



Kinetic studies for the biosorption of lead and copper ions by *Penicillium simplicissimum* immobilized within loofa sponge

Xiao-ming Li*, De-xiang Liao, Xue-qin Xu, Qi Yang,
Guang-ming Zeng, Wei Zheng, Liang Guo

College of Environmental Science and Engineering, Hunan University, Changsha 410082, PR China

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ABSTRACT

Biosorption potential of *Penicillium simplicissimum* (*Penicillium* sp.) immobilized within loofa sponge (PSILS) for lead and copper from aqueous media was explored. The effects of pH, contact time and initial concentration were studied in batch experiments. The maximum uptake of metal ions was obtained at pH 5.0. Biosorption equilibrium was established by 60 min. The pseudo-first-order, pseudo-second-order and intraparticle diffusion kinetic models were applied to study the kinetics of the biosorption processes. The pseudo-second-order kinetic model provided the best correlation ($R^2 > 0.999$) of the experimental data compared to the pseudo-first-order and intraparticle diffusion kinetic models. The maximum heavy metal ions adsorbed was found to be 152.6 and 112.3 mg/g for Pb(II) and Cu(II), respectively. It was found that the biosorption of both Pb(II) and Cu(II) on PSILS was correlated well ($R_{Pb}^2 = 0.999$ and $R_{Cu}^2 = 0.9978$) with the Langmuir equation as compared to Freundlich isotherm equation under the concentration range studied. PSILS was regenerated by washing with a 100 mM solution of HCl. The desorption efficiency was as high as 98%. The PSILS was reused in five adsorption–desorption cycles with negligible decrease in biosorption capacity. The present work showed that PSILS was an efficient biosorbent for removal of heavy metal ions from aqueous solution.

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1. Introduction

Conventional methods for removing heavy metals such as activated carbon adsorption, chemical oxidation/reduction, precipitation, ion exchange, electrochemical processes, membrane filtration and reverse osmosis from waste streams encountered a few major disadvantages such as high energy requirements, incomplete metal removal and generation of toxic sludge which needs proper disposal in addition to financial constraints [1,2]. Biosorption, using low-cost biomaterials and microorganisms for removing and recovering toxic metals from wastewaters, has emerged as a potential alternative method to conventional techniques [2]. The process has gained importance due to its advantages such as the reusability of biomaterial, low operating cost, improved selectivity for specific metals of interest, removal of heavy metals from effluent irrespective of toxicity, short operation time, and no production of secondary compounds which might be toxic [3,4].

During past few decades, biosorption has been studied extensively using various biomasses such as white-rot fungus [5–7], *Saccharomyces cerevisiae* [8,9], *Cladosporium* sp. [10], *Bacillus sub-*

tilis [11,12] and *Chlorella sorokiniana* [13,14]. However, one major problem associated with microbial biosorbents is separation and harvesting of the biomass after metal removal. Immobilization of the biomass on to a more rigid and open support matrix can overcome this problem. A number of different synthetic polymeric agents have been used as supporting materials for the immobilization of microbial biosorbents [15–17], however, the production of large amounts of polymeric gel beads for commercial application is expensive and results in closed structures with low mechanical strength, restrictive diffusion and mechanical breakdown in the presence of certain ions [18]. Loofa sponge, an alternative immobilization matrix, has been used successfully to immobilize fungal hyphae and yeast cells to remove toxic metal from aqueous solution [14]. Loofa sponge can be used as matrix due to its advantages such as low cost, physically strong, rigid and highly porous.

In the present study, PSILS was chosen as a biosorbent material, because information on its ability to remove Pb(II) and Cu(II) from aqueous solution is not available. The biosorption potential of PSILS for Pb(II) and Cu(II) from aqueous media was investigated as a function of initial pH, contact time and initial metal ion concentration. The biosorption data have been analyzed by the pseudo-first-order, pseudo-second-order and intraparticle diffusion kinetic models as well as the Langmuir and Freundlich isotherm models. These studies may be useful for low-cost industrial wastewater treatment.

* Corresponding author. Tel.: +86 731 8823967; fax: +86 731 8822829.
E-mail address: xmli@hnu.cn (X.-m. Li).

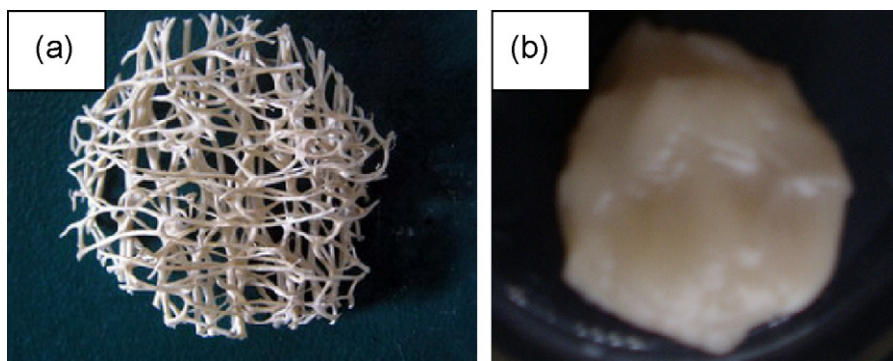


Fig. 1. Immobilization of *Penicillium* sp. within loofa sponge disc (a: loofa sponge disc; b: loofa sponge disc covered with *Penicillium* sp.).

2. Materials and methods

2.1. Microorganism and culture medium

Penicillium sp., isolated from a composting fermentation system in our laboratory was used in this study. Mycelium suspensions for immobilization were prepared from 7-day-old cultures, grown on potato dextrose agar slants at 303 K. The growth medium for immobilization consisted of (g/L distilled water): FeSO_4 , 0.005; NaHCO_3 , 0.05; CaCl_2 , 0.1; KCl , 0.1; NaCl , 0.2; $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 0.25; KH_2PO_4 , 0.5; NH_4Cl , 2.0; Peptone, 10.0; Glucose, 20.0; pH 5.7.

2.2. Immobilization

Loofa sponge were cut into discs of approximately 2.5 cm diameter, 2–3 mm thick, soaked in boiling water for 30 min, thoroughly washed under tap water, and left for 24 h in distilled water and continuously rinsed. Then, the discs were dried in an oven at 378 K and stored in desiccators before further use.

Immobilization of the *Penicillium* sp. in loofa sponge was carried out as described by Iqbal and Edyvean [19] with some modifications. Some pre-weighed loofa sponge discs as an immobilizing matrix were added into 250 mL Erlenmeyer flasks containing 100 mL of the growth medium and then autoclaved (394 K, 30 min). The matrix was then inoculated with 5 mL of *Penicillium* sp. (10^6 spores/mL) suspension followed by incubation under shaking (100 rpm) at 303 K. After 4 days of incubation, immobilized *Penicillium* sp. was harvested from the medium, washed thrice with distilled water and stored at 277 K until use. Dry weight of biomass

was determined by weighing dried (24 h at 343 K) discs before and after fungal growth.

2.3. Characteristics of PSILS

In the optimal condition, the biomass of *Penicillium* sp. grew rapidly in the biomatrix of loofa sponge and formed a compact block of fungal mass (Fig. 1a and b). The surrounding of the immobilized disc was clear and no free hyphal growth was observed in the medium.

SEM analysis reveals that even though the *Penicillium* sp. hyphal is packed tightly, there is still sufficient microchannel and void volume for free movement of solute thus increasing the accessibility of metal ions to the binding sites on the fungal biomass (Fig. 2).

2.4. Preparation of metal solutions

The synthetic solutions were all prepared by diluting Pb(II) and Cu(II) standard stock solutions (concentration 1000 ± 2 mg/L) obtained by dissolving $\text{Pb}(\text{NO}_3)_2$ and $\text{Cu}(\text{NO}_3)_2$ in deionized water. Fresh dilutions were used in each experiment.

2.5. Biosorption studies

To determine the optimum Pb(II) and Cu(II) biosorption conditions, the batch experiments were conducted with PSILS and naked loofa sponge (NLS) at 303 K in 250 mL Erlenmeyer flasks. The effect of pH on the biosorption capacity was investigated at initial pH values range of 2.0–6.0 and the desired pH of the suspensions was maintained by adding HCl or NaOH at the beginning of the experiment and not controlled afterwards. Biosorbent was added to medium and the reaction mixture was shaken in ther-

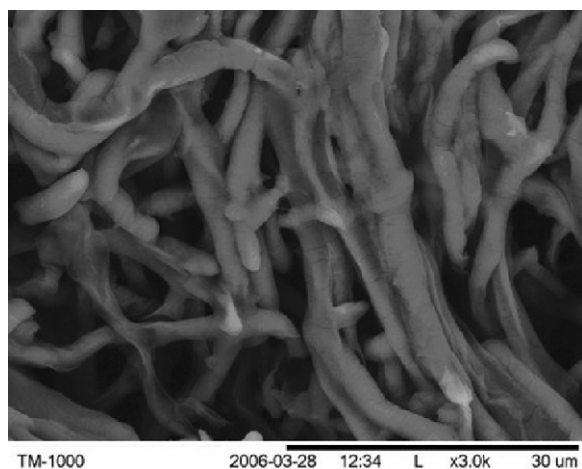


Fig. 2. The SEM characterization of immobilized *Penicillium* sp. biomass ($\times 3000$).

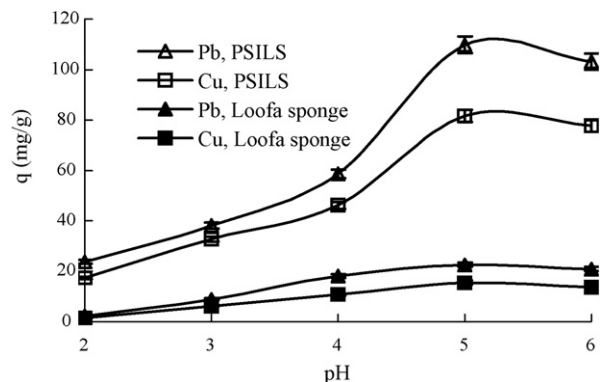


Fig. 3. Effect of pH on the adsorption capacities of PSILS and naked loofa sponge for Pb(II) and Cu(II) ions.

mostated water bath shaker at 100 rpm for 60 min. In the latter experiments the pH of the Pb(II) solutions were adjusted to optimum pH value (5.0 ± 0.1). The effect of contact time was studied in the range of 5–180 min. Similarly above, single metal solutions with the concentration range of 10–500 mg/L were used to assess the effect of initial Pb(II) and Cu(II) ion concentrations. At the end of the biosorption process biosorbent was separated from the solution and supernatant, and the solution was diluted with deionized water then analyzed for residual Pb(II) and Cu(II) concentrations by AAS (Agilent 3510, USA). Three replicates were used for each Pb(II) and Cu(II) biosorption experiments and the results given were the average values. The biosorption capacity of immobilized biomass was calculated using the general equation:

$$q_e = \frac{(C_0 - C_t)V}{M} \quad (1)$$

where q_e is the amount of Pb(II) and Cu(II) ions biosorbed on the biomass (mg/g), C_0 and C_t are the Pb(II) and Cu(II) concentrations in solution before and after biosorption (mg/L), V the volume of the medium (L) and M is the amount of the biomass used in the reaction mixture (g).

2.6. Biosorbent regeneration

The regeneration of biosorbent is directly related to the application potential of biosorption technology. The performance of HCl in the biosorbent regeneration was examined in five biosorption–desorption cycles to determine the PSILS regeneration. For this purpose, PSILS was contacted with 100 mL of 50 mg/L of single metal solution for biosorption and 100 mM HCl for desorption in 250 mL flasks, shaken on constant temperature oscillator at 100 rpm and 303 K. The contact time of each biosorption and desorption cycle was maintained 60 min for achieving biosorption or desorption equilibrium. The initial and final metal concentrations of the solution were recorded for each cycle. After each cycle of adsorption–desorption, the PSILS were thoroughly washed with deionized distilled water to neutrality and reconditioned for biosorption in the succeeding cycle.

The desorption efficiency was calculated using the following equation:

$$\text{Desorption efficiency} = \left(\frac{\text{amount of metal ions desorbed}}{\text{amount of metal ions adsorbed}} \right) \times 100\% \quad (2)$$

2.7. Adsorption isotherms

2.7.1. Langmuir isotherm

Langmuir's isotherm model [20] is valid for monolayer adsorption onto a surface containing a finite number of identical sites. The Langmuir treatment is based on the assumption that a maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface, that the energy of adsorption is constant, and that there is no transmigration of adsorbate in the plane of the surface, which is represented as Eq. (3):

$$\frac{C_e}{q_e} = \frac{1}{bq_{\max}} + \frac{C_e}{q_{\max}} \quad (3)$$

where q_e and q_{\max} are the observed and maximum uptake capacities (mg/g); C_e is the equilibrium concentration (mg/L); b is the equilibrium constant (L/mg).

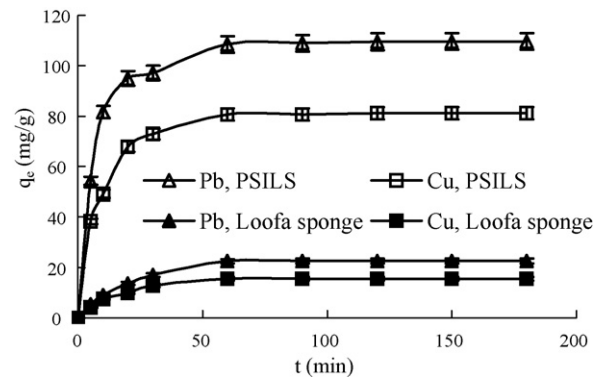


Fig. 4. Effect of time on the adsorption capacities of PSILS and naked loofa sponge for Pb(II) and Cu(II) ions.

2.7.2. Freundlich isotherm

The Freundlich equation [21] proposes an empirical model that is based on sorption on heterogeneous surface and has the form:

$$\ln q_e = \ln K_f + \frac{1}{n(\ln C_e)} \quad (4)$$

where K_f (L/g) and n are Freundlich isotherm constants; q_e is the observed uptake capacity (mg/g); C_e is the equilibrium concentration (mg/L).

3. Results and discussion

3.1. Effect of pH

The acidity of solution (pH) is one of the most important parameters controlling uptake of heavy metals from wastewater and aqueous solutions [22]. In this group of experiments, the concentration of single metal 100 mg/L, and contact time (60 min) were kept constant. Fig. 3 describes the effects of pH on biosorption of Pb(II) and Cu(II) onto PSILS and NLS at initial pH value range between 2.0 and 6.0. The results showed that the biosorption of Pb(II) and Cu(II) on PSILS increased significantly as the pH increased from 2.0 to 5.0, however, the increase was slightly on NLS, and then decreased at pH 5.0–6.0. The low Pb(II) and Cu(II) biosorption capacity at pH values below 3.0 may be attributed to hydrogen ions that compete with metal ions on the sorption sites [23]. This means that at higher hydrogen ions concentrations, the biosorbent surface becomes more positively charged, thus reducing the attraction between biosorbent and metal ions. In contrast, as the pH increases, more negatively charged surfaces become available thus facilitating greater metal uptake [24]. Yan and Viraraghavan [25] found that the Pb(II) biosorption capacity of *Mucor rouxii* cells increased with increasing pH of the solution and reached a constant value at pH 5.0. Chang et al. [23], reported that, the optimum pH value for the biosorption of Pb(II) and Cu(II) by *Pseudomonas aeruginosa* cells was 6.0. Since the optimum pH for Pb(II) and Cu(II) biosorption by PSILS was found to be 5.0, therefore, this pH was used for further study.

3.2. Kinetic study

The kinetics of Pb(II) and Cu(II) sorption were studied using solution containing 100 mg/L concentration of each metal using PSILS and NLS at optimum pH up to a contact time of 3 h. Fig. 4 shows the plot of the metal ion sorbed (q_e , mg/g) as a function of the time. Rapid accumulation of both metals was observed for PSILS, reaching 90% of total biosorption capacity in the first 30 min. Equilibrium was reached in approximate 60 min for lead and copper, which showed saturation of the active points. NLS adsorbed Pb(II) and Cu(II) far

Table 1

Parameter values calculated using the pseudo-first-order and the pseudo-second-order models for the biosorption of Pb²⁺ and Cu²⁺ on PSILS

Metal ion	Pseudo-first-order model			Pseudo-second-order model			
	q_e	K_1	R^2	v_0	q_e	K_2	R^2
Pb ²⁺	58.88	0.0546	0.9757	29	112.36	0.0023	0.9998
Cu ²⁺	48.83	0.0560	0.9496	16.9	84.03	0.0024	0.9995

less than PSILS, indicating little effect of the immobilization matrix on metal uptake.

In order to investigate the biosorption mechanism of PSILS, characteristic constants of biosorption were determined using a pseudo-first-order equation of Lagergren [26,27] based on solid capacity, a pseudo-second-order equation (Ho equation) [28,29] based on solid phase sorption and an intraparticle diffusion model.

The pseudo-first-order equation of Lagergren can be expressed as Eq. (5):

$$\log(q_e - q_t) = \log q_e - \frac{K_1 t}{2.303} \quad (5)$$

where q_t is the amount of metal ions adsorbed (mg/g) at any given time t (min), q_e is the amount of metal ion adsorbed (mg/g) at equilibrium and K_1 is the pseudo-first-order reaction rate constant for adsorption (min^{-1}).

The pseudo-second-order reaction rate equation has the form:

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{K_2 q_e^2} \quad (6)$$

where q_t is the amount of metal ions adsorbed (mg/g) at any given time t (min), q_e is the amount of metal ion adsorbed (mg/g) at equilibrium and K_2 is the second-order reaction rate constant for adsorption ($\text{g}/(\text{mg min})$). The following expression denotes the initial sorption rate v_0 ($\text{mg}/(\text{g min})$) [30]:

$$v_0 = K_2 q_e^2 \quad (7)$$

The intraparticle diffusion model [31,32] was considered in order to determine the participation of this process in the sorption of lead and copper by PSILS. According to this model, the plot of uptake (q_t), versus the square root of time ($t^{0.5}$) should be linear if intraparticle diffusion is involved in the overall adsorption mechanism. Furthermore, if this line passes through the origin then the intraparticle diffusion is the rate controlling step of the process [33]. The initial rate of intraparticle diffusion, K_d , can be calculated in the following way:

$$q_t = K_d t^{0.5} \quad (8)$$

where q_t is the amount of sorbate on the surface of the sorbent at time t (mg/g), K_d is the intraparticle rate constant ($\text{mg}/(\text{g min}^{0.5})$) and t is the time (min).

Fig. 5a and b show linear plots of the linearized forms of the pseudo-first-order model in Eq. (5) and the pseudo-second-order model in Eq. (6) for the sorption of Pb(II) and Cu(II) onto PSILS. K_1 , K_2 and q_e calculated from the slopes and intercepts of the lines obtained by plotting $\log(q_e - q_t)$ against t and t/q_t against t are listed in Table 1. As shown in Table 1, the pseudo-second-order model fits better the biosorption kinetics of heavy metal ions on PSILS than the pseudo-first-order model. This suggests that the rate-limiting step of this sorption system may be chemical sorption or chemisorption involving valency forces through sharing or exchange of electrons between sorbent and sorbate [34,35]. The q_e calculated from the pseudo-second-order rate model of Pb(II) and Cu(II) are 112.36 and 84.03 mg/g, respectively, in the order of Pb(II) > Cu(II), which are consistent with the results in Fig. 4. The initial biosorption rate (v_0) values of Pb(II) and Cu(II) ions are 29 and 16.9 mg/(g min), in the order of Pb(II) > Cu(II). The differences in the initial biosorption rate

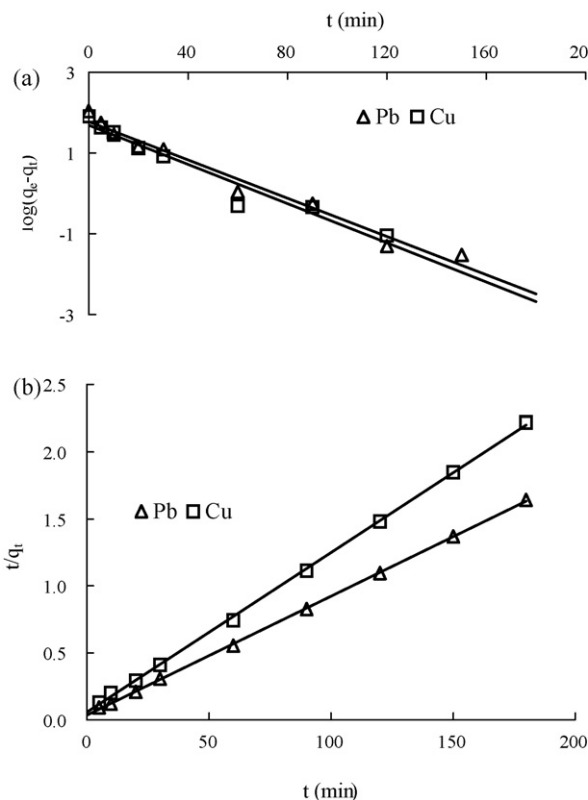


Fig. 5. (a) linear fit of experimental data obtained using pseudo-first-order model and (b) linear fit of experimental data obtained using pseudo-second-order model.

of lead and copper may be due to the nature and distribution of active groups on the adsorbent and the affinity between the metal ions and the adsorbent [36–38].

The plot of uptake (q_t), versus the square root of time ($t^{0.5}$) was not linear (not shown), which indicated that the intraparticle diffusion was not the rate-controlling step in these biosorption systems.

3.3. Effect of initial metal ion concentration

The experiments were carried out using various concentrations of Pb(II) and Cu(II) solution under the determined optimum pH values and contact time. The effect of initial single metal ion concentration was investigated in the range of 10–500 mg/L. The results were presented in Fig. 6. The Pb(II) and Cu(II) biosorption capacity of the immobilized biomass firstly increased with increasing of the initial concentration of metal ion and then reached a saturation value at about 200 mg/L and the maximum equilib-

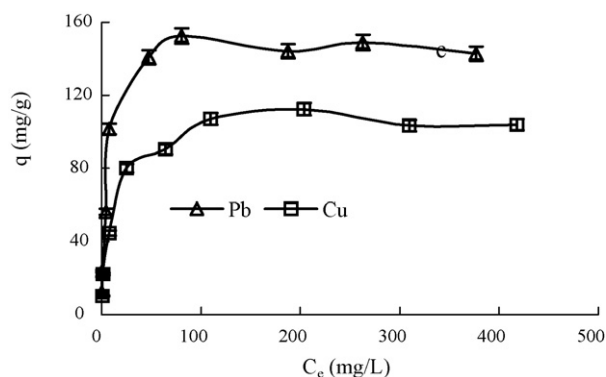


Fig. 6. Effect of initial concentration on the adsorption.

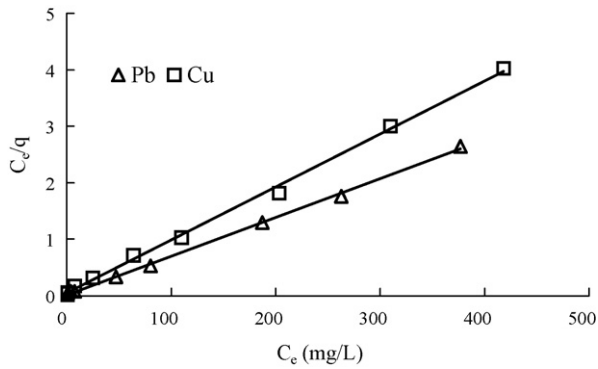


Fig. 7. Langmuir plot of Pb(II) and Cu(II) ions on PSILS.

Table 2

Langmuir and Freundlich constants and correlation coefficients for biosorption of Pb(II) and Cu(II) on PSILS

Metal ions	Langmuir			Freundlich		
	q_{max}	b	R^2	K_f	n	R^2
Pb ²⁺	144.9	0.59	0.999	33.0	3.27	0.9016
Cu ²⁺	106.4	0.193	0.9978	19.3	3.02	0.9102

rium uptake for Pb(II) and Cu(II) were 152.6 and 112.3 mg/g. Then the value did not significantly change with the initial metal ion concentration.

3.4. Adsorption isotherms studies

The linear plots of Langmuir and Freundlich equation representing Pb(II) and Cu(II) biosorption by the PSILS are illustrated in Fig. 7 and Fig. 8. The adsorption constants of Langmuir and Freundlich equation and their correlation coefficients (R^2) are calculated and represented in Table 2. The correlation regression coefficients show that the biosorption process is better defined by Langmuir than by the Freundlich equation. The Langmuir fit is consistent with strong monolayer sorption onto specific sites. According to Langmuir isotherm, the monolayer saturation capacity of PSILS is 144.9 mg/g for Pb(II) and 106.4 mg/g Cu(II).

3.5. Desorption and regeneration

Biosorption capability of fungal biomass and its regeneration would decide its potential as a biosorbent for commercial application. The capacity of the PSILS to adsorb metal ions was

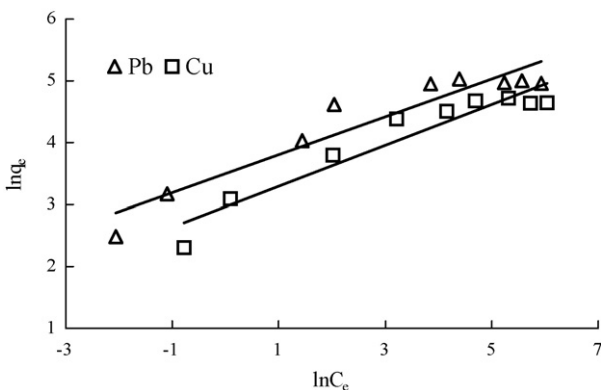


Fig. 8. Freundlich plot of Pb(II) and Cu(II) ions on PSILS.

Table 3

Biosorption and desorption of heavy metal ions by PSILS in five consecutive cycles

Cycle No.	Metal adsorbed (mg/g)		Metal desorbed (%)	
	Pb(II)	Cu(II)	Pb(II)	Cu(II)
1	91.08 ± 1.35 ^a	76.29 ± 2.06	98.3 ± 0.59	98.1 ± 0.51
2	89.79 ± 1.52	75.73 ± 1.97	99.1 ± 0.34	99.5 ± 0.16
3	90.13 ± 1.29	76.08 ± 1.31	97.9 ± 1.08	99.0 ± 0.21
4	89.67 ± 1.43	75.57 ± 2.13	99.1 ± 0.25	97.8 ± 0.51
5	89.24 ± 2.03	75.32 ± 1.46	97.2 ± 0.41	98.2 ± 0.93

^a Data denote mean ± S.D. of three replicates.

determined by repeating the biosorption experiments in five-consecutive cycles. HCl (100 mM) solution was used as a desorption agent. As illustrated in Table 3, the PSILS undergoing successive adsorption–desorption processes retained good metal biosorption capacity even after 5 cycles and higher than 97% desorption was obtained after five-adsorption–desorption cycles. The total decrease in biosorption efficiency of PSILS for Pb(II) and Cu(II) after five cycles were 2.02% and 1.27%, respectively, which showed that PSILS had good potential to adsorb metal ions repeatedly from aqueous solution.

4. Conclusions

In this study, biosorption of Pb(II) and Cu(II) on PSILS was investigated as a function of pH, equilibration time and initial metal concentration. The experiments have shown that:

- (1) The experimental data were fitted by the second-order kinetic model, and the rate-limiting step of this sorption system may be chemical sorption inside of mass transfer. The contact time of approximately 60 min was required to reach the equilibrium.
- (2) The sorption isotherm could be well defined by Langmuir equation. The calculated capacity obtained by Langmuir equation were 144.9 mg/g for Pb(II) and 106.4 mg/g Cu(II).
- (3) The adsorbed metals were effectively eluted with dilute HCl. The PSILS was reused in five adsorption–desorption cycles with negligible decrease in biosorption capacity. The present work showed that PSILS was a new biosorbent to be used for treatment of metal-bearing solutions.

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