Article

Removal of metal ions from aqueous solutions using thermally activated biosorbent: Column study

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Abstract

Biosorption potential of thermally activated biosorbent prepared from *Hydrilla verticillata* biomass was investigated for the removal of Cu^{++}, Zn^{++}, Cd^{++} and Pb^{++} ions using a packed-bed column. Bed height (15-25 cm), flow rate (10-30 mL min^{-1}) and influent metal concentrations (5-25 mg L^{-1}) were variable parameters for the column study. Results revealed that highest bed height (25 cm), lowest flow rate (10 mL min^{-1}) and lowest influent metal concentration (5 mg L^{-1}) were favorable for column biosorption. The maximum biosorption capacity for Cu^{++}, Zn^{++}, Cd^{++} and Pb^{++} removal were observed to be 174.14, 184.36, 176.55 and 179.14 mg g^{-1} respectively. The breakthrough curves obtained from column process were successfully correlated with Bed Depth Service Time (BDST) and Thomas models. Regeneration studies revealed good reusability of activated biosorbent during three cycles of sorption and desorption studied.

Keywords Bed Depth Service Time model; breakthrough curve; regeneration; Thomas model.

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1 Introduction

Rapid expansion of industrial activities in the developing countries has resulted in the discharge of metal contaminated wastewater (Al-Farraj et al., 2013; Raju et al., 2013; Zojaji et al., 2014). Concentration of these metals beyond the threshold values is responsible for various environmental and public health hazards (Aziz et al., 2014). Occurrence of these metals in aqueous environment is of major concern because of their toxic, non-biodegradable and bio-accumulative tendency in the food chain even at fairly low concentrations (Su et al., 2014). Among the metals, copper, zinc, cadmium and lead are documented as hazardous pollutants (Xue et al., 2009; Limcharoensuk et al., 2015). Although, Cu and Zn are recognized as essential to plants, humans and animals, but their presence in wastewater beyond the permissible limit can also adversely affect various ecosystems on which human life relies on. For the removal of these metals from contaminated water numerous methods are available such as chemical precipitation, electrochemical treatment, flotation, ion exchange,

membrane filtration, reverse osmosis, sedimentation and solvent extraction (Hasfalina et al., 2012). But, these techniques are inefficient in removing the toxic metals in the low concentration range of 1-100 mg L^{-1} (Kobya et al., 2005) because of high capital cost, non-specificity, generation of toxic secondary waste etc. (Limcharoensuk et al., 2015). In recent years, metal removal using biosorption approach have stimulated increased interest because of their high efficacy, simplicity of design, ease of operation, economic viability and environment friendly nature (Ma et al., 2015). Removal of metals using biosorption process can be achieved either in a batch mode or continuous mode. Various studies have been published documenting the utilization of numerous materials as low cost biosorbent for the removal of metals in batch mode. However, the equilibrium data obtained from batch experiments were not suitable in predicting the performance of biosorbent at industrial scale (Karunarathne and Amarasinghe, 2013). Therefore, in order to overcome the drawbacks of batch biosorption data, present work was carried out to examine the potential of thermally activated biosorbent prepared from *Hydrilla verticillata* biomass in removing Cu^{++}, Zn^{++}, Cd^{++} and Pb^{++} ions using up-flow packed-bed column. In the present endeavour, *H. verticillata* was selected for the preparation of biosorbent because of its wide spread availability and very fast growth rate (Naveen et al., 2011; Nigam et al., 2013; Mishra et al., 2015). The biosorption capacity of activated biosorbent was investigated as a function of different column operating parameters such as bed height, flow rate and influent metal concentrations. Bed Depth Service Time (BDST) and Thomas models were used to fit the experimental biosorption results. Furthermore, regeneration experiments were carried out to explore the possible reuse of the activated biosorbent.

2 Materials and methods

2.1 Preparation of biosorbent

H. verticillata used in the current experiment was collected from the pond located inside the university campus. The plant biomass was thoroughly washed under tap water followed by distilled water to remove dirt. The washed biomass was sliced into pieces and dried by exposure to the sunlight for three days. The sun dried biomass was further heated in an oven at 80 ºC for 5 h (Nigam et al., 2013). The resultant dried biomass was milled to form powder and further subjected to thermal activation process in a muffle furnace at 500 ºC under nitrogen flow for 1 h as described elsewhere (Baral et al., 2009). The carbonized biomass was cooled under nitrogen to prevent complete combustion (Baral et al., 2009). The carbonized biomass thus obtained was grounded and sieved through mesh to get particles below 1 mm in size. The average particle size and specific surface area of the biosorbent was observed to be 0.00571 cm and 21.4 m^2 g^{-1} respectively.

2.2 Metal solutions

Stock solutions of Cu^{++}, Zn^{++}, Cd^{++} and Pb^{++} were prepared by dissolving required amount of $Cu(NO_3).2.5H_2O$, $ZnSO_4.7H_2O$, $CdCl_2.0.5H_2O$, and $PbNO_3$ respectively in distilled water. The working solutions of different metals were prepared by diluting the stock solutions.

2.3 Column design and experiment

Glass column with an internal diameter of 4 cm and length 35 cm was used to execute the continuous flow packed bed column experiments. Thermally activated biosorbent was packed in the column between two supporting layers of glass wool. To facilitate the uniform flow of influent metal solutions, a 3 cm high layer of glass beads was also placed at the bottom end of the packed column. Adjustable plunger (20 µm) with selective filter was fixed at the top of the column. The influent metal solutions were pumped upward at different flow rates ranging from 10 to 30 mL min^{-1} using a peristaltic pump. To increase the retention time and avoid the channelling effect, upward flow of the influent solutions was preferred (Chen et al., 2014). The pH of the influent solution was constantly maintained using 0.1 M NaOH and/or HNO_3 at desired value throughout the column experiment. Thermostatic bath was used to maintain the temperature of stream feeding

influent of the column at 25 ºC. The sampling of effluent was done at regular interval to investigate the breakthrough curve. The column operations were continued until the concentration of metals in the final effluent exceeded 95% of the concentration at the inlet (Vijayaraghavan and Yun, 2008). The concentration of metals in the effluent samples was analyzed using standard protocols (APHA, 2012). All the experiments were executed in duplicate and for the calculation average results were taken (Baral et al., 2009).

2.4 Analysis of column data

The effectiveness of packed bed column was analyzed using the breakthrough curve obtained from the plot between time (T) or throughput volume (V_T) for a given bed height and the ratio of measured effluent concentration (C_E) to inlet concentration (C_O) (normalized concentration) (Kumar and Chakraborty, 2009). Throughput volume (V_T) was determined by using the subsequent equation:

$$V_T = F \times T$$

The breakthrough time (T_B) for the current study was represented as the time at which the outlet concentration of copper, zinc, cadmium and lead reached 3.0 mg L^{-1}, 5.0 mg L^{-1}, 2.0 mg L^{-1} and 0.1 mg L^{-1} respectively, considering the maximum permissible discharge limit for all the metals into inland surface waters. Correspondingly, the bed exhaustion time (T_E) was represented as the time at which the outlet concentration of different metal ions exceeded 95% of the inlet concentration (Vijayaraghavan and Yun, 2008; Kumar and Chakraborty, 2009). The total quantity of metals adsorbed in the packed bed column was calculated using the equation given below (Luo et al., 2011; Cruz-Olivares et al., 2013):

$$M_{ADS} = \frac{F.A}{1000} = \frac{F}{1000}\int_0^{T_B} C_{ADS}.dT$$

The metal uptake capacity (Q_{ADS}) of biosorbent was calculated by dividing the quantity of different metals adsorbed (M_{ADS}) by the mass (M) of biosorbent.

$$Q_{ADS} = \frac{M_{ADS}}{M}$$

The total amount of different metals sent to packed bed column (M_{TOT}) was obtained from the following equation:

$$M_{TOT} = \frac{C_O \times F \times T_E}{1000}$$

The total removal percentage (R) of different metals was computed by using subsequent equation:

$$R(\%) = \frac{M_{ADS}}{M_{TOT}} \times 100$$

2.5 Column regeneration experiment

0.5 mol L^{-1} Na_2CO_3 (Chathuranga et al., 2014) was used to regenerate the metals loaded biosorbent packed column at the flow rate of 8 mL min^{-1}. After passing the eluting agent, packed bed column was washed several times with distilled water to neutralize and to regenerate for further experiment. The column was again fed with influent solution for further biosorption studies. After saturation of packed bed the eluting agent was pumped again into the column and regeneration processes were studied. To evaluate the reusability of thermally activated biosorbent column, three cycles of sorption-desorption experiments were carried out.

3 Results and Discussion

3.1 Influence of bed height

Fig. 1 illustrates the breakthrough curves (C_E/C_O versus time) for biosorption of Cu^{++}, Zn^{++}, Cd^{++} and Pb^{++} ions at varying bed heights (15, 20, 25 cm). The flow rate and influent metal concentrations were kept constant

at 10 mL min^{-1} and 5 mg L^{-1} respectively. As the bed height increased from 15 to 25 cm, increase in breakthrough and exhaustion time was detected. This may be attributed to the availability of more active binding sites, which resulted in a longer time for achieving the breakthrough and exhaustion. Increased column bed height is also accountable for broadened mass transfer zone (Vijayaraghavan et al., 2006). It was also observed that with increase in bed height of the packed column from 15 to 25 cm, the slope of the curve from T_B to T_E decreased, suggesting that curve becomes steeper with decrease in column bed height (Vijayaraghavan and Yun, 2008).

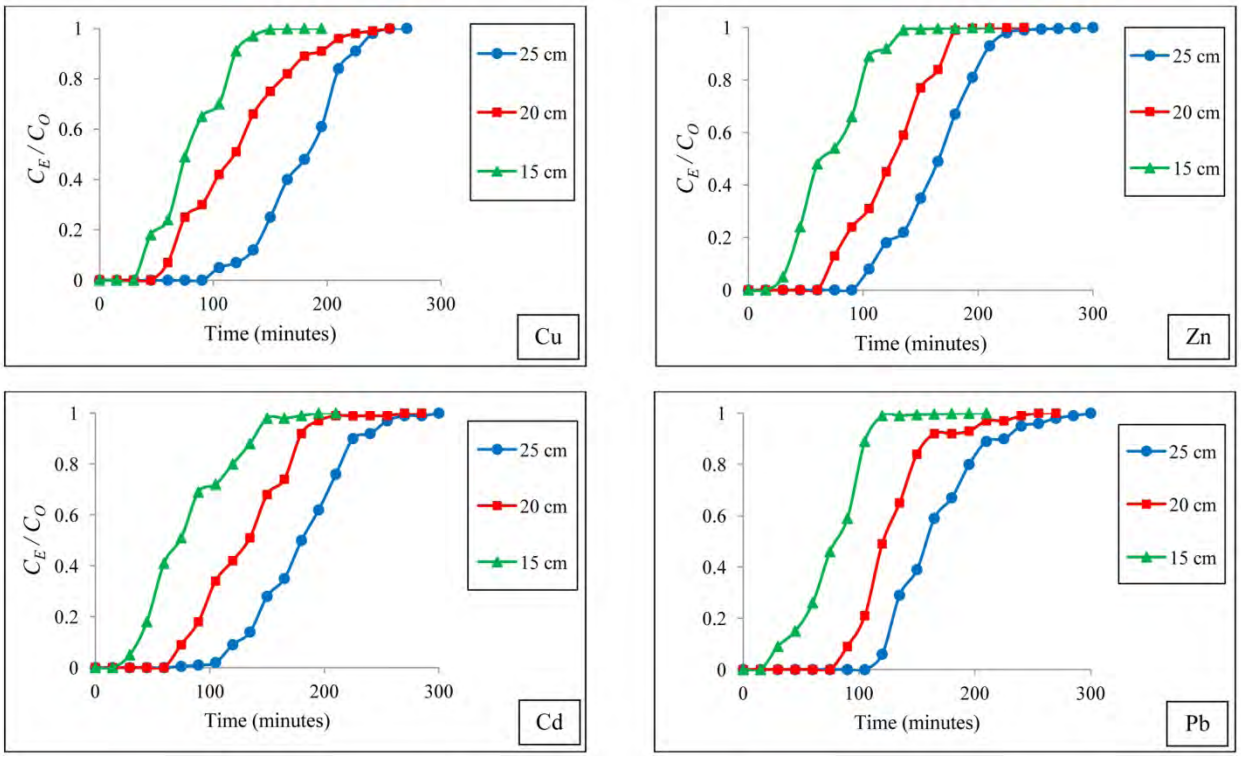

Fig. 1 Breakthrough curve for biosorption of Cu^{++}, Zn^{++}, Cd^{++} and Pb^{++} at different bed heights.

3.2 Influence of flow rate

To examine the influence of flow rate on the biosorption of Cu^{++}, Zn^{++}, Cd^{++} and Pb^{++} onto thermally activated biosorbent, column experiments were executed at flow rates ranging from 10 to 30 mL min^{-1} and maintaining the bed height and influent metal concentration constant at 25 cm and 5 mg L^{-1} respectively (Fig. 2). Very early breakthrough as well as exhaustion of bed was found at highest flow rate, this is more likely to result due to insufficient residence time of the adsorbate in the column and diffusion restriction of the adsorbate into the pores of thermally activated biosorbent at highest flow rates (Ko et al., 2000; Vijayaraghavan et al., 2006). Even though, shortened mass transfer zone was found at highest flow rate but metal uptake capacity and removal efficiency was observed maximum at lowest flow rate (10 mL min^{-1}).

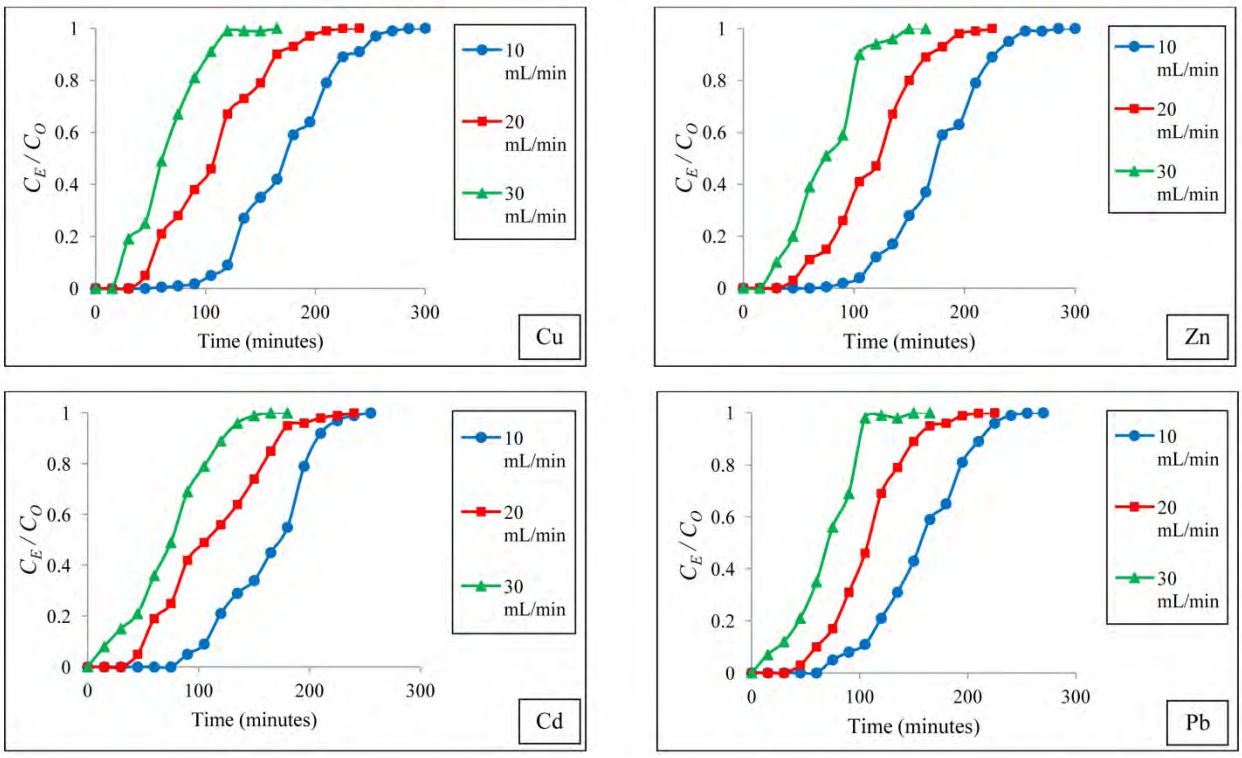

Fig. 2 Breakthrough curve for biosorption of Cu^{++}, Zn^{++}, Cd^{++} and Pb^{++} at different flow rates.

3.3 Influence of influent metal ions concentration

The influence of influent Cu^{++}, Zn^{++}, Cd^{++} and Pb^{++} concentrations (5 to 25 mg L^{-1}) on the shape of breakthrough curve is presented in Fig. 3. The bed height and flow rate were kept constant at 25 cm and 10 mL min^{-1} respectively. It can be concluded from Fig. 3 that with increase in metal concentration from 5 to 25 mg L^{-1}, the breakthrough as well as bed exhaustion time decreases. The plausible explanation for this behaviour might be the fast saturation of thermally activated biosorbent at highest influent metal concentration, which eventually will lead to steeper breakthrough curve. These results illustrate that concentration gradient is the driving force for biosorption and affects the saturation rate and breakthrough time (Vijayaraghavan and Yun, 2008). Thus, the high driving force due to highest influent metal concentration resulted in better metal uptake. But, decrease in metal removal efficiency was observed with increase in influent metal concentration. This might be because of the fact that, at lowest influent metal concentration, adequate binding sites are present to accommodate the different metal ions but with increase in influent metal concentration number of binding sites becomes lesser (Vijayaraghavan et al., 2006).

3.4 Application of models

3.4.1 Bed Depth Service Time (BDST) model

The BDST model can be represented as below (Muhamad et al., 2010):

$$T_E = \frac{N_O Z}{C_O U} - \frac{1}{k C_O} ln\left(\frac{C_O}{C_E} - 1\right)$$

where, T_E is the service time at breakthrough point, N_O is the dynamic bed capacity (mg L^{-1}), Z is the packed bed column depth of (cm), U is the linear flow rate of feed to bed (cm h^{-1}) which is defined as the ratio of the volumetric flow rate F (cm^3 h^{-1}) to the cross-sectional area of the bed A (cm^2), C_O and C_E are the influent and the breakthrough metal concentration (mg L^{-1}) respectively and k is the adsorption rate constant (L mg^{-1} h^{-1}) which represents the rate of solute transfer from the liquid phase to the solid phase. The values of dynamic bed

capacity and adsorption rate constant were calculated from the slope and intercept of the plot of T_E versus Z. The values of adsorption rate constants (k), dynamic bed capacity (N_O) and correlation coefficient (r^2) are shown in Table 1. The results presented in the Table 1 illustrate that the correlation coefficient values ranged from 0.990 to 0.999, representing a good agreement between the experimental data and column data calculated using the BDST model. Also, decrease in the dynamic bed capacity or volumetric adsorption capacity (N_O) with increase in influent metal concentration was observed for all the metals studied.

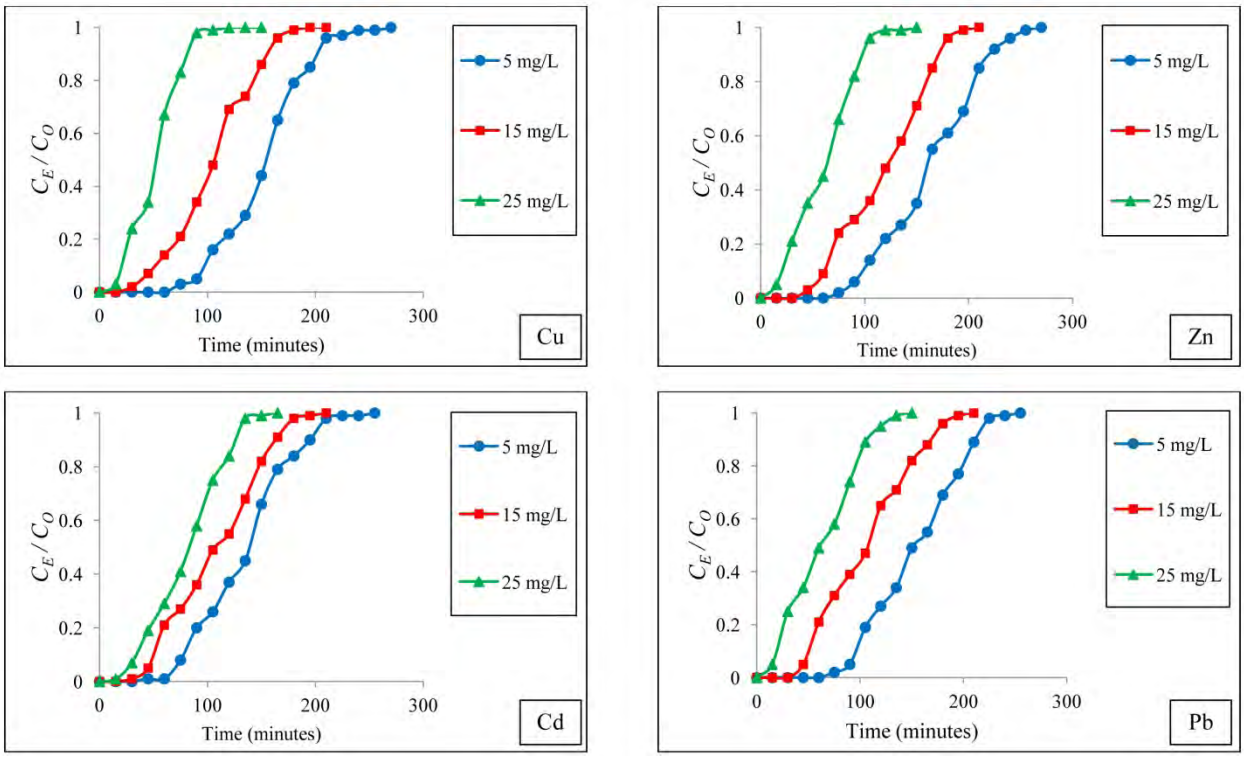

Fig. 3 Breakthrough curve for biosorption of Cu^{++}, Zn^{++}, Cd^{++} and Pb^{++} at different influent metal concentration.

Table 1 Estimated parameters of BDST and Thomas model for the biosorption of Cu^{++}, Zn^{++}, Cd^{++} and Pb^{++}.

		BDST Model			Thomas Model		
Metal	C_o (mg L^{-1})	k (L mg^{-1} h^{-1})	N_o (mg L^{-1})	r^2	k_{Th} (mL min^{-1} mg^{-1})	Q_o (mg g^{-1})	r^2
Cu^{++}	05	0.071	2232	0.999	0.0135	187.36	0.989
	15	0.043	1941	0.996	0.0110	188.24	0.998
	25	0.031	1896	0.999	0.0088	192.38	0.998
Zn^{++}	05	0.090	1906	0.998	0.0328	157.64	0.996
	15	0.071	1824	0.997	0.0188	172.41	0.999
	25	0.057	1548	0.999	0.0095	185.14	0.997
Cd^{++}	05	0.401	2156	0.994	0.0107	172.66	0.991
	15	0.326	1992	0.991	0.0076	176.71	0.991
	25	0.254	1627	0.996	0.0061	184.19	0.998
Pb^{++}	05	0.103	2047	0.998	0.0086	169.50	0.999
	15	0.079	1745	0.990	0.0071	170.38	0.999
	25	0.026	1588	0.997	0.0048	187.86	0.998

3.4.2 Thomas model

The linearized form of Thomas model is represented as below (Muhamad et al., 2010):

$$ln\left(\frac{C_O}{C_E}-1\right)=\frac{k_{Th}Q_OM}{F}-\frac{k_{Th}C_O}{F}V$$

where, C_O and C_E are influent and effluent metal concentration (mg L^{-1}), k_{Th} is the Thomas rate constant (mL min^{-1} mg^{-1}), Q_O is the maximum metal uptake per gram of the biosorbent (mg g^{-1}), M is the amount of biosorbent in the column (g), F is the volumetric flow rate (mL min^{-1}), V is the throughput volume (L).

Table 1 demonstrates the values of Thomas rate constant (k_{Th}), maximum metal uptake per gram of the biosorbent (Q_O) and correlation coefficient (r^2). It can be observed from the Table 1 that the value of k_{Th} decreases with increase in influent metal concentration. In contrast, metal uptake per gram of the biosorbent increases with increasing influent metal concentration from 5 to 25 mg L^{-1}.

3.5 Regeneration of biosorbent

In order to ensure the long term use of thermally activated biomass for the reduction of overall treatment cost and possible recovery of metals, it is desirable to desorb the sorbed metals and regenerate the column for another cycle (Vijayaraghavan and Yun, 2008). For this purpose, column regeneration experiments were performed and results are presented in Table 2 for all the three cycles studied. It is evident from the Table 2 that more than 90% of the adsorbed metals were desorbed in each successive cycle. During the regeneration experiment slight decrease in biosorption capacity of the activated biosorbent was also observed.

Table 2 Performance of packed column during three cycles of Cu^{++}, Zn^{++}, Cd^{++} and Pb^{++} sorption and desorption.

Cycle	Cu^{++}		Zn^{++}		Cd^{++}		Pb^{++}	
	Sorption (mg g^{-1})	Desorption (mg g^{-1})	Sorption (mg g^{-1})	Desorption (mg g^{-1})	Sorption (mg g^{-1})	Desorption (mg g^{-1})	Sorption (mg g^{-1})	Desorption (mg g^{-1})
1.	257.44	251.22	178.24	171.42	158.42	155.60	191.36	185.90
2.	242.19	240.18	166.52	159.15	151.24	147.52	182.87	176.54
3.	238.66	228.65	157.86	148.55	150.38	142.72	176.14	171.96

4 Conclusions

Thermally activated biosorbent showed high efficiency for Cu^{++}, Zn^{++}, Cd^{++} and Pb^{++} removal from aqueous solutions. Experimental results confirmed that highest bed height (25 cm), lowest flow rate (10 mL min^{-1}) and lowest influent metal concentration (5 mg L^{-1}) were favourable for biosorption. Breakthrough curves modeling indicated that both Bed Depth Service Time (BDST) model and Thomas model fitted the experimental data fairly well. Regeneration studies revealed good reusability of activated biosorbent during three cycles of sorption and desorption studied.

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