

55 (2015) 163–172 June



# Utilization of immobilized distillation sludges for bioremoval of Pb(II) and Zn(II) from hazardous aqueous streams

Muhammad Idrees Jilani<sup>a</sup>, Raziya Nadeem<sup>a</sup>, Muhammad Asif Hanif<sup>a,\*</sup>, Tariq Mahmood Ansari<sup>b</sup>, Asid Majeed<sup>a</sup>

<sup>a</sup>Department of Chemistry of Biochemistry, University of Agriculture, Faisalabad 38040, Pakistan, Tel. +92419200161 3309; Fax: +92 419200765; emails: midreesjilani1star@yahoo.com (M.I. Jilani), raziyanalyst@yahoo.com (R. Nadeem), muhammadasifhanif@ymail.com (M.A. Hanif), asidchemist@yahoo.com (A. Majeed) <sup>b</sup>Institute of Chemical Sciences, Bahauddin Zakariya University, Multan 60800, Pakistan, Tel. +92419200161 3309; email: drtariq2000@gmail.com (T. Mahmood Ansari)

Received 8 October 2013; Accepted 11 March 2014

#### ABSTRACT

The present study was carried out to investigate the metal sorption potential of low-cost distillation sludges of caraway (DSC), basil (DSB), fennel (DSF), clove (DSCl), jasmine (DSJ); and immobilized distillation sludges of caraway (IDSC), basil (IDSB), fennel (IDSF), clove (IDSCl), and jasmine (IDSJ). The maximum equilibrium uptake of Pb(II) and Zn(II) ions was 0.80 and 0.30 mmol/g by IDSJ and IDSF, respectively. The optimum pH was 4.5 for Pb(II) and Zn(II) uptake was noticed with increase in shaking speed. The metal uptake capacity of Zn(II) sharply decreased with increase in temperature. Experiments revealed that sorption equilibrium reached much faster in case of textile industrial wastewater than synthetic effluents. Pseudo-first-order model fitted well to the kinetics data of Pb(II) at  $30-50^{\circ}$ C and of Zn(II) at  $30-40^{\circ}$ C. Metal uptake increased with increase in initial concentration of metal ions up to 200 mg/L. Acidic desorbents were found to be suitable as compared to EDTA in metal desorbing studies.

Keywords: Pb(II); Zn(II); Immobilization; Distillation sludge; Removal

#### 1. Introduction

Natural reserves are being contaminated due to toxic substances generated by industrial, agricultural, and domestic activities. Heavy metals present in wastewater may affect survival, development, growth, reproduction, and behavior of the aquatic organisms. Most of heavy metals are non-degradable into nontoxic end products. Heavy metal concentrations must be reduced

\*Corresponding author.

to acceptable levels before their discharge into environment. These could pose threats to public health and/or affect the esthetic quality of potable water [1,2]. Heavy metals such as zinc and lead have a number of applications in basic engineering works, paper and pulp industries, leather tanning, organo-chemicals, petrochemicals, fertilizers, etc. Pb(II) is a potent neurotoxic metal. Once free in the system, lead may cause nephrotoxicity, neurotoxicity, and hypertension [3]. Too much intake of Zn(II) can lead to respiratory incapacitation, as indicated by increased respiratory activity such as

<sup>1944-3994/1944-3986 © 2014</sup> Balaban Desalination Publications. All rights reserved.

breathing rate, volume and frequency of ventilation, coughing, decrease in oxygen uptake efficiency [4]. Zn (II) travels through the food chain via bioaccumulation [5].

Conventional methods for removing metals from aqueous solutions comprise chemical precipitation, chemical oxidation or reduction, ion exchange filtration, electrochemical treatment, reverse osmosis, membrane technologies, and evaporation recovery [6,7]. These processes may be ineffective or extremely expensive especially when the metals in solution are in the range of 1–100 mgL<sup>-1</sup>. Biosorption is most promising technique to remove heavy metals from wastewater [8]. Although freely suspended biomass may have better contact with adsorbate during biosorption process, the suspended biomass is normally not the practical form for the direct use in the removal of heavy metals. Since cell immobilization can enhance its stability, mechanical strength, reusability, and the ease of treatment, the technique has been well used to remove toxic heavy metals [9].

Caraway (Carum carvi L.), basil (Ocimum basilicum), fennel (Foeniculum vulgare), clove (Syzygium aromaticum L.), and jasmine (Jasmine sambac) essential oils are important for cosmetics as well as for medical industries. Essential oil from these plants is usually extracted using steam distillation. The biomass left after extraction of essential oil does not have any potential use. The present study was planned: (i) to assess the biosorption potential of these waste materials (DSC, DSB, DSF, DSCl, and DSJ) for uptake of Zn(II) and Pb(II) from aqueous as well as real hazardous streams; (ii) to study the effect of different parameters such as pH, biosorbent dose, biosorbent bead size, initial concentration of Pb(II) and Zn(II), contact time, stirring speed, and temperature; and (iii) to investigate the potential of immobilized distillation sludges for treating industrial effluents.

#### 2. Materials and methods

# 2.1. Biomass collection and preparation

DSC, DSB, DSF, DSCl, and DSJ used in this study were collected from Extraction Unit of Rosa Lab, Institute of Horticultural Sciences, University of Agriculture, Faisalabad, Pakistan. Distillation sludge was soaked overnight in distilled water to remove particulate matter and other waste soluble residues. Thus, obtained biomass was first sun-dried and then ovendried at 60°C till constant weight. One kilogram of biomass was sub-sampled for use in the experiments. Dried biomass was grounded using food processor (MJ 176, Japan) and then sieved through Octagon siever (OCT-DIGITAL 4527-01) to obtain adsorbent with homogenous known particle size. The fraction with <0.250–1.00 mm was selected for use in the sorption tests. The sieved sorbent was stored in an air tight plastic container for further experiments. For immobilization studies, one gram of sieved biosorbent (particle size 0.250 mm) was suspended in 2% sodium alginate solution to form a homogeneous mixture. Beads were formed by introducing this solution dropwise into the 0.1 M solution of calcium chloride. The biosorbent beads were preserved in 50 mM CaCl<sub>2</sub> solution till further use [10].

# 2.2. Preparation of Zn(II) and Pb(II) stock solutions

Stock Molar solutions (1,000 mg/L) were prepared by dissolving 4.549 g of  $Zn(NO_3)_2 \cdot 6H_2O$ , and dissolving 1.598 g of Pb(NO<sub>3</sub>)<sub>2</sub> in 1,000 mL of deionized water separately. Stock solution pH of  $Zn(NO_3)_2 \cdot 6H_2O$  and Pb(NO<sub>3</sub>)<sub>2</sub> was found to be 3.71 and 3.20, respectively. The solutions of different concentrations were prepared by adequate dilution of the stock solution with deionized water. Glassware and polypropylene flasks used were overnight immersed in 10% (v/v) HNO<sub>3</sub> and rinsed several times with deionized water.

# 2.3. Batch biosorption studies

In all sets of experiments fixed volume of Zn(II) and Pb(II) solutions (100 mL of 100 mg/L) were taken in each 250 mL conical flasks. The initial pH of each metal solution was adjusted to the required pH value using 0.1 N NaOH and 0.1 N HCl. Weighed amount of immobilized biosorbent was added to each conical flask. Conical flasks were over sealed with aluminum foil. After 24 h samples were filtered with Whatman No. 40, ashless, and stored in plastic sample bottles at 4°C. The concentrations of Zn(II) and Pb(II) were determined using Perkin Elmer AAnalyst 300 Atomic Absorption Spectrophotometer.

#### 2.4. Industrial effluents collection

The wastewater samples were collected from textile industry (dying and printing units) from Faisalabad, Pakistan. Triplicate samples were collected in polyethylene bottles and transported to research laboratory.

#### 2.5. Desorption

The reusability of biosorbent is directly related to the application potential of biosorption technology. The desorption of Pb(II) and Zn(II) from the loaded beads of IDSJ and

IDSF were carried by the 0.1 M HCl, H<sub>2</sub>SO<sub>4</sub>, CH<sub>3</sub>COOH, and EDTA which were used as desorbing agent.

# 2.6. Determination of Zn(II) and Pb(II) contents in the solutions

Zn(II) and Pb(II) contents in sample and control assays before and after the equilibrium were analyzed by flame atomic absorption spectrometry, using a Perkin-Elmer AAnalyst 300 atomic absorption spectrometer equipped with an air–acetylene burner and controlled by Intel Pentium-4 personal computer. Before analyzing samples, standard aqueous solutions of Zn(II) and Pb(II) were prepared. Standard solutions having Zn(II) (0.5–2 mg/L) and Pb(II) (1–20 mg/L) were used for plotting standard calibration curve ( $R^2 = 0.9999$ ). The hollow cathode lamps were operated at analytical wavelengths of 213.9 nm for Zn(II) and 342.8 nm for Pb(II) and slit as 0.2 nm for both metals.

# 2.7. Determination of uptake capacity and percentage removal

The Zn(II) and Pb(II) uptake was calculated by the simple concentration difference method. Adsorption capacity q is amount of metal ion (mg) biosorbed per g (dry weight) of biomass. The initial concentration,  $C_i$  (mg/L) and equilibrium metal concentrations,  $C_e$  (mg/L), respectively, were determined. The following equations were used to compute the percent metal uptake by the sorbent (Eq. (1)) and sorbent uptake capacity at equilibrium  $q_e$  (mg/g) (Eq. (2)) [9].

% Sorption 
$$= (C_i - C_e) 100/C_i$$
 (1)

$$q_e = (C_i - C_e) V / 1000w$$
<sup>(2)</sup>

where V is the volume of the solution in mL and w is the mass of the sorbent in g.

### 2.8. Statistical analysis

All data represent the mean of three independent measurements. Results were discussed using standard deviation. All statistical analysis was done using Microsoft Excel 2007, Version Office Xp.

# 3. Results and discussion

#### 3.1. Effect of pH on metal biosorption

Solution pH is the most important variable affecting metal uptake in metal biosorption [11]. The site dissociation and chemistry of heavy metal such as hydrolysis, complexation by organic and/or inorganic ligands, redox reactions, and precipitation are strongly influenced by pH and on the other side strongly influenced the speciation and the biosorption availability of the heavy metal [12,13]. In order to evaluate the influence of pH batch equilibrium studies were carried out with different initial pH value ranges Pb(II) (1-4.5) and Zn(II) (1-6) in order to avoid precipitation of metal hydroxides which have been estimated to occur at pH > 4.5 for  $Pb(OH)_2$  and pH > 6 for  $Zn(OH)_2$  [5,14]. Solution pH was found to play a vital role in the biosorption of Pb(II) and Zn(II) by DSC, DSB, DSF, DSCl, DSJ; and IDSC, IDSB, IDSF, IDSCl, IDSJ. Effect of pH on the boisorption Pb(II) and Zn(II) is depicted in (Fig. 1(a)–(d)). The result shows that as the pH enhanced metal uptake increased. The maximum equilibrium uptake of Pb(II) and Zn(II) ions was 165.74 and 19.26 mg/g by IDSJ and IDSF, respectively. The pH was 4.5 for Pb(II) and 6 for Zn(II). At low pH, H<sup>+</sup> ions increase in solution and H<sup>+</sup> ions coordinate with -OH group to from -OH<sub>2</sub><sup>+</sup> [15]. Due to high proton concentration at low pH values heavy metal uptake was decreased because of positive charge density on biosorbent metal binding site. Hydrogen ions effectively compete with metal ions to bind the site [16]. Thus, there is reduction in metal uptake capacity at low pH values. As the pH of solution increases the number of protons dissociated from functional group on the cell wall increase and thus more negative groups for complexation of metal cations are provided [17]. One of the most important aspects that have to be evaluated in metal biosorption study is the selection of suitable part of biomass able to sequester the largest amounts of metal of interest from its solution. One possible preliminary test that may be used to perform this selection is the effect of pH on metal uptake capacity of biomass (Fig. 1). This experimental procedure has also been used in other studies [18] and it can give a rough characterization of the selected biomass mainly when ionic exchange is the prevalent mechanism for the removal of heavy metals from their solutions [19]. Keeping previous studies in mind, IDSJ having maximum adsorption for Pb(II) and IDSF having maximum adsorption for Zn(II) at pH 4.5 and 6, respectively, were selected for further studies.

# 3.2. Effect of bead size

The effect of varying the biosorbent bead size ranging from 3.1 to 4.6 mm is presented in Fig. 2. The optimum bead size for Pb(II) and Zn(II) uptake by IDSJ and IDSF, respectively, was 3.5 mm. The bead



Fig. 1. (a) Effect of pH on uptake of Pb(II) by native distillation waste biomass. (b) Effect of pH on uptake of Zn(II) by native distillation waste biomass. (c) Effect of pH on uptake of Pb(II) by immobilized distillation waste biomass. (d) Effect of pH on uptake of Zn(II) by immobilized distillation waste biomasses.



Fig. 2. Effect of biosorbent bead size on uptake of Pb(II) and Zn(II).

size smaller than 3.5 mm showed less Pb(II) and Zn(II) uptake due to reduction in metal diffusion inside the bead pores. Whereas bead size larger than 3.5 mm showed reduction in metal uptake capacity due to reduced surface area. Thus, all the further experiments were conducted using 3.5 mm beads as it is always preferable to use rigid and slightly larger particles/ beads in sorption processes [20].

# 3.3. Effect of biosorbent dose

Biosorbent dose is a significant factor to be considered for effective metal sorption. It determines the sorbent–sorbate equilibrium of the system [6]. Biosorption of Pb(II) and Zn(II) with varying biosorbent concentration from 0.025 to 0.15 g/100 ml is



Fig. 3. Effect of biosorbent dose on uptake of  $\mbox{Pb(II)}$  and  $\mbox{Zn(II)}.$ 

shown in Fig. 3. The results indicated that the amount of % metals removed increased with an increase in adsorbent concentration, while the q (mg/g) (sorptive capacity) reduced, similar result has been found in work of [6,11]. The maximum uptake capacity of Pb(II), Zn(II) was achieved with a biomass concentration of 0.025 g/L and the result demonstrated that the biomass concentrations strongly affected the amount of metal removal from aqueous solutions [21]. Increase in % biosorption with an increase biosorbent dosage. This is because of the availability of more binding sites for complexation of metal ion.

# 3.4. Effect of shaking speed

The effect of altering the shaking speed from 0 to 250 rpm on uptake of Pb(II) and Zn(II) ions by IDSJ and IDSF, respectively, was evaluated at constant values of pH (pH 4.5 for Pb(II) and pH 6 for Zn), biosorbent dose, initial metal concentration, contact time, and temperature depicted in Fig. 4. The result revealed that as the shaking speed was increased, the metal uptake was reduced slightly. A slow decrease in Pb(II) and Zn(II) uptake was observed with increase in shaking speed. Uptake of Pb(II) and Zn(II) by IDSJ and IDSF were found to be maximum without shaking. With increase in shaking speed some metal ions may desorb into solution due to agitation, as the metal uptake process is reversible in nature [22].

#### 3.5. Effect of temperature

Biosorption of Pb(II) and Zn(II) ions was found as a function of the temperature. Experiments were carried out at five different temperatures ranging from



Fig. 4. Effect of shaking speed on uptake of Pb(II) and Zn (II).



Fig. 5. Effect of Temperature on uptake of Pb(II) and Zn(II).

30 to 60°C was revealed in Fig. 5. This figure demonstrate that Pb(II) uptake increase from 30 to 40°C, beyond this temperature an increase in temperature had negative effect on metal uptake process. The result has correlation with a previous study [17]. The metal uptake capacity of Zn(II) sharply decreases with increase in temperature. According to adsorption theory, adsorption decreases with increase in temperature and molecules adsorbed earlier on surface tend to desorb from the surface at elevated temperature [23]. A reasonable explanation might be that the actual attachment of metal ion on the cellular surface included not only chemisorption and ion exchange, but also physical adsorption [24]. It is also possible that as the temperature increases, denaturation of active sites of biomass also increase [21]. The results are in accordance with earlier reported work [17,22].

#### 3.6. Effect of contact time

Time course profile for the biosorption of Pb(II) and Zn(II) for a solution of 100 mg/L concentration is shown in Fig. 6(a) and (b). The experiment was carried out with different time intervals while keeping the other parameter (pH, biosorbent dose, and initial metal concentration) constant. According to result Pb(II) and Zn(II) uptake enhanced with increase in contact time. The sharp increase was observed in first 30 min, and equilibrium was attained after 120 min. The similar explanation was proposed by several earlier workers [10,22,25]. In first 30 min biosorption was sharp probably due to decrease in pH of solution. It might be because of proton released by the biosorbent. The rapid initial sorption was likely due to extra cellular binding and slow sorption phase likely resulted from intracellular binding [5]. The result is important as equilibrium time is one of the important parameters for an economical wastewater treatment [26].



Fig. 6. Effect of contact time on uptake of Pb(II) (a) and Zn(II) (b).

#### 3.7. Hazardous aqueous streams

Sorption kinetic experiments were performed at optimized conditions in order to investigate sorption time for Pb(II) and Zn(II) biosorption from hazardous aqueous streams elaborated in (Fig. 7(a) and (b)). This figure has indicated that sorption equilibrium reached much faster in case of textile industrial wastewater from bleaching and printing units samples (60 min for Pb(II)) and (100 min for Zn(II) in comparison to synthetic wastewater (120 min) using IDSJ and IDSF, respectively. This may be due to the presence of cometal ions in the industrial effluents [7].

#### 3.8. Biosorption kinetic models

In order to investigate the mechanism of biosorption and potential rate controlling step, such as mass transport and chemical reaction processes, kinetic models have been used to test the experimental data. Kinetics of absorption by any biological material has been widely tested by first-order expression given by



Fig. 7. Effect of contact time on uptake of Pb(II) (a) and Zn(II) (b) from industrial effluents.

Lagergren and pseudo-second-order approach (Fig. 8(a)–(d)). The first-order Lagergren [6] equation is:

$$\log\left(q_{e} - q\right) = \log q_{e} - (k_{1.\text{ads}}t/2.303) \tag{3}$$

The pseudo-second-order [6] equation is:

$$t/q = (1/k_{2,\text{ads}}q_e^2) + (t/q_t)$$
(4)

where  $q_e$  is the mass of metal absorbed at equilibrium (mg/g),  $q_t$  the mass of metal at time t (min),  $k_{1,ads}$  the first-order reaction rate constant of adsorption (per min),  $k_{2,ads}$  the pseudo-second-order rate constant of adsorption (mg/g min). A comparison between Lagergren pseudo-first-order and pseudo-second-order kinetic models is tabulated in Table 1. The results obtained suggest that pseudo-first-order model fitted well to the kinetics data of Pb(II) at 30–50 °C and of Zn



Fig. 8. Kinetic isotherms for uptake of metals: (a) Pseudo-first-order kinetic model for Pb(II). (b) Pseudo-second-order kinetic model for Pb(II). (c) Pseudo-first-order kinetic model for Zn(II). (d) Pseudo-second-order kinetic model for Zn(II).

(II) at 30–40 °C. It is suggested because the value of  $q_e$  obtained from pseudo-first-order kinetics model was in close agreement with that of experimental value and correlation coefficient  $R^2$  was also close to one at these temperatures. Interestingly, pseudo-second-order kinetic model fitted well to kinetic data above 50 °C for Pb(II) and above 40 °C for Zn(II). This is suggested on the basis of close agreement between the estimated q values to experimental  $q_e$  values and due to high value of correlation coefficient [27]. In case of industrial effluents (Table 2) the estimated  $q_e$  value of pseudo-second-order reaction agreed well with experimental  $q_{max}$  value. Secondly, the  $R^2$  coefficient of the model was also close to one.

# 3.9. Effect of initial metal concentrations

Starting concentration of metal in effluent is an important factor when studying biosorption of metal ions in aqueous system [23]. Initial metal concentration provides important driving force to overcome all mass

transfer resistance of the metal between the aqueous solution and solid phase [24]. The influence of initial concentration on uptake capacities of both metals by IDSJ and IDSF was studied at pH 4.5 and 6 for Pb(II) and Zn(II), respectively, by changing the concentration of the system from 25 to 1,000 mg/L (Fig. 9).

Metal uptake increased with increase in initial concentration of metal ions up to 200 mg/L. The observation can be explained by the fact that at very low concentration of metal ions, the ratio of sorption surface area to the total metal ions available is high and there is a greater chances for metal removal [5]. At higher concentration low adsorption yield is due to the saturation of adsorption sites [28]. Though an increase in metal uptake was observed, the decrease in percentage adsorption may be attributing to lack of sufficient surface area to accumulate much more metal available in solution [28]. The results obtained from this study were found to be comparable with many other reported work for Pb(II) [4,13,25] and Zn(II) [5,28,29]. Table 1

Metal	Temperature (°C)	Pseudo-first-order kinetic model			Fynerimental	Pseudo-second-order kinetic model		
		$q_e (\mathrm{mg}/\mathrm{g})$	$K_{1,\mathrm{ads}} \ (\mathrm{min}^{-1})$	$R^2$	q (mg/g)	$q_e (\mathrm{mg/g})$	$K_{2,ads}$ (g/mg min)	$R^2$
Pb(II)	30	199.85	$1.8 \times 10^{-2}$	0.969	178.38	256.14	$4.39 \times 10^{-5}$	0.9413
	40	299.16	$2 \times 10^{-2}$	0.985	245.06	250	$6.55 \times 10^{-5}$	0.9105
	50	221.92	$1.1 \times 10^{-2}$	0.9564	225.2	238.09	$5.47 \times 10^{-5}$	0.9497
	55	229.93	$2.2 \times 10^{-2}$	0.9764	212.42	200	$1.45 \times 10^{-4}$	0.9634
	60	144.71	$1.8 \times 10^{-2}$	0.995	188.26	172.14	$3.40 \times 10^{-4}$	0.9977
Zn(II)	30	16.23	$8.98 \times 10^{-3}$	0.9536	19.26	26.66	$4.55 \times 10^{-4}$	0.9227
	40	5.90	$1.2 \times 10^{-5}$	0.9854	7.92	9.49	$2.48 \times 10^{-3}$	0.9797
	50	5.16	$2.4 \times 10^{-2}$	0.9062	5.86	6.69	$5.26 \times 10^{-3}$	0.9918
	55	5.40	$3 \times 10^{-2}$	0.9462	5.76	6.40	$7.05 \times 10^{-3}$	0.9953
	60	1.66	$2.2 \times 10^{-2}$	0.9889	0.64	0.75	$3.4 \times 10^{-2}$	0.9914

Comparison between Lagergren pseudo-first-order and pseudo-second-order kinetic models for Pb(II) and Zn(II) biosorption

Table 2

Comparison between Lagergren pseudo-first-order and pseudo-second-order kinetic models for Zn(II) biosorption from industrial effluents

Industry	Pseudo-first-order kinetic model			Experimental	Pseudo-second-order kinetic model			
maasay	$q_e (\mathrm{mg/g})$	$K_{1,\mathrm{ads}}$ (min <sup>-1</sup> )	$R^2$	q (mg/g)	$q_e (\mathrm{mg}/\mathrm{g})$	$K_{2,ads}$ (g/mg min)	$R^2$	
Bleaching	195.61	$8 \times 10^{-1}$	0.9839	86.5	87.70	$8.42 \times 10^{-4}$	0.9905	
Printing	166.11	$7.5 \times 10^{-2}$	0.9388	72.46	73.65	$8.96 \times 10^{-4}$	0.9913	
Bleaching	6.84	$1.4 \times 10^{-2}$	0.9864	8.66	10.36	$3.32 \times 10^{-3}$	0.9838	
Printing	6.24	$3 \times 10^{-2}$	0.9166	6.48	7.37	$5.10 \times 10^{-3}$	0.9834	



Fig. 9. Effect of initial metal concentration on uptake of Pb (II) and Zn(II).

#### 3.10. Adsorption isotherms

Initial metal concentration data was fitted to Langmuir and Freundlich adsorption isotherms. The Langmuir model [30] takes the form of equation:

$$C_e/q_e = (1/X_m K_L) + (C_e/X_m)$$
 (5)

where  $q_e$  is the metal ion sorbed (mg/g),  $C_e$  the equilibrium concentration of metal ion solution,  $X_m$  and  $K_L$ are Langmuir constants. Results obtained from initial metal ion concentration were found to be in better correlation with Langmuir isotherm. Well-fitting of Langmuir isotherm revealed that metal ions are taken up separately on a single type of binding site, in accordance with this the uptake of first metal ion does not affect the sorption of next ion.

Freundlich equation is:

$$\log q_e = 1/n \log C_e + \log k \tag{6}$$

where  $q_e$  is the metal ion adsorbed (mg/g),  $C_e$  the equilibrium concentrations of metal ion solutions (mg/L), *K* and *n* are Freundlich constant.  $R^2$  values obtained by Freundlich model indicated that Freundlich isotherm model is not applicable because  $R^2$  value is less than 0.98 (Table 3).

0		1			1				
	Immobilized	Langmuir isotherm parameters			Experimental	Freundlich isotherm parameters			
Metals	distillation waste	$X_m (q_{\max}) mg/g$	$K_L$ (L/mg)	$R^2$	q (mg/g)	q (mg/g)	<i>K</i> (mg/g)	$R^2$	1/n
Pb(II)	Jasmine	263.15	0.059	0.9578	232.06	245.22	31.63	0.8531	0.4609
Zn(II)	Fennel	26.45	0.023	0.9891	21.3	23.63	2.21	0.9014	0.4526

Table 3 Langmuir and Freundlich isotherm parameters for Pb(II) and Zn(II) biosorption



Fig. 10. Desorption of Pb(II) and Zn(II) from biomass.

# 3.11. Desorption

The IDSJ and IDSF could be reused several times to decrease material cost. The regeneration of the biosorbent is one of the key factors in assessing their potential for commercial application. Desorption of the biosorbed Pb(II) and Zn(II) ions from IDSJ and IDSF, respectively, were studied in a batch system (Fig. 10). The metal ions adsorbed onto IDSJ and IDSF were eluted with 0.1 M of HCl, H<sub>2</sub>SO<sub>4</sub>, CH<sub>3</sub>COOH, and EDTA. The effectiveness of desorbing agents was found in following order:  $H_2SO_4 > HCl > EDTA >$ CH<sub>3</sub>COOH. Acid eluents removed adsorbed metals from biomass beads by lowering pH [31]. EDTA removes metal from biomass surface by chelation. EDTA was found less effective eluent in comparison to strong acids. The use of strong acids was better due to easier proton release and promptly reached equilibrium. EDTA solution is harder to produce due to its higher molecular weight and lower solubility in water. The use of EDTA in comparison to other eluents is also not economically feasible as referred by [32].

### 4. Conclusions

The results indicated that immobilization improved the metal uptake capacity of the waste. After preliminary evaluation, it was found that IDSJ was the best biosorbent for Pb(II) uptake at pH 4.5. In case of Zn (II) the most suitable biosorbent was IDSF at pH 6. The effect of various experimental parameters on Pb (II) and Zn(II) uptake was evaluated. The optimized bead size, biosobent dose, contact time, and initial metal concentration were 3.5 mm, 0.05 g/100 mL, 120 min, and 200 mg/L, respectively. On agitation the uptake of both metals was found to decrease. The uptake of Pb(II) was maximum at 40°C and Zn(II) at 30°C. The kinetic data of Pb(II) fitted at 30-50°C to pseudo-first-order and from 55-60°C to pseudo-second-order kinetic model. Whereas, Zn(II) kinetic data was better described by pseudo-first-order kinetic model at 30-40°C and pseudo-second-order kinetic model at 50-60°C. The kinetic data of bleaching and printing textile industries fitted well to pseudo-second-order kinetic model. The Langmuir sorption isotherm model fitted both to the Pb(II) and Zn(II) concentration data. The desorption studies suggested that H<sub>2</sub>SO<sub>4</sub> was the best metal eluent for both Pb(II) and Zn(II).

# References

- A. Kausar, H.N. Bhatti, G. MacKinnon, Equilibrium, kinetic and thermodynamic studies on the removal of U(VI) by low cost agricultural waste, Colloid Surface B 111 (2013) 124–133.
- [2] Shan Um-e-Ammara, N. Ikram, Heavy metals in human scalp hair and nail samples from Pakistan: Influence of working and smoking habits, Int. J. Chem. Biochem. Sci. 1 (2012) 54–58.
- [3] M. Alam, R. Nadeem, M.I. Jilani, Pb(II) removal from wastewater using Pomegranate waste biomass, Int. J. Chem. Biochem. Sci. 1 (2012) 24–29.
- [4] A. Babarinde, G. Omisore, Application of kinetic, isothermal and thermodynamic models in the biosorption of Cd(II), Pb(II) and Zn(II) from solutions onto Melon (*Citrillus lanatus*) seed husk, Int. J. Chem. Biochem. Sci. 5 (2014) 72–85.
- [5] H.N. Bhatti, A. Saleem, M.A. Hanif, Utilization of *Mentha arvensis* waste biomass for the removal of Pb (II) and Co(II) from aqueous solutions, Desalin. Water Treat. 51 (2013) 3335–3343.
- [6] M.A. Hanif, R. Nadeem, H.N. Bhatti, N.R. Ahmad, T.M. Ansari, Nickel biosorption by *Cassia fistula* (Golden shower) biomass, J. Hazard. Mater. 139 (2007) 345–355.

- [7] M.S. Mohammadnia, P. Salaryan, N. Ghasemi, The study of nonlinear isotherms for Mn(II) adsorption from aqueous solution, Int. J. Chem. Biochem. Sci. 5 (2014) 55–58.
- [8] M. Kashefi, P. Salaryan, N. Hazeri, J. Valizadeh, A. Abdi, M.S. Mohammadnia, Biosorption of Cr(VI) from aqueous solutions using *Carum copticum* stem, Int. J. Chem. Biochem. Sci. 1 (2012) 48–53.
- [9] F. Zhao, E. Repo, D. Yin, M. Sillanpää, Adsorption of Cd(II) and Pb(II) by a novel EGTA-modified chitosan material: Kinetics and isotherms, J. Colloid Interface Sci. 409 (2013) 174–182.
- [10] M. Riaz, R. Nadeem, M.A. Hanif, T.M. Ansari, K.U. Rehman, Pb(II) biosorption from hazardous aqueous streams using *Gossypium hirsutum* (Cotton) waste biomass, J. Hazard. Mater. 161 (2009) 88–94.
- [11] A. Sari, M. Tuzen, O.D. Uluözlü, M. Soylak, Biosorption of Pb(II) and Ni(II) from aqueous solution by lichen (*Cladonia furcata*) biomass, Biochem. Eng. J. 37 (2007) 151–158.
- [12] A. Özer, D. Özer, Comparative study of the biosorption of Pb(II), Ni(II) and Cr(VI) ions onto *S. cerevisiae*: Determination of biosorption heats, J. Hazard. Mater. 100 (2003) 219–229.
- [13] R. Nadeem, M.A. Hanif, F. Shaheen, S. Perveen, M.N. Zafar, T. Iqbal, Physical and modification of distillery sludge for Pb(II) biosorption, J. Hazard. Mater. 150 (2007) 335–342.
- [14] M. Martinez, N. Miralles, S. Hidalgo, N. Fiol, I. Villaescusa, J. Poch, Removal of lead(II) and cadmium (II) from aqueous solutions using grape stalk waste, J. Hazard. Mater. 133 (2006) 203–211.
- [15] Y.S. Ho, A.E. Ofomaja, Pseudo-second-order model for lead ion sorption from aqueous solutions onto palm kernel fiber, J. Hazard. Mater. 129 (2006) 137–142.
- [16] S. Tunali, A. Çabuk, T. Akar, Removal of lead and copper ions from aqueous solutions by bacterial strain isolated from soil, Chem. Eng. J. 115 (2006) 203–211.
- [17] M. Iqbal, R.G.J. Edyvean, Biosorption of lead, copper and zinc ions on loofa sponge immobilized biomass of *Phan*erochaete chrysosporium, Miner. Eng. 17 (2004) 217–223.
- [18] F. Vegliò, Å. Esposito, A.P. Reverberi, Standardisation of heavy metal biosorption tests: Equilibrium and modelling study, Process Biochem. 38 (2003) 953–961.
- [19] F. Veglio, F. Beolchini, Removal of metals by biosorption: A review. Hydrometallurgy 44(3) (1997) 301–316.
- [20] R. Nadeem, T.M. Ansari, A.M. Khalid, Fourier transform infrared spectroscopic characterization and

optimization of Pb(II) biosorption by fish (*Labeo rohita*) scales, J. Hazard. Mater. 156 (2008) 64–73.

- [21] A.R. Iftikhar, H.N. Bhatti, M.A. Hanif, R. Nadeem, Kinetic and thermodynamic aspects of Cu(II) and Cr (III) removal from aqueous solution using rose waste biomass, J. Hazard. Mater. 161(2009) 941–947.
- [22] H.N. Bhatti, R. Khalid, M.A. Hanif, Dynamic biosorption of Zn(II) and Cu(II) using pretreated *Rose gruss an teplitz* (red rose) distillation sludge, Chem. Eng. J. 148 (2008) 434–443.
- [23] A. Zubair, H.N. Bhatti, M.A. Hanif, F. Shafqat, Kinetic and equilibrium modeling for Cr(III) and Cr(VI) removal from aqueous solutions by *Citrus reticulata* waste biomass, Water Air Soil Poll. 191 (2008) 305–318.
- [24] X. Wang, S. Xia, L. Chen, J-F. Zhao, J-M. Chovelon, N. Jaffrezic-Renault, Biosorption of cadmium(II) and lead(II) ions from aqueous solutions onto dried activated sludge, J. Environ. Sci. 18(5) (2006) 840–844.
- [25] M.A. Javed, H.N. Bhatti, M.A. Hanif, R. Nadeem, Kinetic and equilibrium modeling of Pb(II) and Co(II) sorption onto rose waste biomass, Sep. Sci. Technol. 42 (2007) 3641–3656.
- [26] N. Saifuddin, A.Z. Raziah, Removal of heavy metals from industrial effluent using *Saccharomyces Cerevisiae* (Baker's yeast) immobilised in chitosan/lignosuphonate matrix, J. Appl. Sci. Res. 3(12) (2007) 2091–2099.
- [27] B. Preetha, T. Viruthgir, Biosorption of zinc (II) by *Rhizopus arrhizus* equilibrium and kinetic modelling, Afr. J. Biotechnol. 4(6) (2005) 506–508.
- [28] P. King, N. Rakesh, S. Beenalahari, Y.P. Prasanna Kumar, V.S.R.K. Prasad, Removal of lead from aqueous solution using *Syzygium cumini* L.: Equilibrium and kinetic studies, J. Hazard. Mater. 142 (2007) 340–347.
- [29] M. Arshad, M.N. Zafar, S. Younis, R. Nadeem, The use of Neem biomass for the biosorption of zinc from aqueous solutions, J. Hazard. Mater. 157 (2008) 534–540.
- [30] M.H. Jnr, A.I. Spiff, Effect of metal ion concentration on the biosorption of Pb (ii) and Cd (iii) by *Caladium bicolor* (wild cocoyam), Afr. J. Biotechnol. 4(2) (2005) 191–196.
- [31] R.S. Bia, T.E. Abraham, Studied on Cromium(VI) adsorption-desorption using immobilized fungal biomass, Bioresource Technol. 87 (2003) 17–26.
- [32] A. Ferraz, T. Tavares, J. Teixeira, Cr(III) removal and recovery from, Chem. Eng. J. 105 (2004) 11–20.