



Investigation of the biosorption characteristics of lead(II) ions onto *Symphoricarpus albus*: Batch and dynamic flow studies

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ABSTRACT

This work reports the results of the study for lead(II) binding by the natural and low cost biosorbent *Symphoricarpus albus*. Batch biosorption experiments demonstrated the high rate of lead(II) biosorption and the kinetic data were successfully described by a pseudo-second-order model. Biosorption of lead(II) onto *S. albus* biomass showed a pH-dependent profile and lead(II) biosorption was higher when pH or temperature was increased. As much as 88.5% removal of lead(II) is also possible in the multi-metal mixture. The Langmuir isotherm better fits the biosorption data and the monolayer biosorption capacity was $3.00 \times 10^{-4} \text{ mol g}^{-1}$ at 45 °C. The biomass was characterized with FTIR and SEM analysis. Desorption studies revealed that the natural biomass could be regenerated using 10 mM HNO₃ solution with about 99% recovery and reused in five biosorption–desorption cycles. Therefore, *S. albus* which is cheap, highly selective and easily regenerable seems to be a promising substrate to entrap lead(II) ions in aqueous solutions.

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1. Introduction

The contamination of the aquatic systems with toxic heavy metal ions is a problem of global concern. The potential hazard because of their accumulation in the food chain and their persistence in nature has resulted in a significant increase of studies directed at developing for useful and alternative technologies for the treatment of contaminated effluents [1,2].

Biosorption is a promising technology for the treatment of pollutant streams. It is based on the metal–biomaterial interactions [3]. This process has several advantages such as low cost of materials, easy of operation and selectivity against the alkaline metals when compared with existing conventional physicochemical process such as chemical precipitation, reverse osmosis, ion-exchange and activated carbon adsorption [4].

The plant origin biomaterials contain hemicellulose, lignin, extractives, lipids, proteins, simple sugars, water hydrocarbons, and starch. The functional groups of these components play an important role in the heavy metal removal by the mechanism of complexation [5].

Fungal [6–8], algal [9–11], bacterial [12–14] and agricultural [15,16] biomasses have been employed for the biosorptive removal

of different pollutants from contaminated solutions. However, information about feasibility of regenerating spent biomasses is still scarce [17]. In the practical application of the biosorption process the regeneration ability of the biosorbent may be significantly important to keep the process cost down and to open the possibility of recovering the metal ions extracted from the biosorption medium [18].

Symphoricarpus albus (snowberry) is cheap and easily available plant in many countries and is commonly planted as ornamentals in parks and gardens. It is reported that *S. albus* berries can act as secologanin, carbon and nitrogen source [19]. There is currently no research regarding the biosorption potential of this biomass.

The goal of our study is to assess the lead(II) biosorption potential of *S. albus* berries. For this purpose, biosorption process was characterized under different operating conditions such as initial pH and sorbent dosage. Experimental data as functions of temperature and time were evaluated with the pseudo-first-order and the pseudo-second-order kinetic models. The Freundlich, Langmuir and Dubinin–Radushkevich (D–R) isotherm models were applied to the equilibrium data obtained at different concentration and temperature ranges. The continuous biosorption studies were conducted with different flow rates and internal diameters of column. Further, the desorption performance and regeneration ability of the biosorbent were studied. The biosorption mechanism was evaluated using FTIR and SEM analysis.

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2. Experimental

2.1. Preparation of the biosorbent

The fresh berries of *S. albus* were naturally collected in September 2007. The samples were repeatedly washed with deionized water to remove adhering dirt and soluble impurities. They were then dried at 80 °C for 24 h and grounded and sieved, using an ASTM Standard sieve, to select the particle sizes of less than 150 μm. The biosorbent was stored in a glass bottle for further use.

2.2. Preparation of lead(II) solutions

A stock solution of lead(II) was prepared by dissolving appropriate amount of anhydrous Pb(NO₃)₂ in 1 L of deionized water, and the concentrations of lead(II) used in this study (50–500 mg L⁻¹) were obtained by dilution of the stock solution. The pH of the solutions was adjusted to the desired value by adding a small quantity of 0.1 mol L⁻¹ HCl, or 0.1 mol L⁻¹ NaOH.

2.3. Batch biosorption experiments

The batch biosorption experiments were performed on a digital magnetic stirrer at 200 rpm, using 100 mL beakers to elucidate the optimum conditions. The effect of initial pH on the biosorption process was examined by equilibrating the mixture containing 0.025 g of biosorbent samples, and 25 mL of 100 mg L⁻¹ lead(II) solutions, at different pH values ranging from 1.0 to 5.5. The biosorbent dosage was varied between 0.6 and 10.0 g L⁻¹, to predict the effect of biosorbent concentration on the removal of lead(II) ions. The contact time between the lead(II) ions and the biomass was ranged from 10 to 70 min, and the temperatures were ranged from 15 to 45 °C. The pseudo-first-order and the pseudo-second-order kinetic models were applied to data. After the each biosorption procedure completed, the samples were centrifuged at 4500 rpm for 3 min to separate the solid phase from the liquid phase. The supernatants were analyzed for residual lead(II) concentrations by an Atomic Absorption Spectrophotometer (Hitachi 180-70, Japan). Deuterium background correction was used and the spectral slit width was 1.3 nm. The working currents/wavelengths were 7.5 mA/283.3 nm. The instrument response was periodically checked by using standard lead(II) solutions. The biosorption capacity was determined by using the following equation.

$$q_e = \frac{V(C_i - C_e)}{m} \quad (1)$$

where C_i and C_e represent the initial and equilibrium concentrations of lead(II), respectively; V is the volume of the lead(II) solution (L) and m is the amount of biosorbent (g).

The Langmuir, Freundlich and Dubinin–Radushkevich isotherm models were investigated in batch mode using an initial lead(II) concentration range of 50–500 mg L⁻¹ and varying operating temperatures. In addition, the thermodynamic parameters of biosorption were also extracted using a distribution constant (K_D).

2.4. Column biosorption experiments

The lead(II) biosorption performance of the natural biosorbent *S. albus* was investigated in a continuous mode using an up flow packed glass column. A known quantity of dried *S. albus* was packed between two layers of glass wool into the column to provide the desired bed height. The lead(II) solution was pumped upward through the column at a desired flow rate using a peristaltic pump (Ismatec ecoline). Firstly, the flow rate of sorbate was altered in a

range between 1.0 and 10.0 mL min⁻¹, while all of the other parameters, such as pH, amount of biosorbent, temperature, initial lead(II) concentration, column i.d., and sorbate volume were kept constant. The effect of column i.d. on the biosorption performance of the biomass was investigated by using different columns (9–19 mm i.d. and 100 mm height). The effluent samples left the column were collected (in a 25 mL volume) and analyzed for the residual lead(II) concentration as described above. The Langmuir, Freundlich and Dubinin–Radushkevich isotherm models were also investigated in continuous mode.

2.5. Desorption and reusability studies

Different mineral acids revealed metal elution efficiency close to 100%. In this work *S. albus* biomass was subjected to 10 mM HCl, 10 mM HNO₃ and 10 mM EDTA solutions (25 mL) in order to select the most suitable desorption agent for lead(II) ions. Consecutive biosorption–desorption cycles were repeated five times using the same biosorbent. For this purpose fixed bed experiments were performed in a glass column (13.0 mm i.d. and 100 mm height) loaded with 0.1 g of the biosorbent material. Lead(II) solutions (100 mg L⁻¹) were pumped through the column at a flow rate of 1.0 mL min⁻¹. The effluent was analyzed for the residual lead(II) concentration by FAAS as described above. Desorption yield was calculated by using the following equation:

$$\text{Desorption yield} = \frac{\text{Amount of Pb(II) ions desorbed}}{\text{Amount of Pb(II) ions biosorbed}} \times 100 \quad (2)$$

2.6. Matrix effect

In order to evaluate the matrix effect on the removal of lead(II) by *S. albus*, an optimized biosorption procedure was tested with model solutions containing Pb²⁺, Ca²⁺, Mg²⁺, Na⁺, K⁺, Ni²⁺, Co²⁺, Cu²⁺ ions at a concentration of 100 mg L⁻¹.

2.7. Characterization of the biosorbent

FTIR spectral analysis of unloaded and lead(II)-loaded biosorbent was recorded in a PerkinElmer Spectrum 100IR infrared spectrometer in the region of 400–4000 cm⁻¹ and the samples were prepared as KBr pellets under high pressure. The surface structure and morphology of the biosorbent material before and after lead(II) biosorption were characterized using a scanning electron microscope (JEOL 560 LV SEM), at 20 kV and 1000× magnification. Prior to analysis, the samples were coated with a thin layer of gold under an argon atmosphere to improve electron conductivity and image quality. The surface charge of the biomass was measured using a Zeta potential analyzer (Malvern Zetasizer nano ZS).

3. Results and discussion

3.1. Effect of pH

It is well documented that pH of the biosorption medium is an important parameter affecting the uptake of heavy metal ions from aqueous solutions by biosorbent [20,21]. Therefore the batch equilibrium studies were carried out with different initial pH values ranging from 1.0 to 5.5 in order to study the effect of initial pH on the biosorption capacity of *S. albus* biomass. The results presented in Fig. 1 indicated that the maximum biosorption capacity of biomass was observed at pH 5.5. Under highly acidic conditions little biosorption occurred. Especially at pH 1.0 almost no biosorption took place. The lead(II) biosorption capacity of *S. albus* biomass increased from 0.73 to 31.48 mg g⁻¹ when the solution pH was

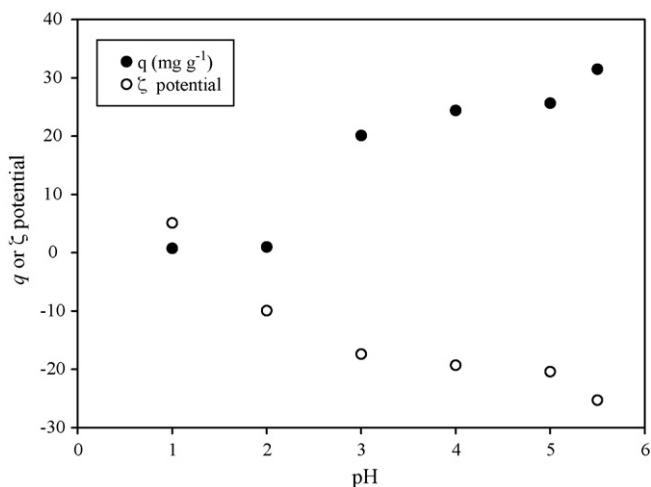


Fig. 1. Effect of initial pH on the biosorption of lead(II) ions and ζ potential values of biosorbent at various pH values (m : 0.025 g, V : 25 mL, and C_0 : 100 mg L⁻¹).

increased from 1.0 to 5.5. It was indicated that there was a close relationship between the zeta potential and the biosorption capacity of biomaterials [22]. Therefore, the zeta potentials of the biomass under different pH conditions were determined and the results were shown in Fig. 1. When the pH of the solution was increased the number of positively charged available sites decreased and the number of negatively charged sites increased. The surface of the biosorbent becomes negatively charged, and this increases the biosorption of the positively charged lead(II) ions through electrostatic forces of attraction. Therefore, the biosorption of lead(II) ions increased at higher pH values. The lower biosorption capacity of the biomass observed at acidic pH is due to the competition between the excess hydronium (H₃O⁺) ions and the positively charged metal ions for the biosorption sites. When the initial pH of the solution was adjusted to a higher value of pH 5.5, lead(II) ions precipitated because of the higher concentration of OH⁻ ions in the biosorption medium. For this reason, the experiments were not conducted beyond pH 5.5.

3.2. Effect of biosorbent concentration

Data obtained from the experiments with varying biosorbent concentrations are presented in Fig. 2. It showed that increasing biosorbent dosage resulted in a sharply increase in the biosorption yield. The biosorption yield for lead(II) onto *S. albus* biomass increased from 15.34 to 88.55% when the biomass dosage was increased from 0.6 to 4.0 g L⁻¹. The observed enhancement in lead(II) biosorption yield with increasing biomass concentration could be due to an increase in the number of possible binding sites and surface area of the biosorbent [23]. A further increase in biomass concentration over 4.0 g L⁻¹ did not lead to a significant improvement in biosorption yield due to the saturation of the biosorbent surface with lead(II) ions. Therefore, the optimal biomass concentration was selected as 4.0 g L⁻¹ for the further experiments.

3.3. Effects of contact time and temperature

In order to determine the biosorption equilibrium time for lead(II) ions, the contact time was varied from 10 to 70 min at different temperatures, and the results are shown in Fig. 3. From this figure it was observed that lead(II) biosorption onto *S. albus* biomass relatively occurs rapidly and equilibrium was reached within 20 min at all temperatures. The rapid biosorption rate that

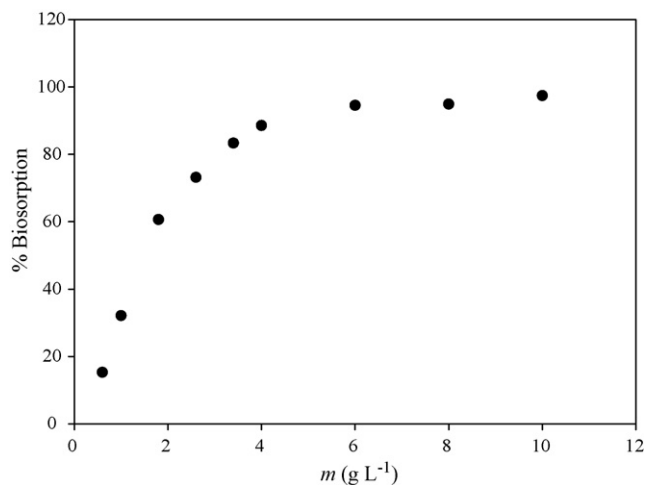


Fig. 2. Effect of biosorbent concentration on the biosorption of lead(II) ions onto *S. albus* biomass (pH: 5.5, V : 25 mL, and C_0 : 100 mg L⁻¹).

was observed at the beginning of biosorption process may be explained by an increase in the number of active metal binding sites on the biosorbent surface, which would result in an increased concentration gradient between sorbate in the solution and on the biomass surface. After an increase in contact time, the occupation of the remaining vacant sites will be difficult due to the repulsive forces between the Pb(II) ions on the solid and the liquid phases [24,25]. The rate of metal-biosorption is of great significance for developing a microbial origin sorbent material for water-treatment technology [26] and practical application of process [27]. The equilibrium biosorption of lead(II) ions was favored at higher temperatures. An increase in the temperature from 15 to 45 °C leads to an increase in the biosorption capacity from 19.26 to 21.78 mg g⁻¹ at an equilibrium time of 20 min. After this period, lead(II) biosorption was virtually constant. The observed trend with increasing temperature suggests that biosorption of lead(II) ions by natural biosorbent is kinetically controlled by an endothermic process.

3.4. Biosorption kinetics

The kinetic studies have carried out to determine the efficiency of lead(II) biosorption onto *S. albus* biomass and indicated that the

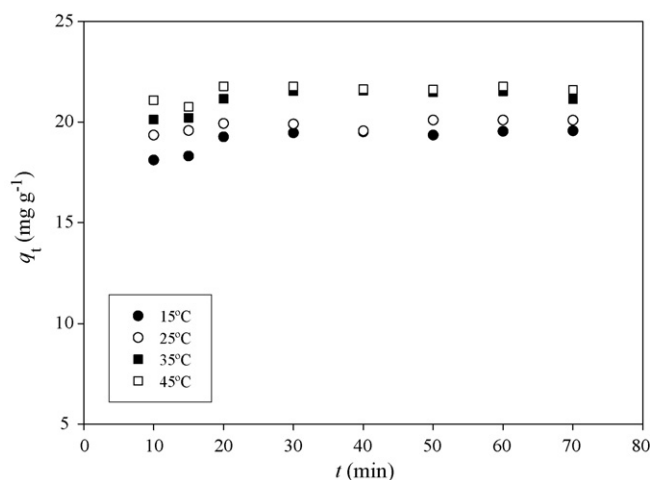


Fig. 3. Effect of contact time on the biosorption of lead(II) ions onto *S. albus* biomass at various temperatures (pH: 5.5, m : 0.1 g, V : 25 mL, and C_0 : 100 mg L⁻¹).

Table 1Kinetic parameters for the biosorption of lead(II) ions onto *S. albus* biomass at various temperatures (pH: 5.5, m: 0.1 g, V: 25 mL, C₀: 100 mg L⁻¹).

T (°C)	q _{exp} (mg g ⁻¹)	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
		K _L (min ⁻¹)	q _{e,cal} (mg g ⁻¹)	r ₁ ²	k ₂ (g mg ⁻¹ min ⁻¹)	q _{e,cal} (mg g ⁻¹)	r ₂ ²
15	19.26	7.87 × 10 ⁻⁴	1.04	0.098	6.0 × 10 ⁻²	19.81	0.999
25	19.93	-1.75 × 10 ⁻²	0.24	0.102	9.56 × 10 ⁻²	20.22	0.999
35	21.16	3.86 × 10 ⁻²	2.55	0.374	1.05 × 10 ⁻¹	21.54	0.999
45	21.78	4.61 × 10 ⁻²	0.82	0.292	1.58 × 10 ⁻¹	21.78	0.999

biosorption capacity increased with an increase in the temperature. The Lagergren pseudo-first-order [28] and the pseudo-second-order [29] kinetic models were tested to elucidate the biosorption mechanism.

The kinetic data in Table 1 demonstrate that the biosorption of lead(II) onto *S. albus* biomass does not follow the pseudo-first-order kinetics. The pseudo-second-order kinetic model with r² values of 0.999 showed good agreement with the experimental values at all temperatures studied.

3.5. Sorption isotherms

The equilibrium biosorption isotherms are one of the most important data for understanding the mechanisms of the biosorption process. The Freundlich [30], Langmuir [31] and Dubinin–Radushkevich [32] isotherms were selected in this study.

The numerical values of the Freundlich constant *n*, which is a measure of the deviation from linearity of the biosorption [33], were between 2.623 and 2.823. Values of *n* greater than unity indicated that lead(II) ions are favorably biosorbed by *S. albus* at all of the temperatures studied.

The r² and q_{max} values in Table 2 suggested that the Langmuir isotherm may be a suitable model for our data due to the high correlation coefficients. It was concluded that the removal process of lead(II) by natural biosorbent was monolayer biosorption, and the maximum monolayer biosorption capacities were found between 2.24 × 10⁻⁴ mol g⁻¹ (46.41 mg g⁻¹) and 3.00 × 10⁻⁴ mol g⁻¹ (62.16 mg g⁻¹) at the various temperatures in the batch studies. The biosorption capacity of *S. albus* obtained for lead(II) ions in this study was found to be comparable to and moderately higher than those of many corresponding sorbents [34–46] in the literature (Table 3). The batch biosorption capacity of *S. albus* is also comparable with those obtained from the continuous mode (Table 2).

The Langmuir constant, K_L, can be used to determine the suitability of the biosorbent for the sorbate and to calculate the Hill separation factor (R_L, dimensionless) [47]. R_L values can be used for interpretation of the sorption type [47–49]. In this study, we found values of R_L between 5.15 × 10⁻² and 5.39 × 10⁻², and this indicated that the biosorption of lead(II) onto *S. albus* is favorable.

The magnitude of *E* value gives information about biosorption mechanism as chemical ion-exchange or physical sorption [50–53]. The mean free energy of lead(II) biosorption was found to range between 18.64 and 21.59 kJ mol⁻¹ in this study which indicates a

Table 2Isotherm model constants for the biosorption of lead(II) ions onto *S. albus* biomass at various temperatures (pH: 5.5, m: 0.1 g, V: 25 mL).

Process	Langmuir constants				Freundlich constants			Dubinin–Radushkevich (D–R) constants			
	q _{max} (mol g ⁻¹)	K _L (L mol ⁻¹)	r _L ²	R _L	<i>n</i>	K _F (L g ⁻¹)	r _F ²	q _{max} (mol g ⁻¹)	β (mol ² kJ ⁻²)	r _{D–R} ²	<i>E</i> (kJ mol ⁻¹)
Batch (15 °C)	2.24 × 10 ⁻⁴	7.63 × 10 ³	0.998	5.15 × 10 ⁻²	2.823	2.33 × 10 ⁻³	0.903	5.73 × 10 ⁻⁴	1.95 × 10 ⁻³	0.935	18.64
Batch (25 °C)	2.55 × 10 ⁻⁴	7.48 × 10 ³	0.999	5.25 × 10 ⁻²	2.623	3.27 × 10 ⁻³	0.921	7.06 × 10 ⁻⁴	1.94 × 10 ⁻³	0.949	18.81
Batch (35 °C)	2.79 × 10 ⁻⁴	7.42 × 10 ³	0.995	5.29 × 10 ⁻²	2.672	3.31 × 10 ⁻³	0.893	7.35 × 10 ⁻⁴	1.86 × 10 ⁻³	0.927	20.50
Batch (45 °C)	3.00 × 10 ⁻⁴	7.27 × 10 ³	0.995	5.39 × 10 ⁻²	2.632	3.69 × 10 ⁻³	0.878	7.96 × 10 ⁻⁴	1.81 × 10 ⁻³	0.915	21.59
Column	1.68 × 10 ⁻⁴	3.44 × 10 ³	0.967	1.07 × 10 ⁻¹	2.025	4.20 × 10 ⁻³	0.979	6.28 × 10 ⁻⁴	2.27 × 10 ⁻³	0.984	13.77

Table 3

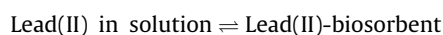
Biosorption results for lead(II) ions by various sorbents from the literature.

Sorbent material	Sorption capacity (mg g ⁻¹)	References
Grape stalk waste	49.93	[34]
<i>Cladonia furcata</i>	12.30	[35]
Tree fern	40.00	[36]
Mustard husk	30.48	[37]
Expanded perlite	13.39	[38]
<i>Ganoderma carnosum</i>	22.79	[39]
<i>Penicillium simplicissimum</i>	76.90	[40]
Saw dust (<i>Pinus sylvestris</i>)	22.22	[41]
<i>Saccharomyces cerevisiae</i> (immobilized on cone biomass)	30.04	[42]
Modified peanut husk	29.14	[43]
Tea waste	65.00	[44]
<i>Rhizopus arrhizus</i>	2.64	[45]
Bagasse fly ash (Hydrogen peroxide treated)	2.50	[46]
<i>Symphoricarpos albus</i>	62.16	This study

physical biosorption of lead(II) ions onto *S. albus*.

3.6. Biosorption thermodynamics

Thermodynamic parameters (energy and entropy) are used to determine whether a biosorption process will spontaneously occur. Lead(II) biosorption may be represented by the following reversible process [54]:



For such equilibrium reactions, K_D, the distribution constant, can be used to estimate the thermodynamic parameters due to its dependence on temperature. The changes in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) of biosorption process were determined by using following equations:

$$K_D = \frac{q_e}{C_e} \quad (10)$$

$$\Delta G^\circ = -RT \ln K_D \quad (11)$$

$$\ln K_D = -\frac{\Delta G^\circ}{RT} = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (12)$$

A Van't Hoff plot of ln K_D as a function of 1/T yields a straight line, from which ΔH° and ΔS° were calculated from the slope and intercept, respectively. The negative values of ΔG° at different temperatures (Table 4) indicate that lead(II) biosorption is a

Table 4
Thermodynamic parameters for the biosorption of lead(II) ions onto *S. albus* biomass.

$T (^{\circ}\text{C})$	K_D	$\Delta G^{\circ} (\text{kJ mol}^{-1})$	$\Delta H^{\circ} (\text{kJ mol}^{-1})$	$\Delta S^{\circ} (\text{kJ K}^{-1} \text{mol}^{-1})$
15	3.812	-3.215	17.179	68.40
25	4.227	-3.899		
35	6.236	-4.583		
45	6.771	-5.267		

spontaneous process, and the biosorbent used in this study has higher affinity at higher temperatures. The change in the standard enthalpy, ΔH° is $17.179 \text{ kJ mol}^{-1}$ and the positive value of ΔH° indicates that biosorption of lead(II) onto *S. albus* is an endothermic process. The positive value of ΔS° ($68.40 \text{ kJ mol}^{-1}$) suggests that randomness at the solid/solution interface increases with biosorption of lead(II) onto *S. albus* [55].

3.7. Column biosorption

A continuously operating system has advantages such as simple operation, high yield, is easily scaled up from the laboratory and the packed bed of biosorbent is easy to regenerate [56]. Therefore, the natural biosorbent, *S. albus* was also evaluated for lead(II) biosorption in a continuous mode.

In order to investigate the effect of flow rate on the biosorption capacity of biosorbent, the flow rate of sorbate was varied from 1.0 to 10.0 mL min^{-1} . The results shown in Fig. 4 indicated that the flow rate strongly influenced lead(II) biosorption capacity. Lower flow rates favor lead(II) biosorption. The biosorption capacity of the biomass significantly decreased from 11.58 to 5.02 mg g^{-1} with increased flow rate from 1.0 to 10.0 mL min^{-1} [57]. At lower flow rates, lead(II) ions had more time in contact with the biosorbent and this was resulted in more lead(II) being removed from the column. Higher flow rates reduce the contact time between the lead(II) ions and biosorbent by reducing the solute residence time [58]. Therefore the optimum flow rate for lead(II) biosorption was selected as 1.0 mL min^{-1} in this study.

In the second stage of the column studies, the internal diameter of column was changed from 9 to 19 mm in order to evaluate the effect of column size on biosorption performance. The results are shown in Fig. 5. The lead(II) biosorption capacity of *S. albus* increased from 11.82 to 16.54 mg g^{-1} when the column i.d. was increased from 9 to 19 mm . As the column i.d. was increased, the surface area of biosorbent in the column increased because the

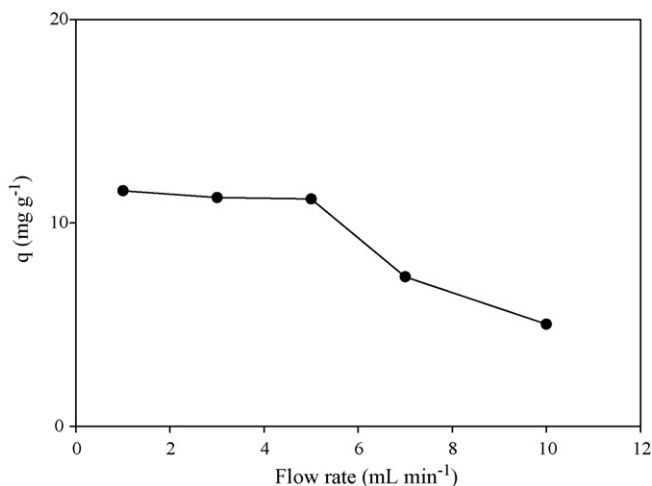


Fig. 4. Effect of flow rate on the continuous biosorption of lead(II) ions onto *S. albus* biomass (pH: 5.5, m : 0.1 g, and C_0 : 100 mg L^{-1}).

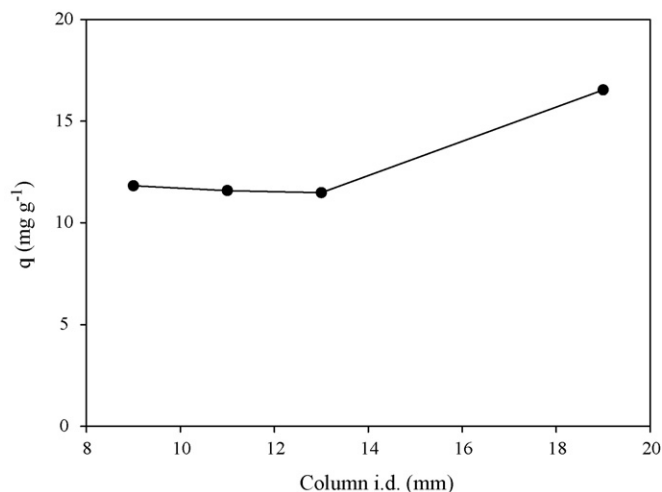


Fig. 5. Effect of internal diameter of column on the continuous biosorption of lead(II) ions onto *S. albus* biomass (pH: 5.5, m : 0.1 g, C_0 : 100 mg L^{-1} , and flow rate: 1 mL min^{-1}).

amount of loading biomass into column was kept constant. Therefore, more lead(II) ions had in contact with the biosorbent and the maximum biosorption capacity was observed when a column with the highest i.d. was used.

3.8. Desorption and reuse

The regeneration of the biosorbent is one of the key factors in assessing of their potential for commercial applications. Three different desorption agents, HCl (10 mM), HNO_3 (10 mM) and EDTA (10 mM) were used to recover the lead(II) ions from the biosorbent and the results were shown in Fig. 6. Since the best regeneration was achieved with 10 mM HNO_3 solution it was selected as desorption agent for lead(II) ions. Higher than 99% of the biosorbed Pb(II) ions were desorbed from the biosorbent. The reusability of the biosorbent was tested in five consecutive biosorption–desorption cycles using the same preparation (Fig. 7). These results indicated that the natural biosorbent *S. albus* offers potential to be used repeatedly in lead(II) biosorption studies without any significant loss in the total biosorption capacity.

The fate of biosorbent after complete utilization is relatively unanswered question. Although the biosorbent materials can be

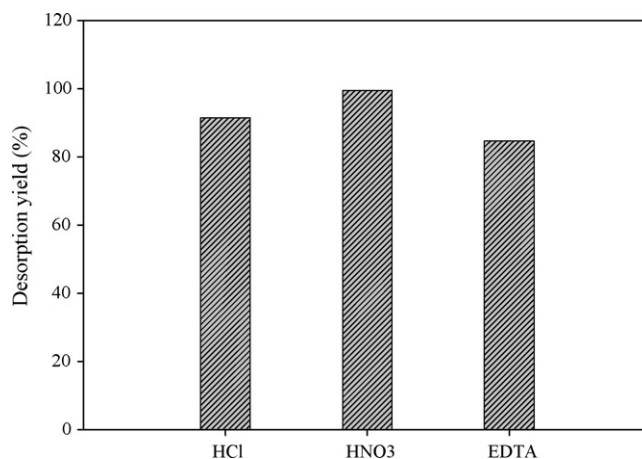


Fig. 6. Effect of the type of desorption agent on the desorption of lead(II) ions from *S. albus* biomass (m : 0.1 g, C_0 : 100 mg L^{-1} , and flow rate: 1 mL min^{-1}).

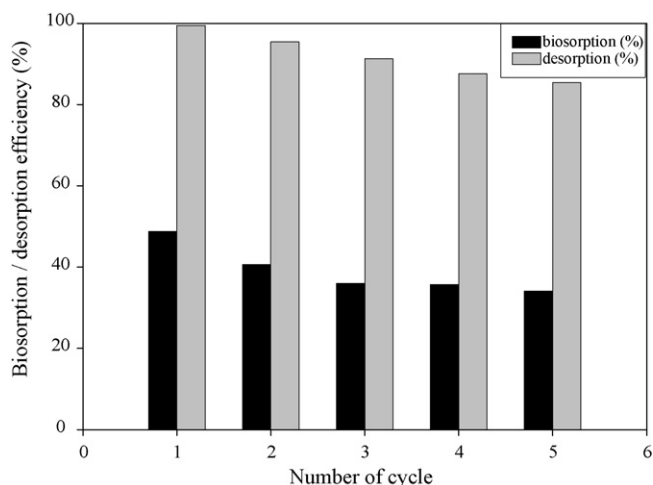


Fig. 7. Biosorption–desorption cycles for lead(II) ions by *S. albus* biomass (m : 0.1 g, C_0 : 100 mg L⁻¹, and flow rate: 1 mL min⁻¹).

successfully used in many biosorption/desorption cycles, the final disposal of the biosorbents should be addressed. It was suggested that the final biosorbents may be disposed via land-fill or by incineration. If the biosorbent material is cheap and abundant, it can be used as fertilizer and animal feed after biosorbed metals were completely removed or reused for the sorption of the other pollutants [59,60].

3.9. Effect of interference by metal ions

Since interference by other ions may have an effect on the biosorption of lead(II) by *S. albus*, biosorption experiments were conducted for a model solution containing 100 mg L⁻¹ of Pb²⁺, Ca²⁺, Mg²⁺, Na⁺, K⁺, Ni²⁺, Co²⁺, Cu²⁺ ions. The medium containing each metal ion was treated with *S. albus* at determined optimum biosorption conditions for single lead(II) ion solution. The biosorption capacity of the biomass in multi-metal solution (21.45 mg g⁻¹) was slightly lower than single condition (22.14 mg g⁻¹). Competition among metal ions can hinder the metal binding ability of biomass, as expected. But the results indicated that the presence of the other metal ions has almost no effect on the biosorption of lead(II) onto *S. albus* biomass. The observed trend for multi-metal solution would be an important advantage for the usability of the proposed biosorption system in real wastewater conditions.

3.10. Characterization of the biosorbent and mechanism of lead(II) biosorption

In order to examine the textural structure of biomass, SEM micrographs were taken before (Fig. 8(a)) and after (Fig. 8(b)) lead(II) biosorption onto *S. albus* biomass. These micrographs indicated clearly the deformation and presence of many new shiny bulky particles over the surface of lead(II)-loaded *S. albus* biomass, which were absent on the corrugated surface of biomass before loading with lead(II). The unloaded biomass has irregular pores with a diameter higher than 10 μm, which indicates that the biosorbent has a macro-porous structure [61]. There was also a decrease in pore sizes in lead(II)-loaded biomass, and this may be attributed to the fact that the macro-porous structure plays a role in lead(II) biosorption.

The FTIR spectra of unloaded and lead(II)-loaded *S. albus* biomass in the range of 400–4000 cm⁻¹ were taken to obtain information on the nature of the possible biosorbent–lead(II) ions interactions and presented in Fig. 9. Band positions for each sam-

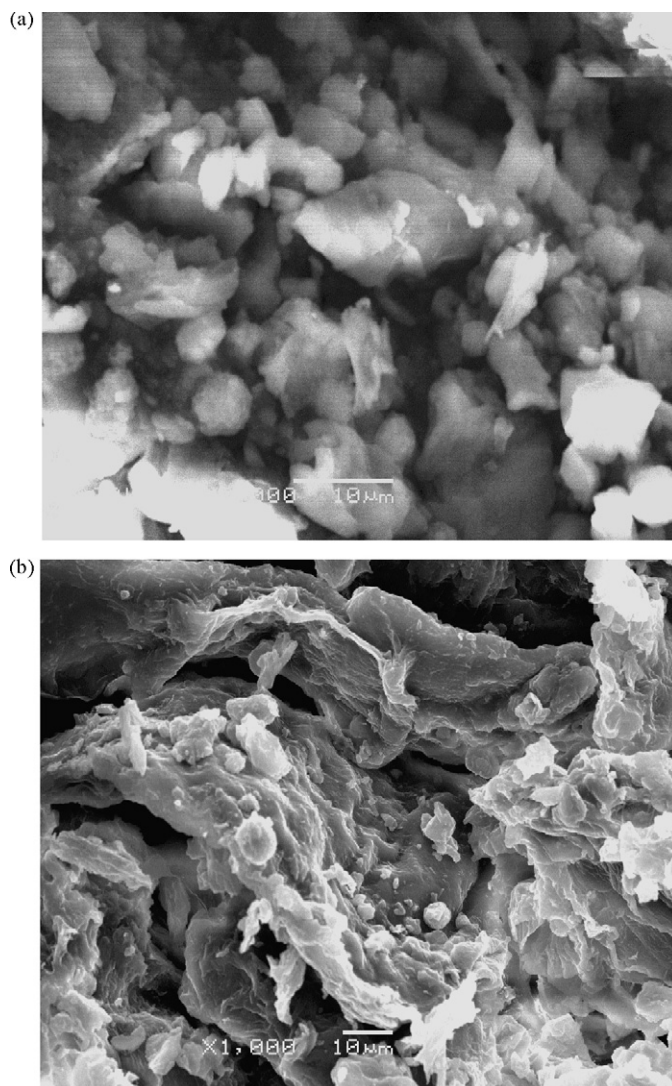


Fig. 8. SEM micrographs for unloaded (a) and lead(II)-loaded (b) *S. albus* biomass.

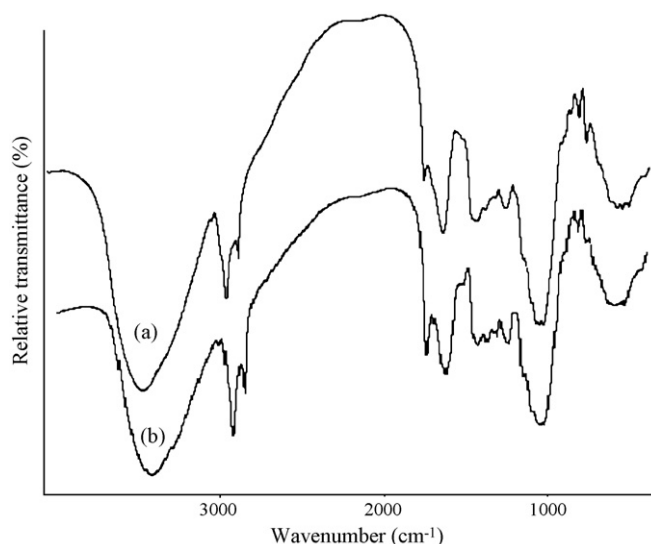


Fig. 9. Infrared spectra of unloaded (a) and lead(II)-loaded (b) *S. albus* biomass.

Table 5
Band positions before and after lead(II) biosorption.

Suggested assignment	Band positions (cm ⁻¹)	
	Unloaded biomass	Lead(II)-loaded biomass
—OH and/or—NH ₂ stretching	3424	3422
—CH ₂ —symmetric stretching	2925	2924
—CH ₂ —asymmetric stretching	2853	2852
—C=O stretching	1743	1744
—OH bending vibrations ^a	1630	1626
—C—O stretching	1432	1432
—CH ₂ —bending vibrations	1376	1377
—SO ₃ group ^a	1257	1246
—P=O stretching ^a	1151	1158
—P—OH stretching ^a	1030	1033
—N-containing bioligands ^a	<775	<771

^a Denotes band shifting after lead(II) biosorption.

ple are also listed in Table 5. It has previously been reported that all of the biological sorbent materials have intense absorption bands around 3500–3200, which represent the stretching vibrations of amino groups. These bands are superimposed onto the side of the hydroxyl group band at 3500–3300 cm⁻¹ [62]. A similar and very strong absorption peak was observed for both unloaded and lead(II)-loaded biomass at 3424 and 3422 cm⁻¹, respectively. The —CH₂ stretching vibrations showed a characteristic absorption peaks at about 2925 and 2853 cm⁻¹ for unloaded and at 2924 and 2852 cm⁻¹ for lead(II)-loaded biomass. The spectra of the unloaded and lead(II)-loaded biomass also display absorption peaks at 1743 and 1744 cm⁻¹, corresponding to stretching of the carboxyl groups. Strong absorption band at 1630 cm⁻¹ (indicative of —OH bending vibrations) slightly shifted to 1626 cm⁻¹ in the FTIR spectrum of lead(II)-loaded biomass. The band shift was observed for —SO₃ groups moving from 1257 to 1246 cm⁻¹ with a difference of 11 cm⁻¹. The absorption peaks around 1151 and 1030 cm⁻¹ are indicative of P=O stretching and P—OH stretching vibrations, respectively [63]. These peaks shifted to 1158 and 1033 cm⁻¹ after lead(II) biosorption onto *S. albus* biomass. These results indicated the involvement of these functional groups in biosorption process. Finally, it should be noted that peaks in the region of lower wavenumbers (under 800 cm⁻¹) appeared as a broad peak and this could be attributed to an interaction between lead(II) ions and N-containing bioligands [13,27,64].

4. Conclusions

From this investigation on the biosorption of lead(II) ions using natural biosorbent, *S. albus*, the following conclusions can be drawn:

1. The natural biomass of *S. albus* was found to be an excellent and low cost biosorbent for lead(II) ions.
2. The batch biosorption of lead(II) was highly dependent on the initial pH and biosorbent concentration and pH 5.5 was found to be most suitable. Maximum removal of lead(II) ions was achieved with 4.0 g L⁻¹ of biomass dosage.
3. Biosorption was very fast and equilibrium was established within 20 min. The kinetic data were successfully described by a pseudo-second-order model with rate constants ranging from 6.0 × 10⁻² to 1.58 × 10⁻¹ g mg⁻¹ min⁻¹, as a function of temperature.
4. Continuous biosorption of lead(II) onto *S. albus* was found to depend on flow rate and column i.d.
5. Biosorption isotherms were modeled using the Langmuir, Freundlich and D-R models. Based on the correlation coefficients the Langmuir model adequately described the biosorption of lead(II) under all examined conditions.

6. The 10 mM HNO₃ solution was able to elute 99% of lead(II) from the metal-loaded biomass, and allowed the *S. albus* to be regenerated and reused for five sorption–desorption cycles.
7. 88.5% of lead(II) ions was also removed from multi-metal solutions by natural biosorbent *S. albus*.
8. Thermodynamic studies on the lead(II) biosorption revealed that the process was endothermic and spontaneous. The FTIR spectroscopic analysis confirmed that the functional groups on the biosorbent surface were involved in lead(II) biosorption.

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