

Remediation of soil contaminated with the heavy metal (Cd^{2+})

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Abstract

Soil contamination by heavy metals is increasing. The biosorption process for removal of the heavy metal Cd^{2+} from contaminated soil is chosen for this study due to its economy, commercial applications, and because it acts without destroying soil structure. The study is divided into four parts (1) soil leaching: the relationships between the soil leaching effect and agitation rates, solvent concentrations, ratios of soil to solvent, leaching time and pH were studied to identify their optimum conditions; (2) adsorption Cd^{2+} tests of immobilized *Saccharomyces pombe* beads: different weight percentages of chitosan and polyvinyl alcohol (PVAL) were added to alginate (10 wt.%) and then blended or cross-linked by epichlorohydrin (ECH) to increase their mechanical strength. Next, before blending or cross-linking, different weight percentages of *S. pombe 806* or *S. pombe ATCC 2476* were added to increase Cd^{2+} adsorption. Thus, the optimum beads (blending or cross-linking, the percentages of chitosan, PVAL and *S. pombe 806* or *S. pombe ATCC 2476*) and the optimum adsorption conditions (agitation rate, equilibrium adsorption time, and pH in the aqueous solution) were ascertained; (3) regeneration tests of the optimum beads: the optimum beads adsorbing Cd^{2+} were regenerated by various concentrations of aqueous HCl solutions. The results indicate that the reuse of immobilized *pombe* beads was feasible; and (4) adsorption model/kinetic model/thermodynamic property: the equilibrium adsorption, kinetics, change in Gibbs free energy of adsorption of Cd^{2+} on optimum beads were also investigated.

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Keywords: Soil leaching; Cadmium; Chitosan; Immobilized *Saccharomyces pombe* bead; Regeneration

1. Introduction

Soil contamination by heavy metals is increasing. Heavy metals in farm land have been of great concern due to their toxic nature and other adverse effects. Crops which are raised on land contaminated by heavy metals may take up heavy metals. Heavy metals accumulate easily in crops and therefore may be transferred from crops to animals (and hence to humans).

According to the literature [1], remediation methods for soil contaminated with heavy metals include chemical methods, engineering solutions, and biological methods, etc. However, chemicals utilized in the chemical methods may destroy soil structure and result in secondary pollution. Besides, Cline and Reed [2] noted that soil contaminated by heavy metals

is effectively leached by EDTA or HCl, but that these may destroy the soil structure. In contrast, soil contaminated by heavy metals leached by CaCl_2 does not destroy the soil structure although it is not very effective. Therefore, in this study, among engineering solutions, CaCl_2 was chosen to leach soil contaminated with heavy metals due to its lower cost. After soil leaching, this method produced large quantities of leaching solutions whose composition was complex. Furthermore, Mackenbrock [3] mentioned that it is more economic and competitive to remove heavy metals from leaching solutions by a biosorption process. So, in this research, among biological methods, the biosorption process was chosen to treat leaching solutions containing heavy metals.

Chitosan is a biopolymer, which is of interest to researchers concerning the adsorption of metals. It is the deacetylated form of chitin, which is a natural polymer extracted from crustacean shells, such as prawns, crabs, shrimp, and insects. Liu et al. [4] noted that chitosan is a suitable natural polymer for the concentration of metals, such as Cd^{2+} ,

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Zn²⁺, Cu²⁺, Pb²⁺, etc., since amine groups on chitosan can act as chelating sites for heavy metals. However, the mechanical strength of chitosan is poor. It is, therefore, necessary to modify chitosan to improve its mechanical properties and chemical stability, etc. In order to improve its mechanical strength, polymers such as PVAL can be added to chitosan. In addition, Wan Ngah et al. [5] and Alupeu et al. [6] showed that in order to maintain the NH₂ groups of chitosan, CH₂OH groups of chitosan combine with O groups of ECH when chitosan is cross-linked by ECH. Thus, cross-linked chitosan beads still retain NH₂ groups with which to adsorb heavy metals. Moreover, Mi et al. [7], Chang et al. [8], Pozzo et al. [9], and Zhang et al. [10] stated that mechanical strength and pore size of cross-linked chitosan beads are a function of cross-linking agents used and polymers added.

In spite of cross-linking enhancing the mechanical strength of chitosan beads, it may reduce their adsorption capacity. Herein, some types of biomass added to cross-linked chitosan beads may improve adsorption performance. David [11] mentioned that *S. pombe 806* and *S. pombe ATCC 2476* can be used as biosorbents for removal of Cd²⁺. In addition, Puranik and Paknikar [12], Bolesky and Holan [13], Chang and Chen [14] showed that immobilized biomass appeared to effectively adsorb heavy metals. Furthermore, Stoll and Duncan [15] mentioned that it appeared technically feasible to remove heavy metals from aqueous solutions by immobilized *Saccharomyces pombe* beads. Moreover, the advantages of the process based on immobilized biomass include enhancing microbial cell stability, allowing the reuse of biomass, and avoiding the biomass-liquid separation requirement. Thus, in order to enhance adsorption capacity, the inactivated cells of *S. pombe 806* or *S. pombe ATCC 2476* was added in this research.

In this study, in order to enhance mechanical strength, different amounts of chitosan and PVAL were added to alginate (10 wt.%) and then they were blended or cross-linked by 0.5 M ECH. In addition, different amounts of *S. pombe 806* or *S. pombe ATCC 2476* were also added before blending or cross-linking to increase their adsorption capacity. The aim of this research was to ascertain the optimum beads (blending or cross-linking, the percentages of chitosan, PVAL and *S. pombe 806* or *S. pombe ATCC 2476*) and the optimum adsorption conditions (agitation rate, equilibrium adsorption time, and pH in the aqueous solution). In addition, we also investigated the equilibrium adsorption and kinetics of adsorption of Cd²⁺ on optimum beads. The Langmuir equation was used to fit equilibrium adsorption. The adsorption rates were determined quantitatively and compared by pseudo-first-order and second-order models. Furthermore, thermodynamic parameters, such as change in Gibbs free energy (ΔG^0) were also determined to indicate whether the adsorption is spontaneous or not. Moreover, immobilized *S. pombe* beads containing adsorbed Cd²⁺ were regenerated by HCl aqueous solutions. Finally, this information would also be used to further application in the treatment of soil leaching solutions containing Cd²⁺.

Table 1
Soil leaching parameters and their conditions

Parameters	Conditions
CaCl ₂ concentration (M)	0.00, 0.01, 0.03, 0.05, 0.10, 0.20, 0.30, 0.40, 0.50
Agitation rate (rpm)	5000, 8000
Soil/solvent	1/2, 1/4, 1/6, 1/8
pH	3, 6, 9, 10, 11, 12

2. Experimental methods

2.1. Soil leaching

The soil was sampled from farm land contaminated by Cd²⁺ and dried in air. Then the soil was sieved by a Taylor's standard sieve mesh to constant size (<1 mm) for use. Before soil leaching, the total concentration of Cd²⁺ in the soil was measured by the digestion method of aqua regia. Next, influence of soil leaching parameters on soil leaching was studied employing progressive steps to identify their optimum operating conditions. Soil leaching parameters and their conditions are given in Table 1. Their steps included (1) changing CaCl₂ concentration, fixing other conditions (agitation rate = 5000 rpm, soil/solvent = 1/2, sampling time = 1 h), and measuring concentrations of Cd²⁺ in the leaching solutions by inductively coupled plasma-mass spectrometer (ICP-MS); (2) changing agitation rates, selecting the optimum CaCl₂ concentration from step (1) and soil/solvent = 1/2, taking samples at time intervals (0.5, 1.0, 2.0, and 4.0 h) after leaching, and measuring Cd²⁺ concentrations; (3) changing soil/solvent, choosing the optimum CaCl₂ concentration, agitation rate, sampling time from above steps, and measuring Cd²⁺ concentrations; and (4) changing pH, choosing the optimum CaCl₂ concentration, agitation rate, sampling time, soil/solvent from above steps, and measuring concentrations Cd²⁺. In this way, the optimum conditions for soil leaching parameters could be determined.

2.2. Culture of *Saccharomyces*

In general, the culture methods for *Saccharomyces* include agar-agar culture and liquid culture. In this study, *S. pombe 806* was grown on the culture medium YTG and *S. pombe ATCC 2476* was grown on the culture medium YMG. Besides, *S. pombe 806* and *S. pombe ATCC 2476* belong to aerobic split reproduction fungi. Furthermore, influence of culture parameters on growth of *Saccharomyces* was studied. Culture parameters and their conditions are given in Table 2. Their steps included (1) changing agitation rates, fixing other conditions ($T = 303$ K, *S. pombe 806*: pH 5.45 and $t = 15$ h, *S. pombe ATCC 2476*: pH 5.65 and $t = 24$ h), analyzing it at wavelength 600 nm by an UV-vis spectrometer (Model: SP 830) and observing the number of fungi by blood cell counter; (2) changing temperatures, choosing the optimum agitation rate from step (1), fixing

Table 2
Culture parameters and their conditions

Parameters	Conditions
Agitation rate (rpm)	0, 50, 100, 150, 200
Temperature (K)	298, 299, 300, 301, 302, 303
Time (h)	2, 4, 6, 8, 10, ... (until the number of fungi reached a maximum)
pH	2, 3, 4, 5, 6, 7

pH and time as step (1), observing the number of fungi; (3) changing time until the number of fungi reached a maximum, choosing the optimum agitation rate and temperature from above steps, fixing pH as step (1), observing the number of fungi; and (4) changing pH, choosing the optimum agitation rate, temperature, and time from above steps, and again observing the number of fungi. Thus, the optimum culture conditions for *S. pombe* 806 and *S. pombe* ATCC 2476 could be determined and these optimum culture conditions were utilized to culture *S. pombe* 806 and *S. pombe* ATCC 2476 for the required inactivated *Saccharomyces* to be used in immobilized *pombe* beads.

2.3. Preparation of immobilized pombe beads and their batch adsorption experiments/property tests

Chitosan with a deacetylation percentage of approximately 86% was supplied by Fluka Enterprises Company, which also supplied the reagent ECH. Chitosan solutions were prepared by dissolving chitosan into 5 wt.% acetic acid solutions. The preparation of immobilized *pombe* beads (an equal weight of alginate, PVAL, and chitosan) and their batch adsorption experiments involved (1) changing percentages (5, 10, and 15 wt.%) of PVAL, fixing other chemicals (10 wt.% alginate and 1 wt.% chitosan), blending or cross-linking with 0.5 M ECH to prepare immobilized beads, and adding 10 g of immobilized beads to 50 ml of aqueous solutions with different initial concentrations and changing their pH (2–6) and agitation rates (200–700 rpm) to conduct experiments of batch equilibrium adsorption, taking sample at every 3 min until reaching equilibrium adsorption and measuring concentrations of Cd^{2+} in the aqueous solutions by ICP-MS; (2) changing percentages (1, 1.5, and 2 wt.%) of chitosan, fixing 10 wt.% alginate and choosing the optimum percentage of PVAL from step (1), following step (1) to prepare immobilized beads and conduct adsorption experiments; (3) adding different percentages (1–4 wt.%) of inactivated cells of *S. pombe* 806 or *S. pombe* ATCC 2476 before blending or cross-linking, choosing the optimum percentages of PVAL and chitosan from above steps, following step (1) to prepare immobilized *pombe* beads and to conduct adsorption experiments for those beads at the optimum pH and agitation rate according to results of above steps. Therefore, the optimum beads (blending or cross-linking, percentages of PVAL, chitosan, *S. pombe* 806 or *S. pombe* ATCC 2476) and

adsorption conditions (pH in the aqueous solution, agitation rate, and equilibrium adsorption time) could be determined. Furthermore, in order to ascertain the influence of bead properties on adsorption performance, mechanical strength of beads was measured by dynamic mechanical analyzer (DMA).

In experiments of batch kinetic adsorption, 10 g of the optimum beads were added to 50 ml of aqueous solutions with different initial concentrations at the optimum adsorption conditions (pH and agitation rate). A sample was taken every 3 min until reaching equilibrium adsorption. Then concentrations of Cd^{2+} in samples were measured by ICP-MS.

2.4. Batch equilibrium desorption experiments of optimum beads

Ten grams of optimum beads containing Cd^{2+} were regenerated by 50 ml of various concentrations (0.1, 0.5, 1.0, and 1.5 M) HCl aqueous solutions at the agitation rate of the optimum adsorption for 1 h. Thus, the optimum HCl concentration was determined.

2.5. Efficiencies of batch equilibrium adsorption and desorption experiments of optimum beads

Ten grams of optimum beads were added to 50 ml of 150 mg/l Cd^{2+} aqueous solution to investigate experiments of batch equilibrium adsorption by the optimum adsorption conditions (pH in the aqueous solution, agitation rate, and equilibrium adsorption time). Then beads containing Cd^{2+} were regenerated using 50 ml of the optimum HCl concentration according to the result of Section 2.4 at the agitation rate of the optimum adsorption for 1 h. Next, the regenerated beads were reused to investigate experiments of batch equilibrium adsorption and then regenerated beads containing Cd^{2+} were regenerated again as before. Adsorption and desorption steps were repeated again and again. Finally, we may confirm that the beads can be reused according to efficiencies of adsorption and desorption.

2.6. Batch equilibrium adsorption experiments of optimum beads for the soil leaching solution

Different amounts (0.1, 0.2, and 0.3 g) of optimum beads were added to 50 ml of the soil leaching solution containing Cd^{2+} to investigate experiments of batch equilibrium adsorption at the optimum adsorption conditions (pH in the aqueous solution and agitation rate) and then a sample was taken at every 3 min until equilibrium adsorption. In this way, we ascertained what were the amount of beads required to reach the discharge standard concentration of Cd^{2+} in discharge waste water.

3. Results and discussion

3.1. Soil leaching

There was little difference in effect between 0.1 and 0.5 M CaCl_2 used as a solvent on soil leaching at the conditions (5000 rpm, 1 h, and soil/solvent ratio of 1/2), since the ratio of soil and solvent was too large to flow for the mixture of soil and solvent, then the collision frequency between functional groups with negative charges of soil and Ca^{2+} was small, thus the cation exchange of Ca^{2+} for Cd^{2+} was limited. So, due to economical considerations, 0.1 M was chosen as the optimum CaCl_2 concentration for soil leaching. In addition, the results of soil leaching show that the higher the agitation rate, the shorter the leaching time, and that leaching time could be reduced to about 0.5 h when the agitation rate was set to 8000 rpm (the maximum agitation rate of the agitator). Furthermore, they show that the higher the ratio of soil and solvent, the higher the efficiency of soil leaching, and that the efficiency of soil leaching reached 95% when the ratio of soil and solvent was 1/8 [due to the maximum capacity (400 g of soil and 3200 g of CaCl_2 aqueous solution) of the mixer], the CaCl_2 concentration was 0.1 M, the value of pH was 3–9, leaching time was 0.5 h, and the agitation rate was 8000 rpm.

3.2. Culture of *Saccharomyces*

The optimum agitation rate was 200 rpm (the maximum agitation rate of low-temperature shaker incubator) for *S. pombe 806* and *S. pombe ATCC 2476*. This evidence proves that these two *Saccharomyces* are aerobic fungi. The optimum culture temperatures for *S. pombe 806* and *S. pombe*

ATCC 2476 were 303 and 302 K, respectively. In addition, optimum culture time for *S. pombe 806* and *S. pombe ATCC 2476* was 16 and 32 h, respectively. Furthermore, the optimum pH for these two *Saccharomyces* lay between 5 and 6.

3.3. Preparation of immobilized beads and their batch adsorption experiments/property tests

Fig. 1 shows the effect of pH on equilibrium adsorption of Cd^{2+} onto 10 g immobilized beads containing 10 wt.% alginate as well as different percentages of PVAL and chitosan cross-linked by 0.5 M ECH at the adsorption conditions (400 rpm, 30 min, and 50 ml of the aqueous solution with the initial concentration of 100 mg Cd^{2+} /l). It shows that equilibrium adsorption concentrations approximately increase with increasing pH of the solution except for the immobilized beads (10 wt.% alginate + 2 wt.% chitosan + 5 wt.% PVAL) at pH 6 due to higher wt.% of chitosan [because of the higher wt.% of chitosan, the more solidity of immobilized beads at higher pH (6), this phenomena is similar to that of the literature [5], and then the equilibrium adsorption concentration decreases at pH 6]. The phenomena of equilibrium adsorption concentrations increasing with increasing pH of the solution might be explained because at lower pH, more protons are available to amine groups of chitosan molecules to form NH_3^+ groups, then competition existed between protons and Cd^{2+} for adsorption sites (NH_2 groups) and adsorption capacity was decreased. At pH higher than 6, precipitation of cadmium hydroxide occurs, affecting adsorption of Cd^{2+} onto immobilized beads. Thus, the optimum pH for immobilized beads (an equal weight of 10 wt.% alginate, 1.5 wt.% chitosan, and 10 wt.% PVAL cross-linked by 0.5 M ECH)

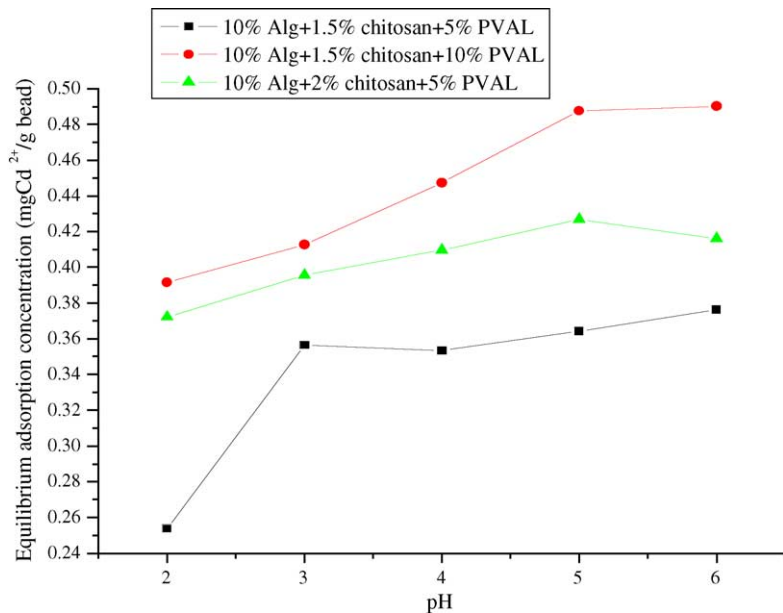


Fig. 1. Effect of pH in the aqueous solution (50 ml and 100 mg Cd^{2+} /l) on equilibrium adsorption of Cd^{2+} onto 10 g beads cross-linked by 0.5 M ECH at the adsorption conditions (400 rpm and 30 min).

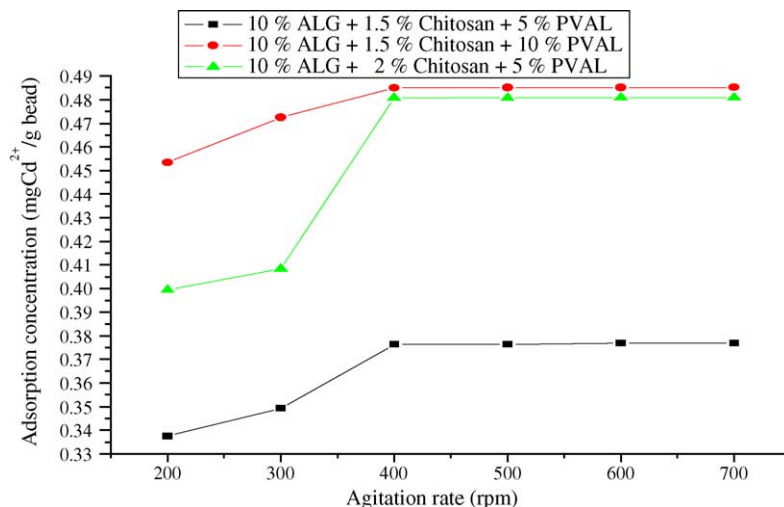


Fig. 2. Effect of agitation rates on adsorption of Cd²⁺ onto 10 g beads cross-linked by 0.5 M ECH at the adsorption conditions (pH 6, 30 min and 50 ml of the aqueous solution with the initial concentration of 100 mg Cd²⁺/l).

with higher adsorption capacity was 6. The result is similar to that of the literature [5] which has noted chitosan beads with higher adsorption capacity at pH 3–6.

Fig. 2 shows effect of agitation rates on adsorption of Cd²⁺ onto 10 g of immobilized beads containing 10 wt.% alginate as well as different percentages of PVAL and chitosan cross-linked by 0.5 M ECH at the adsorption conditions (pH 6, 30 min, and 50 ml of the aqueous solution with the initial concentration of 100 mg Cd²⁺/l). The adsorption of Cd²⁺ increases with agitation rates and attains a near constant value at 400–700 rpm for all immobilized beads and thus an agitation rate of 400 rpm was chosen for economical reasons.

Fig. 3 shows effect of percentages of two *Saccharomyces* on equilibrium adsorption of Cd²⁺ onto 10 g of immobilized beads containing optimum percentages (an equal weight of 10 wt.% alginate, 1.5 wt.% chitosan, and 10 wt.% PVAL)

determined from Figs. 1–2 and different percentages (1, 2, 3, and 4 wt.%) of *S. pombe 806* or *S. pombe ATCC 2476* cross-linked by 0.5 M ECH at the adsorption conditions (pH 6, 400 rpm, 30 min, and 50 ml of the aqueous solution with the initial concentration of 150 mg Cd²⁺/l). It shows that for the same percentage of *Saccharomyces*, adsorption capacity of immobilized beads containing *S. pombe 806* are higher than that of immobilized beads containing *S. pombe ATCC 2476* and the higher the percentage of *Saccharomyces*, the higher the adsorption capacity. In addition, the percentage increase in the equilibrium adsorption concentrations for adding 1 and 4 wt.% of *S. pombe 806* is 20 and 40%, respectively, so the optimum percentage of *S. pombe 806* added is 1 wt.% taking economical factors into consideration.

In addition, Fig. 4 shows that the higher the initial concentration in the aqueous solution, the shorter the time to reach equilibrium adsorption and the larger the amount of

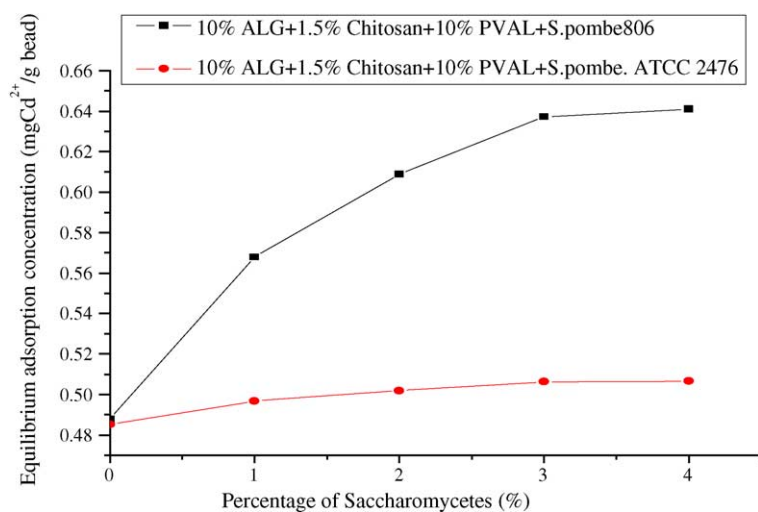


Fig. 3. Effect of percentages of *Saccharomyces* on equilibrium adsorption of Cd²⁺ onto 10 g beads cross-linked by 0.5 M ECH at the adsorption conditions (pH 6, 400 rpm, 30 min and 50 ml of the aqueous solution with the initial concentration of 150 mg Cd²⁺/l).

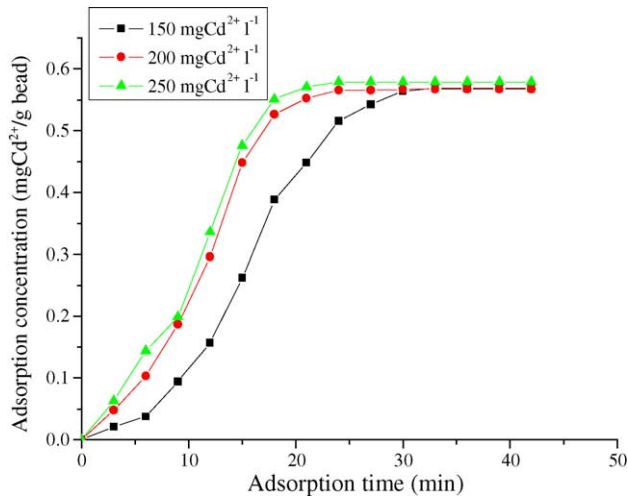


Fig. 4. Effect of adsorption time on adsorption of Cd^{2+} onto 10 g optimum beads at the adsorption conditions (pH 6, 400 rpm, and 50 ml of aqueous solutions with initial concentration of 150 mg Cd^{2+}/l , 200 mg Cd^{2+}/l , and 250 mg Cd^{2+}/l).

adsorbed Cd^{2+} before reaching equilibrium adsorption due to the higher collision frequency between Ca^{2+} in the aqueous solution and the NH_2 groups of chitosan in optimum beads, and that the maximum amounts of adsorbed Cd^{2+} after reaching equilibrium adsorption were almost the same in spite of initial concentrations in the aqueous solution and equilibrium adsorption time was about 30 min which confirmed adsorption time used before.

Furthermore, from Table 3, it found that mechanical strength for beads cross-linked with 0.5 M ECH is about four times of that for blended beads and cross-linked beads

Table 3
Mechanical strength $\text{N}/\mu\text{m}$ of beads blended and beads cross-linked with 0.5 M ECH

Composition (wt.%) of beads	Immobilized methods	
	Beads blended	Beads cross-linked with 0.5 M ECH
99 wt.% of alginate (10 wt.%) + 1 wt.% of <i>S. pombe 806</i>	0.061	
49.5 wt.% of alginate (10 wt.%) + 49.5 wt.% of chitosan (1 wt.%) + 1 wt.% of <i>S. pombe 806</i>	0.058	0.071
33 wt.% of alginate (10 wt.%) + 33 wt.% of chitosan (1 wt.%) + 33 wt.% of PVAL (5 wt.%) + 1 wt.% of <i>S. pombe 806</i>	0.093	0.385
33 wt.% of alginate (10 wt.%) + 33 wt.% of chitosan (1 wt.%) + 33 wt.% of PVAL (10 wt.%) + 1 wt.% of <i>S. pombe 806</i>	0.117	0.564
33 wt.% of alginate (10 wt.%) + 33 wt.% of chitosan (1.5 wt.%) + 33 wt.% of PVAL (5 wt.%) + 1 wt.% of <i>S. pombe 806</i>	0.131	0.703
33 wt.% of alginate (10 wt.%) + 33 wt.% of chitosan (1.5 wt.%) + 33 wt.% of PVAL (10 wt.%) + 1 wt.% of <i>S. pombe 806</i>	0.188	0.856
33 wt.% of alginate (10 wt.%) + 33 wt.% of chitosan (2 wt.%) + 33 wt.% of PVAL (5 wt.%) + 1 wt.% of <i>S. pombe 806</i>	0.202	0.407

Table 4
Parameters of the Langmuir adsorption equation

Composition (wt.%) of beads cross-linked with 0.5 M ECH	Parameters		
	X_{max} (mg/g)	b (l/mg)	R^2
33 wt.% of alginate (10 wt.%) + 33 wt.% of chitosan (1.5 wt.%) + 33 wt.% of PVAL (10 wt.%) + 1 wt.% of <i>S. pombe 806</i>	231.48	1.18682	0.99976

containing 33 wt.% of alginate (10 wt.%), 33 wt.% of chitosan (1.5 wt.%), 33 wt.% of PVAL (10 wt.%), and 1 wt.% of *S. pombe 806* had the highest mechanical strength ($0.856 \text{ N}/\mu\text{m}$) whose property is optimum for reuse of cross-linked beads. Thus, these kinds of cross-linked beads were chosen as optimum beads.

The equilibrium adsorption behaviour can be described with the Langmuir adsorption equation as

$$\frac{C_e}{X} = \frac{C_e}{X_{\text{max}}} + \frac{1}{X_{\text{max}}b} \quad (1)$$

where C_e is the equilibrium concentration of Cd^{2+} in the solution (mg/l), X is the amount of Cd^{2+} adsorbed per unit weight of optimum beads at the equilibrium concentration (mg/g), X_{max} is maximum adsorption at monolayer coverage (mg/g), and b is the Langmuir adsorption equilibrium constant (l/mg) and is a measure of adsorption energy.

A linearized plot of C_e/X versus C_e gives X_{max} and b . Table 4 shows computation results. It shows that the Langmuir adsorption equation fitted well with equilibrium data from experiments of batch kinetic adsorption (correlation coefficient $R^2 > 0.999$).

First-order adsorption and second-order adsorption kinetic models were utilized to investigate experimental data of batch kinetic adsorption and determine the mechanism of adsorption. The first-order adsorption kinetic model is expressed as

$$\log(q_e - q) = \log q_e - \frac{k_1 t}{2.303} \quad (2)$$

where q_e is the amount of Cd^{2+} adsorbed on optimum beads at equilibrium (mg/g), q is the amount of Cd^{2+} adsorbed on

Table 5
Rate constants and change in Gibbs free energy of adsorption

Initial Cd ²⁺ concentration (mg/l)	First-order reaction		Second-order reaction		Change in Gibbs free energy (ΔG^0 , kJ/mol)
	k_1 (min ⁻¹)	R^2	k_2 (g/(mg min))	R^2	
150	0.140	0.823	0.031	0.139	-2.838
200	0.254	0.891	0.05	0.061	-0.668
250	0.282	0.893	0.09	0.144	-0.361

optimum beads at time t (mg/g) and k_1 is the rate constant of first-order adsorption (min⁻¹).

The slope ($-k_1/2.303$) of a plot of $\log(q_e - q)$ versus t was used to calculate k_1 . Table 5 shows the results.

The second-order adsorption kinetic model is given as

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (3)$$

where k_2 is the rate constant of second-order adsorption (g/(mg min)).

The slope and intercept of a plot of t/q versus t were used to determine k_2 . Table 5 shows the results.

The thermodynamic property ΔG^0 [change in Gibbs free energy (J/mol)] was determined using the following equation. Table 5 shows the results.

$$\Delta G^0 = -RT \ln K_C \quad (4)$$

where K_C is an equilibrium constant ($K_C = C_{Ae}/C_e$), C_{Ae} is the amount of Cd²⁺ adsorbed on optimum beads per volume of the solution at equilibrium (mg/l), C_e is the equilibrium concentration of Cd²⁺ in the solution (mg/l), R is an ideal gas constant (8.314 J/(mol K)), and T is the temperature (K).

From Table 5, we found that adsorption of Cd²⁺ onto optimum beads was a first-order (larger correlation coefficient) and spontaneous ($\Delta G^0 < 0$) reaction.

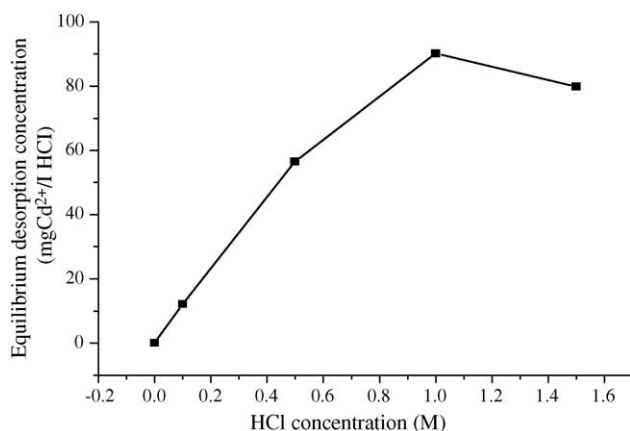


Fig. 5. Effect of HCl concentrations in 50 ml aqueous solutions on equilibrium desorption concentrations of Cd²⁺ desorbed from 10 g optimum beads at the desorption conditions (400 rpm and 1 h).

3.4. Batch equilibrium desorption of optimum beads

Desorption would help to recover Cd²⁺ from optimum beads and regenerate the beads so that they can be used again. Fig. 5 shows that the higher the HCl concentration, the higher the equilibrium desorption concentration except when HCl concentrations were higher than 1 M due to the immobilized chitosan (dissolved in 5 wt.% acetic acid solutions) beads which were destroyed at high HCl concentrations, and that the equilibrium desorption concentration can reach a maximum of 90.27 mg Cd²⁺/l HCl, when 1 M HCl was used to regenerate the beads, so 1 M HCl was chosen as the optimum concentration for bead regeneration.

3.5. Efficiencies of batch equilibrium adsorption and desorption experiments of optimum beads

From Fig. 6, we found that the adsorption efficiency was still about 70% after six cycles of adsorption and desorption. This could be explained by amine groups of chitosan in the beads being destroyed gradually in each cycle, and a few of the adsorbed Cd²⁺ not being desorbed in the previous cycle and still occupying adsorption sites. Thus, the amount of adsorbed Cd²⁺ in the next cycle decreased. In addition, Fig. 7 shows that the greater the cycle of adsorption and desorption, the higher the desorption efficiency, and that the desorption

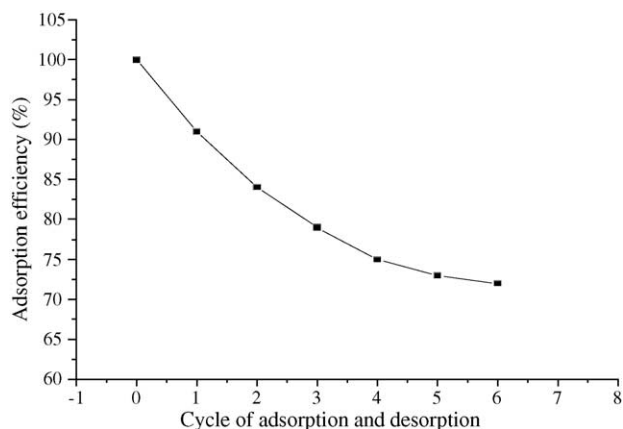


Fig. 6. Effect of cycles of adsorption and desorption on adsorption efficiencies of Cd²⁺ onto 10 g optimum beads in 50 ml of the aqueous solution with initial concentration of 150 mg Cd²⁺/l at optimum adsorption and desorption conditions [adsorption efficiency (%) = 100 × (initial Cd²⁺ concentration in the aqueous solution - residual Cd²⁺ concentration in the aqueous solution)/initial Cd²⁺ concentration in the aqueous solution].

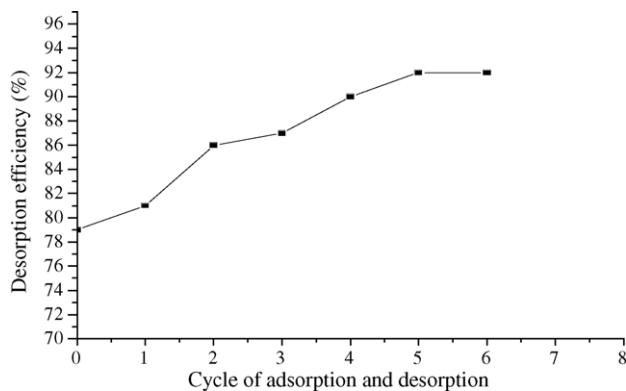


Fig. 7. Effect of cycles of adsorption and desorption on desorption efficiencies of Cd^{2+} from 10 g optimum beads in 50 ml of the aqueous solution at optimum adsorption and desorption conditions (desorption efficiency (%) = $100 \times$ the ratio of the amount of desorbed Cd^{2+} and the amount of adsorbed Cd^{2+} in each cycle of adsorption and desorption).

efficiency reached 92% after six cycles of adsorption and desorption. This could be explained by a few of the adsorbed Cd^{2+} not being desorbed in the previous cycle and still occupying adsorption sites. Thus, the amount of adsorbed Cd^{2+} in the next cycle decreased. So the desorption efficiency increased with increasing the cycle of adsorption and desorption. Finally, from efficiencies of adsorption and desorption, we found that the reusability of optimum beads was feasible.

3.6. Batch equilibrium adsorption experiments of optimum beads for the soil leaching solution

From Fig. 8, it shows that the more beads that were added to the soil leaching solution, the lower the residual Cd^{2+} concentration in the soil leaching solution was. The residual Cd^{2+} concentrations in the soil leaching solution decreased with time, when 0.3 g of optimum beads were added to the soil leaching solution, its Cd^{2+} concentration

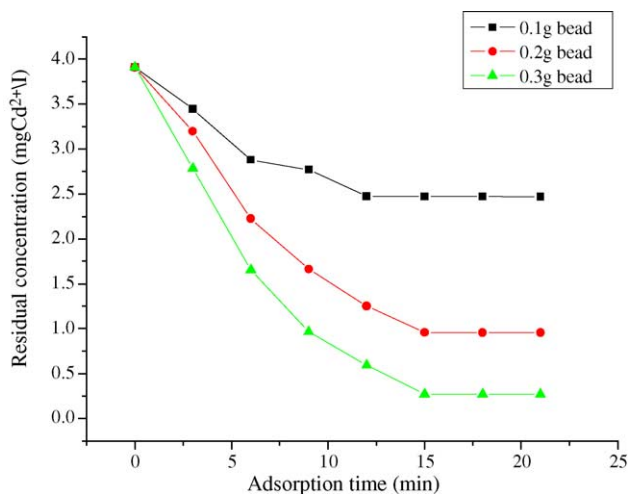


Fig. 8. Effect of adsorption time on residual Cd^{2+} in the soil leaching solution with initial concentration of $3.91 \text{ mg Cd}^{2+}/\text{l}$ by adding different amounts of optimum beads at the optimum adsorption conditions.

can decrease from 3.91 to 0.269 mg/l , which is below the Cd^{2+} discharge standard.

4. Conclusions

For soil leaching, the efficiency of soil leaching was up to 95% at soil/solvent = $1/8$, pH 3–9, 0.1 M CaCl_2 , 8000 rpm, and 0.5 h. The optimum culture conditions for *S. pombe 806* were at 200 rpm, 303 K, 16 h, and pH 5–6. However, the optimum conditions for *S. pombe ATCC 2476* were 200 rpm, 302 K, 32 h, and pH 5–6. In addition, optimum beads containing 33 wt.% of alginate (10 wt.%), 33 wt.% of chitosan (1.5 wt.%), 33 wt.% of PVAL (10 wt.%), and 1 wt.% of *S. pombe 806* were cross-linked by 0.5 M ECH. The optimum adsorption conditions for optimum beads were pH 6, 400 rpm, and 30 min. Furthermore, mechanical strength of cross-linked beads was four times that of blended beads, and optimum beads had the highest mechanical strength. Moreover, the Langmuir adsorption equation fitted well with equilibrium adsorption data and adsorption of Cd^{2+} onto optimum beads was a first-order/spontaneous reaction. Besides, the desorption efficiency achieves 79% when 1 M HCl was used to regenerate the beads. The adsorption efficiency was still as high as 70% after six cycles of adsorption and desorption, so optimum beads were reusable. Finally, after treating the soil leaching solution with optimum beads, its Cd^{2+} concentration reached the discharge standard.

References

- [1] M.J. Mench, V.L. Didier, M. Loffler, A. Gomez, P. Masson, A mimicked in-situ remediation study of metal-contaminated soils with emphasis on cadmium and lead, *J. Environ. Qual.* 23 (1994) 58–63.
- [2] S.R. Cline, B.E. Reed, Lead removal from soils bench scale soil washing techniques, *J. Environ. Eng.* October (1995) 700–705.
- [3] K. Mackenbrock, Treatment of contaminated soils by a combination of suitable, proven technologies contaminated soil, Kluwer Academic Publishers, Netherlands, 1993.
- [4] X.D. Liu, S. Tokura, M. Haruki, N. Nishi, N. Sakairi, Surface modification of nonporous glass beads with chitosan and their adsorption property for transition metal ions, *Carbohydr. Polym.* 49 (2002) 103–108.
- [5] W.S. Wan Ngah, C.S. Endud, R. Mayanar, Removal of copper ion from aqueous solution onto chitosan and cross-linked chitosan beads, *React. Funct. Polym.* 50 (2002) 181–190.
- [6] I.C. Alupeii, M. Popa, M. Hamcerencu, M.J.M. Abadie, Superabsorbent hydrogels based on xanthan and poly (vinyl alcohol). 1. The study of the swelling properties, *Eur. Polym. J.* 38 (2002) 2313–2320.
- [7] F.L. Mi, S.S. Shyu, C.T. Chen, J.Y. Lai, Adsorption of indomethacin onto chemically modified chitosan beads, *Polymer* 43 (2002) 757–765.
- [8] J.S. Chang, J.C. Huang, C.C. Chang, T.J. Tarn, Removal and recovery of lead by fixed bed biosorption with immobilized bacterial biomass, *Water Sci. Technol.* 38 (1998) 171–178.
- [9] A.D. Pozzo, L. Vanini, M. Fagnoni, M. Guerrini, R.A.A. Muzzarelli, Preparation and characterization of polyethylene glycolcross-linked reacylated chitosans, *Carbohydr. Polym.* 42 (2000) 201–206.

- [10] M. Zhang, X.H. Li, Y.D. Gong, N.M. Zhao, X.F. Zhang, Properties and biocompatibility of chitosan films modified by blending with PEG, *Biomaterials* 23 (2002) 2641–2648.
- [11] W.O. David, Purine biosynthetic genes are required for cadmium tolerance in *Schizosaccharomyces pombe*, *Mol. Cell. Biol.* 12 (1992) 5301–5310.
- [12] P.R. Puranik, K.M. Paknikar, Biosorption of lead, cadmium, and zinc by *Citrobacter* strain MCM B.181 characterization studies, *Biotechnol. Prog.* 15 (1999) 228–237.
- [13] B. Bolesky, Z.R. Holan, Biosorption of heavy metals, *Biotechnol. Prog.* 11 (1995) 235–250.
- [14] J.S. Chang, C.C. Chen, Biosorption of lead, copper, and cadmium with continuous hollow fiber micro filtration processes, *Sep. Sci. Technol.* 34 (1999) 1607–1627.
- [15] A. Stoll, J.R. Duncan, Implementation of a continuous flow stirred bioreactor system in the bioremediation of heavy metals from industrial wastewater, *Environ. Pollut.* 97 (1997) 247–251.