

A novel biosorbent: characterization of the spent mushroom compost and its application for removal of heavy metals

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Abstract: The spent mushroom compost of *Lentinus edodes* was used as a biosorbent for adsorbing cadmium, lead and chromium from solutions under batch conditions for the first time. Titration of the biomass revealed that it contained at least three types of functional groups. The Fourier transform infrared spectrometry showed that the carboxyl, phosphoryl, phenolic groups were the main groups. The simulated values of pK_H and molar quantity were 5.00 and 0.44 mmol/g, 7.32 and 1.38 mmol/g, 10.45 and 1.44 mmol/g, respectively. The biosorption ability increased with pH in acid condition. When 10 mg/L biomass dosage was added in, there was no significant increment of metal uptake. The maximum uptake estimated with the Langmuir isotherm model were 833.33 mg/g for Cd(II), 1000.00 mg/g for Pb(II) and 44.44 mg/g for Cr(III), respectively. All the results showed that vast potential sorption capacity was existed in the biomass for adsorbing these three kinds of metals studied.

Keywords: spent mushroom compost; characterization; biosorption; heavy metals

Introduction

Heavy metals are toxic and non-biodegradable pollutants released into the environment by industrial, mining and agricultural activities (Esposito, 2001). The major sources of heavy metals released are electroplating, smelting, alloy manufacturing, pigments, battery, mining and refining processes (Tsezos, 2001). The soils surrounding many military bases are also contaminated, which poses a risk to groundwater and surface water. Some metals associated with these activities are cadmium (Cd), lead (Pb), chromium (Cr), and mercury (Hg) (Bailey, 1999).

Treatment processes for metal-contaminated water include chemical precipitation, membrane filtration, ion exchange, carbon adsorption, and coprecipitation/adsorption. However, there are some limitations of these processes, such as expensive, low efficiency, labor-intensive operation, or lack of selectivity of the precipitation process (Tarley, 2004). Alternative technologies or sorbents of cost-effective for treating metal-contaminated water are needed. Natural materials available in large quantities, or certain waste products from industrial or agricultural operations, may be of potential as inexpensive sorbents. Due to their low cost, after these materials have been expended, they can be disposed without expensive regeneration.

Many new materials have been reported to remove heavy metals, such as cone biomass (Ucun, 2002), dead *Sargassum* sp. biomass (Cruz, 2004), rice milling by-products (Tarley, 2004), brown seaweed biomass (Yun, 2001) and chitin (Benguella, 2002), with large specific surface area and plenty of binding sites, carboxyl and thiol groups, phosphate and sulfonate groups make them possible for the bioresources to sorb ions from aqueous solutions. Their high efficiency of heavy metal removal and their low cost attract people to exploit more bioresources to alternate traditional processes.

The production of mushroom is the biggest solid-state-fermentation industry in the world. Spent mushroom compost (SMC) is the waste substrate after the production of mushroom. Great bulk of SMC 5 kg will be generated from

the production of 1 kg of mushrooms (Semple, 2001). They are usually thrown into fields as fertilizer. But plenty of biomass species in the spent mushroom compost, such as bacteria, fungi and actinomycetes (Watabe, 2004), high levels of enzymes and other oxidants, made it be more important benefits to human people, such as degrading organopollutants (Chiu, 1998; Law, 2003; Kuo, 1998). There are no reports about the application of its biosorption ability in removing heavy metals. In this sense, the aim of this work was to characterize and apply the spent mushroom compost as a biosorbent for removing cadmium, chromium and lead in laboratory batch systems.

1 Materials and methods

1.1 Preparation of the biosorbent and reagents

The spent mushroom compost (SMC) of *Lentinus edodes* was kindly provided by the Hunan Academy of Agricultural Sciences. The biomass was oven-dried at 80°C for 12 h, ground and homogenised using a sample mill (Foss Tecator, Sweden). Particle sizes $\leq 450 \mu\text{m}$ were obtained by passing the milled materials through a copper sieve. The ground SMC was stored in polyethylene bottle in vacuum dryer and used as biosorbent in the following experiments.

All reagents were of analytical grade (Labconco, Water Pro Plus, USA) and deionised distilled water was used throughout. The stock solutions of Cd(II), Pb(II), Cr(III) 1000 mg/L were prepared using $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Pb}(\text{NO}_3)_2$, $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ respectively (Shanghai Pharmaceutical Co. Ltd, China). Final concentrations of heavy metals were determined by the flame atomic absorption spectrometry (FAAS, Agilent3510).

1.2 Characterization of spent mushroom compost

The functional groups present in the spent mushroom compost were characterized by a Fourier transform infrared (FTIR) spectrometer (WQF-410). The spectral range varied from 4000 to 400 cm^{-1} . Some biomass ($\leq 450 \mu\text{m}$) was encapsulated in KBr in order to prepare the translucent sample disks.

The morphological characterization of the SMC was obtained by using the scanning electron microscope (JSM-

5610LV, JEOL, Japan). The SMC samples were covered with a thin layer of gold and an electron acceleration voltage of 20 kV was applied.

The contents of lignin, semi-cellulose, cellulose in the spent mushroom compost were determined with Fibertec 2010 (Foss, Sweden) according to the method of van Soest (van Soest, 1985).

1.3 Potentiometric titration of spent mushroom compost

The potentiometric titration was carried out for 20 g/L of the SMC. The weighted SMC and 25 ml deionized distilled water (CO₂-free) were put into the Erlenmeyer flasks. Different volume of 1 mol/L NaOH or 0.5 mol/L H₂SO₄ was added into each bottle containing the biosorbent suspension. Sealed bottles were then agitated using an incubator at 200 r/min and 25°C (± 0.5°C) for 24 h. Preliminary tests showed that 24 h was sufficient for the sorption equilibrium (data not shown). After that, the equilibrium pH was measured using an electrode (E-201-C, China). The software of MATLAB 6.5 was used to simulate the quantity of each functional group.

1.4 Biosorption experiments by spent mushroom compost

To optimize the biosorption conditions, dose of biomass, pH, initial concentrations of cadmium, lead and chromium were investigated.

Certain biomass, range from 1 g/L to 25 g/L, was added to 150 ml Erlenmeyer flasks. Following the additions of 100 mg/L of Cd(II), Pb(II), Cr(III), the sealed flasks was agitated in an incubator as described above. The samples were removed from the flasks with filter papers on the pre-determined time. The filtrates were collected to analyze the contents of Cd(II), Pb(II), Cr(III) by FAAS. All treatments were conducted by duplicate.

To ascertain the best pH range during adsorption, 1 mol/L NaOH or 0.5 mol/L H₂SO₄ was used to adjust the solution pH. The solution containing biomass and Cd(II), Pb(II) or Cr(III) were added to the flasks and different volumes of acid or alkali were used. The experiment procedures were the same as described before.

A series of Cd(II), Pb(II), Cr(III) solution ranging from 20 mg/L to 1000 mg/L was prepared to determine the equilibrium isotherms following the addition of the spent mushroom compost. The acid or alkali was added to maintain the best adsorption pH range determined above.

The metal uptake q (mg metal ion/g SMC) was calculated from the mass balance as follows:

$$q = \frac{(C_0 - C_t) V}{W} \times 1000, \quad (1)$$

$$\text{Removal efficiency}(\%) = \frac{C_0 - C_t}{C_0} \times 100. \quad (2)$$

Where C_0 and C_t are the initial and final metal concentrations (mg/L); W and V are the biomass weight (g) and the solution volume (ml) respectively. The change of working volume due to additions of NaOH or H₂SO₄ was negligible in these experiments.

2 Results and discussion

2.1 Characterization of spent mushroom compost

The spent mushroom compost of *Lentinus edodes* was the wood compost products rich of lignin, semi-cellulose, cellulose and chitin (Law, 2003). In this way, high values

(%, g/g) of lignin (10.24), cellulose (22.86) and semi-cellulose (19.71) were obtained in the biomass materials used in the studies.

The FTIR technique was an important tool to identify some characteristic functional groups in the SMC, which were capable of adsorbing metal ions. According to Fig. 1, the broad absorption peak around 3348 cm⁻¹ indicates the existence of bound hydroxyl group (3400–2500 cm⁻¹) (Tarley, 2004; Yun, 2001). The peak observed at 2929 cm⁻¹ could be assigned to the CH₂ group bound by the stretching of the OH groups. The peaks at 1716 cm⁻¹ and 1630 cm⁻¹ were the characteristics of carbonyl group stretching from aldehydes and ketones. These groups could be conjugated or non-conjugated to aromatic rings (1716 and 1630 cm⁻¹ respectively). The spectrum also displayed the absorption peak at 1508 cm⁻¹ corresponding to the stretching band of the aromatic rings. Summing up the characteristic spectra shown in the group frequency region and the fingerprint region, the carboxylic acid was determined by the absorptions of ν_{OH} (3348 cm⁻¹, m), $\nu_{C=O}$ (1630 cm⁻¹, m), δ_{OH} (1423 cm⁻¹, w) and ν_{CO} (1257 cm⁻¹, m). The phosphate group could also be found by some characteristic absorption peaks around $\nu_{P=O}$ (1111 cm⁻¹, s), ν_{PO} (1043 cm⁻¹, vs) and ν_{POC} (895 cm⁻¹, w) (Pagnanelli, 2000). The phenolic group could be defined by the absorptions of ν_{OH} (3404 cm⁻¹, m), $\nu_{C=C}$ (1508 cm⁻¹, w), δ_{OH} (1375 cm⁻¹, m) and ν_{CO} (1321 cm⁻¹, m), which was often found in microbes and distributed widely in the lignin, cellulose and semi-cellulose. The spectrum of the SMC was very similar to that of the rice milling by-products observed by Tarley (Tarley, 2004).

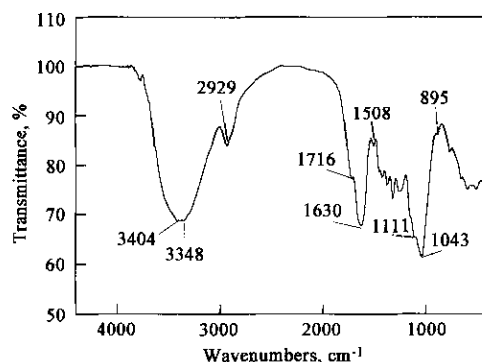


Fig.1 Fourier transform infrared absorption spectra of the spent mushroom compost of *Lentinus edodes*. The lines show the maximum signal obtained

Scanning electron micrographs of SMC are shown in Fig. 2. The porous and irregular inner structure made it possible for heavy metals to adsorb on the vast different surface of the materials.

2.2 Determination of binding sites

The method of potentiometric titration was often used to estimate the functional groups on binding sites (Davis, 2000; Yun, 2001). The titration curve of the SMC is shown in Fig. 3. Considering that the equilibrium pH would be less dependent on the added hydroxide concentration in high biomass concentration (Yun, 2001), 20 g/L SMC was employed to explore the binding characterization. Under this condition, three evident mutations, at pH 4–6, pH 7–8 and pH 9–11, indicated the existence of three functional

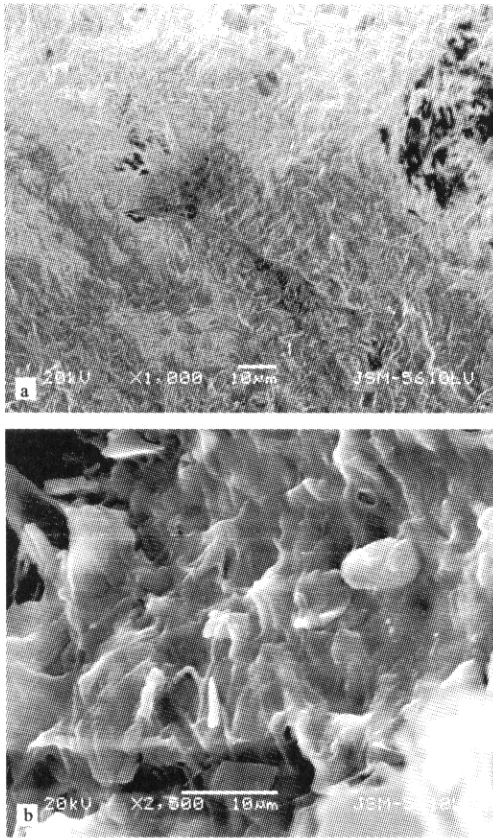


Fig.2 Scanning electron micrograph of spent mushroom compost of *Lentinus edodes* with (a) 1000 times of the surface, (b) 2500 times of the structure. The bar indicates the dimension of 10 μm ; other numbers indicate the acceleration voltage, the magnification and the machine model.

groups with the $\text{p}K_{\text{H}}$ value between 4–6, 7–8 and 9–11, respectively. To evaluate the mole quantities of functional groups, the binding sites on the biomass were deduced from some equations below.

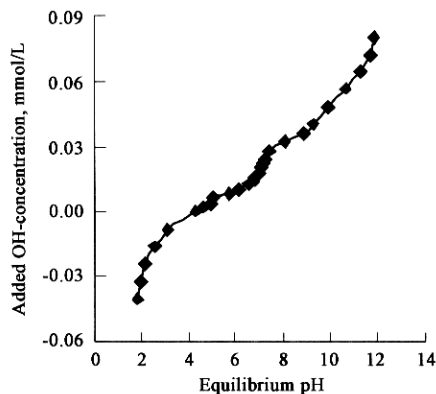
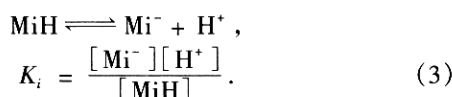


Fig.3 Potentiometric titration of spent mushroom compost of *Lentinus edodes*. 20 g/L of the biomass concentration was used.

A certain group (MiH) reaction with a proton and the related dissociation constant (K_i) might be defined as follows:



The total concentration $[\text{Mi}]$ of the functional group was equal to the sum of the protonated and ionized configurations. The protonated group could be expressed using Eq. (3) as:

$$[\text{MiH}] = \frac{[\text{Mi}^-][\text{H}^+]}{K_i}.$$

Therefore,

$$[\text{Mi}]_{\text{T}} = [\text{MiH}] + [\text{Mi}^-] = [\text{Mi}^-] \left(1 + \frac{[\text{H}^+]}{K_i} \right). \quad (4)$$

Consequently, Eq. (4) could be transformed as follow:

$$[\text{Mi}^-] = \frac{[\text{Mi}]_{\text{T}}}{1 + [\text{H}^+]/K_i}.$$

The law of proton balance must be satisfied in the titration experiments. So

$$[\text{Na}^+] + [\text{H}^+] = \sum_{i=1}^N [\text{Mi}^-] + [\text{OH}^-]. \quad (5)$$

In Eq. (5), the $\sum_{i=1}^N [\text{Mi}^-]$ represented a sum of the concentrations of all types (1st–Nth) of ionized groups, $[\text{Na}^+]$ was the concentration of added hydroxide ions. Therefore

$$[\text{Na}^+] = \sum_{i=1}^N \frac{m_i X}{1 + [\text{H}^+]/K_i} + \frac{K_w}{[\text{H}^+]} - [\text{H}^+]. \quad (6)$$

Where m_i represented the quantity of the specific functional groups per unit mass of biomass (mmol/g) and X was the biomass concentration (g/L).

There were two parameters for each specific functional group in Eq. (6), which were the equilibrium constant (K_i) and the amount of the functional group per unit (m_i). To evaluate the number of functional groups and the concrete value of K_i and m_i , technical software of MATLAB 6.5 was used to simulate the titration model (Eq. (6)) to fit the titration curve.

As a result, there are at least three main types of functional groups in the SMC (Fig. 3). The estimated parameters were summarized in Table 1. The negative logarithm of the equilibrium constant ($\text{p}K_{\text{H}}$) for proton binding to the first group was estimated to 5.00, and the amount was 0.44 mmol/g. Carboxyl groups in biological polymers had $\text{p}K_{\text{H}}$ values ranging from 3.5 to 5.0 (Yun, 2001). The first functional group might be carboxyl for the obvious adsorbing peak of carboxyl group found in FTIR spectrum. The $\text{p}K_{\text{H}}$ of the second group was 7.32. There were many kinds of functional groups of biological polymers that had this $\text{p}K_{\text{H}}$ value such as phosphoryl, amino, and imidazole groups. From the FTIR spectrum, the characteristic absorption peaks of phosphate group could be found (1111 cm^{-1} , P=O stretching; 1043 cm^{-1} , P–OH stretching; 895 cm^{-1} , P–O–C stretching), so the second group might be phosphoryl group. The third group ($\text{p}K_{\text{H}}$ of 10.45) was surely phenolic group because the $\text{p}K_{\text{H}}$ was generally between 9.5 and 10.5 depending on the structure of main chains. The stretching bond of the aromatic rings (1508 cm^{-1}) was also explained by the existence of phenolic group. Meanwhile, the phenolic group was widespread in the lignin, semi-cellulose, cellulose.

Table 1 Constants of K_{H} and m of three functional groups in SMC of *Lentinus edodes*

Functional groups	$\text{p}K_{\text{H}}$	m_i , mmol/g
1st group	5.00	0.44
2nd group	7.32	1.38
3rd group	10.45	1.44

The titration and FTIR studies revealed some characterization of chemical groups in the biomass of SMC,

which could participate the metal binding in the next batch experiments. Since cations of Cd^{2+} , Pb^{2+} , Cr^{3+} would be precipitated in alkaline condition, the heavy metal biosorption experiments were carried out in the range of pH 1–7. In this condition, the second and third functional groups were completely protonated. Therefore, it could be concluded that all of the three titrable sites should play the same important roles in the biosorption studies under the given experimental conditions.

2.3 Biosorption potential by the spent mushroom compost

To make clear the biosorption potential of $\text{Cd}(\text{II})$, $\text{Pb}(\text{II})$ and $\text{Cr}(\text{III})$ by the spent mushroom compost of *Lentinus edodes*, the parameters of pH, dose of biomass and the initial concentration of metals were considered by the next experiments.

pH was one of the most important parameters on biosorption of metal ions from aqueous solutions (Cruz, 2004; Low, 2000; Tarley, 2004). At very low pH value (pH < 2), only few adsorption (Pb and Cr) or even no adsorption (Cd) was observed (Fig. 4). But with the increase of pH in the solution, higher metal biosorption was achieved, indicating better adsorption capacity of the SMC in high pH condition. Then a slight increase of adsorption capacity was got when pH increased from 5 to 7. The highest biosorption capacities of these metals by the SMC were 58.00 mg/g for $\text{Cd}(\text{II})$ at pH 6.95, 82.48 mg/g for $\text{Pb}(\text{II})$ at pH 6.04 and 12.61 mg/g for $\text{Cr}(\text{III})$ at pH 4.82, respectively.

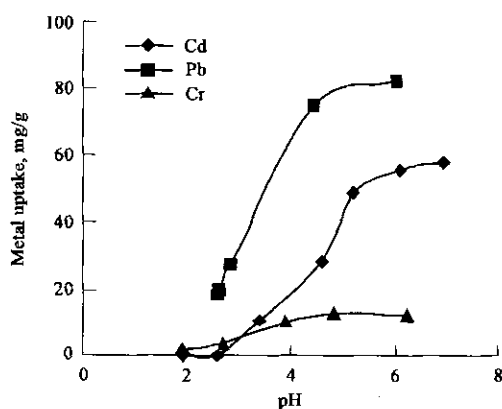


Fig. 4 Effect of pH on removal of $\text{Cd}(\text{II})$, $\text{Pb}(\text{II})$, $\text{Cr}(\text{III})$ by SMC. The initial concentration was 100 mg/L, biomass concentration was 1 g/L for $\text{Pb}(\text{II})$, $\text{Cd}(\text{II})$ and 5 mg/L for $\text{Cr}(\text{III})$ respectively

The phenomenon of biosorption capacity increasing with pH of solution was mostly induced by the surface charge density. From the FTIR spectrum and the titration curve, many functional groups such as phosphoryl, hydroxyl and phenolic existed on the surface of the SMC. With the increasing of pH, the surface charge density of the SMC decreased for the neutralization effect of hydroxide radicals. The electrostatic attraction between the positively charged metal ions and the negative surface of the SMC increased (Tarley, 2004; Boddu, 2003). This resulted in the stronger biosorption ability observed when pH of the solution increased. Similar results were also observed by Tarley (Tarley, 2004) and Yun (Yun, 2001).

In order to make clear the least biomass dosage for a maximal removal of heavy metals, the dosage effect of SMC was examined. As results shown in Fig. 5, the biosorption capacities of $\text{Cd}(\text{II})$, $\text{Pb}(\text{II})$ and $\text{Cr}(\text{III})$ increased with

the concentration of the biomass (while less than 10 g/L of SMC). When the dosage of the biomass was more than 10 g/L, the curves reached a plateau in the figure. But it was reverse when expressed with metal uptake (q). The increase of biomass dosage corresponded to the decrease of the metal uptake. The highest biosorption capacity occurred in the lowest biomass dosage of 1 mg/L with the biosorption capacities of 57.95 mg/g for $\text{Cd}(\text{II})$, 58.78 mg/g for $\text{Pb}(\text{II})$ and 10.96 mg/g for $\text{Cr}(\text{III})$.

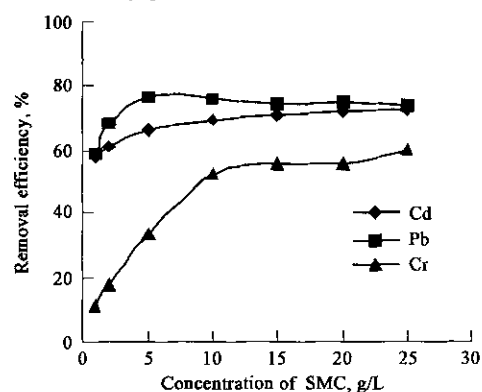


Fig. 5 Effect of concentration of SMC on removal of $\text{Cd}(\text{II})$, $\text{Pb}(\text{II})$, $\text{Cr}(\text{III})$

The initial concentration of metals was 100 mg/L

Metal uptakes in different initial concentrations by the SMC are shown in Fig. 6. Significant differences among these metal cation uptake were observed. There was a decrease order among them: $\text{Pb}(\text{II}) > \text{Cd}(\text{II}) > \text{Cr}(\text{III})$. The surface complex formation related to the valence metals and ionic radius may be induced this phenomenon. $\text{Pb}(\text{II})$ and $\text{Cd}(\text{II})$ offered bigger coordination sphere than $\text{Cr}(\text{III})$ because $\text{Pb}(\text{II})$ and $\text{Cd}(\text{II})$ were of a bigger ionic radius than $\text{Cr}(\text{III})$, which were 120, 97 and 52 mg/L, respectively (Weast, 1988). The bigger the coordination sphere was, the more the hydroxyls and carboxyls embraced. In the other hand, the electronegativity of heavy metals was also an important factor that posed impact on the biosorption ability of the SMC. The electronegativity of $\text{Pb}(\text{II})$, $\text{Cd}(\text{II})$ and $\text{Cr}(\text{III})$ was 2.33, 1.69 and 1.66, respectively. The higher the electronegativity was, the stronger attraction the element had. So $\text{Pb}(\text{II})$ had stronger adsorption profile than the other two metals. Similar results were also found by Chen (Chen, 2002) and Tarley (Tarley, 2004). While in the results given by Chen (2002), the decreasing order of metal binding on calcium alginate-based ion exchange resin was $\text{Pb}(\text{II}) > \text{Cu}(\text{II}) > \text{Ca}(\text{II})$. And the order on rice milling by-

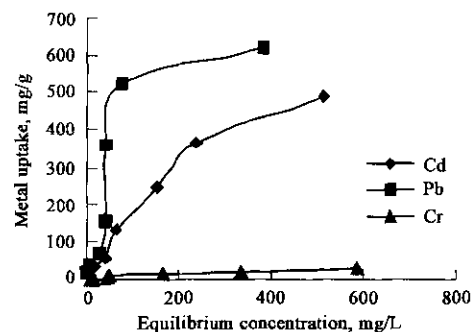


Fig. 6 Isothermal adsorption curves on SMC. The concentration of SMC was 1g/L for $\text{Cd}(\text{II})$, $\text{Pb}(\text{II})$ and 10 g/L for $\text{Cr}(\text{III})$

products was $Pb(II) > Cd(II)$ (Tarley, 2004).

The Langmuir sorption model was usually used to simulate the experimental data when the solute uptake occurs by a monolayer sorption. The model could be described as follows:

$$\frac{C_e}{q} = \frac{k}{q_m} + \frac{C_e}{q_m},$$

where C_e is the equilibrium concentration of the metals (mg/L) and q is the uptake density obtained from experiments (mg/g); q_m is the maximum uptake simulated by the Langmuir model (mg/g) and k is the constant got from the model (L/mg).

Although the model could not provide mechanistic information of the sorption phenomena, it might be used to estimate the maximum uptake of metals (q_m). From the experimental data, the estimated Langmuir parameters for these metals biosorption by the SMC are shown in Table 2. The maximum uptake (q_m) of $Cd(II)$ and $Pb(II)$ were 833.33 mg/g and 1000.00 mg/g, which were much greater than some other biosorbents described in Table 2. And the maximum uptake of $Cr(III)$ was in the middle level.

Table 2 Estimated parameters with Langmuir model by different biosorbents

Metal	Absorbent	q_m , mg/g	k , L/mg	Reference
$Cd(II)$	Chitin	14.71	0.0376	Benguella, 2002
	Dead <i>T. versicolor</i>	164.8	0.0072	Arýca, 2001
	<i>Schizomeris leibleinii</i>	49.25	0.0210	Özer, 1999
	<i>L. tayloriiphos</i>	283.25	0.178	Klimmek, 2001
	Spent mushroom compost	833.33	0.141	This study
$Pb(II)$	<i>Schizomeris leibleinii</i>	63.52	0.0325	Özer, 1999
	<i>L. tayloriiphos</i>	638.18	0.275	Klimmek, 2001
	<i>S. cerevisiae</i>	232.6	0.0168	Özer, 2003
	Immobilized heat inactivated fungus	395	0.00561	Arýca, 2001
	Spent mushroom compost	1000.00	0.488	This study
$Cr(III)$	Brown seaweed biomass	34.1	0.0142	Yun, 2001
	Brown seaweed <i>Sargassum wightii</i>	81.7	0.024	Aravindhan, 2004
	Spent mushroom compost	44.44	0.399	This study

3 Conclusions

The spent mushroom compost was firstly used as a biosorbent for heavy metals of $Cd(II)$, $Pb(II)$ and $Cr(III)$. Vast specific surface area was observed by the scanning electron microscope. Fourier transform infrared spectrometry revealed at least three main kinds of functional groups existing in the biomaterials. Results of titration and model simulation showed that carboxyl, phosphoryl and phenolic groups were proportionally shared the sorption sites. All these characteristics showed that the SMC had vast applicable potential to removal heavy metals from solutions.

The adsorption ability of the SMC increased with the solution pH in acid condition. The highest uptake of metals occurred in pH 4.8—7.0.

Maximum dosage of the biomass was 10 g/L, more quantity could not bring higher adsorbability for three kinds of metals studied.

Isothermal adsorption with series of initial concentrations revealed the adsorbing ability order as follow: $Pb(II) > Cd(II) > Cr(III)$, related to the coordination sphere and

electronegativity. Maximum uptake capacity simulated with the Langmuir sorption model showed the SMC had the superior biosorption ability to some other biomaterials.

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