(II), Cd(II) and Cu(II) by fruiting bodies and spores of *O. radicata*.

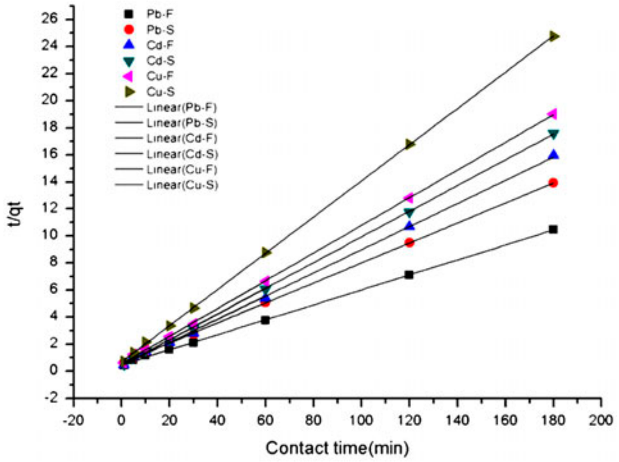

Fig. 6. Pseudo-second-order plots for uptake of Pb(II), Cd(II) and Cu(II) by fruiting bodies and spores of *O. radicata*.

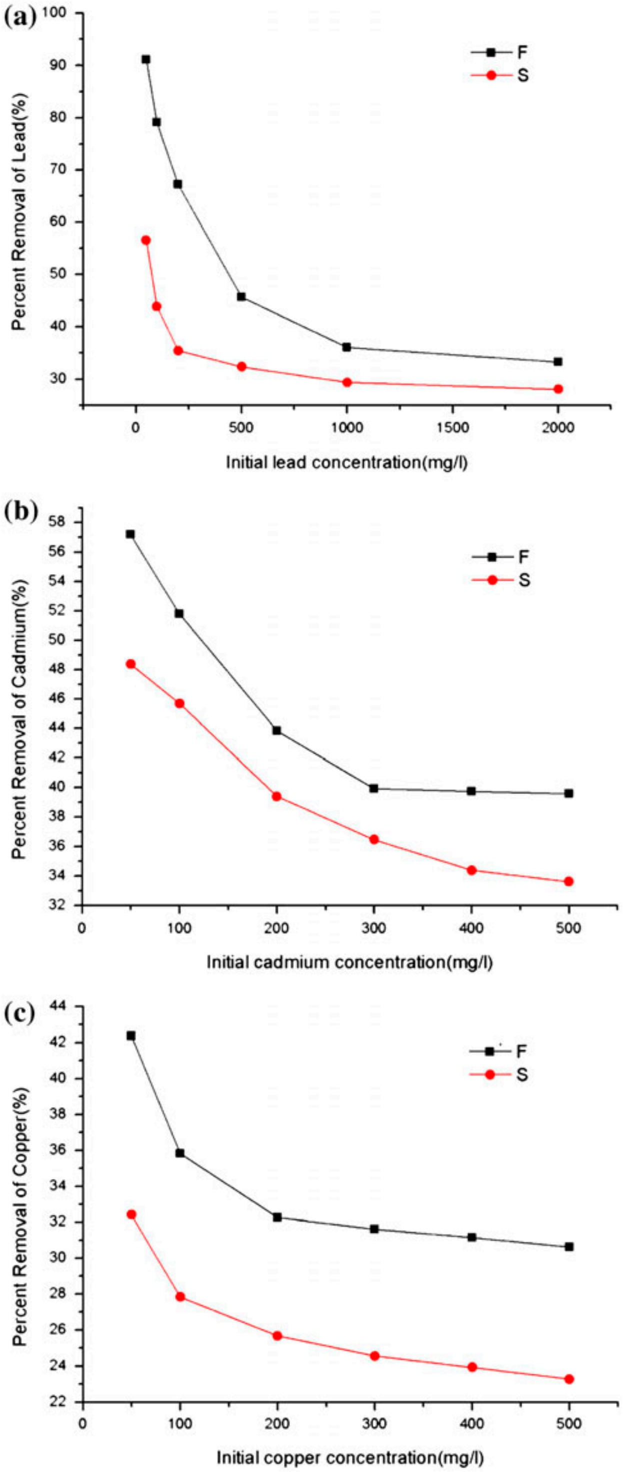

Fig. 7. Effect of initial metal concentration on uptake of (a) Pb(II), (b) Cd(II) and (c) Cu(II) by fruiting bodies and spores of *O. radicata* (biosorbent dosage = 2 g/L, contact time = 3 and pH 5.0).

Table 2
Maximum adsorption capacities (q_{max} in mg/g) obtained from initial concentration of heavy metals adsorption experiments

Biosorbents material	Metal	q_{max} (q_{max} in mg/g)
Fruiting bodies	Pb	332.31
	Cd	98.93
	Cu	76.55
Spores	Pb	280.42
	Cd	84.05
	Cu	58.17

and copper ions is set to 50–500 mg/L. Fig. 7 shows the effect of initial metal concentration on uptake of the three metals by fruiting bodies and spores of *O. radicata*. The figure shows, with the increase of the initial concentration of heavy metals, the uptake of metals decreases, but they both have a good adsorption for high concentrations of heavy metals.

Table 2 shows the maximum adsorption capacities obtained from initial concentration of heavy metals adsorption experiments. As can be seen from the table, they both have a very large adsorption capacity for lead ion adsorption. For cadmium and copper ions, the adsorption capacity is higher than other adsorbents [18–20] and shows great potential in the future industrial effluents purifications. This indicates that the *O. radicata* as a new biosorbent has a good prospect for future applications.

Adsorption isotherm models were used to characterise the interactions of metal ions with the sorbents. In this study, two isotherm models: Langmuir and Freundlich, were used to simulate the biosorption process.

Langmuir model is the best known isotherm model for sorptions from liquid solutions. It is based on the assumptions that maximum adsorption occurs when a saturated monolayer of solute molecules is present on the adsorbent surface, that the energy of adsorption is constant and that there is no migration of adsorbate molecules in the surface of plane, and it is expressed as:

$$q_{eq} = \frac{q_{max} b C_{eq}}{1 + b C_{eq}}$$

where q_{eq} is the amount of metal ions adsorbed at equilibrium (mg/g), C_{eq} the equilibrium concentration of metal ions in solution (mmol/L), q_{max} the maximum adsorption capacity of metal ions for a complete monolayer (mg/g) and b is the Langmuir constant related to the energy of sorption. q_{max} and b can be calculated from the experimental data. The equation can be transformed to a linear form:

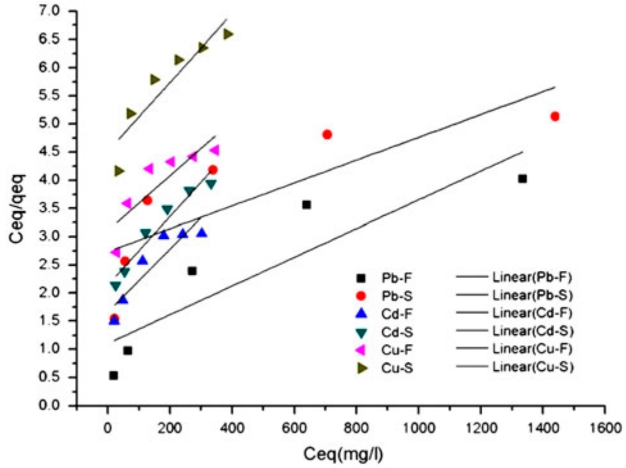

Fig. 8. Langmuir isotherm plots for the biosorption of Pb(II), Cd(II) and Cu(II) by fruiting bodies and spores of *O. radicata*.

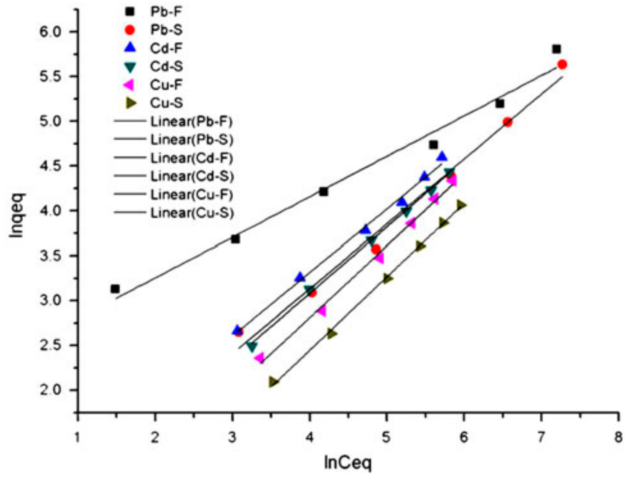

Fig. 9. Freundlich isotherm plots for the biosorption of Pb(II), Cd(II) and Cu(II) by fruiting bodies and spores of *O. radicata*.

Table 3
Isotherm parameters for lead(II), cadmium(II) and copper (II) sorption

Biosorbents material	Metal	Langmuir parameters (R^2)	Freundlich parameters (R^2)
Fruiting bodies	Pb	0.8202	0.9830
	Cd	0.6508	0.9857
	Cu	0.8389	0.9953
Spores	Pb	0.9436	0.9985
	Cd	0.7455	0.9952
	Cu	0.8461	0.9985

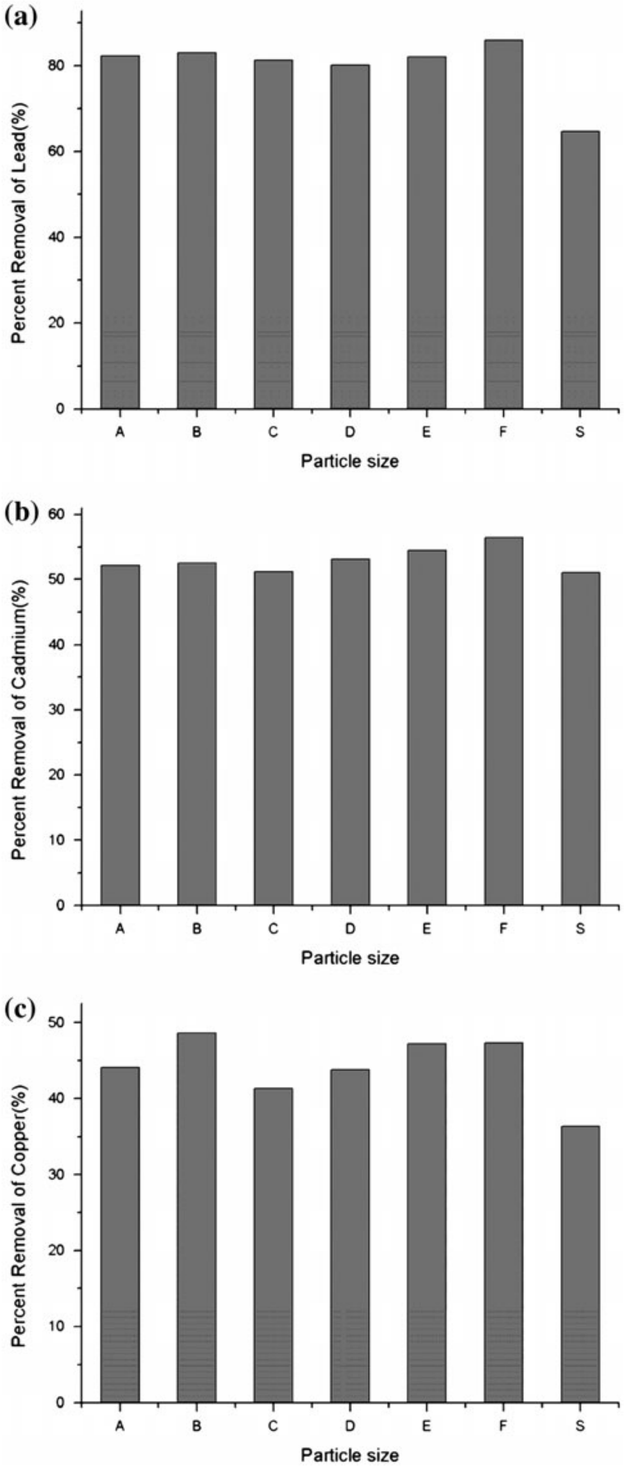

Fig. 10. Effect of partical size on uptake of (a) Pb(II), (b) Cd(II) and (c) Cu(II) by fruiting bodies and spores of *O. radicata* (biosorbent dosage = 5 g/L, initial metal concentration = 100 mg/L, contact time = 3 h and pH 5.0).

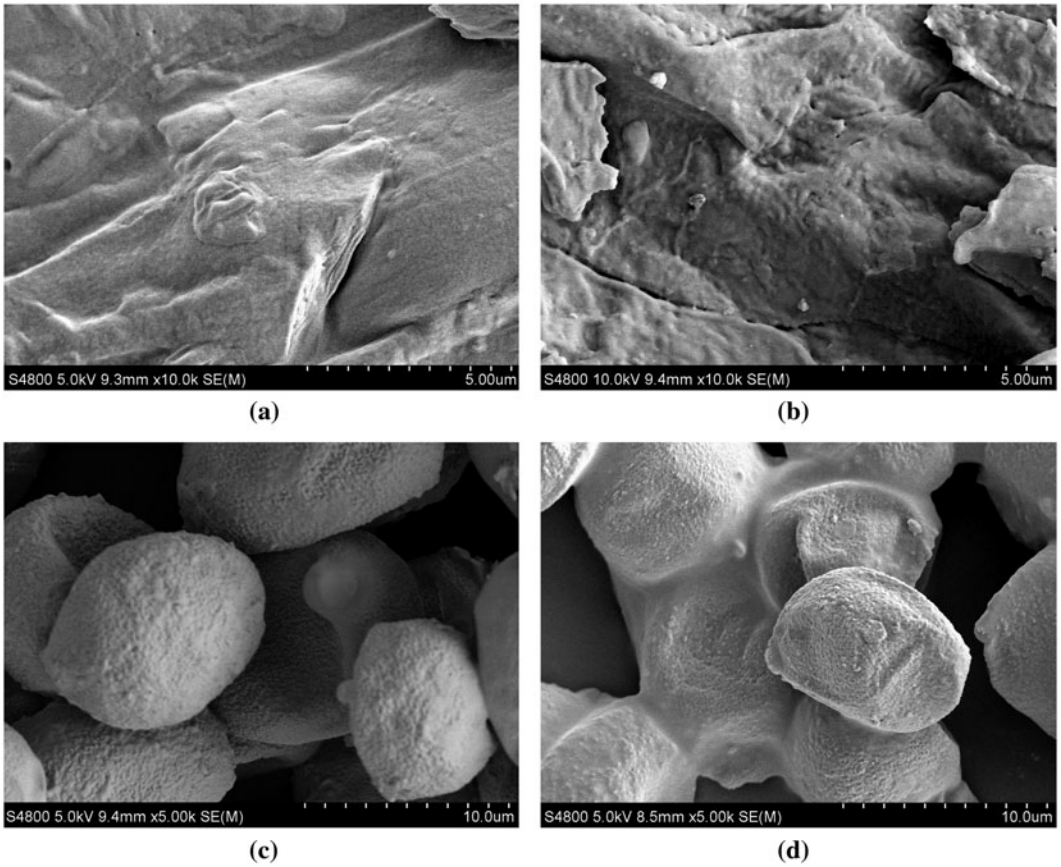

Fig. 11. SEM images of fruiting bodies and spores of *O. radicata* biomass before and after biosorption. (a) Fruiting bodies and (c) spores before Pb(II) biosorption, (b) fruiting bodies and (d) spores after Pb(II) biosorption.

$$\frac{C_{\mathrm{eq}}}{q_{\mathrm{eq}}} = \frac{1}{bq_{\max}} + \frac{C_{\mathrm{eq}}}{q_{\max}}$$

if a biosorption process fits the Langmuir model, a plot of $C_{\mathrm{eq}}/q_{\mathrm{eq}}$ vs. C_{eq} should give a straight line.

The Freundlich isotherm is also commonly used in describing the adsorption on solid sorbent in liquid solutions. It is based on the assumption of heterogeneous surfaces and that the binding sites are not equivalent. This equation is presented as:

$$q_{\mathrm{eq}} = KC_{\mathrm{eq}}^{1/n}$$

where K and n are the Freundlich constant related to sorption capacity and sorption intensity, respectively. The equation can also be transformed to a logarithmic form:

$$\mathrm{In}\, q_{\mathrm{eq}} = \mathrm{In}\, K + \frac{1}{n}\mathrm{In}\, C_{\mathrm{eq}}$$

and a plot of ln q_{eq} vs. ln C_{eq} should give a straight line if an adsorption process fits the Freundlich model.

Figs. 8 and 9 show the Langmuir and Freundlich isotherms obtained for biosorption of lead(II), cadmium(II) and copper(II) ions onto the fruiting bodies and spores. In view of the values of linear regression coefficients (R^2) given in Table 3, it was noted that the Freundlich isotherm model exhibited better fit to the sorption data of all metals for fruiting bodies and spores than the Langmuir isotherm model.

3.5. *Influence of particle size*

The effects of adsorbent particle size on the removal of metal are indicated in Fig. 10. As the result shows, the effect of size on the adsorption rate is small. In the case of copper biosorption, the removal rate of power B is higher than power F. This situation was also observed in previous studies [21]. The results indicated that the effect of particle size on the metal ions biosorption by *O. radicata* is inconspicuous.

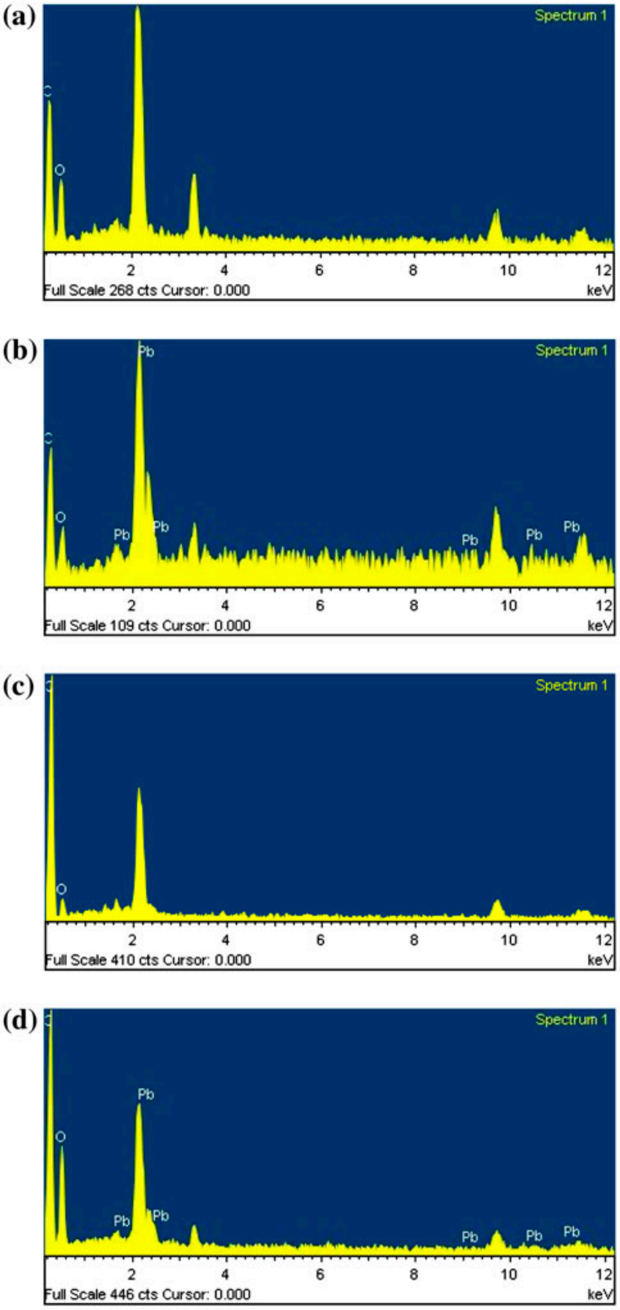

Fig. 12. EDS images of fruiting bodies and spores of *O. radicata* biomass before and after biosorption. (a) Fruiting bodies and (c) spores before Pb(II) biosorption, (b) fruiting bodies and (d) spores after Pb(II) biosorption.

3.6. SEM/EDS analysis

The surface morphologies and elemental compositions of fruiting bodies and spores of *O. radicata* before and after Pb(II) biosorption were examined by SEM coupled with EDS. The SEM results are presented in Fig. 11. It is observed that the surface morphology of the powders changed obviously after Pb biosorption. The functional groups were also characterised by EDS to further understand the role of functional groups in biosorption of Pb(II) in detail. The EDS results are presented in Fig. 12. The EDS analysis confirmed the presence of metal ions on the biosorbent.

Before Pb(II) biosorption, it can be seen that C and O constitute the major elements of fruiting bodies and spores of *O. radicata*. As for heavy metals, element Pb was not detected in pristine fruiting bodies and spores of *O. radicata*. After Pb(II) biosorption, a large amount of Pb was adsorbed by fruiting bodies and spores of *O. radicata*.

3.7. The FT-IR analysis

FT-IR spectra of dried unloaded biomass and Pb (II)-loaded biomass were recorded at 400–4,000 cm^{-1} wavenumber range by using a FT-IR spectrometer.

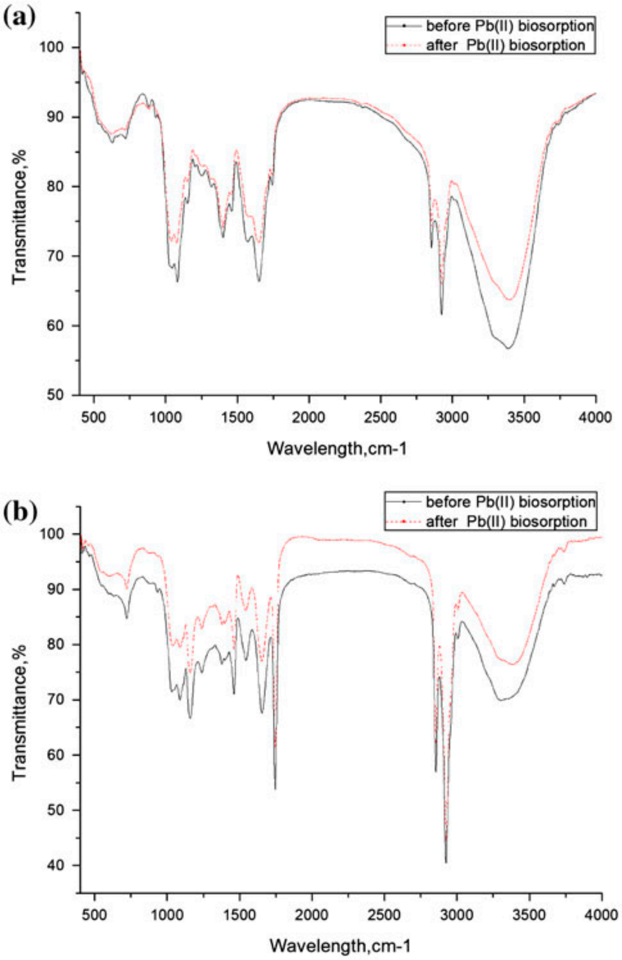

Fig. 13. FT-IR spectrum of unloaded and Pb(II)-loaded biomass (a) fruiting bodies of *O. radicata* biomass and (b) spores of *O. radicata* biomass.

This spectroscopic analysis was used to obtain information on the nature of possible cell–metal ions interactions and the results are presented in Fig. 13. For fruiting bodies of *O. radicata*, the peak at 3,390 was due to bounded hydroxul (–OH) groups. The bands peaks at 1,566 and 1,740 may be attributed to asymmetric and symmetric stretching vibration of carboxyl (–C=O) groups. After biosorption, the stretching vibration bands of hydroxyl were shifted to 3,394. The asymmetric and symmetric stretching vibration bands of carboxyl groups were shifted to 1,577 and 1,743. The similar changes can be seen in FT-IR spectra of spores of *O. radicata*. The results indicated that the chemical interactions as ion-exchange between the metal ions and the hydrogen atoms of carboxyl and hydroxyl of the biomass were mainly involved in the biosorption.

4. Conclusion

O. radicata as a biosorbent for lead, cadmium and copper ions have a high adsorption capacity, especially for lead ion adsorption, the capacity is higher than many biosorbents studied before, it has a good future prospects for practical application. In the pH range of 2–5, for all three metals the adsorption increased along with the increase of pH of the adsorbate solution. The metal biosorption steeply increases with the biomass dosage up to 10 g/L. Increase in the biosorption rate with increase in biomass dosage was attributed to abundant availability of sorption sites. At high biomass dosage, the biosorption rate of the two biosorbents was almost the same. The results revealed that the pseudo-second-order reaction model provided the best description these data; Freundlich isotherm model exhibited better fit to the sorption data than the Langmuir isotherm model. The different sizes of the adsorbent particles were found to have an irregular influence on the adsorption. SEM and EDS analysis confirmed the obvious change of the surface morphology and the presence of metal on the biosorbent after biosorption. The FT-IR analysis results reveal that ion-exchange is the most important biosorption mechanism, but other mechanisms to some extent like electrostatic interaction, involving in functional groups, may also play a part.

Based on the results, it may be concluded that the *O. radicata* biomass could be used as an alternative biosorbent for the removal of lead(II), cadmium(II) and copper(II) from aqueous solution due to its being low-cost biomass and having a considerable high sorption capacity.

Acknowledgements

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