

Adsorption and recovery of lead(II) from aqueous solutions by immobilized *Pseudomonas Aeruginosa* PU21 beads

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Abstract

In this study, immobilized *Pseudomonas aeruginosa* PU21 beads were used as an adsorbent for lead(II). Different weight percentages of chitosan were added to polyethylene glycol (PEG, 0.5 wt.% in aqueous solution) and alginate (18 wt.% in aqueous solution), and then blended or cross-linked using different concentrations of epichlorohydrin (ECH) to prepare beads of different sizes and increased mechanical strength. Before blending or cross-linking, different weight percentages of *P. aeruginosa* PU21 were added to increase lead(II) adsorption. Subsequently the optimized bead composition (concentration of ECH, percentages of chitosan and *P. aeruginosa* PU21) and the optimum adsorption conditions (agitation rate and pH in the aqueous solution) were ascertained. Finally, the optimized beads adsorbing lead(II) were regenerated by 0.1 M aqueous HCl solutions and the most effective desorption agitation rate was ascertained. The results indicate that the reuse of immobilized *P. aeruginosa* PU21 beads was feasible. In addition, the equilibrium adsorption, kinetics, changes in the thermodynamic properties of adsorption of lead(II) on optimized beads were also investigated.

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1. Introduction

Methods for the removal of heavy metals from aqueous solutions include ion exchange, chemical precipitation, and reverse osmosis, etc. However, these methods are expensive and may result in secondary pollution when compared with biosorption processes [1]. Furthermore, Mackenbrock [2] noted that it is more economic and competitive to remove heavy metals from aqueous solutions by biosorption processes. Consequently, in this research, a biosorption process was chosen to treat aqueous solutions containing lead(II).

Liu et al. [3] noted that chitosan is a suitable natural polymer for the concentration of metals, such as Cd^{2+} , Zn^{2+} , Cu^{2+} , Pb^{2+} , etc. In addition, Shi and Tian [4] noted that heavy metal ions form chelates with the NH_2 and OH groups of chitosan. However, the mechanical strength of chitosan is poor, and it is therefore necessary to modify chitosan to improve its mechan-

ical properties and chemical stability, etc. In order to improve its mechanical strength and increase porosity, polymers such as PEG can be added to chitosan [5,6]. Furthermore, Wan Ngah et al. [7] and Alupei et al. [8] showed that the NH_2 groups of chitosan can be preserved by combining its OH groups with O groups in ECH when chitosan is cross-linked with ECH. Thus cross-linked chitosan beads still retain NH_2 groups with which to chelate heavy metals. Moreover, Mi et al. [9], Chang et al. [10], Pozzo et al. [11], and Zhang et al. [12] stated that both the mechanical strength and pore size of cross-linked chitosan beads are a function of the 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 due to reducing the number of OH groups in the chitosan molecule. Alternatively, some types of biomass added to cross-linked chitosan beads may improve adsorption performance. Skountzou et al. [13] showed that biomass such as yeast appeared to effectively adsorb heavy metals. In addition, Chang and Huang [14] observed that *Pseudomonas aeruginosa* PU21 appeared to effectively adsorb heavy metals because of very strong negatively

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charged SH groups on their cell walls and higher lead(II) selectivity due to a cation exchange effect. Furthermore, Chang et al. [15] stated that the inactivated cells of *Pseudomonas aeruginosa* PU21 which are chemically stable and easy to handle (e.g. requiring no nutrients, etc.) still have the capacity to adsorb Pb^{2+} from aqueous solutions. Thus, in this research, inactivated cells of *Pseudomonas aeruginosa* PU21 were added to prepare chitosan beads in order to enhance adsorption capacity.

In this study, in order to enhance mechanical strength, different amounts of chitosan were added to PEG 6000 (0.5 wt.%) and alginate (18 wt.%), and then blended or cross-linked by different concentrations of ECH. In addition, different amounts of *P. aeruginosa* PU21 were also added before blending or cross-linking to increase the Pb^{2+} adsorption capacity. The ultimate aim of this research was to ascertain the optimized bead composition and the optimum adsorption conditions. Subsequently, the Langmuir and Freundlich equations were used to fit equilibrium adsorption. The adsorption rates were determined quantitatively and compared with pseudo-first-order and second-order models. Changes in the thermodynamic properties of different beads were also determined to indicate whether the adsorption is spontaneous or not. Chang et al. [15] showed 0.1 M HCl-induced desorption achieved nearly 98% efficiency, but that higher concentrations of HCl would destroy the negatively charged SH groups on the immobilized biomass. Thus, in this research, optimized beads containing adsorbed Pb^{2+} were regenerated with 0.1 M HCl aqueous solutions and the most effective desorption agitation rate was subsequently ascertained.

2. Experimental methods

2.1. Preparation of immobilized *Pseudomonas aeruginosa* PU21 beads and determination of their batch adsorption/properties

Chitosan with a deacetylation percentage of approximately 80% was supplied by Merck Enterprises Company. Chitosan solutions were prepared by dissolving chitosan into 5 wt.% acetic acid solutions. Besides, PEG 6000 was supplied by Fluka Enterprises Company, which also supplied the ECH reagent. The preparation of immobilized beads is summarized in Table 1. In stage one, beads were synthesized from equal amounts of alginate, PEG, and chitosan solutions but the concentrations of each component in the aqueous solutions were varied in a systematic way. Three different percentages (1, 1.5, and 2 wt.%) of chitosan were used, while fixing other chemicals (18 wt.% algi-

Table 1
Optimized bead composition

Parameters	Operating variables	Optimized bead composition
Percentage of chitosan	1, 1.5, and 2 wt.%	1.5 wt.%
Concentration of ECH	0.055, 0.110, 0.220, 0.332, 0.444, 0.554, and 0.667 M	0.554 M
Percentage of <i>P. aeruginosa</i> PU21	1, 2, 3, and 4 wt.%	1 wt.%

nate and 0.5 wt.% PEG), then blending or cross-linking with different concentrations of ECH. Beads of two different diameters (3–3.5 and 4–4.5 mm) were synthesized. Batch adsorption experiments involved adding 10 g of immobilized beads to 50 ml of aqueous solutions with different temperatures (293–323 K), pHs (4–6) and agitation rates (400–600 rpm). Sample were taken at every 5 min until reaching equilibrium adsorption and concentrations of Pb^{2+} in the aqueous solutions were determined by ICP-MS. Stage two involved adding different percentages (1–4 wt.%) of inactivated biomass of *Pseudomonas aeruginosa* PU21, before blending or cross-linking, while employing the optimum percentage of chitosan, etc., from stage one. Employing this orthogonal array experimental design, the optimized bead composition (concentration of ECH, percentages of chitosan and *P. aeruginosa* PU21) and the optimum adsorption conditions (agitation rate and pH in the aqueous solution) could be determined. Furthermore, in order to ascertain the influence of mechanical properties on bead adsorption performance, the mechanical strength of wet beads was measured by dynamic mechanical analyzer (DMA).

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

2.2. Batch equilibrium desorption experiments of optimized beads

A 10 g of optimized beads containing Pb^{2+} were regenerated using 50 ml of the 0.1 M HCl aqueous solution at different temperatures (293, 303, 313, and 323 K) and agitation rates (300, 400, 500, and 600 rpm) were varied. Sample were taken every 2 min until equilibrium desorption was reached. Concentrations of Pb^{2+} in samples were measured by ICP-MS. Thus the most effective desorption agitation rate was ascertained.

2.3. Efficiencies of batch equilibrium adsorption and desorption experiments on optimized beads

A 10 g of optimized beads were added to 50 ml of the aqueous solution with an initial concentration of 73.4 mg Pb^{2+} /l to investigate batch equilibrium adsorption at the optimum conditions. The beads containing Pb^{2+} were regenerated using 50 ml of 0.1 M HCl aqueous solutions at the most effective desorption agitation rate (according to the result of Section 2.2). Adsorption and desorption steps were repeated in an iterative process to investigate the potential for effective reuse of the beads.

3. Results and discussion

3.1. Determination of optimized beads and their optimum adsorption conditions

The optimized bead composition (concentration of ECH, percentages of chitosan and *P. aeruginosa* PU21) and the optimum

Table 2
Optimum adsorption conditions for optimized beads

Parameters	Adsorption conditions	Optimum adsorption conditions
pH in the aqueous solution	4, 5, and 6	5
Agitation rate	400, 500, and 600 rpm	400 rpm

adsorption conditions (agitation rate and pH in the aqueous solution) were determined using the orthogonal array experimental design. Tables 1 and 2 show the results.

Regarding the sizes of beads, the smaller the diameter of beads, the larger the surface area per unit mass of beads, and hence the higher Pb^{2+} adsorption capacity. Thus, the smaller beads (3–3.5 mm) were chosen as the optimized beads.

From Table 3, we can see that the optimized beads cross-linked with 0.554 M ECH had the highest Pb^{2+} adsorption efficient (73.4%) and higher mechanical strength (0.0.405 N/mm)—a property that is clearly important in the reuse of beads.

Fig. 1 shows effect of percentages of *P. aeruginosa* PU21 on equilibrium adsorption of Pb^{2+} onto 10 g of optimized beads (3–3.5 mm) except the percentage of *P. aeruginosa* PU21. It shows that the percentage increase in the equilibrium adsorption concentrations for adding 1 and 4 wt.% of *P. aeruginosa* PU21 is 30 and 43%, respectively, suggesting that the optimum percentage of *P. aeruginosa* PU21 is 1 wt.% after taking economical factors into consideration.

In addition, Fig. 2 shows that the higher the temperature in the aqueous solution, the higher the adsorption efficiency due to the positive activation energy for adsorption (see Table 6), and that the adsorption efficiency of cross-linking beads with 1 wt.% *P. aeruginosa* PU21 was higher than that of cross-linking or blending beads without biomass. Fig. 3 shows the effect of pH on adsorption of Pb^{2+} onto optimized beads. It shows that the optimum pH for the adsorption concentrations was pH 5 and equilibrium adsorption time was about 15 min. This might be explained because at lower pHs, more protons are available to form NH_3^+ groups with amine groups in the chitosan molecule. A competition existed between protons and Pb^{2+} for potential adsorption sites (NH_2 groups) and adsorption capacity

Table 3
Mechanical strength and Pb^{2+} adsorption efficient (adsorption of Pb^{2+} onto 10 g optimized beads in 50 ml of the aqueous solution with the initial concentration of 73.4 mg Pb^{2+} /l and $T=298$ K at optimum adsorption conditions) of optimized beads (3–3.5 mm) except being cross-linked with different concentrations of ECH

ECH (M)	Mechanical strength (N/mm)	Pb^{2+} adsorption efficient (%)
0.055	0.372	65.4
0.110	0.435	62.5
0.220	0.402	64.1
0.332	0.409	65.1
0.444	0.410	65.1
0.554	0.405	73.4
0.667	0.360	73.4

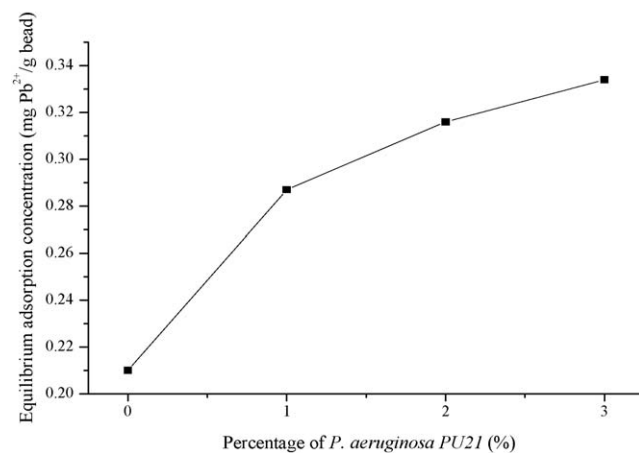


Fig. 1. Effect of percentages of *Pseudomonas aeruginosa* PU21 on equilibrium adsorption of Pb^{2+} onto 10 g of optimized beads (3–3.5 mm) except the percentage of *P. aeruginosa* PU21 at the adsorption conditions (pH 5, 400 rpm, 15 min, 293 K and 50 ml of the aqueous solution with the initial concentration of 73.4 mg Pb^{2+} /l).

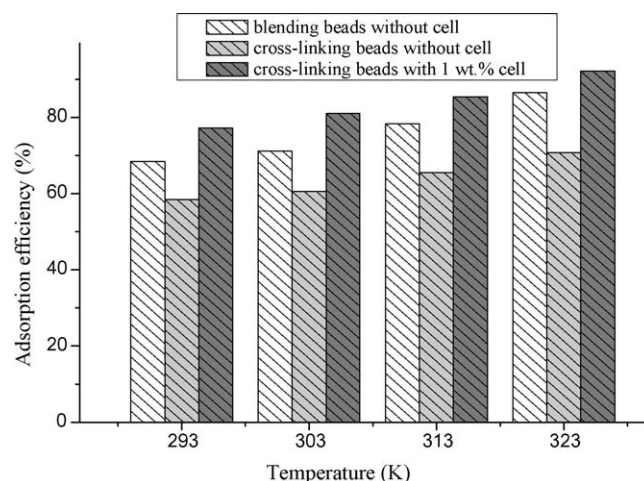


Fig. 2. Effect of temperatures in the aqueous solution on the adsorption efficiencies of Pb^{2+} onto 10 g of optimized beads (3–3.5 mm) at the adsorption conditions (pH 5, 400 rpm, 15 min and 50 ml of the aqueous solution with the initial concentration of 73.4 mg Pb^{2+} /l).

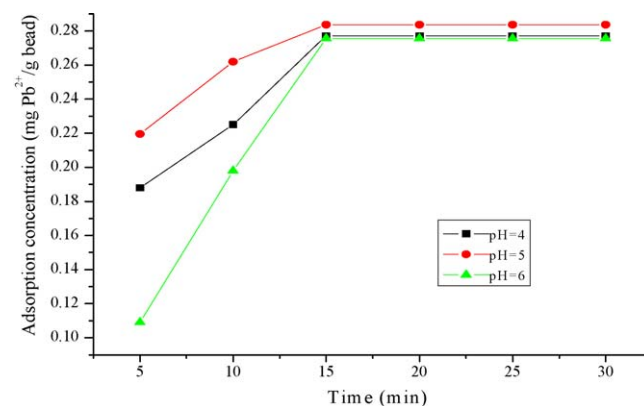


Fig. 3. Effect of pH in the aqueous solution (50 ml and 293 K) on the adsorption concentrations of Pb^{2+} onto 10 g of optimized beads (3–3.5 mm) at the adsorption condition (400 rpm).

Table 4
Parameters of the Langmuir adsorption equation and Freundlich isothermal equation [adsorption of Pb²⁺ onto 10 g of optimized beads (3–3.5 mm) in 50 ml of the aqueous solution with the different initial concentrations (73.4, 128, 192, 224, 273, and 329 mgPb²⁺/l) and temperatures at optimum adsorption conditions]

T (K)	Langmuir parameters			Freundlich parameters		
	q_m (mg/g)	K_d (mg/l)	R^2	$K \{ \text{mg}^{1-(1/n)} \} [^{(1/n)}/\text{g}]$	n	R^2
293	0.503	7.663	0.998	0.198	5.605	0.716
303	0.624	9.388	0.995	0.196	4.401	0.703
313	0.723	7.487	0.995	0.208	3.906	0.749
323	0.735	3.125	0.994	0.267	4.594	0.812

was effectively decreased. Conversely, at higher pHs, precipitation of lead hydroxide occurs, affecting adsorption of Pb²⁺ onto the immobilized beads. However, the maximum adsorption concentrations of Pb²⁺ after reaching equilibrium adsorption were almost equal (only a small difference) in spite of pH in the aqueous solution. This result is similar to that described in the literature [7] which has noted that chitosan beads have higher adsorption capacity in the range pH 3–6. We show that the optimum agitation rate for Pb²⁺ adsorption capacity was 400 rpm.

The equilibrium adsorption behaviour can be described by the Langmuir adsorption equation:

$$\frac{C}{q} = \frac{C}{q_m} + \frac{K_d}{q_m} \quad (1)$$

where C is the equilibrium concentration of Pb²⁺ in the solution (mg/l); q the amount of Pb²⁺ adsorbed on optimized beads at equilibrium (mg/g); q_m the maximum adsorption assuming monolayer coverage (mg/g) and K_d is a dissociation constant (mg/l).

A linearized plot of C/q versus C gives q_m and K_d . Table 4 shows the results.

The equilibrium adsorption behaviour also can be described with the Freundlich isothermal equation as

$$\log q = \left(\frac{1}{n} \right) \log C + \log K \quad (2)$$

where n is adsorption strength and $K \{ \text{mg}^{1-(1/n)} \} [^{(1/n)}/\text{g}]$ is an index of adsorption capacity.

A linearized plot of $\log q$ versus $\log C$ gives values for n and K , shown in Table 4. Our results show that the Langmuir adsorption equation fitted better (larger correlation coefficient R^2) with equilibrium data from experiments of batch kinetic adsorption (see Table 4).

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

$$\log(q - q_t) = \log q - \frac{k_1 t}{2.303} \quad (3)$$

where q_t is the amount of Pb²⁺ adsorbed on optimized beads at time t (mg/g) and k_1 is the rate constant of first-order adsorption (min^{-1}).

Table 5
Rate constants and change in Gibbs free energy of adsorption (adsorption of Pb²⁺ onto 10 g of optimized beads (3–3.5 mm) in 50 ml of the aqueous solution with the different initial concentrations and temperatures at optimum adsorption conditions)

Initial Pb ²⁺ concentration, C_0 (mg/l)	First-order reaction		Second-order reaction		Change in Gibbs free energy (ΔG° , kJ/mole)
	k_1 (min^{-1})	R^2	k_2 [g/(mg min)]	R^2	
Temperature, 293 K					
73.4	0.143	0.943	0.516	0.441	−2.985
128	0.110	0.915	0.422	0.495	−2.119
192	0.187	0.967	0.268	0.443	−0.232
Temperature, 303 K					
73.4	0.176	0.978	1.005	0.762	−3.510
128	0.157	0.952	0.248	0.415	−3.207
192	0.241	0.905	0.415	0.706	−1.400
Temperature, 313 K					
73.4	0.203	0.963	1.116	0.820	−4.618
128	0.187	0.986	0.697	0.826	−3.816
192	0.245	0.854	0.523	0.822	−2.716
Temperature, 323 K					
73.4	0.200	0.978	1.628	0.902	−6.625
128	0.180	0.975	0.945	0.894	−4.861
192	0.232	0.902	0.589	0.864	−3.102

The slope ($-k_1/2.303$) of a plot of $\log(q - q_t)$ versus t was used to calculate k_1 . Results are given in Table 5.

The second-order adsorption kinetic model [16] is given as:

$$\frac{t}{q_t} = \left[\frac{1}{(k_2 q^2)} \right] + \left(\frac{t}{q} \right) \quad (4)$$

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

The slope and intercept of a plot of t/q_t versus t were used to determine k_2 . Table 5 shows that adsorption of Pb^{2+} onto optimized beads was first-order (i.e. larger correlation coefficient).

Finally, the thermodynamic property ΔG° [change in Gibbs free energy (kJ/mole)] was determined using the following equation. Table 5 shows the results.

$$\Delta G^\circ = -RT \ln K_C \quad (5)$$

where K_C is an equilibrium constant ($K_C = C_{\text{Ae}}/C_e$); C_{Ae} the amount of Pb^{2+} adsorbed on optimized beads per volume of the solution at equilibrium (mg/l); C_e the equilibrium concentration of Pb^{2+} in the solution (mg/l); R the ideal gas constant [8.314×10^{-3} kJ/(mole K)] and T is temperature (K).

The thermodynamic properties ΔH° [change in enthalpy (kJ/mole)] and ΔS° {change in entropy [kJ/(mole K)]} were determined using the following equation.

$$\log K_C = \frac{\Delta S^\circ}{(2.303R)} - \frac{\Delta H^\circ}{(2.303RT)} \quad (6)$$

A linearized plot of $\log K_C$ versus $1/T$ gives ΔS° and ΔH° . Table 6 shows the results.

The rate constant k_1 (Table 5) for first-order adsorption shows an Arrhenius dependence on reciprocal temperature. The relationship can be expressed by:

$$k_1 = k_{10} \exp \left[\frac{-E_{\text{ad}}}{RT} \right] \quad (7)$$

where k_{10} is a temperature invariant factor (min^{-1}) and E_{ad} is the activation energy (kJ/mole) for adsorption.

E_{ad} is calculated from the slope of a plot of $\ln k_1$ versus $1/T$. Table 6 shows the result.

The relationship between E_{ad} and E_{de} [activation energy (kJ/mole) for desorption] is expressed by

$$\Delta H^\circ = E_{\text{ad}} - E_{\text{de}} \quad (8)$$

Then E_{de} can be calculated and its value is shown in Table 6. From Tables 5 and 6, we see that adsorption of Pb^{2+} onto optimized beads was a spontaneous reaction due to $\Delta G^\circ < 0$ and $\Delta S^\circ > 0$.

Table 6

Thermodynamic properties of adsorption and active energy (adsorption of Pb^{2+} onto 10 g of optimized beads (3–3.5 mm) in 50 ml of the aqueous solution with the different initial concentrations and temperatures (293, 303, 313, and 323 K at optimum adsorption conditions)

Initial Pb^{2+} concentration (mg/l)	Thermodynamic properties		Active energy	
	ΔH° (kJ/mole)	ΔS° [J/(mole K)]	E_{ad} (kJ/mole)	E_{de} (kJ/mole)
73.4	32.03	118.4	9.216	-22.81
128	23.74	88.45	13.15	-10.59
192	194.0	667.7	10.38	-188.5

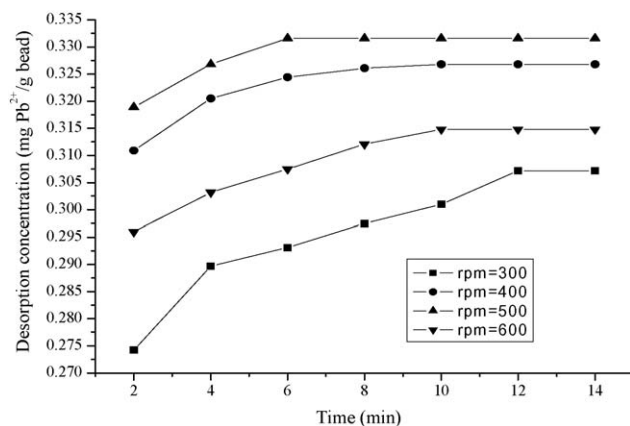


Fig. 4. Effect of agitation rates on the desorption concentrations of Pb^{2+} from 10 g of optimized beads (3–3.5 mm) by 50 ml of the 0.1 M HCl aqueous solution with 293 K.

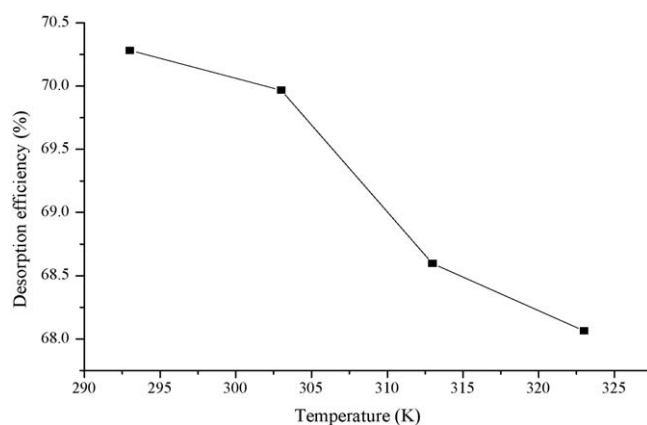


Fig. 5. Effect of temperatures on the ninth desorption efficiencies (after eight cycles of adsorption and desorption) of Pb^{2+} from 10 g of optimized beads (3–3.5 mm) by 50 ml of the 0.1 M HCl aqueous solution at the most effective desorption agitation rate and 10 min (desorption efficiency = 100% \times the ratio of the amount of desorbed Pb^{2+} and the amount of adsorbed Pb^{2+} in each cycle of adsorption and desorption).

3.2. Batch equilibrium desorption for optimized beads

Desorption would allow recovery of Pb^{2+} from optimized beads and regenerate the beads so that they can be used again. Fig. 4 shows that the desorption concentration reaches a maximum at an agitation rate of 500 rpm. However, the difference of desorption efficiencies between 400 and 500 rpm is only 1%, suggesting the most effective desorption agitation rate of 400 rpm when taking economical factors into consideration. Equilibrium desorption time was about 10 min. Fig. 5 shows that

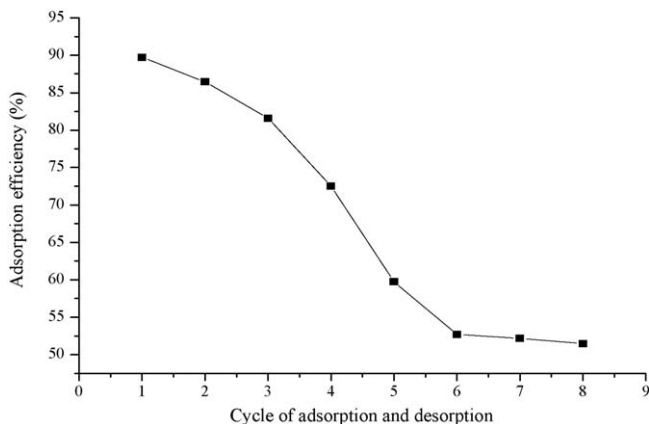


Fig. 6. Effect of cycles of adsorption (15 min) and desorption (10 min) on adsorption efficiencies of Pb^{2+} onto 10 g of optimized beads (3–3.5 mm) in 50 ml of the aqueous solution with the initial concentration of $73.4 \text{ mgPb}^{2+}/\text{l}$ and $T=323 \text{ K}$ at the optimum adsorption conditions and desorption agitation rate [adsorption efficiency = $100\% \times (\text{initial } Pb^{2+} \text{ concentration in the aqueous solution} - \text{residual } Pb^{2+} \text{ concentration in the aqueous solution})/\text{initial } Pb^{2+} \text{ concentration in the aqueous solution}$].

the higher the temperature in the aqueous solution, the higher the desorption efficiency due to the negative activation energy for desorption (refer to Table 6).

3.3. Efficiencies of batch equilibrium adsorption and desorption of optimized beads

From Fig. 6, we found that the adsorption efficiency was still approximately 55% after six to eight cycles of adsorption and desorption. This can be explained by amine groups of chitosan in the beads being destroyed gradually in each cycle and a few of the adsorbed Pb^{2+} not being desorbed in the previous cycle, thus still occupying adsorption sites. Fig. 7 shows that the

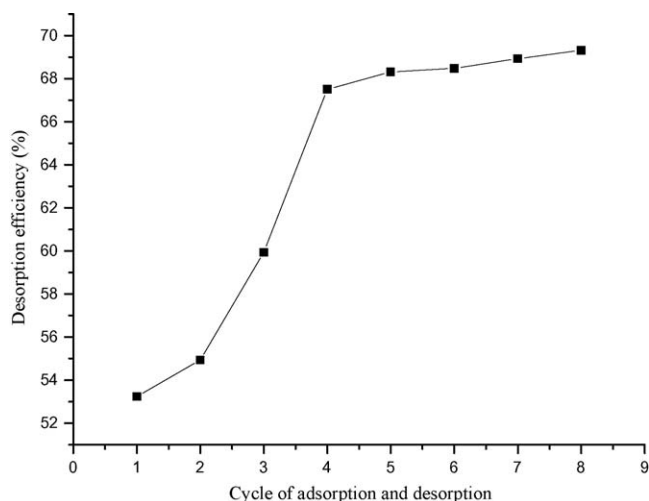


Fig. 7. Effect of cycles of adsorption (15 min) and desorption (10 min) on desorption efficiencies of Pb^{2+} from 10 g of optimized beads (3–3.5 mm) in 50 ml of the 0.1 M HCl aqueous solution ($T=293 \text{ K}$) at the optimum adsorption conditions and the most effective desorption agitation rate (desorption efficiency = $100\% \times \text{the ratio of the amount of desorbed } Pb^{2+} \text{ and the amount of adsorbed } Pb^{2+} \text{ in each cycle of adsorption and desorption}$).

greater the cycle of adsorption and desorption, the higher the desorption efficiency, and that the desorption efficiency reached 70% after six to eight cycles of adsorption and desorption. This can also be explained by a number of the adsorbed Pb^{2+} not being desorbed in the previous cycle and still occupying adsorption sites. Examining the relative efficiencies of adsorption and desorption, we find that the reusability of optimized beads is feasible.

4. Conclusions

Optimized beads contained 33 wt.% of alginate (18 wt.% in aqueous solution), 33 wt.% of chitosan (1.5 wt.% in aqueous solution), 33 wt.% of PEG (0.5 wt.% in aqueous solution), and 1 wt.% of *Pseudomonas aeruginosa* PU21, cross-linked by 0.554 M ECH. The optimum adsorption conditions for these optimized beads were pH 5 and 400 rpm agitation, and equilibrium adsorption time was about 15 min. Furthermore, the optimized beads also had higher mechanical strength which is a property that facilitates potential reuse of the beads. The Langmuir adsorption equation fitted better with equilibrium adsorption data and adsorption of Pb^{2+} onto optimized beads was consistent with a first-order/spontaneous reaction. Finally, the most effective desorption agitation rate was 400 rpm and equilibrium desorption time was about 10 min when 0.1 M HCl was used to regenerate optimized beads.

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