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Selection of optimum formulation for biosorbing lead and cadmium from aquatic solution by using PVA-SA's immobilizing *Lentinus edodes* residue

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

[a]*The Key Lab of Mountain Environment Diversity & Control, Institute of Mountain Hazards and Environment, Chinese Academy of Sciences and Ministry of Water Conservancy, Chengdu 610041, China*
Tel. +86 (28) 85230076; Fax +86 (28) 85222258; email: daniezhang@imde.ac.cn
[b]*Graduate University of Chinese Academy of Sciences, Beijing 100049, China*
[c]*Research Group of Environmental Chemistry, Ecotoxicology & Food Toxicology, Institute of Environmental Sciences & Public Health, University of Gdańsk, Gdańsk, Poland*

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ABSTRACT

This study focused on macrofungi *Lentinus edodes* residue immobilized by polyvinyl alcohol (PVA)-Na-alginate (SA) for lead (Pb) and cadmium (Cd) adsorption. Based on the ability of absorbing Pb^{2+} and Cd^{2+} from aqueous solution, the mechanical strength and balling property, an orthogonal experiment was done to confirm the optimum formulation of PVA-SA's immobilizing *L. edodes*. The optimum immobilization formulation for absorbing Pb^{2+} was 8% (m/V) PVA + 1% SA + 3% *L. edodes* + 2% $CaCl_2$ in saturated H_3BO_3 solution with adsorption rate of 95.4%, while that for absorbing Cd^{2+} was 5% PVA + 1% SA + 3% *L. edodes* + 2% $CaCl_2$ in saturated H_3BO_3 with adsorption rate of 63.7%. The Langmuir isotherm model best described free *L. edodes* for Pb^{2+} adsorption with R^2 of 0.9939. Freundlich isotherm model best described free *L. edodes* for Cd^{2+} adsorption with R^2 of 0.9993 and best described Pb^{2+} and Cd^{2+} adsorption by immobilized *L. edodes* with R^2 of 0.9587 and 0.9823 respectively. The adsorption for Pb^{2+} and Cd^{2+} by *L. edodes* reached equilibrium within 1 h with equilibrium quantity (q_e) of 0.8440 mg Pb^{2+}/g and 1.8120 mg Cd^{2+}/g respectively, while that by immobilized *L.edodes* reached equilibrium within 3 h and 7 h separately with q_e of 0.4925 mg Pb^{2+}/g and 0.2008 mg Cd^{2+}/g respectively. The pseudo-second-order model fit well Cd^{2+} and Pb^{2+} adsorption kinetics by free *L. edodes* and immobilized *L. edode*s. The rate constant k_2 of the pseudo-second-order model was 1.2531 for Cd^{2+} adsorption and was 1.3241 for Pb^{2+} by free *L. edodes*, and that was 0.7805 for Pb^{2+} and 0.2310 for Cd^{2+} by immobilized *L. edodes* respectively. The theoretic maximum adsorption quantity (q_m) of of 6.4475 mg/g for Cd^{2+} by immobilized *L. edodes* was higher than q_m of 2.8321 mg/g for Cd^{2+} by free *L. edodes* calculated from the Langmuir model and the *k* value of 3.0401 by immobilized *L. edodes* calcuated from the Freundlich model for Pb^{2+} adsorption was higher than the *k* value of 0.7704 for Cd^{2+} adsorption by free *L. edodes* indicated that after immobilization treatment, the capacity of *L. edodes* for Pb^{2+} and Cd^{2+} adsorption increased, and the adsorption ability for Pb^{2+} was stronger than Cd^{2+} by immobilized *L. edodes*.

Keywords: PVA-SA; Immobilization; *Lentinus edodes* residue; Thermodynamics

* Corresponding author.

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1. Introduction

Immobilized cell technology, developed in 1960s, is a kind of biotechnology which has a broad application prospect in wastewater treatment [1]. In wastewater treatment by free fungus, there exists a disadvantage with a small cell which was hard to separate from aqueous solution and easy to cause secondary pollution. But immobilized cell technology prevents those disadvantages and has advantages as high treatment efficiency, less land occupation and reuse of adsorptive materials. At present, there are three common immobilization methods including carrier combination, crosslinking and entrapping methods [2,3]. The entrapping method appears to be the best, because the entrapping agent immobilizes microorganisms inside through the process of high molecular polymer forming gel. Exploiting and utilizing an immobilization carrier with low price, sufficient mechanical stability, physical and chemical stability is a very important part in determining whether the immobilized cell technology can be applied to wastewater treatment. Polyvinyl alcohol (PVA) is considered to be one of the best immobilizing carriers because of its characteristics such as nontoxicity, low price, resistance to microbial decomposition and high mechanical strength [4–6]. The immobilization technology can be affected by carrier property, absorbent characteristics, carrier type and concentration. The granularity of fungus powder affects the mixture degree of fungus powder with immobilizing agents, as well as its adsorption capability for heavy metal. Gao found that smaller granule diameter had stronger adsorption capability in research of Pb^{2+} and Cd^{2+} adsorption by fungus *Flammulina velutipes* residue [7]. The carrier concentration also directly affects the property of immobilized cells. The higher concentration of the carrier contributes a stronger strength to immobilized cells, but its viscosity increases, which makes operation more difficult and obstructs the substrate transfer [8]. The concentration of microorganisms is related to the balling property, mechanical strength and acid tolerance. Higher concentration of microorganisms increases their contact percent with the carrier. Immobilization conditions include the type and concentration of immobilizing agents, which has an impact on the immobilizing process. Commonly used immobilizing agents are H_3BO_3, $CaCl_2$ and $AlCl_3$ [9,10]. The balling property of PVA can be markedly improved by adding sodium alginate (SA), and addition of SA into PVA prevents adhesion in the preparation process of PVA–SA's immobilizing fungus. But SA should not be added too much, because it is extremely unstable in solution with cations such as Mg^{2+} and Ca^{2+}, and easily breaks up and dissolves [11–13].

Edible fungus, a kind of microfungi, has been proved for its great ability in accumulating large quantity of heavy metal [14,15]. *Lentinus edodes* are widely cultivated in China, which has brought broad source of materials for utilization of *L. edodes* residue. Meanwhile, the carrier is nontoxic and of no limitation to biological activity in immobilized dead biomass. Most researchers focused on the immobilization of mold and active biomass compared with less attention on immobilizing dead biomass. The objective of this study is to confirm optimal conditions for immobilizing *L. edodes* by an orthogonal experiment with 4 factors plus 4 levels including concentration of PVA, SA, $CaCl_2$ and *L. edodes* powder, selecting the main factors influencing Pb^{2+} and Cd^{2+} adsorption, and giving out some useful data on heavy metal contaminated water treatment by *L. edodes* residue.

2. Materials and methods

2.1. Materials

Chemicals are pure Cd powder of 99.99%, HNO_3, PVA, SA, anhydrous $CaCl_2$, NaOH, HCl, H_3BO_3 (analysis purity).

The preparation of biosorbent was as follows. The inedible part of fungal stripe of *L. edodes* fruiting body residue attached to the substrate was cut off and cleaned up. The residue biomass was dried at 50±2°C to constant weight in an oven, then cooled, grinded into fine powder, stored in a jar for biomass components of biosorbents.

Stock solution of Cd^{2+} (ρ = 1000 mg/L): dissolving pure Cd of 0.1000 g in the solution of HCl (V/V = 1:1) of 30 mL, absolutely dissolved, adding 1 mL of concentrated HNO_3, then diluted with deionized water and transferred into a 100 mL flask and shaken up.

Stock solution of Pb^{2+} (ρ = 1000 mg/L): weighing $Pb(NO_3)_2$ of 1.5990 g in deionized water containing 100 mL of HNO_3 (density of 1.42 g/cm³), transferred into a 1000 mL flask and shaken up.

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

2.2. Instruments

Cycle-vibrator (HY-5), electronic balance (FA2001N, sense quantity 0.001), thermostatic drying chamber (DFG801), atomic absorption spectrometer (AAS, made in Australia, GBC9322AA), qualitative medium-speed filter (∅ = 9 cm), extensive pH indicator paper (pH 1–14), grinder (FZ102).

2.3. Experimental methods

The concentration of PVA, SA, $CaCl_2$ in saturated H_3BO_3 solution and *L. edodes* powder were the 4 influencing factors with 4 levels respectively for designing an orthogonal experiment. The adsorption rate of Pb^{2+} and Cd^{2+} was taken as the main criteria combining with other physico-chemical properties such as balling property, mechanical strength and acid tolerance of PVA-SA's immobilizing *L. edodes*. On the basis of comprehensive

Table 1
Levels and factors in orthogonal experiment design (m/V/%)

Level	Factors			
	PVA	SA	$CaCl_2$	*L. edodes*
1	5	0.2	2	0.5
2	8	0.5	3	1.0
3	10	0.8	4	2.0
4	12	1.0	5	3.0

evaluation, optimal conditions for immobilized *L. edodes* by PVA-SA was selected. The experimental levels and factors in orthogonal design are shown in Table 1.

2.3.1. The process of making immobilized L. edodes *by PVA–SA and test of its physico-chemical properties*

According to the levels, factors (Table 1) and detailed scheme (Table 2) in the orthogonal experiment design, PVA-SA's immobilizing *L. edodes* was made. Weighed out PVA and SA were placed into a beaker with 100 mL of distilled water, heated, stirred, dissolved, cooled to 45–50°C, then *L. edodes* powder of 0.5–3% was added in the beaker and the mixture was stirred until a homogeneous mixture (fungus–alginate mixture) was formed. The mixture was pressed into a saturated H_3BO_3 aqueous solution containing 2–5% $CaCl_2$ with a syringe needle of the size 7–9, continuously stirred till formation of adsorption pellets. After standing for 24 h, the pellets were cleaned by distilled water, then dried to constant weight in the oven (50±2°C), and stored in a jar for use. Fig. 1 depicts the concrete process of making immobilized *L. edodes*.

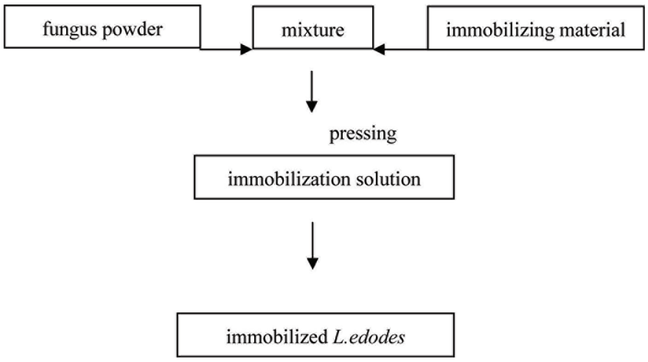

Fig. 1. The process of making immobilized *L. edodes*.

The test of physico-chemical properties of immobilized *L. edodes* included mechanical strength, acid tolerance and its adsorption capacity for heavy metals.

The test of mechanical strength was carried out by pinching immobilized *L. edodes* and describing the strength of pellets qualitatively. The test of acid tolerance was carried out by putting 50 granules of the pellets in HCl aqueous solution with pH 2 for 2 h after the test of the mechanical strength. The test of adsorption capacity for Pb^{2+} and Cd^{2+} was implemented by the following experiment. 25 mL of heavy metal solution (Pb^{2+}: $\rho = 10$ mg/L, pH 5–6; Cd^{2+}: $\rho = 5$ mg/L, pH 5–6) and 0.5 g of immobilized

Table 2
Design and results of orthogonal experiment

Mark	Factors				Balling property	Mechanical strength	Acid tolerance	Sorbtion rate (%)	
	A (PVA)	B (SA)	C ($CaCl_2$)	D (*L. edodes*)				Pb^{2+}	Cd^{2+}
1	1 (5%)	1 (0.2%)	1 (2%)	1 (0.5%)	Poor	Poor	Poor	92.34	61.00
2	1	2 (0.5%)	2 (3%)	2 (1.0%)	Moderate	Poor	Poor	90.50	39.98
3	1	3 (0.8%)	3 (4%)	3 (2.0%)	Excellent	Moderate	Moderate	89.15	51.44
4	1	4 (1.0%)	4 (5%)	4 (3.0%)	Moderate	Moderate	Poor	90.15	51.76
5	2 (8%)	1	1	1	Poor	Excellent	Excellent	87.05	47.88
6	2	2	2	2	Excellent	Good	Good	92.42	54.04
7	2	3	3	3	Good	Excellent	Good	85.86	42.18
8	2	4	4	4	Excellent	Excellent	Good	89.92	54.38
9	3 (10%)	1	1	1	Excellent	Good	Good	87.89	39.58
10	3	2	2	2	Good	Good	Moderate	85.39	36.23
11	3	3	3	3	Excellent	Excellent	Excellent	89.44	44.70
12	3	4	4	4	Good	Excellent	Excellent	88.76	46.54
13	4 (12%)	1	1	1	Poor	Good	Excellent	71.63	28.71
14	4	2	2	2	Good	Excellent	Excellent	88.68	34.75
15	4	3	3	3	Poor	Moderate	Good	92.24	36.58
16	4	4	4	4	Moderate	Good	Good	92.39	35.40

L. edodes was added into a 250 mL Erlenmeyer flask with a stopper, then shaken for 3 h at room temperature, filtered with medium-speed qualitative filters. The concentrations of Pb^{2+} and Cd^{2+} in the filtrates were analyzed by AAS.

2.3.2. Kinetic experiment for Pb^{2+} and Cd^{2+} biosorption

The kinetic experiment of free *L. edodes*: 25 mL solution of Pb^{2+} (ρ = 10 mg/L, pH 5–6) and Cd^{2+} (ρ = 5 mg/L, pH 5–6) was added into the 250 mL Erlenmeyer flask with a stopper respectively, and *L. edodes* concentration was adjusted to 4 mg/L by adding 100 mg of *L. edodes*, shaken at room temperature for different time intervals (1, 3, 5, 10, 40, 60, 100, 140, 180, 240, 300, 360, 420, 480, 540 min), filtered immediately after shaking for adsorption. The concentrations of Pb^{2+} and Cd^{2+} in the filtrates were analyzed by AAS.

The kinetic experiment of immobilized *L. edodes*: 25 mL solution of Pb^{2+} (ρ = 10 mg/L, pH 5–6) and Cd^{2+} (ρ = 5 mg/L, pH 5–6), and 500 mg of immobilized *L. edodes* were added into the 250 mL Erlenmeyer flask with a stopper respectively, shaken at room temperature for different time intervals (1, 3, 5, 10, 30, 50, 60, 80 min), filtered immediately after shaking for adsorption. The concentrations of Pb^{2+} and Cd^{2+} in the filtrates were analyzed by AAS.

2.3.3. Thermodynamic experiment for Pb^{2+} and Cd^{2+} biosorption

The thermodynamic experiment of free *L. edodes*: 25 L of Pb^{2+} and Cd^{2+} solution with different concentrations (10, 20, 40, 60, 80, 100 mg/L, pH 5–6) and 100 mg of free *L. edodes* were added into the 250 mL Erlenmeyer flask with a stopper respectively, shaken for 1 h at constant temperature of 30°C, filtered after shaking for adsorption. The concentrations of Pb^{2+} and Cd^{2+} in the filtrates were analyzed by AAS.

The thermodynamic experiment of immobilized *L. edodes*: 25 mL of Pb^{2+} and Cd^{2+} solution with different concentrations (10, 20, 40, 60, 80, 100 mg/L, pH 5–6) and 200 mg of immobilized *L. edodes* were added into the 250 mL Erlenmeyer flask with a stopper respectively, shaken for 1 h at constant temperature of 30°C, filtered after shaking. The concentrations of Pb^{2+} and Cd^{2+} in the filtrates were analyzed by AAS.

2.4. Chemical quantity and data processing

The rate of adsorbed Pb^{2+} and Cd^{2+} was calculated by using the following equation.

$$X = \left(C_0 - C_e\right) / C_0 \quad (1)$$

where X (%) is the adsorption rate of heavy metal ions, C_0 (mg/L) is the initial concentration of metal ions in the aqueous solution, C_e (mg/L) is the metal concentration at adsorption equilibrium, V (L) is the volume of the metal solution.

3. Results and analysis

3.1. Determination of the optimal immobilization method

The specific experimental design with 4 experimental factors and 4 levels was implemented by means of the orthogonal experiment, in which the 4 factors were PVA (A), SA (B), $CaCl_2$ (C) and *L. edodes* powder (D) and the 4 concentrations of the above 4 factors constituted 4 levels (Table 2).

3.1.1. Physico-chemical properties of immobilized L. edodes

Table 2 indicates that the balling property of immobilized *L. edodes* was optimal at the concentration of 8% and 10% PVA. When concentration of PVA was too high or too low, such as pellets #1 and #13, pellet's formation was difficult. The increase of concentration in SA could markedly improve the ball's formation of PVA–H_3BO_3 pellet. For example, at concentrations of 5% PVA and 0.2% SA, the ball's formation of pellet #1 became worse, while at the concentration of 0.8% SA, the ball's formation of pellet #3 without occurrence of adhesion phenomenon was better than #1. Under certain quantity of PVA, the more amount of fungus powder was expectantly immobilized, but the increase of fungus powder would lead to tailing of PVA–H_3BO_3 pellets. For example, when the concentration of fungus powder in pellet #8 was increased to 4%, the obvious tailing of pellets appeared and the ball's formation was not optimal. In addition, the increase in concentration of fungus powder would interfere with the complete crosslink of PVA and H_3BO_3, which would reduce mechanical strength of pellets. It can be said that mechanical strength and acid tolerance of PVA–H_3BO_3 pellets gradually increased with the increase of PVA concentration.

3.1.2. Optimal formulation of immobilized L. edodes *for Pb^{2+} and Cd^{2+} biosorption*

Table 3 shows the variance analysis for the orthogonal experiment of Pb^{2+} and Cd^{2+} adsorption rate by immobilized *L. edodes*. The higher the sum of square is, the greater the effect of this factor on the adsorption rate is by immobilized *L. edodes*. In 4 factors, the order of influencing Cd^{2+} adsorption capability by immobilized *L. edodes* was the concentration of PVA > $CaCl_2$ > SA > *L. edodes*. The influence of concentrations of the above 4 factors on Pb^{2+} adsorption rate by immobilized *L. edodes* was not significant and the influence of PVA concentration on Cd^{2+} adsorption rate by immobilized *L. edodes* was significant with no significance of other 3 factors.

Table 4 presents the mean value of metal ion adsorption rate by immobilized *L. edodes* with 4 factors and 4 levels. Regarding each factor, the larger the mean is, the higher the rate of metal ion adsorption is under its relevant level. At concentration of 8% PVA, Pb^{2+} adsorption rate by immobilized *L. edodes* was 90.34% which was

Table 3
Variance analysis of Pb^{2+} and Cd^{2+} adsorption by immobilized *L.edodes*

Source of variance (concentration)	Pb^{2+}			Cd^{2+}		
	Degree of freedom	Sum of square	*F*	Degree of freedom	Sum of square	*F*
PVA	3	44.38	0.742	3	914.37	16.050*
SA	3	54.75	0.915	3	29.61	0.520
$CaCl_2$	3	158.83	2.654	3	167.65	2.943
L. edodes	3	57.03	0.953	3	26.21	0.460
Error	3	59.84		3	56.97	
Total	15	374.83		15	1194.81	

Table 4
Mean adsorption rate by immobilized *L. edodes* from orthogonal experiment (*r*/%)

Level	Pb^{2+}				Cd^{2+}			
	A	B	C	D	A	B	C	D
1	89.98	85.57	91.69	89.09	53.55	44.29	48.79	44.57
2	90.34	89.17	90.35	85.54	49.62	43.75	45.25	44.44
3	87.87	89.14	88.99	89.12	41.76	43.73	45.04	42.74
4	86.24	90.57	83.41	90.69	33.86	47.02	39.72	45.49

higher than at any other levels of PVA. At concentration of 5% PVA, Cd^{2+} adsorption rate was 53.55% which was higher than at any other levels. At concentration of 1% SA, both Pb^{2+} and Cd^{2+}adsorption rates by immobilized *L. edodes* were the highest which were 90.57% and 47.02% respectively. At concentration of 2% $CaCl_2$, both Pb^{2+} and Cd^{2+} adsorption rates of immobilized *L. edodes* were the highest which were 91.69% and 48.79% respectively. At concentration of 3% *L. edodes* powder, both Pb^{2+} and Cd^{2+} adsorption rates were the highest which were 90.69% and 45.49% respectively. Therefore, the optimal formulation of PVA-SA's immobilizing *L. edodes* for absorbing Pb^{2+} was 8% (m/V) PVA + 1% SA + 2% $CaCl_2$ in saturated H_3BO_3 solution + 3% *L. edodes* powder, while for absorbing Cd^{2+} was 5% PVA + 1% SA + 2% $CaCl_2$ in saturated H_3BO_3 solution + 3% *L. edodes* powder.

At concentration of 8% PVA, the balling property, mechanical strength and acid tolerance of immobilized pellets were all preferable. At concentration of 5% PVA, the physico-chemical properties of made pellets were poor, while at concentrations of 5% PVA with 0.8% SA or 1.0% SA, the physico-chemical properties of immobilized pellets were better. The concentration of SA in optimal formulation was 1% for absorbing Cd^{2+} from the orthogonal experiment and the physico-chemical properties of immobilized pellets were considered to be good. The adsorption rates of Pb^{2+} and Cd^{2+} by immobilized *L. edodes* made on the above two optimal formulation were 95.4% and 63.7% respectively. Meanwhile, the physico-chemical properties of the 2 kinds of pellets were also preferable.

3.2. Kinetic studies for Pb^{2+} and Cd^{2+} biosorption by immobilized L. edodes

3.2.1. Kinetic process for Pb^{2+} and Cd^{2+} biosorption

Fig. 2 illustrates the change of Pb^{2+} and Cd^{2+} adsorption process by immobilized *L. edodes* with time and from the figure, the adsorption process could be divided into rapid and slow steps. In the first hour of adsorption, Pb^{2+} adsorption rate rapidly increased from 0 to 93% while Cd^{2+} from 0 to 53.51%, after that the adsorption rate of both increased gently. Pb^{2+} and Cd^{2+} adsorption by immobilized *L. edodes* reached equilibrium within 3 and 7 h separately with equilibrium quantity (q_e) of 0.4925 and 0.2008 mg/g respectively.

There were two steps in the process of Pb^{2+} and Cd^{2+} adsorption by free *L. edodes* (Fig. 3). In the first step, Pb^{2+} and Cd^{2+} adsorption by free *L. edodes* rapidly increased up to 67% and 58% within 10 min separately and in the second step, the adsorption rates of both Pb^{2+} and Cd^{2+} increased gently, which reached equilibrium within 60 min with q_e of 1.812 and 0.844 mg/g respectively.

The equilibrium time of immobilized *L. edodes* was much longer than that of free *L. edodes* (1 h), which was in accordance with the results obtained by some other researchers. The equilibrium time of ^{241}Am by immobi-

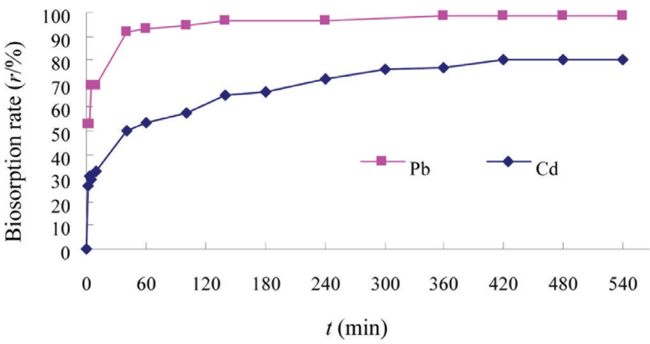

Fig. 2. Effect of time on Pb^{2+} and Cd^{2+} adsorption rate by immobilized *L. edodes*.

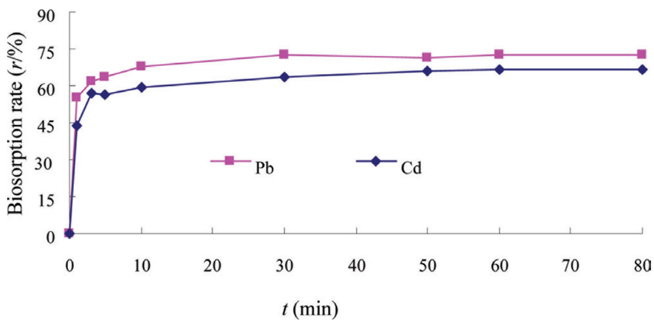

Fig. 3. Effect of time on Pb^{2+} and Cd^{2+} adsorption rate by free *L. edodes*.

lized *Rhizopus arrihizus* was 1 h longer than that of free *R. arrihizus* from research of Liu et al. [8]. Meanwhile, the same result was obtained by Wang et al. in research of Zn^{2+} adsorption by free and immobilized sludge of SRB [16]. This phenomenon might be associated with the process of heavy metal adsorption by immobilized adsorbent, including adsorption of heavy metal ions by the surface of immobilized microorganism carrier, the diffusion mass transfer of heavy metal ions to the inner part of carrier, the adsorption of heavy metal ions by the fungi and the function of exchange resin in biological ions [17]. Also, the adsorption process also could be affected by the porous structure and size of the carrier.

3.2.2. Kinetic model for Pb^{2+} and Cd^{2+} biosorption

The adsorption equilibrium analysis was the basis for inspecting the affinity of the adsorbent and adsorption capacity. Pseudo-first-order equation and pseudo-second-order equation were commonly used in description of the kinetic process for metal ion adsorption [18–20]. Zhang et al. found that Cu^{2+} and Pb^{2+} adsorption by fungus mycelium *Auricularia polytricha* obeyed the pseudo-second-order equation [21]. Fan et al. gave the research result that pseudo-second-order equation was more suitable than pseudo-first-order equation when using the two equations in description of Zn^{2+} adsorption by *Bacillus clausii* S-4 [22].

Table 5 shows the results of the pseudo-second-order model fit with the kinetic process of Pb^{2+} and Cd^{2+} adsorption by immobilized *L. edodes* with the correlation coefficient (R^2) of 0.9999 and 0.9946 separately, and theoretic q_e of 0.4536 and 0.2060 mg/g respectively. The rate constant (k_2) calculated from the model was 0.7805 for Pb^{2+} adsorption higher than 0.2130 for Cd^{2+} adsorption by immobilized *L. edodes*, which means that the adsorption speed of Pb^{2+} was faster than that of Cd^{2+} by immobilized *L. edodes*.

The pseudo-second-order model also well describes the kinetic process of Pb^{2+} and Cd^{2+} adsorption by free *L. edodes* with R^2 of 0.9999 and 0.9998 separately, and with theoretic q_e of 1.817 and 0.8425 mg/g respectively. The k_2 by free *L. edodes* was 1.3241 for Pb^{2+} and 1.2531 for Cd^{2+} which was higher than that for Pb^{2+} of 0.7805 and 0.2130 of Cd^{2+} by immobilized *L. edodes*. It could be said that the needed time for reaching equilibrium of Pb^{2+} and Cd^{2+} adsorption by immobilized *L. edodes* was longer than that by free *L. edodes*.

3.3. Thermodynamics for Pb^{2+} and Cd^{2+} biosorption by immobilized L. edodes

The essence of the adsorption process could be learnt and the maximum adsorption quantity of heavy metal ions by absorbent could be determined with the help of the thermodynamic study. Langmuir and Freundlich adsorption isotherm models were used to imitate the

Table 5
Parameters of pseudo-second-order kinetic for Pb^{2+} and Cd^{2+} adsorption

Adsorbent	Adsorbate	Parameters of pseudo-second-order			Equation
		q_e (mg/g)	k_2	R^2	
Immobilized *L. edodes*	Pb^{2+}	0.4536	0.7805	0.9999	$y = 2.0247x + 6.2277$
	Cd^{2+}	0.2061	0.2130	0.9946	$y = 4.8526x + 110.54$
Free *L. edodes*	Pb^{2+}	1.8172	1.3241	0.9999	$y = 0.5503x + 0.2287$
	Cd^{2+}	0.8425	1.2531	0.9998	$y = 1.1869x + 1.1242$

thermodynamic process of Pb^{2+} and Cd^{2+} adsorption by immobilized *L. edodes* and free *L. edodes* in this study, for inquiring into the influence of immobilization treatment on Pb^{2+} and Cd^{2+} adsorption capacity by *L. edodes*.

Both Langmuir and Freundlich adsorption isotherm models were able to suitably describe the thermodynamic process of Pb^{2+} adsorption by free *L. edodes* with R^2 of 0.9939 and 0.9794 respectively, in which the Langmuir model was more appropriate than the Freundlich model (Table 6). These two models are also able to well describe the thermodynamic process of Cd^{2+} adsorption by free *L. edodes*, with R^2 of 0.9391 with the Langmuir model and 0.9993 with the Freundlich model, in which the Freundlich model was more appropriate than the Langmuir model.

The Freundlich model was able to well describe the thermodynamic process of Pb^{2+} adsorption by immobilized *L. edodes* with R^2 of 0.9587, while the Langmuir model was unsuitable to describe the process of Pb^{2+} with the theoretic maximum adsorption quantity (q_m) of –0.4624 that was impractical. Both Langmuir and Freundlich models were able to well describe the thermodynamic process of Cd^{2+} adsorption by immobilized *L. edodes* with R^2 of 0.9981 and 0.9823 separately, in which the Langmuir model was more appropriate than the Freundlich model.

For Cd^{2+} adsorption, calculated from the Langmuir model, the theoretic q_m of 6.4475 mg/g by immobilized *L. edodes* was higher than q_m of 2.8321 mg/g by free *L. edodes*. For Pb^{2+} adsorption, calculated from the Freundlich model, the *k* value of 3.0401 by immobilized *L. edodes* was higher than the *k* value of 0.7704 by free *L. edodes*. For both ion adsorptions by immobilized *L. edodes*, calculated from the Freundlich model, the *k* value (3.0401) of Pb^{2+} was higher than *k* value (0.4310) of Cd^{2+}. The above results indicate that after immobilization treatment, the adsorption capacity of *L. edodes* for Pb^{2+} and Cd^{2+} increased, and the ability of immobilized *L. edodes* for Pb^{2+} adsorption was stronger than for Cd^{2+}.

4. Conclusion

Among the 4 factors the degree of influencing Pb^{2+} adsorption was $CaCl_2$ > *L. edodes* > PVA > SA in concentration, while influencing Cd^{2+} adsorption was PVA > $CaCl_2$ > SA > *L. edodes* in concentration. The influence of all the 4 factors on Pb^{2+} adsorption was not significant and the influence of PVA on Cd^{2+} adsorption was significant.

The optimal formulation of making immobilized *L. edodes* for absorbing Pb^{2+} was 8% (m/V) PVA + 1% SA + 3% *L. edodes* + 2% $CaCl_2$ in saturated H_3BO_3 solution with the adsorption rate of 95.4%, while for absorbing Cd^{2+} it was 5% PVA + 1% SA + 3% *L. edodes* + 2% $CaCl_2$ in saturated H_3BO_3 solution with the adsorption rate of 63.7%, and with preferable balling property, mechanical strength and acid tolerance of immobilizing pellets.

The adsorption for Pb^{2+} and Cd^{2+} by free *L. edodes* reached equilibrium within 60 min with q_e of 1.812 mg/g and 0.844 mg/g respectively, while by immobilized *L. edodes* the adsorption for Pb^{2+} and Cd^{2+} reached equilibrium after 3 h and 7 h later with q_e of 0.201 mg/g and 0.493 mg/g respectively.

The pseudo-second-order model well fits to describe the kinetic process of Pb^{2+} and Cd^{2+} adsorption by both immobilized *L. edodes* and free *L. edodes* with R^2 of 0.9999 for Pb^{2+} and 0.9946 for Cd^{2+}, and theoretic q_e of 0.4536 mg Pb^{2+}/g and 0.2060 mg Cd^{2+}/g by immobilized *L. edodes* and with R^2 of 0.9999 for Pb^{2+} and 0.9998 for Cd^{2+}, and theoretic q_e of 1.8172 mg Pb^{2+}/g and 0.8425 Cd^{2+}mg/g by free *L. edodes* respectively. The time of reaching equilibrium for Pb^{2+} and Cd^{2+} adsorption by immobilized *L. edodes* was longer than that by free *L. edodes*.

The Langmuir adsorption isotherm model best fits the thermodynamic process of Pb^{2+} adsorption by free *L. edodes* with R^2 of 0.9939 and the second one is the Freundlich model with R^2 of 0.9794. The Freundlich model well fits the thermodynamic process of Cd^{2+} adsorption by free *L. edodes* with R^2 of 0.9993 and the second one is the Langmuir model with R^2 of 0.9391. The Freundlich model well fits the thermodynamic process of Pb^{2+} and Cd^{2+} adsorption by immobilized *L. edodes* with R^2 of 0.9587 and 0.9823 respectively. After immobilization treatment,

Table 6
Isotherm parameters of model for Pb^{2+} and Cd^{2+} adsorption

Isotherm model	Parameter	Free *L. edodes*		Immobilized *L. edodes*	
		Pb^{2+}	Cd^{2+}	Pb^{2+}	Cd^{2+}
Langmuir	q_m (mg/g)	72.9927	2.8321	–0.4624	6.4475
	b×100 (constant)	0.8375	3.1762	100.9500	5.9160
	R^2	0.9939	0.9391	0.9898	0.9981
Freundlich	k (constant)	0.7704	0.3127	3.0401	0.4310
	n (constant)	1.1675	1.0314	0.1281	1.5099
	R^2	0.9794	0.9993	0.9587	0.9823

the adsorption capacity for both Pb^{2+} and Cd^{2+} by *L. edodes* increased. The adsorption ability for Pb^{2+} was stronger than for Cd^{2+} by immobilized *L. edodes*.

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