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The sorption of Cd(II) from aqueous solutions by fixed *Lentinus edodes* mushroom flesh particles

Dan Zhang[a,*], Xuedan Zeng[a,b], Pei Ma[b], Haijiang He[a,b], Jerzy Falandysz[c]

[a]*The Key Laboratory of Mountain Environment Diversity and Control, Institute of Mountain Hazards and Environment, Chinese Academy of Sciences and Ministry of Water Conservancy, Chengdu 610041, China*
Tel. +86 13708008342; Fax: +86 28 85222258; email: daniezhang@imde.ac.cn
[b]*Graduate University of Chinese Academy of Sciences, Beijing 100081, China*
[c]*Research Group of Environmental Chemistry, Ecotoxicology and Food Toxicology, University of Gdańsk, 18 Sobieskiego Str., Gdańsk PL 80-952, Poland*

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ABSTRACT

Lentinus edodes residue that is immobilized with polyvinyl alcohol–Na-alginate was studied as a sorbent for Cd(II) removal from solutions to discover a cost-effective and more practical sorption material for heavy metal ion removal from sewage. Results demonstrated that the sorption of Cd ions by immobilized *L. edodes* reached equilibrium within 7 h. The kinetics of Cd ion sorption were best described with a pseudo-second-order model with an equilibrium sorption capacity (q_e) of 0.2008 mg/g. The optimal pH for Cd ion sorption ranged from 4 to 7. The sorption capacity for Cd ions gradually increased with increasing initial Cd concentration from 0 to 120 mg/L. When the Cd ion concentration was fixed at 10 mg/L and the interfering metal Cu or Pb ion concentration in the same solution was varied from 0 to 30 mg/L, the sorption rate of Cd ions decreased significantly, as determined with variance analysis. The Langmuir model was the most suitable for describing Cd ion sorption with a correlation coefficient (R^2) of 0.9981 and a theoretical maximum sorption capacity (q_m) of 6.4475 mg/g, which was similar to the experimentally observed q_m of 6.046 mg/g. The Langmuir–Freundlich and Freundlich models were also suitable for describing the Cd ion sorption process. Scanning electron microscopy was used for observing the contractive change of the cell surface before and after absorbing Cd ions by immobilized *L. edodes* beads. Fourier transform infrared spectroscopy analysis demonstrated –OH, –CO, and –CO–NH in the cell wall of *L. edodes* plays an important role in Cd ion sorption.

Keywords: Immobilized *L. edodes* residue beads; Cd ion; Sorption; FTIR; SEM

1. Introduction

Immobilized microorganism technology concentrates free cells or enzymes into a limited area, which maintains the activity of the cell and allows for its repeated utilization in chemical or physical methods of recycling [1]. This technology, which was first used in fermentation and water treatment in the late 1970s, has become the focus of substantial research in recent years. Immobilized microorganism technology shows great promise in wastewater treatment. It prevents some of the disadvantages of bioremediation, such as the difficulty in separating the cells from the aqueous solution and the potential for secondary pollution,

*Corresponding author.

and possesses several advantages, such as high efficiency and stability as well as ease of purification. Polyvinyl alcohol (PVA) has several characteristics; it is strong, inexpensive, chemically stable, resistant to microbial decomposition, nontoxic to microorganisms, and results in little loss in cell activity [2–4], although it has poor ball-forming properties and is readily adherent. To improve the PVA gel, polysaccharides, such as sodium alginate (SA), can be added during the process of gel formation [5–8]. Most previous research into immobilization technology has centered on enzyme catalysis, whereas studies seldom examine the use of immobilization technology in wastewater treatment and, even less frequently, in heavy metal wastewater treatment using dead cells [9].

Many recent reports have shown that macrofungi, including edible fungi, have the capacity to collect heavy metals [10–12]. In this study, we used small beads containing dead *Lentinus edodes* cells immobilized on PVA–SA as a sorbent for adsorbing Cd^{2+} ions in solution to increase the sorption capacity of the *L. edodes* residue and to develop an effective method for Cd^{2+} wastewater treatment, which have the characteristics of low cost, high efficiency, and abundant raw materials without secondary pollution. The influence of pH, initial Cd^{2+} concentration, and interfering ions on the sorption capacity of immobilized *L. edodes* beads was investigated. The kinetics and thermodynamics of adsorption were analyzed to investigate the mechanism of Cd^{2+} sorption by the beads. Saturated *L. edodes* beads were treated with HCl to desorb the Cd^{2+}, and desorbed beads were tested for their sorption ability.

2. Materials and methods

2.1. Materials

The inedible portion of the fungal stipe of *L. edodes* was separated from its growth substrate and cleaned. The residue biomass was dried in an oven (50 ± 2℃) to a constant weight and was then cooled, ground into a fine powder, and stored in a jar as biological components of sorbents. Next, 5 g of PVA and 1 g of SA were combined in a beaker with 100 mL of distilled water and then heated and mixed to homogeneity. After the PVA–SA mixture was cooled to 45–50℃, 3 g of *L. edodes* powder was added to the beaker and was stirred. The fungus, alginate, and alcohol solution, at a concentration of 3 g of fungus powder/mL, were subsequently pressed into 100 mL of a saturated H_3BO_3 solution containing 20 mg/mL $CaCl_2$ using a #7–9 syringe needle and was continuously stirred until sorption beads were formed. After they were left standing for 24 h, the sorption beads were cleaned with distilled water, dried to a constant weight in an oven (50 ± 2℃), and stored in a jar for the subsequent experiments.

A stock solution of Cd^{2+} (ρ = 1,000 mg/L) was prepared as follows: 0.1000 g pure Cd was dissolved in a solution of HCl (V:V = 1:1) and 1 mL of concentrated HNO_3 was added upon complete dissolution. The solution was then diluted to 100 mL with deionized water and mixed.

A stock solution of Pb^{2+} (ρ = 1,000 mg/L) was prepared as follows: 1.5990 g of $Pb(NO_3)_2$ was dissolved in 100 mL of HNO_3 (density of 1.42 g/mL), transferred to a 1,000 mL flask, diluted with deionized water to graduation, and then mixed.

A stock solution of Cu^{2+} (ρ = 1,000 mg/L) was prepared as follows: 0.1000 g of pure Cu was dissolved in a small volume of HNO_3 (V:V = 1:1). Once completely dissolved, the solution was diluted to 100 mL with deionized water and then mixed.

The pH of each solution was adjusted with 1 M NaOH or 1 M HCl.

2.2. Experimental methods

2.2.1. Effect of pH

Two hundred milligrams of immobilized beads were added into 25 mL of a 10 mg/L Cd^{2+} solution, and the pH was adjusted to 1, 2, 4, 5, and 7. The immobilized beads in Cd^{2+} solution in flasks were allowed to adsorb heavy metals for 7 h at room temperature with shaking. The Cd^{2+} solution with beads was subsequently filtered by a qualitative medium-speed filter paper , and the concentration of Cd^{2+} in filtrates was determined by atomic absorption spectroscopy (AAS).

2.2.2. Effect of initial Cd^{2+} concentration on sorption

Two hundred milligrams of immobilized beads were added to solutions (pH 5–6) of varying Cd^{2+} concentrations: 5, 20, 40, 80, or 120 mg/L. Flasks containing immobilized beads and the indicated Cd^{2+} solution were shaken at room temperature for 7 h. Solutions were subsequently filtered, and the concentration of Cd^{2+} in filtrates was determined by AAS.

2.2.3. Competitive sorption experiment

A 10 mg/L Cd^{2+} solution was combined with solutions of 0, 1, 5, 10, and 30 mg/L Cu^{2+} or Pb^{2+}, pH 5–6. Flasks containing 200 mg of immobilized beads combined with a solution of interfering Cu^{2+} or Pb^{2+} were

shaken at room temperature for 7 h. The solutions were subsequently filtered, and the concentration of Cd^{2+} in filtrates was determined with AAS.

2.2.4. Determination of sorption kinetics

Five hundred milligrams of immobilized beads was combined with 25 mL of a 5 mg/mL Cd^{2+} solution at a pH of 5–6. Flasks containing immobilized beads and Cd^{2+} solution were shaken at room temperature for different lengths of time: 1, 3, 5, 10, 40, 60, 100, 140, 180, 240, 300, 360, 420, 480, and 540 min. After shaking, the mixture of solution and beads was filtered immediately by a qualitative medium-speed filter paper . The concentration of Cd^{2+} in the filtrates was determined using AAS.

2.2.5. Sorption isotherm

Immobilized beads (200 mg) were combined with 25 mL of a solution of 5, 20, 40, 80, or 120 mg/L Cd^{2+}. After shaking at 25°C for 7 h, solutions were filtered and the concentration of Cd^{2+} in filtrates was determined with AAS.

2.2. Analysis of sorbent by scanning electron microscope (SEM) and Fourier transform infrared spectroscopy (FTIR)

L. edodes powder and PVA–SA-immobilized *L. edodes* beads (both before and after Cd^{2+} sorption) were dried and ground, and the microscopic surface characteristics of samples were observed by SEM (JSM-5900LV, Japan). In addition, *L. edodes* powder and immobilized *L. edodes* beads (both before and after Cd^{2+} sorption) were dried and homogenized, then pressed into slices with KBr. Slices were observed by FTIR (NEXUS 670, Thermo Nicolet Corporation, America).

2.2.7. Desorption experiment

Twenty-five milliliters of a Cd^{2+} solution ($\rho = 5$ mg/L, pH 5–6) was added to a 250 ml Erlenmeyer flask with a stopper. After adding 200 mg of immobilized beads, the flasks were shaken for 3 h at room temperature. After filtration, the immobilized beads were immersed in a 10 mM HCl solution for 2 h to desorb the Cd^{2+} [12], then cleaned with distilled water and dried to a constant weight in an oven (50 ± 2°C). All sorption–desorption procedures were repeated three times with the same batch of beads, and the Cd^{2+} concentration of solutions after absorption was measured between each desorption cycle, so that the rate of change in Cd^{2+} sorption by immobilized *L. edodes* beads could be determined.

The above experiments were replicated three times. Results are expressed as dry biomass.

2.3. Data processing

The equilibrium sorption capacity (q_e) was calculated using the following formula (1):

$$q_e = (C_0 - C_e)V/M \quad (1)$$

where q_e (mg/g) is the sorption capacity per unit sorbent; C_0 (mg/L) is the initial concentration of heavy metal ions; C_e (mg/L) is the metal ion concentration at sorption equilibrium; V (L) is the volume of the metal ion solution; and M (g) is the fungal biomass in dry weight.

The sorption rate (X) of heavy metal ions was calculated using the following formula (2):

$$X = (C_0 - C_e)/C_0 \times 100\% \quad (2)$$

where X (%) is the sorption rate of adsorbed heavy metal ions; and C_0 and C_e are the same as in formula (1).

3. Results and discussion

3.1. Effect of pH on sorption

It is well known that biosorption of heavy metal ions by biosorbents depends on the pH of the solution [13]. The pH affects the availability of metal ions in solution and the metal binding sites on biosorbent surface [14]. The relationship between Cd^{2+} sorption and pH is described in Fig. 1. The sorption rate of Cd^{2+} was comparatively low at a low pH. When the pH increased from 0 to 4, the sorption rate of Cd^{2+} increased sharply

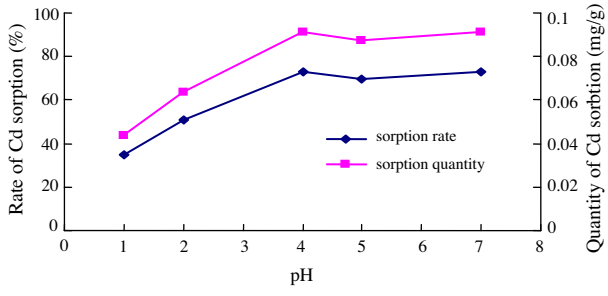


Fig. 1. Effect of pH on Cd^{2+} sorption by immobilized *L. edodes* (the initial Cd^{2+} concentration of solution: 10 mg/L; temperature: room temperature of 25°C; pH of solution: 1, 2, 4, 5, and 7; shaking time: 30 min).

from 35 to 73%. Changes in adsorbed quantity with changes in pH were similar to those of the sorption rate. The quantity of adsorbed Cd^{2+} increased from 0.04385 to 0.09121 mg/g as the pH increased from 1 to 4. At a pH above 4, the sorption curve tended to be relatively constant. The optimal pH range for Cd^{2+} sorption by immobilized *L. edodes* was 4–7, which was much wider than that of free *L. edodes* [15]. The observed increase in the biosorption levels with increasing pH can be explained by the strong relation of biosorption to the number of surface negative charges, which depends on the dissociation of functional groups. Acidic conditions did not favor the sorption of cations. The low biosorption capacity at pH values below 4 was attributed to hydrogen ions that compete with metal ions on the sorption sites [16,17]. In other words, at lower pH, due to protonation of binding sites resulting from a high concentration of protons, negative charge intensity on the sites was reduced, resulting in the reduction or inhibition of the binding of metal ions [18]. It also can be understood that H^+ and H_3O^+ ions in the solution compete with metal cations for binding sites on the surface of the sorbent, which results in a decline in metal ion sorption. The maximum Cd^{2+} biosorpton occurred at pH 4 and the interaction of the Cd^{2+} with the alginate and entrapped fungal cell wall component could primarily be with the carboxyl groups, both alginate and fungal cell wall components. The fungi cell wall, in our case *L. edode*, consists mainly of a number polymers containing various acidic groups, which may deprotonate with rising pH values of biosorption medium [12]. The dependence of heavy metal sorption on pH here implies protonation or deprotonation of these carboxyl groups, and it was proposed that the groups responsible for metal are carboxyl groups. Comparing the increase in binding that occurred at pH 4 shows they are deprotonated and negatively charged, which means that negative charge attracts positively charged Cd^{2+} and more Cd^{2+} binding occurs. Also, the electrostatic and/or coordinative interactions between functional groups on an organism's surface and the metal ions in solution may play a significant role in the process of heavy metal sorption [19]. It has to be mentioned that at alkaline region, metals precipitate as insoluble hydroxides onto the cell surfaces. From the application point of view, precipitation may desirably augment and act complimentary with the application of biosorption to achieve the required high removal of metals [20].

3.2. Effect of initial Cd^{2+} concentration on sorption

With an increasing initial concentration of Cd^{2+}, the sorption capacity also increased (Fig. 2) reaching

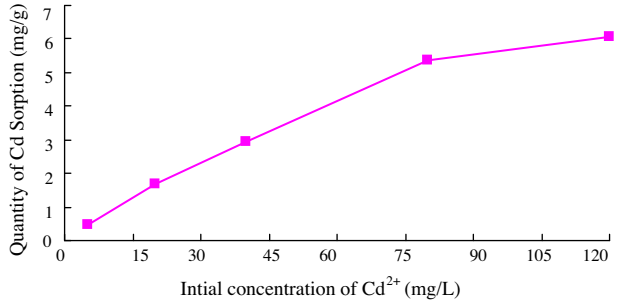


Fig. 2. Effect of metal ion concentration on Cd^{2+} sorption (the initial Cd^{2+} concentrations of solution: 5, 20, 40, 80, and 120 mg/L; temperature: room temperature of 25℃; pH: 5–6; shaking time: 7 h).

6.0469 mg/g at an initial Cd^{2+} concentration of 120 mg/L. The rate of increase in the sorption capacity signifies the affinity between sorbent and metal ion with a faster rate of increase indicating a stronger affinity. When the initial Cd^{2+} concentration was comparatively high (>90 mg/L), the sorption capacity for Cd^{2+} by immobilized *L. edodes* beads declined significantly, which indicates that the competitive exclusion of Cd^{2+} itself had a significant effect on sorption capacity.

3.3. Competitive sorption

Various metal ions often coexist in sewage [21]. Fig. 3 illustrates the influence of Cu^{2+} on the Cd^{2+} sorption rate, which was similar to the effect of Pb^{2+}. A significant change in the Cd^{2+} sorption rate occurred when interfering Cu^{2+} or Pb^{2+} ions at a low concentration, while the opposite occurred at a high concentration. Zhang et al. [22] used mycelia of *Auricularia polytricha* to absorb Cd^{2+} in solution, and found that Cd^{2+} sorption by *A. polytricha* mycelia declined in the presence of Cd^{2+} and Pb^{2+}. When Cu^{2+} was pres-

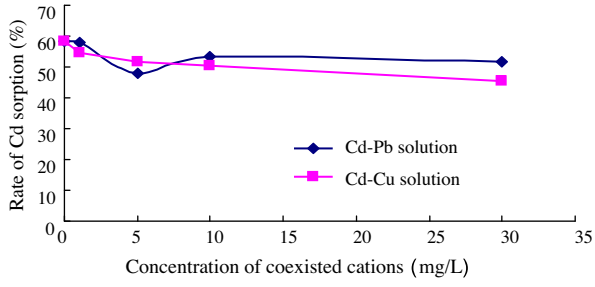


Fig. 3. Effect of interfering ions on Cd^{2+} sorption (the initial Cd^{2+} concentration: 10 mg/L, Cu^{2+} or Pb^{2+} concentration: 0, 1, 5, 10, and 30 mg/L; temperature: room temperature of 25℃; pH 5–6; shaking time: 7 h).

ent in a 10 mg/mL Cd^{2+} solution, the Cd^{2+} sorption rate by *A. polytricha* mycelia initially decreased and then increased with increasing Cu^{2+} concentration. When the concentration of Cu^{2+} and Pb^{2+} was varied from 10 to 30 mg/L, the sorption rate of Cd^{2+} decreased from 50.40 to 45.53%, and from 53.20 to 51.75%, respectively. Thus, the negative influence of Cu^{2+} on Cd^{2+} sorption by immobilized *L. edodes* beads was greater than that of Pb^{2+}. One possible explanation for this observation is that the mechanism of sorption is related to the physico-chemical properties of Cu^{2+}, Pb^{2+}, and Cd^{2+}, such as the element's atomic number, atomic radius, and bonding form between ions and the surface hydroxyl groups of the sorbent, etc. Alternatively, the differences could be related to the functional groups of the sorbent [23].

The variance analysis of the effects of Pb^{2+} and Cu^{2+} on Cd^{2+} sorption is presented in Table 1. The sorption of Cd^{2+} by immobilized *L. edodes* beads was clearly suppressed by Pb^{2+} and Cu^{2+} ions in the solution, which was similar to their effect on the Cd^{2+} sorption capacity of *A. polytricha* [22].

Table 1
Variance analysis of the effects of Pb^{2+} and Cu^{2+} on Cd^{2+} sorption

Source of treatments	Sum of squares		Degrees of freedom		Mean square		*F* value		Significance ($p<0.01$)	
	Pb	Cu	Pb	Cu	Pb	Cu	Pb	Cu	Pb	Cu
Between treatments	226.041	277.535	4	4	56.51	69.384	72.818	155.922	**	**
Within treatments	7.76	4.45	10	10	0.776	0.445				
Total	233.801	281.985	14	14						

3.4. Kinetic analysis of Cd^{2+} sorption

Fig. 4 describes the change in Cd^{2+} sorption rate by immobilized *L. edodes* over time, which can be divided into rapid and slow phases. Within the first hour, the Cd^{2+} sorption rate rapidly increased from 0 to 53.51%; subsequently, the sorption rate increased only slightly, finally reaching equilibrium within 7 h with a q_e of 0.2008 mg/g. Compared to SA, PVA–SA-immobilized *L. edodes* beads were less expensive and more easily obtained. The fact that the equilibrium time of sorption by immobilized *L. edodes* (7 h) was much longer than that of free *L. edodes* (1 h) might be due to slowing the process of diffusion of Cd^{2+} to immobilized *L. edodes* beads compared to free *L. edodes* in solution [15].

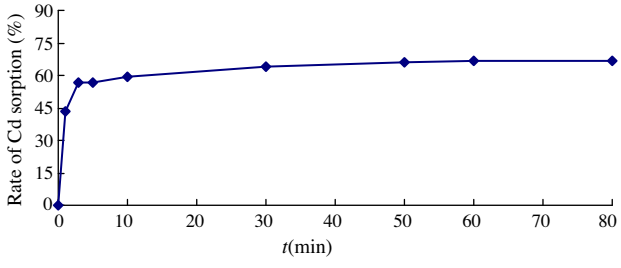


Fig. 4. Change in sorption rate of Cd^{2+} over time (the initial Cd^{2+} concentration of solution: 5 mg/L; temperature: room temperature of 25°C; pH of solution: 5–6; shaking time: 1, 3, 5, 10, 40, 60, 100, 140, 180, 240, 300, 360, 420, 480, and 540 min).

In studying the rules of change in heavy metal concentration over time during a sorption process, many researchers prefer to use a pseudo-first-order model and a pseudo-second-order model to describe the experimental data [24–29]. The pseudo-second-order model, which is commonly used for sorption of divalent heavy metal cations is expressed in formula (3) [24,25,30]:

$$t/q_t = 1/(k_2 q_e^2) + t/q_e \quad (3)$$

where q_t (mg/g) and q_e (mg/g) are the relative sorption capacities of t time and equilibrium time, respectively; and k_2 is the rate constant of the pseudo-second-order model.

A straight line was obtained by plotting t/q_t vs. t (Fig. 5), demonstrating that the pseudo-second-order equation fit the experimental results well, with a correlation coefficient (R^2) of 0.9946. A theoretical q_e of 0.2061 mg/g by immobilized *L. edodes* beads and a k_2 of 0.2130 were obtained from the slope and intercept of the line.

3.5. Sorption isotherms

The capacity of a biomass can be described by equilibrium sorption isotherm, which is characterized by certain constants whose values express the surface properties and affinity of the biomass. The biosorption isotherms were investigated using four equilibrium models, which are namely the Langmuir, Freundlich, Langmuir–Freundlich, and Dubinin–Radushkevich (D–R) isotherm models [31,32].

The Langmuir equation, which is most widely used equation for modeling equilibrium data in dilute solutions, is valid for monolayer sorption on to a surface with a finite number of identical sites and the equation has the following formula (4):

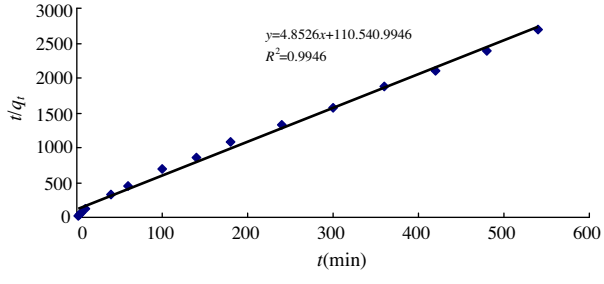


Fig. 5. Pseudo-second-order of Cd^{2+} sorption (the initial Cd^{2+} concentration of solution: 5 mg/L; temperature: room temperature of 25℃; pH: 5–6; shaking time: 1, 3, 5, 10, 40, 60, 100, 140, 180, 240, 300, 360, 420, 480, and 540 min).

$$q_e = q_m b C_e/(1 + bC_e) \quad (4)$$

where q_e is the amount of adsorbed metal at time t (mg/g); q_m is the maximum capacity of adsorbed metal per unit sorbent (mg/g); b is a constant related to the affinity of combining sites for metal adsorption (L/mg); C_e is the equilibrium concentration (mg/L).

The Freundlich expression is an empirical equation based on adsorption on a heterogeneous surface. The Freundlich is commonly presented as formula (5):

$$q_e = KC_e^{1/n} \quad (5)$$

where q_e is the amount of adsorbed metal at time t (mg/g); K and n are equilibrium constants indicative of adsorption capacity and adsorption intensity, respectively; C_e is the equilibrium concentration (mg/L).

The Langmuir–Freundlich isotherm equation is presented as formula (6):

$$q_e = q_m b_{LF} C_e^{\theta}/(1 + b_{LF} C_e^{\theta}) \quad (6)$$

where b and θ are sorption constants; other parameters are the same as formula (4).

The equilibrium data were also subjected to the D–R isotherm model to determine the nature of biosorption processes as physical or chemical. The D–R sorption isotherm is more general than Langmuir isotherm, as its derivation is not based on ideal assumptions such as equiponderance of the sorption sites, absence of steric hindrance between sorbed and incoming particles, and surface homogeneity on microscopic level [33]. The linear presentation of the D–R isotherm equation is expressed by the formula (7) [34]:

$$\ln q_e = \ln q_m - \beta\varepsilon^2 \quad (7)$$

where β is the activity coefficient related to biosorption mean free energy (mol^2/J^2); ε is Polanyi potential (coulomb); other parameters are the same as formula (4). In formula (7), ε can be obtained by formula (8).

$$\varepsilon = RT\ln(1 + 1/C_e) \quad (8)$$

where R is the gas constant (J/mol/K); T is absolute temperature (K); other parameters are the same as formulae (4) and (7):

$$E_s = (2\beta)^{-1/2} \quad (9)$$

Table 2
Parameters of isotherm models for Cd^{2+} sorption

Kinetic model	Parameters	Parameter values	R^2
Langmuir	q_m (mg/g)	6.4475	0.9981
	b	0.05916	
Freundlich	K	0.4310	0.9823
	n	1.5099	
Langmuir–Freundlich	q_m (mg/g)	11.3,636	0.9913
	θ	0.8485	
	b_{LF}	0.03437	
D–R	q_m (mg/g)	53.4529	0.4072
	β	–	
	E_s (kJ/mol)	10,000	

where E_s is absorption energy (kJ/mol); another parameter is the same as formula (7).

The Langmuir equation, Freundlich equation, and Langmuir–Freundlich equation described the process of Cd^{2+} sorption well (Table 2). Among the four models, the Langmuir model was the best fitting with R^2 of 0.9981 and the calculated theoretical maximum sorption capacity (q_m) of 6.4475 mg/g was slightly higher than the practical q_m of 6.0469 mg/g at the initial Cd^{2+} concentration of 120 mg/L. The maximum capacity q_m determined from the Langmuir isotherm defines the total capacity of the biosorbents for Cd^{2+}.

Different biosorbents having a wide range of biosorption capacities for Cd^{2+} have been reported. For example, the heat-treated fungal biomass of *Pleurotus sajor-caju* for biosorption of Cd^{2+} has been used and the biosorption capacity of the biosorbent was 29.6 mg/g dry biomass [35]. The Cd^{2+} biosorption capacity of the NaOH treated fungus biomass, *Aspergillus niger*, was 3.43 mg Cd/g [36]. The fungal biomass of white rot fungus *Phanerochaete chry sosporium* used for heavy metal removal from artificial wastewater had a Cd^{2+} removal capacity of the dry fungal biomass of 23.4 mg Cd/g [37]. The adsorption capacities obtained for both entrapped dead and live *L. sajur-caju* were 120.6 and 104.8 mg Cd^{2+}/g biosorbent, respectively [12]. The maximum uptake obtained at initial concentration of Cd^{2+} 50 mg/L could reach 15.2 mg/g [38]. Yan et al. used live and dead *Mucor rouxii* as sorbents for cadmium removal from aqueous solution and the maximum biosorption capacity was 8.46 and 8.36 mg/g, respectively, when using different culture media, the biosorption capacity of *M. rouxii* obtained was from 2.34 to 9.60 mg Cd/g [18]. The maximum biosorption capacity for immobilized live and inactivated mycelia of wood-rotting fungus *Funalia trogii* was found as 164.8 and 191.6 mg/g, respectively [14]. Under the same experimental conditions, the Cd^{2+} adsorption amounts by *Tremella fuciformis* and *Auriculari polytricha* were 1.4 and 2.3 mg/g, respectively, and Cd^{2+} adsorption amount by *L. edodes* was 1.11 mg/g [39]. The maximum adsorption amounts of Cd^{2+} by *Agaricu bisporus* and *L. edodes* were 2.08 and 0.716 mg/g, respectively [40]. Guo et al. [10] obtained a q_e of 0.6806 mg/g for Cd^{2+} sorption by SA-immobilized bacteria. However, it must be cautious to compare the results in the literature because the experimental conditions used (metal concentrations, solution volumes pH, temperature, amount of biosorbent, etc.) can be widely different. The absence of uniform methodology often makes quantitative comparisons almost impossible [41].

The cost of the adsorbent is an important issue that must be considered while selecting an adsorbent. The cost of commercial activated carbon varies from \$5 to \$6/kg (approximately) [40] and the cost of cultivated mushrooms such as *Pleurotus platypus*, *A. bisporus*, and *Calocybe indica* chosen for some researcher's studies is around \$3 [42], whereas the cost of fixed *L. edodes* mushroom flesh particles for the present study is quite low (<\$1/kg) with no cost for obtaining *L. edodes* residue from mushroom processing factory. So, it can be concluded that fixed *L. edodes* mushroom as cost-effective biosorbents may play an important role for removing Cd^{2+} from aqueous environment.

The magnitudes of K and n (Freundlich constants) show easy separation of metal ions from aqueous medium and indicate favorable adsorption. Also, the magnitude of K and n showed easy uptake of Cd^{2+} from aqueous medium with a high adsorption capacity of entrapped dead fungus. As seen from Table 2 for all experimentally tested biosorbents, n values were found high enough for separation. The experimental equilibrium data fits both Langmuir and Freundlich models well. In mean time, Langmuir–Freundlich model is also suitable for describing the

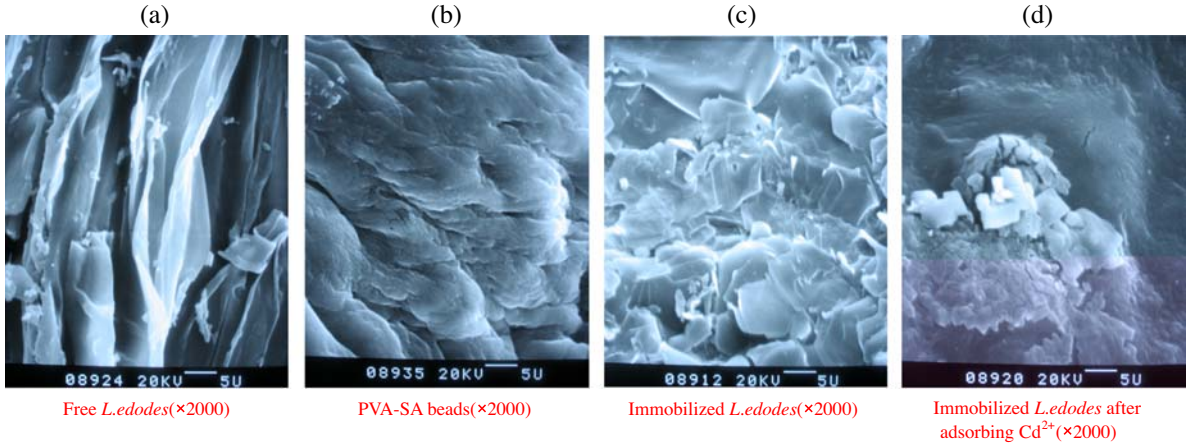


Fig. 6. Spectra of free *L. edodes* (a), blank PVA–SA beads (b) and immobilized *L. edodes* before (c) and after (d) Cd^{2+} absorption (the initial Cd^{2+} concentration in solution: 5 mg/L; temperature: room temperature of 25˚C; pH of solution: 5–6; shaking time: 30 min).

sorption process of Cd^{2+}, thus illustrating the fact that the use of PVA and SA as an entrapment matrix for biosorption of Cd^{2+} could be modeled using the Langmuir, Freundlich, and Langmuir–Freundlich models, whereas the D–R isotherm model not fitted the equilibrium data since the R^2 value was found to be 0.4072. The q_m value calculated was 53.4529 mg/kg, which is largely different from the experimental data.

3.6. Sorbent analysis by SEM and FTIR

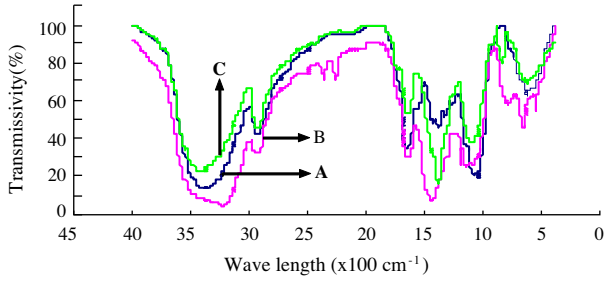
3.6.1. Analysis with SEM

The micro-morphology of *L. edodes*, which has a large, specific surface area of naked and damaged cell walls, is described in Fig. 6(a). The loose and porous structure of the cell walls allows for the free diffusion of molecules and ions. Fig. 6(b) depicts empty PVA–SA beads with a smooth surface and small pores. In contrast, PVA–SA-immobilized *L. edodes* beads were shaggy and porous (Fig. 6(c)); however, after absorbing Cd^{2+}, immobilized *L. edodes* beads became close-grained (Fig. 6(d)) due to the sedimentation of Cd crystals inside the pores, which was confirmed by FTIR. In other words, the immobilized beads could absorb heavy metal contaminants onto their cell walls via physical sorption or by forming inorganic sediments.

3.6.2. Analysis with FTIR

The FTIR spectroscopy method was used to obtain information on the nature of possible cell–metal ions interaction. The FTIR spectra of unloaded and Cd^{2+} loaded forms of biosorbent (free *L. edodes* and PVA–SA-immobilized *L. edodes* beads) in the range of 400–4,000 cm^{-1} were taken and presented in Fig. 7. From Fig. 7(A), the broad and strong band absorption peaks at 3,381 cm^{-1} were due to bounded hydroxyl (–OH) or amine ($–NH_2$) groups. The peaks at 2,927 cm^{-1} were attributed to stretching vibration of –CH group of carbohydrate methylene. The bands observed at 1,551–1,646 cm^{-1} were assigned to –CO–NH, representing the protein absorption peak caused by –CO and –NH. The bands observed at 1,377 cm^{-1} were assigned to –C=O stretching of alcohols and carboxylic acids. The peaks observed at 1,254 cm^{-1} can be assigned to the hydroxyl (–OH) group. The peaks at 1,132 cm^{-1} and 1,041 cm^{-1} were induced by the elastic vibrations of ring saccharides with C–O–C bonds. Therefore, the active groups –OH and –CO–NH were among the main components of *L. edodes* cell walls.

After *L. edodes* being immobilized, the spectral bands at 2,927 and 1,646 cm^{-1} of free *L. edodes* moved



A: free *L. edodes*; B: PVA-SA immobilizing *L. edodes*; C: PVA-SA immobilizing *L. edodes* after adsorbing Cd^{2+}

Fig. 7. FTIR spectra of (A) free *L. edodes* and immobilized *L. edodes* (B) before and (C) after Cd^{2+} adsorption (the initial Cd^{2+} concentration in solution: 5 mg/L; temperature: room temperature of 25˚C; pH of solution: 5–6; shaking time: 30 min).

to 2,923 and 1,634 cm^{-1} of immobilized *L. edodes* with more strongly stretching out and drawing back. Meanwhile, the new peaks emerged at 3,321 and 1,437 cm^{-1} which were characteristic peaks of PVA and H_3BO_3, respectively, and the peak of ring saccharide C–O–C at 1,041 cm^{-1} disappeared (Fig. 7(B)).

After adsorbing Cd^{2+}, the spectral bands of immobilized *L. edodes* beads weakened at 3,381, 2,927, and 1,646 cm^{-1} (Fig. 7(C)). The carboxyl peak was shifted to 1,379 cm^{-1} and the peak at 3,221 cm^{-1} disappeared. The spectral band between 2,500 and 3,500 cm^{-1} had the most obvious change. This results indicated that the chemical interactions as ion exchange between the hydrogen atoms of carboxyl (–COOH), hydroxyl (–OH), and amine ($–NH_2$) groups of the biosorbents and metal ions were mainly involved in the biosorption of Cd^{2+} onto immobilized *L. edodes* biosorbents. In addition, the disappearance of some bands indicated that there was also clear possibly belonging to monosubstituted aromatic protons of the biosorbent indicating possibly the involvement of aromatic amino acids in the sorption of Cd^{2+}. The similar FT-IR results were reported [33,43–45].

3.7. Recycling of sorbent

Sorbent recycling is important for improving efficiency and reducing the initial cost when applying the technology to industrial practice. Fig. 8 depicts the changes in the rate of Cd^{2+} sorption by immobilized *L. edodes* beads in solution after one, two, or three rounds of sorption and desorption. The sorption rate of Cd^{2+} by immobilized *L. edodes* beads declined with an increasing number of sorption–desorption cycles, and the sorption rate decreased from 80.27% for the first recycle to 69.07% after the third recycle, resulting in an overall decrease of 11.20%. Consequently, immobilized *L. edodes* residue can be repeatedly recycled for the effective removal of Cd^{2+} from contaminated water. The decrease in sorption rate may be due to the incomplete desorption of adsorbed Cd^{2+} during the desorption process, which would reduce the number of available binding sites on the beads. We cannot exclude that the number of binding sites for Cd^{2+} sorption decreased due to a transformation in the structure of the immobilized *L. edodes* beads during the desorption process. Further research on the optimal conditions of sorption and desorption by immobilized *L. edodes* beads, methods for increasing their capacity for Cd^{2+} sorption, and techniques for prolonging their lifespan are required.

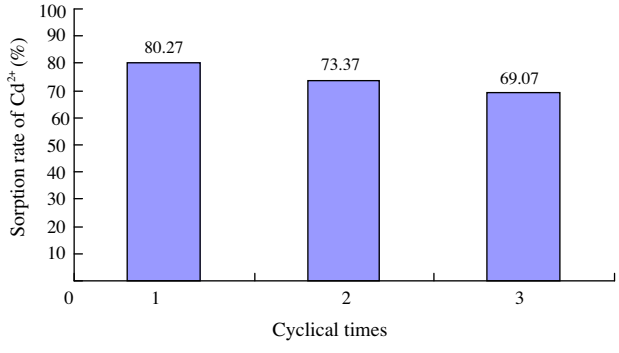


Fig. 8. Reuse of immobilized *L. edodes beads* (the initial Cd^{2+} concentration in solution: 5 mg/L; temperature: room temperature of 25°C; pH of solution: 5–6; shaking time: 3 h; the immobilized beads were immersed in a 10 mM HCl solution for 2 h to desorb the Cd^{2+}; three cycles).

4. Conclusion

The sorption of Cd^{2+} by immobilized *L. edodes* beads reached equilibrium within 7 h with a q_e of 0.2008 mg/g, and the time to reach equilibrium was longer than that of free *L. edodes*. A pseudo-second-order kinetic equation fit the Cd^{2+} sorption process by immobilized *L. edodes* beads well with an R^2 of 0.9946. With an increase in pH from 0 to 4, the sorption rate for Cd^{2+} increased rapidly, reaching a plateau at a pH above 4. The suitable pH range for Cd^{2+} sorption by immobilized *L. edodes* was from 4 to 7, which was much wider than that of free *L. edodes*. The presence of Cu^{2+} or Pb^{2+} ions noticeably reduced Cd^{2+} sorption capacity. Furthermore, low concentrations of interfering ions had a greater impact on the q_c compared to high concentrations. The sorption capacity of the beads increased with increasing initial Cd^{2+} concentration. The Langmuir sorption isotherm model provided the best fit for the process of Cd^{2+} sorption with an R^2 of 0.9981 and a theoretical q_m of 6.4475 mg/g, which was higher than the practical q_m of 6.0469 mg/g at the initial Cd^{2+} concentration of 120 mg/L. After immobilization by PVA–SA, *L. edodes* beads were shaggy and porous and absorbed the heavy metal contaminants onto their cell walls via physical sorption or formation of inorganic sediments. The functional groups –OH, –CO–NH, and –CO on the cell walls of *L. edodes* and on PVA played a role in the process of Cd^{2+} sorption by immobilized *L. edodes* beads. The sorption rate for Cd^{2+} by immobilized *L. edodes* declined after three cycles of recycling with a dilute solution of HCl, although the beads still maintained a sorption rate of 69.07%. Thus, the use of immobilized *L. edodes* residue is feasible for the purpose of heavy metal sorption. The continuous adsorption will be carried out in practical waste water.

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