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Modeling of Pb(II) adsorption by a fixed-bed column

D. M. R. E. A. Dissanayake^{a,b}, P. K. D. Chathuranga^{a,b}, P. I. Perera^a, M. Vithanage^c, and M. C. M. Iqbal^a

^aPlant Biology Laboratory, National Institute of Fundamental Studies, Kandy, Sri Lanka; ^bPostgraduate Institute of Science, University of Peradeniya, Peradeniya, Sri Lanka; ^cChemical and Environmental Systems Modelling Research Group, National Institute of Fundamental Studies, Kandy, Sri Lanka

ABSTRACT

Removal of Pb(II) from an aqueous environment using biosorbents is a cost-effective and environmentally benign method. The biosorption process, however, is little understood for biosorbents prepared from plant materials. In this study, the biosorption process was investigated by evaluating four adsorption models. A fixed-bed column was prepared using a biosorbent prepared from the aquatic plant Hydrilla verticillata. The effect of bed height and flow rate on the biosorption process was investigated. The objective of the study was to determine the ability of H. verticillata to biosorb Pb(II) from an aqueous environment and to understand the process, through modeling, to provide a basis to develop a practical biosorbent column. Experimental breakthrough curves for biosorption of 50 mg L⁻¹ aqueous Pb(II) using a fixed-bed column with 1.00 cm inner diameter were fitted to the Thomas, Adams-Bohart, Belter, and bed depth service time (BDST) models to investigate the behavior of each model according to the adsorption system and thus understand the adsorption mechanism. Model parameters were evaluated using linear and nonlinear regression methods. The biosorbent removed 65% (82.39 mg g^{-1} of biosorbent) of Pb(II) from an aqueous solution of Pb(NO₃)₂ at a flow rate of 5.0 ml min⁻¹ in a 10 cm column. Na₂CO₃ was used to recover the adsorbed Pb(II) ions as PbCO₃ from the biosorbent. The Pb(II) was completely desorbed at a bed height of 10.0 cm and a flow rate of 5.0 ml min⁻¹. Fourier transform infrared (FT-IR) analysis of the native biosorbent and Pb(II)-loaded biosorbent indicated that the hydroxyl groups and carboxylic acid groups were involved in the metal bonding process. The FT-IR spectrum of Pb (II)-desorbed biosorbent showed an intermediate peak shift, indicating that Pb(II) ions were replaced by Na⁺ ions through an ion-exchange process. Of the four models tested, the Thomas and BDST models showed good agreement with experimental data. The calculated bed sorption capacity N_0 and rate constant k_a were 31.7 g L⁻¹ and 13.6 \times 10⁻⁴ L mg⁻¹ min⁻¹ for the C_t/C_0 value of 0.02. The BDST model can be used to estimate the column parameters to design a large-scale column.

Introduction

Heavy metals are chemical elements with a high specific gravity, usually higher than 5.0 g cm^{-3} . Due to their high specific gravity, heavy metals can accumulate through the food chain and concentrate in the human body. Some heavy metals such as Zn and Cu are required for metabolic reactions in the body (Prasad 2004), and some are toxic and also cause adverse health effects such as mutations, cancers, and birth defects (Athar and Vohora 1995; Ahluwalia and Goyal 2010; Akar et al. 2013). Even though some heavy metals are toxic, they are used in industries such as leather tanning (Netzahuatl-Muñoz et al. 2012), electroplating, and the paint industry

(Hutton and Symon 1986). Lead is one of the major threats to human health from heavy metals, the others being Cd, As, and Hg. The adverse health effect from heavy metal poisoning is usually chronic and hence is ignored. This is so in the greater interest of deriving immediate economic benefits from their use in various manufacturing processes, particularly in developing countries. Pb(II) is commonly used in the paint industry, manufacture of batteries, glazed food containers, and ammunition (Hutton and Symon 1986). Although its use in petrol has declined, it continues to be used in some petrol additives. In Sri Lanka, Pb(II) concentration in sedimentary deposits in Colombo urban areas were

KEYWORDS

Bed depth service time model; biosorption; desorption; fixed-bed column modeling; *Hydrilla verticillata*; Pb(II)

CONTACT D. M. R. E. A. Dissanayake rasikaeranda.shrea@gmail.com Plant Biology Laboratory, National Institute of Fundamental Studies, Hanthana Road, Kandy, Sri Lanka.

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measured at 444 mg L⁻¹ (Herath et al. 2013). In addition Pb(II) concentrations of 7.4 μ g L⁻¹ were measured in a garbage disposal site in the Colombo City and 100–390 μ g L⁻¹ in a city lake in Sri Lanka (Ileperuma 2000). Within the population, children are more vulnerable due to their high gastrointestinal uptake through the permeable blood-brain barrier, leading to subsequent brain damage and diminished intellectual capacity (Järup 2003). Although blood levels below 10 μ g dl⁻¹ in children is considered acceptable, recent data suggest toxicological effects at low levels of exposure. In oral contaminations, the gastrointestinal tract can absorb 5–15% of the Pb(II) ingested and human bones retain most of the Pb(II) adsorbed through the gastrointestinal tract (Athar and Vohora 1995).

Remediation of heavy metals from a contaminated aqueous environment requires several advanced physicochemical methods, such as membrane filtration (Molinari, Argurio, and Poerio 2004), chemical precipitation, ion exchange (Inglezakis and Loizidou 2007), chemical oxidation (Mitra et al. 2011), and electrochemical treatments (Rana, Mohan, and Rajagopal 2004). However, these methods are expensive, consume chemicals and energy, need skilled labor, and produce large amounts of secondary waste. Moreover, these techniques are insufficient at low metal concentrations.

Biosorption is an alternative, cost-effective, and environmentally friendly means of adsorbing pollutants, which utilizes nonliving biomass to remove heavy metals from an aqueous environment. The surface of biological materials is made up of polymers, such as cellulose, lignin, pectin, and hemicelluloses (Gardea-Torresdey, de la Rosa, and Peralta-Videa 2004). In the biosorption process, metal ions in the surrounding environment are adsorbed onto functional groups, such as carboxyl, hydroxyl, and sulfates, of these polymers (Gardea-Torresdey, de la Rosa, and Peralta-Videa 2004; Hasan and Srivastava 2009). This adsorption process is governed by several mechanisms, such as chemisorption, microprecipitation, complexation, adsorption-complexation on the surface and pores, ion exchange, heavy metal hydroxide condensation, and surface adsorption (Gardea-Torresdey, de la Rosa, and Peralta-Videa 2004). Many types of biomaterials, such as tea waste (Amarasinghe and Williams 2007), aquatic weeds such as Hydrilla verticillata (Chathuranga et al. 2014), yellow passion fruit shell (Jacques et al. 2007), marine algae (Jalali et al. 2002), seed powder of Strychnos potatorum L. (Jayaram et al. 2009), and *Enterobacter* spp. (Lu et al. 2006), have been used and reported as potential biosorbents to remove aqueous Pb(II).

The biosorption process can be performed by two major reaction methods: either as a batch reaction or as a fixed-bed column process. In the batch sorption method, the biosorbent, which is dead plant material, is in contact with the heavy metal solution for a desired time and the biosorbent is then removed from the reactor. For example, yellow passion fruit shells were shaken with Pb(II) and Cr(III) solutions for 120 min to complete the adsorption process (Jacques et al. 2007). In the fixed-bed method, biosorbent is subjected to continuous flow of heavy metal-contaminated water until the biosorbent is saturated by the metal (Hasan and Srivastava 2009; Malkoc and Nuhoglu 2006; Volesky, Weber, and Park 2003). In the batch reaction method, metal recovery cannot be performed easily. Here, the biosorbent has to be filtered and the dry heavy metal-loaded biosorbent is then used for metal recovery, which leads to the loss of biosorbent. But in the fixed-bed method, metal recovery is easier by passing the desorbent solution through the metal adsorbed biosorbent to remove the bonded metal ions from the biosorbent. When all the bonded metal ions are removed from the biosorbent, the biosorbent can be reused for another biosorption cycle.

If the metal-loaded biosorbent is discarded, it will decompose and the metal will return to the environment. Therefore, recovery of metals is important in the biosorption process. Recovery or desorption of metals from the biosorbent is usually achieved by utilizing precipitation, complexation, or ion-exchange methods (Gardea-Torresdey, de la Rosa, and Peralta-Videa 2004). Ion-exchange columns use resins to adsorb heavy metals or pollutants, which are regenerated using acids, bases, and salts (Franks et al. 2005). To identify an effective desorbent, it is necessary to consider its performance. An effective desorbent should possess a high eluent capacity (use a small volume to desorb high amount of adsorbate), cause low damage to the biosorbent, be less hazardous to the environment and to the employees, have less effect on metal uptake in a second adsorption cycle, and be cheap (Lezcano et al. 2011; Gardea-Torresdey, de la Rosa, and Peralta-Videa 2004). In previous studies on the desorption of Pb(II) from biosorbents, the desorbents Na₂CO₃, HNO₃, and Na₂EDTA (Chathuranga et al. 2014) showed good results. Although HNO₃ replaced the Pb(II) ions on the biosorbent surface

with highly mobile H⁺ ions, the use of HNO₃ can create occupational hazards as well as damage to the biosorbent and mechanical parts in the treatment system. In this study, Na₂CO₃ was used as the desorbent because it is economical, environmentally friendly, and safer to use than mineral acids. Besides, in several studies (Bai and Abraham 2003; Gardea-Torresdey, de la Rosa, and Peralta-Videa 2004), Na₂CO₃ was used as a desorbent because it possesses a pair of electrons that can complex with the Pb(II) ion and remove it from the adsorbent surface. Na⁺ ions in the solution will replace the metal binding site in the adsorbent. Although precipitation methods use less toxic desorbents such as sulfides (Crist et al. 1994), water-insoluble metal sulfides will form as the end product. Therefore, direct quantification of the percentage of desorption is difficult. Besides, adhesion of particulate metals onto the biosorbent will reduce the surface area of the biosorbent and also may block the adsorbent columns (Gardea-Torresdey, de la Rosa, and Peralta-Videa 2004).

Hydrilla verticillata is a native aquatic plant found in the warmer areas of Asia (Langeland 1996). Due to its extensive adaptations to the environment, H. verticillata has become aggressive and a competitive colonizer in aquatic systems and is considered an invasive species. This submerged aquatic weed is usually rooted at the bottom of the aquatic system and fragments can also grow in free-floating forms, meaning that H. verticillata can reproduce both sexually and asexually. Therefore, it is a serious threat to freshwater habitats, exercising a negative impact on water resources and aquatic life. The plant is easily identified by its leaves. The plants produce leaves 2-4 mm wide and 6-20 mm long, which occur in whorls of 3-8 leaves. Usually H. verticillata is either monoecious or dioecious (Cook and Lüönd 1982). Floating female flowers have whitish petals, which are 10-50 mm long, 4-8 mm wide, and male flowers consist of three whitish red or brown sepals that are up to 3 mm long and 2 mm wide (Langeland 1996). Hence, utilizing H. verticillata as a biosorbent would provide an alternative use and mitigate its impact on the aquatic environment.

This article reports the biosorbent capacity of H. *verticillata* for aqueous Pb(II) using a fixed-bed column. The validity of the four adsorption models are discussed by evaluating the adsorption parameters using linear and nonlinear regression analyses to determine their validity to model the adsorption process. The objective of this study to

determine the ability of *H. verticillata* to biosorb Pb (II) from aqueous environment and to understand the process through modeling to provide a basis to develop a practical biosorbent column. This will provide evidence to understand the behavior of each adsorption model and thereby understand the biosorption mechanism to develop a practical adsorbent column. For the recovery of the adsorbed Pb(II) from the adsorbent, Na₂CO₃ was used as desorbent, as a means of safe disposal of the used biosorbent and the possible reuse of the recovered Pb(II).

Materials and methods

Biosorbent preparation

Fresh *H. verticillata* plants were collected from a fresh water pond. The species was authenticated at the National Herbarium Peradeniya, Sri Lanka. Plants were thoroughly washed with running tap water and deionized water to remove particulate matter from their surface and air dried for 2 days and oven dried at 60°C for 24 h. The dried *H. verticillata* biomass was ground in a mortar with a pestle and sieved to obtain particles with diameter between 250 and 350 μ m. This would maintain a high column inner diameter to particle size ratio (>10) to avoid the channeling effect and to maintain high eluent flow rates without blocking the eluent flow (porosity = 21.74 ± 2.14%). All the experiments were conducted in triplicate and repeated twice.

Chemicals and instrumentation

All the chemicals used were analytical-grade reagents. Pb(II) solutions were prepared using lead nitrate (PbNO₃) (Aldrich, Steinheim, Germany). Sodium carbonate (Na₂CO₃) (BDH Chemicals, Poole, UK) was used to prepare solutions of sodium salts. All the working solutions were prepared in deionized distilled water, and the concentration of the metal solutions was confirmed by analyzing in an atomic absorption spectrophotometer (AAS) (GBC 933 AA; GBC Scientific Equipment, Melbourne, Australia). Pb(II) atomic absorption spectroscopy standard solution (1000 mg L⁻¹) was used to prepare the series of standard solutions for calibration of the AAS during analysis.

Flame AAS was used to determine the concentrations of Pb(II) in solutions at spectral wave lengths 217.0 and

283.3 nm on the acetylene-air flame. Fourier transform infrared (FT-IR) spectrophotometer (Nicolet 6700; Madison, WI, USA) was used for characterization of the native, metal-loaded, and metal-desorbed biosorbent surfaces.

Fixed-bed column biosorption

Continuous fixed-bed experiments were conducted using a glass column of height 50 cm and inner diameter 1 cm (Figure 1). The column was loaded with dried *H. verticillata* biosorbent to a predetermined bed height of 10, 15, and 20 cm with 1.0, 1.5, and 2.0 g of biosorbent, respectively. Pb(II) solution of an initial concentration of 50.0 mg L^{-1} was allowed to flow through the biosorbent column under



Figure 1. Schematic outline of laboratory-scale fixed-bed column reactor for desorption studies. 1, Metal/desorbent reservoir; 2a, metal/desorbent flow rate controller; 2b, eluent flow rate controller; 3, glass tube; 4, eluent collection beaker; 5, biosorbent; 6, nonabsorbing glass wool plugs.

gravity at predetermined flow rates. The eluate was collected at 15 min intervals and analyzed by AAS for Pb(II). The effect of flow rate on breakthrough time was assessed by varying the flow rate from 5.0 to 10.0 ml min⁻¹ for a biosorbent column of height 10.0 cm. Subsequently, the flow rate was measured from the collected eluate in a measuring cylinder. The effect of different bed heights on breakthrough time was investigated at an eluent flow rate of 7.0 ml min⁻¹. The eluate was collected at 15 min intervals and analyzed by AAS for Pb(II).

Fixed-bed column desorption

Desorption studies using a fixed-bed column were conducted in a similar glass column, with the same diameter. Initially several biosorbent columns were loaded with Pb(II) at a flow rate of 10.0 ml min⁻¹ and bed height of 10.0 cm. For desorption experiments, the column was filled with dried Pb(II)-loaded H. ver*ticillata* biosorbent (47.10 mg g^{-1}) to a predetermined height of 10, 15, and 20 cm. Subsequently, a 0.50 mol L^{-1} Na₂CO₃ solution was allowed to flow through the column, under gravity. The effect of flow rates on desorption was investigated by varying the flow rate of the desorbent from 2.5 to 10.0 ml min⁻¹ for a Pb(II)loaded H. verticillata biosorbent column of 10.0 cm height. Different bed heights on desorption were investigated at an eluent flow rate of 5.0 ml min⁻¹, and the eluate was analyzed for Pb(II) using AAS.

Characterization of biosorbent surfaces

The functional groups on the biosorbent responsible for metal uptake were determined by FT-IR. Spectral data were obtained for the native biosorbent, Pb(II)adsorbed biosorbent, and Pb(II)-desorbed biosorbent. FT-IR sample disks were prepared with samples of finely ground biosorbent thoroughly mixed with analytical-grade anhydrous potassium bromide (KBr). The sample disks were stored in a desiccator for 24 h, and the FT-IR spectra were obtained in the 400– 4000 cm⁻¹ wavenumber range.

Recovering of adsorbed Pb(II)

An adsorbent column of 10 cm bed height was prepared using 1 g of dry *H. verticillata* biomass. Thereafter, Pb(II) solution of 50 mg L^{-1} was allowed to flow through the adsorbent column at a flow rate of 7 ml min⁻¹ for the eluate concentration to reach 1.0 mg L⁻¹ ($C_t/C_0 = 0.02$). The column was then washed with 100 ml of distilled water. Subsequently, 0.50 mol L⁻¹ Na₂CO₃ was allowed to flow at 3 ml min⁻¹ flow rate. The eluate was collected in a beaker, and 10.00 ml aliquots were pipetted out for AAS analysis at 15 min intervals.

Implementation of biosorbent column

A synthetic waste water sample was prepared by spiking a sample of natural stream water with 10.0 mg L⁻¹ Pb(II) solution. A biosorbent column of 5.0 cm height was prepared using 0.5 g of dried *H. verticillata* biosorbent. Thereafter, the synthetic wastewater was allowed to flow through the biosorbent column at 7.0 ml min⁻¹ for 10 h. The eluate was collected at 15min intervals and analyzed by AAS for Pb(II).

Error analysis

In this study, linear and nonlinear regression analyses were performed to determine the fixed-bed model parameters for the experimental values and predicted values of C_t/C_0 for each model. Standard error of estimate (SEE; Equation 1) and R^2 values were used to determine the applicability of each fixed-bed adsorption model to the experimental data and nonlinear curve fit and linear curve fit using Origin 9 software (OriginLab, Northampton, MA, USA).

$$SEE = \sqrt{\frac{\sum (Y_e - Y_p)^2}{N}}$$
(1)

where SEE is the standard error of estimation, Y_e is the experimental value, Y_p is the predicted value, and N is the number of observations.

Modeling of biosorption

Since the fixed-bed adsorption method is an effective method for adsorption of heavy metals from an aqueous system, optimization of the fixed-bed column design is important for optimum performance (Xu, Cai, and Pan 2013). Measuring the performance of a large-scale fixed-bed column is not practical, since it is time-consuming and expensive (Xu, Cai, and Pan 2013). This can be overcome by using fixed-bed column models. The amount of Pb(II) adsorbed, q (mg),

was calculated using Equation 2.

$$q = \frac{R}{1000} \int_{t=0}^{t=\text{tot}} C_{\text{ads}} dt$$
 (2)

where C_{ads} is the adsorbed concentration (mg L⁻¹) and $C_{ads} = C_0 - C_t$, C_0 is the eluent Pb(II) concentration (mg L⁻¹) and C_t is the eluate concentration at time t (mg L⁻¹), R is the flow rate (ml min⁻¹), and t is the time (min).

The amount of Pb(II) flowing through the biosorbent (q_{tot}) was calculated using Equation 3, and the adsorption percentage (A%) was determined using Equation 4.

$$q_{\rm tot} = \frac{C_0 \times R \times t}{1000} \tag{3}$$

$$A\% = \frac{q}{q_{\rm tot}} \times 100\% \tag{4}$$

The prediction of what would happen in a full-scale column is done by modeling the data obtained from a laboratory mini-column. Breakthrough curves of the adsorbent column are more important in this process. In this study, four models were evaluated (Thomas model, Belter model, bed depth service time model, and Adams-Bohart model) to assess their suitability to describe the adsorption process.

Thomas model

The Thomas model (Thomas 1944) has been widely used in fixed-bed column performance modeling. The model assumes that the adsorption process follows second-order reversible kinetics and the Langmuir isotherm (Han et al. 2008), and no axial dispersion of the flow is involved (Saadi, Saadi, and Fazaeli 2013). Nonlinear and linearized forms of the Thomas model are given by

$$\frac{C_t}{C_0} = \frac{1}{1 + e^{\left(\frac{k_{\rm Th}q_0 x}{Q} - k_{\rm Th}C_0 t\right)}}$$
(5)

$$ln\left(\frac{C_0}{C_t} - 1\right) = \frac{k_{\rm Th}q_0 x}{Q} - k_{\rm Th}C_0 t \tag{6}$$

where C_0 is the eluent concentration (mg L⁻¹), C_t is the eluate metal concentration (mg L⁻¹), k_{Th} is the Thomas model constant (ml min⁻¹ mg⁻¹), q_0 is the predicted adsorption capacity (mg g⁻¹), x is the mass of the adsorbent (g), and Q is the effluent flow rate of the metal

solution (ml min⁻¹) (Saadi, Saadi, and Fazaeli 2013; Xu, Cai, and Pan 2013; Kumar et al. 2007).

Belter model

Belter model is a semi-empirical two-parameter model that is used to describe the breakthrough curve of a fixed-bed column adsorption system (Chu et al. 2011). The nonlinear form of the Belter model is given by

$$\frac{C_t}{C_0} = \frac{1}{2} \left[1 + \operatorname{erf}\left(\frac{t - t_{0.5}}{\sqrt{2} \times \sigma \times t_{0.5}}\right) \right]$$
(7)

where C_0 is the eluent concentration (mg L⁻¹), C_t is the breakthrough metal concentration (mg L⁻¹), erf(x) is the error function of x, $t_{0.5}$ is the time at which the eluent concentration is half of the inlet concentration, σ is the standard deviation of the linear part of the breakthrough curve, and t is the time in min. The model parameters $t_{0.5}$ and σ can be measured by nonlinear fitting of the equation (Chu et al. 2011; Ramirez et al. 2007; Ghasemi et al. 2011)

Bed depth service time (BDST) model

The BDST model is a mathematical model widely used for fixed-bed column data modeling (Hasan and Srivastava 2009; Balci, Keskinkan, and Avci 2011; Zulfadhly, Mashitah, and Bhatia 2001). It is useful in designing an industrial-scale column using data of a laboratory-scale column (Cooney 1999). In this model, a linear relationship exists between the bed height and the service time of the adsorption column. The relationship between service time and the bed height of the column, where surface chemical reactions between the metal ions and the biosorbent (not yet used for adsorption) control the adsorption kinetics of the column (Taty-Costodes et al. 2005). Usually, the BDST model fits for real adsorption systems where it follows a convex adsorption isotherm (Cooney 1999). A modified version of the BDST model is given as a fixed function of service time by

$$t = \frac{N_0 Z}{C_0 Q} - \frac{1}{K_a C_0} \ln\left(\frac{C_0}{C_t} - 1\right)$$
(8)

where t is the time (min), N_0 is the sorption capacity of the bed (mg L⁻¹), Z is the bed height (cm), Q is the linear flow rate of the metal solution (cm min⁻¹), K_a is the rate constant (L mg⁻¹ min⁻¹), C_0 is the eluent concentration (mg L^{-1}), and C_t is the breakthrough metal concentration (mg L^{-1}) (Balci, Keskinkan, and Avci 2011; Zulfadhly, Mashitah, and Bhatia 2001).

A simplified equation of the BDST model is given by

$$t = aZ - b \tag{9}$$

where a and b are the gradient and intercept, respectively, of the plot of t vs. Z (Taty-Costodes et al. 2005; Balci, Keskinkan, and Avci 2011; Zulfadhly, Mashitah, and Bhatia 2001).

Adams-Bohart model

In the 1920s, Adams and Bohart (Bohart and Adams 1920a; 1920b) developed this model for chlorine adsorption on to charcoal (Han 2008; Xu, Cai, and Pan 2013; Saadi, Saadi, and Fazaeli 2013). This model assumes that the rate of adsorption will depend on both the metal concentration and the available bonding sites in the biosorbent (Xu, Cai, and Pan 2013; Saadi, Saadi, and Fazaeli 2013). The non-linear and linearized form of the Adams-Bohart model are given by

$$\frac{C_t}{C_0} = e^{\left(k_{AB}C_0 t - k_{AB}N_0\frac{z}{Q}\right)} \tag{10}$$

$$ln\left(\frac{C_t}{C_0}\right) = k_{AB}C_0t - k_{AB}N_0\frac{Z}{Q}$$
(11)

where C_0 is the eluent concentration (mg L⁻¹), C_t is the breakthrough metal concentration (mg L⁻¹), k_{AB} is the Adams-Bohart rate constant (L min⁻¹ mg⁻¹), t is the time (min), N_0 is the maximum adsorption capacity (mg g⁻¹), Q is the linear flow rate of the metal solution (cm min⁻¹) and Z is the bed height (Saadi, Saadi, and Fazaeli 2013; Xu, Cai, and Pan 2013; Kumar et al. 2007).

Results and discussion

Effect of flow rate and bed height on breakthrough time

Column breakthrough occurs when the eluate leaving the column shows a gradually increasing metal concentration. The time at which the column breakthrough occurs is the breakthrough time. The breakthrough time was inversely related to the flow rate of the Pb(II) solution and directly related to the bed height of the biosorbent (Figures 2a and 2b). The



Figure 2. Nonlinear (a, b) and linear (c, d) plots of Thomas model for experimental data of adsorption of Pb(II) onto *H. verticillata* biosorbent column: (a, c) at different flow rates; (b, d) at different bed heights (eluent concentration $[C_0] = 50.0 \text{ mg L}^{-1}$, n = 3).

highest breakthrough time of 180 min was observed for a flow rate of 5.0 ml min⁻¹, and the lowest of 60 min was observed at 10.0 ml min⁻¹ for the 10 cm column. The bed porosity of the biosorbent column was 21.74 \pm 2.14%. The gradient of the plot of C_t/C_0 vs. time, which gives an indication of how rapidly saturation is reached, increased with an increasing flow rate, where C_t is the eluate concentration at time *t* and C_0 is the eluent concentration.

The adsorption of Pb(II) was directly dependent on the bed height of the column of the biosorbent inside the

Table 1. Adsorbed Pb(II) percentage at column saturation at different flow rates and different bed heights (eluent concentration 50.0 mg L^{-1} , n = 3).

Bed height (cm)	Biosorbent amount (g)	Flow rate (ml min ⁻¹)	Percentage (%)
10.0	1.0	5.0 7.0	$\begin{array}{c} 65\pm1\\ 56\pm1 \end{array}$
15.0	15	10.0	48 ± 1 60 ± 1
20.0	2.0	7.0	60 ± 1 64 ± 2

fixed-bed column, and the breakthrough time increased with an increase of the bed height (Figure 2b). The highest breakthrough time of 270 min was observed at 20.0 cm bed height, whereas the lowest of 135 min was observed at 10.0 cm bed height. With increasing bed height the gradient of the C_t/C_0 vs. time plot increased, which indicates the saturation of the adsorbent occurs at a slow rate.

The flow rate was inversely proportional to the percentage of Pb(II) adsorbed onto the *H. verticillata* biosorbent (Table 1). The maximum adsorption percentage (65%) was observed at a flow rate of 5.0 ml min⁻¹, and the lowest adsorption percentage (48%) was observed at 10.0 ml min⁻¹. However, the percentage of Pb(II) adsorbed increased with the increase in bed height, where the highest adsorption was observed at a bed height of 20.0 cm (64%) and the lowest (56%) was observed at a bed height of 10.0 cm (Table 1).

Variations in the breakthrough time at different flow rates can be explained with mass transfer fundamentals. The biosorption process is controlled by both intraparticle mass transfer and external mass transfer (Ko, Porter, and McKay 2000). At low flow rates, the metal solution has more residence time and facilitates intraparticle mass transfer. Consequently, the amount of metal adsorbed on the biosorbent increases, increasing the breakthrough time. Similar observations have been reported for methylene adsorption on rice husk and Pb(II) adsorption on Pinus sylvestris sawdust as a biosorbent (Taty-Costodes et al. 2005; Han et al. 2007). However, at high flow rates, the film resistance decreases and the external mass transfer coefficient increases. Therefore, mass transfer becomes faster, enabling breakthrough time to occur early (Ko, Porter, and McKay 2000). Further, column saturation occurs rapidly at high mass transfer rates. The weak distribution of metal solution into the biosorbent column at higher flow rates causes lower diffusivity of the metal ions onto the biosorbent particles and reduces the breakthrough time, as reported for Pb(II) adsorption onto Pinus sylvestris sawdust biosorbent (Taty-Costodes et al. 2005). When the bed height is increased, the amount of metal ions adsorbed and the breakthrough time also increase. This is due to the higher bed heights, which enables metal ions to spend a sufficient period of time to diffuse into the biosorbent mass (Hasan and Srivastava 2009). Further, at higher bed heights, the amount of biosorbent in the column is higher and therefore more vacant sites are available for metal adsorption (Han et al. 2007; Al-Degs et al. 2009; Sadaf and Bhatti 2014). Thus, metal adsorption is increased, and the breakthrough time increases with increasing column bed height. At higher bed heights, longer breakthrough times were observed due to the high intraparticle mass transfer, which leads to higher adsorption capacity of the column (Sadaf and Bhatti 2014). With higher intraparticle mass transfer, axial dispersion of the Pb(II) ions into the H. verticillata biosorbent column increases and this allows Pb(II) ions to diffuse into the entire biosorbent (Sadaf and Bhatti 2014). Hence, at higher bed heights, the amount of contaminated wastewater that can be treated is high (Sadaf and Bhatti 2014; Gupta et al. 1997).

Effect of flow rate on desorption

The flow rate of the 0.50 mol L^{-1} Na₂CO₃ desorbent through the column significantly affected Pb(II) desorption from the biosorbent surface. A complete desorption



Figure 3. Effect of flow rate (a) and bed height (b) on percentage of desorption of Pb(II) from 1.0 g of Pb(II)-loaded *H. verticillata*-packed biosorbent (desorbent = $0.50 \text{ mol } \text{L}^{-1} \text{ Na}_2\text{CO}_3$, n = 3).

was observed at flow rates of 3.0 and 7.0 ml min⁻¹ after 150 and 180 min, respectively (Figure 3a). The optimum flow rate for the desorption of Pb(II) from the biosorbent using Na₂CO₃ was 3.0 ml min⁻¹; it gave 100% desorption within a short period of 150 min, using a low (450 ml) volume of desorbent.

During desorption, Pb(II) is removed in the form of PbCO₃. At low flow rates (2.5 ml min⁻¹), adequate time is available for PbCO₃ to adhere to the biosorbent. Therefore, the amount of Pb(II) in the eluate is reduced. Another reason to observe a low desorption percentage could be that the flow rate is insufficient to wash out the PbCO₃ from the biosorbent. At moderate flow rates (3.0 ml min⁻¹), PbCO₃ flows through the biosorbent column without adhesion. At higher flow rates (10.0 ml min⁻¹), the CO₃²⁻ ions may not have

adequate time to react with adsorbed Pb(II) ions. Therefore, complete desorption would not be achieved because desorption may occur due to rapid flow of the desorbent, which weakens the bonds between the functional group of the biosorbent and the metal ion.

Effect of bed height on desorption

A complete desorption of Pb(II) was obtained using a 15 cm column after 135 min at a flow rate of 5.0 ml min⁻¹ (Figure 3b). When the height of the bed increases, contact time between the biosorbent and the desorbent also increases. Hence, the desorption percentage increases. However, when the contact time is excessively high, metal readsorption can also take place. This may have lowered the desorption percentage at a 20.0 cm bed height in this study. Since the contact time with the desorbent is low at a bed height of 10.0 cm, the desorption percentage is also reduced.

Desorption of Pb(II) ions from the functional groups in the biopolymers of the biosorbent occurs mainly through ion exchange. The ionic radius of Na⁺ is 1.02 Å in octahedral complexes and its hydrated ionic radius is 1.09 Å, which is smaller than the hydrated ionic radius of Pb(II) at 1.20 Å (Persson 2010). Ion exchange readily occurs when the hydrated radii of the metals are different, where metal ions with a larger hydrated radii are easily replaced by ions with a smaller hydrated radii (Trujilla, Sprint, and Zhuang 1995). Therefore, the larger Pb(II) ion is replaced by Na⁺ ions. In aqueous medium, Na₂CO₃ dissociates to give Na⁺ and CO_3^{2-} . The Na⁺ are able to compete out the Pb(II) for the binding sites of the biosorbent due to their smaller size, relatively higher mobility, and higher affinity to the metal bonding sites of the biosorbent. Therefore, Na⁺ can effectively remove Pb(II) ions from the binding site. Since CO_3^{2-} ions are present in the solution, the displaced Pb(II) metal ions form a complex with CO_3^{2-} (Gardea-Torresdey, de la Rosa, and Peralta-Videa 2004; Bai and Abraham 2003). This will prevent the readsorption of Pb(II). In a continuous system, the biosorbent is always subjected to fresh desorbent solution and therefore an equilibrium stage will not be developed; hence, complete desorption can be observed (Volesky 2003).

The equilibrium state can be proposed as follows, where B is the biosorbent with the functional groups

-OH and -COOH:

$$2B - OH + Pb^{2+} \leftrightarrow 2B - OPb + 2H^{+}$$
$$\leftrightarrow 2B - OPb + 2Na^{+} \leftrightarrow 2B - ONa + Pb^{2+}$$
$$2B - COOH + Pb^{2+} \leftrightarrow 2B - COOPb + 2H^{+}$$
$$\leftrightarrow 2B - COOPb + 2Na^{+} \leftrightarrow 2B - COONa + Pb^{2+}$$

Modeling of biosorption

Belter model

The experimental data for time at which the eluent concentration is half of the inlet concentration $(t_{0,5})$ varied from 135 to 326 min for a flow rate of 10.0 to 5.0 ml min⁻¹; similarly, $t_{0.5}$ varied from 210 to 434 min for a bed height from 10 to 20 cm. These data agreed with the predicted $t_{0.5}$ values by the Belter model. The Belter model is a dose-response mathematical model (Chu 2004; Ramirez et al. 2007). Values for standard deviation of the linear section of the breakthrough curve and time at which the eluent concentration is half of the inlet concentration $(t_{0.5})$ are shown in Table 2. The time for eluate concentrations to become half of the effluent concentration $(t_{0.5})$ decreased with an increasing flow rate, due to the reduced residence time of Pb(II) in the adsorbent bed at a high flow rate (Saadi, Saadi, and Fazaeli 2013). This may be due to the adsorption process changing from intraparticle mass transfer to external mass transfer at high flow rates, enabling faster adsorption of Pb(II) onto the biosorbent (Huang et al. 2009). Hence, rapid saturation of the biosorbent column occurs, enabling early breakthrough of the column.

When the bed height increased, $t_{0.5}$ also increased (Table 2). When the bed height increases, the available sites for Pb(II) ions to bond is increased and the biosorbent needs more time to be saturated; therefore, $t_{0.5}$ increases with increasing bed height. When the Pb(II) solution spends more time in the column, the rate of adsorption is reduced, thus increasing the break-through time. It was observed that although the Yoon-Nelson model showed high values of R^2 and low SEE, the predicted data for 50% breakthrough time (τ) deviated much from the experimental value, whereas predicted values of $t_{0.5}$ from the Belter model were more close to the experimental values. It was observed that the Belter model underestimated the eluate metal

		Flow rate (ml min $^{-1}$	5.0	7.0	10.0	7.	0
Model	Parameter	Bed height (cm)		10.0		15.0	20.0
Thomas model	k _{Th (Nonlinear)}		0.45	0.70	0.81	0.55	0.35
	$q_{ m e\ (Nonlinear)}$		85.71	71.65	70.03	79.83	78.83
	R^2		0.995	0.996	0.993	0.996	0.994
	SEE		0.027	0.026	0.032	0.036	0.046
	$k_{\text{Th (Linear)}}$		0.68	0.76	0.88	0.54	0.41
	$q_{ m e}$ (Linear)		87.54	86.91	65.71	86.56	81.96
	q _{e (Exp)}		82.39	67.35	64.42	79.20	76.99
	R∠		0.935	0.967	0.911	0.904	0.936
	SEE		0.717	0.684	0.738	0.691	0.659
Adams-Bohart model 50%	$k_{\rm AB (Nonlinear)} (\times 10^{-4})$		4.361	8.179	6.662	5.810	3.492
	N ₀ (Nonlinear)		9008	7457	7693	8260	8228
	R ²		0.977	0.961	0.962	0.808	0.978
	SEE		0.061	0.027	0.032	0.016	0.020
	$k_{AB (Linear)} (\times 10^{-4})$		10.288	13.058	14.300	10.100	5.986
	N ₀ (Linear)		7716	7042	6374	7768	7638
	R ²		0.927	0.941	0.889	0.937	0.904
	SEE		0.584	0.297	0.456	0.416	0.479
Adams-Bohart model	$k_{AB (Nonlinear)} (\times 10^{-7})$		1.262	1.253	1.338	0.918	0.861
	N_0 (Nonlinear)		12182	12118	12213	12559	11581
	<i>K</i> -		0.893	0.///	0.789	0.808	0.870
	SEE (10 ⁻⁴)		0.129	0.210	0.187	0.192	0.158
	$K_{AB (Linear)} (\times 10^{-1})$		3.628	3.360	2.258	2.292	1.960
	N ₀ (Linear)		11021	/81/	1/161	11514	10544
	R- CFF		0.713	0.535	0.607	0.587	0.676
Deltamore del	SEE		1.201	0.865	0.921	1.057	0.897
Beiter model	L _{0.5}		334	200	132	330	438
	σ_{p^2}		0.311	0.196	0.208	0.175	0.210
	SEE		0.994	0.998	0.995	0.028	0.998

Table 2. Nonlinear and linear model comparison of the Thomas, Adams-Bohart, and Belter models for Pb(II) adsorption onto *H. verticillata* biosorbent column at different flow rates and bed heights (eluent concentration 50.0 mg L⁻¹, n = 3).

Note. $k_{TH} =$ Thomas model constant (ml min⁻¹ mg⁻¹); $q_0 =$ adsorption capacity (mg g⁻¹); $k_{YN} =$ Belter model (min⁻¹); τ and $t_{0.5} =$ time required for 50% adsorbate breakthrough (min); $k_{AB} =$ Adams-Bohart model constant; $N_0 =$ bed sorption capacity (mg L⁻¹); $\sigma =$ standard deviation of the linear part of the breakthrough curve.

concentrations for variations of flow rates and for high bed height. This underestimation of model parameters may be due to the dependency of the Belter model on the physical parameters of the biosorbent column such as flow rate and bed height (Ghasemi et al. 2011). Although the Belter model showed high R^2 values (>0.994) and low SEE (<0.028), it is only valid under the same conditions that were used to obtain the breakthrough curve.

Thomas model

The experimental data followed the Thomas model and the adsorption process followed second-order reversible kinetics (Han et al. 2008), and no axial dispersion of the flow is involved (Saadi, Saadi, and Fazaeli 2013).

The maximum adsorption capacity (q_0) and the Thomas model constant (k_{Th}) for different flow rates and bed heights were calculated using the intercepts and the slopes of the linear plots and using the nonlinear fitting function in Origin software (Table 2). The experimental data fitted with both the nonlinear and

linearized Thomas model equation with a high R^2 and low SEE (Table 2). High values of R^2 indicate that the adsorption process can be modeled using the Thomas model.

When the flow rate increased, the maximum adsorption capacity (q_0) calculated from the model decreased and the Thomas constant (k_{Th}) increased with the increasing flow rate. Similar observation were reported by Nwabanne and Igbokwe (2012) on the kinetic modeling of heavy metal adsorption on a fixed-bed column. When the bed height was increased, q_0 also increased and k_{Th} decreased. Similar observations were reported by Saadi, Saadi, and Fazaeli (2013) for Pb(II) adsorption onto nanostructured alumina.

The variation of k_{Th} at different flow rates and bed heights can be explained using the variation of Pb(II) concentration in the solution and in the adsorbent where the Thomas model assumes that the adsorption follows second-order reversible kinetics, which depends on the Pb(II) concentration gradient. Further, at high flow rates due to the high external mass transfer, the rate of adsorption will increase, which will increase the Thomas constant (Saadi, Saadi, and Fazaeli 2013; Ko, Porter, and McKay 2000; Nwabanne and Igbokwe 2012). At increased bed heights, slow saturation of the column leads to a decrease in the Thomas constant (Ko, Porter, and McKay 2000; Saadi, Saadi, and Fazaeli 2013). Another reason to observe a high Thomas constant at higher flow rate is that the Pb(II) ion concentration gradient between the biosorbent surface and the solution is high, whereas at higher flow rates, Pb(II) metal ions have a low residence time and the biosorbent is always in contact with fresh metal ions (Sadaf and Bhatti 2014; Sadaf et al. 2014). At slow flow rates, Pb(II) ions have a higher residence time and the concentration gradient between the Pb(II) ions on the biosorbent surface and the solution is decreased; hence, the rate of the reaction decreases and a reduced Thomas constant was observed (Sadaf and Bhatti 2014). Similarly at higher bed heights, residence time of Pb(II) ions is increased and comparatively lower Thomas constants were observed. Although the model showed high R^2 values and low SEE, the calculated q_0 value always exceeded the experimental values (Table 2). Similar overestimation of q_0 values was reported in several studies (Saadi, Saadi, and Fazaeli 2013; Ghasemi et al. 2011; Vijayaraghavan et al. 2005). Theoretical estimation of corresponding parameters should adequately describe the experimental data. Deviation of the experimental and calculated q_0 values can be due to the assumptions made during the modeling, that the adsorption process follows the Langmuir isotherm, whereas earlier studies showed that the adsorption process followed a Freundlich isotherm (Huang et al. 2009; Chathuranga et al. 2014). The variation of the Thomas model at different flow rates and bed heights are shown in Figure 2.

Bed depth service time (BDST) model

The BDST model agreed with the experimental data where the linear plot of time vs. Z showed higher R^2

Table 3. Calculated constants for BDST model for the adsorption of Pb(II) onto *H. verticillata* biosorbent column (eluent concentration 50.0 mg L⁻¹, flow rate 7.0 ml min⁻¹, n = 3).

C_t/C_0	Q	Slope	Intercept	No	$k_{\rm a} (imes 10^{-4})$	R ²
0.02	7.0	106.0	42.3	31.7	13.6	0.995
0.20		112.0	64.6	34.5	3.5	0.989
0.60		126.0	92.6	44.2	—1.1	0.995

Note. Q = linear flow rate (cm min⁻¹); $N_0 =$ bed sorption capacity (g L⁻¹); $k_a =$ bed rate constant (L mg⁻¹ min⁻¹).



Figure 4. Isoremoval lines for 0.02, 0.20, and 0.60 breakthrough for different bed heights (influent concentration 50.0 mg L⁻¹, flow rate = 7 ml min⁻¹, n = 3).

values ($R^2 > 0.98$; Table 3). The relative constants for the BDST model were calculated using the gradients and the intercepts of the linear plots (Table 3). The gradients and the intercepts of the linear graphs were higher for higher C_t/C_0 values (Table 3). The highest gradient of 126 min cm⁻¹ was observed at $C_t/C_0 =$ 0.6, and the lowest gradient of 106 min cm^{-1} was observed at $C_t/C_0 = 0.02$. As the C_t/C_0 values increase, the rate constant (k_a) decreases, whereas the bed sorption capacity (N_0) increases. When the C_t/C_0 increases, the concentration gradient between the solution and the biosorbent surface is reduced; thus, the rate of adsorption is reduced and the k_a value decreases. Similarly, when the C_t/C_0 increases, N_0 is also increased due to the continued adsorption of Pb(II) onto the biosorption surface. Higher R^2 values ($R^2 > 0.98$) indicate the validity of the BDST model for adsorption of Pb(II) onto the biosorbent (Table 3). The BDST model constants given in Table 3, which are k_a and N_0 , can be used to scale up the adsorption process for other flow rates and eluent Pb(II) concentrations. The linear relationship for the BDST model is shown in Figure 4.

An ideal fixed-bed adsorption model should provide exact predictions of the breakthrough curves of the process and should describe the variations of parameters at different experimental conditions (Xu, Cai, and Pan 2013). It is necessary to propose a general fixedbed adsorption column model, whereas fixed-bed columns were used for different assumptions to evaluate the parameters. Therefore, some models were unable to predict model parameters. Of the four models that were investigated in this study, the Thomas model and BDST model showed good agreement with the experimental data. Therefore, the Thomas model can be used to evaluate the model parameters, and parameters from the BDST model can be used to design a largescale column. For the implemented adsorption column (at $C_t/C_0 = 0.02$), the breakthrough time was 1978 min, which is over 10 h. Experimental breakthrough time for the adsorption column also exceeded 600 min. These results indicate the suitability of the BDST model in practical column designing.

The BDST model showed a high R^2 (0.995; Table 3) for $C_t/C_0 = 0.6$, but the bed rate constant (k_a) showed a negative value. A negative rate constant for the BDST model showed the unsuitability of the BDST and Adams-Bohart model after 50% saturation of the adsorbent column. Predicted data for Adam-Bohart model are given in Table 2. These models predict data that are not compatible with the experimental data; therefore, these models are not discussed.

Recovering the adsorbed Pb(II)

Recovering of Pb(II) is important because it enables the safe disposal of the used biosorbent and reuse of the Pb(II). In Sri Lanka, the Board of Investment (BOI) standard for Pb(II) in industrial wastewater going to the treatment plant should be less than 1.0 mg L⁻¹ concentration (BOI 2011). Therefore, the adsorbent column has to shut down at this eluent concentration. An effluent solution of 50.0 mg L⁻¹ Pb(II) run through a 10.0-cm biosorbent column after 150 min reached an eluate concentration of 1.0 mg L⁻¹ Pb(II). Using the early experimental data, 0.5 mol L⁻¹ Na₂CO₃ solution at 3.0 ml min⁻¹ flow rate resulted in 100% desorption after 210 min.

The biosorbent in the 5.0-cm-height column adsorbed 60 mg g^{-1} of Pb(II) from synthetic wastewater. Even after 10 h, the biosorbent column did not reach its breakthrough point. Therefore, it is possible to use the biosorbent column even for longer periods without reaching its saturation point. After adsorption, the biosorbent was clumped and compacted, limiting the reusability of the biosorbent for another adsorption cycle. However, due to high adsorption of Pb(II) and possible recovery of Pb(II) as PbCO₃, it is possible to use the biosorbent column for a single cycle and discard the used biosorbent as an organic fertilizer or growth medium without causing any hazardous impact on the environment. Immobilization of the biosorbent can be used to improve the durability of the biosorbent, where the biosorbent is entrapped or encapsulated in a gel or silica medium. Such immobilization methods were used by Akar et al. (2013) for Ni²⁺ removal by the immobilized macrofungus Lactarius salmonicolor and Bai and Abraham (2003) for Cr(VI) removal by immobilized *Rhizopus nigricans*.



Figure 5. FT-IR spectra for the native, Pb(II)-loaded, and Pb(II)-desorbed H. verticillata biosorbent.

FT-IR band wavenumber (cm ⁻¹)						
Native	Metal adsorbed	Metal desorbed	Functional group assignment	References		
3448	3400	3415	Bonded O–H	Jacques et al. 2007; Huang et al. 2009		
1654	1651	1646	C=O stretching of carboxylic acid	Pavia et al. 2009; Huang et al. 2009		
1411	1420	1416	C-O stretching carboxylic acid	Pavia et al. 2009; Jacques et al. 2007; Jayaram et al. 2009; Akar et al. 2013		

Table 4. FT-IR spectral bands for the native, Pb(II)-adsorbed, and Pb(II)-desorbed H. verticillata biosorbent.

FT-IR spectroscopic study

The FT-IR spectra of all the biosorbents (native, Pb(II) loaded, and Pb(II) desorbed) displayed a number of vibrational bands, indicating the complex nature of the biosorbent (Figure 5). The largest peak and the second largest peak were observed at wavenumbers 3448 and 1654 cm^{-1} (Figure 5), which are associated with bonded hydroxyl groups and carboxylic acid groups with intermolecular hydrogen bonds (C=O), respectively (Pavia et al. 2009). Additional peak positions for C-H groups (2925 cm⁻¹), C-O of alcohol (1033 cm^{-1}) , and C–N of amines (1325 cm^{-1}) were also identified (Table 4). The peaks corresponding to bonded O-H groups at 3448 cm⁻¹, to C=O stretching of carboxylic acid at 1654 cm⁻¹ (Jacques et al. 2007; Huang et al. 2009; Pavia et al. 2009), and to C-O stretching of carboxylic group at 1411 cm⁻¹ (Amarasinghe and Williams 2007; Akar et al. 2013; Pavia et al. 2009) were significantly shifted after adsorption and desorption. The decrease in wavenumber of the bonded O-H peak and the C=O carboxylic acid compared with the native biosorbent and the biosorbent after adsorption suggests that these functional groups are participating in the Pb(II) adsorption process by complexation and ion exchange. Hence, it can be concluded that hydroxyl groups and carboxylic acid groups are involved in the Pb(II)-binding process, which is a physisorption process (Chathuranga et al. 2014).

After the desorption process, wavenumbers of the functional groups showed an intermediate peak shift (Table 4), where Pb(II) ions are removed from the binding site (functional groups) of the biosorbent and replaced by Na^+ ions.

Conclusions

This study reports the mechanisms of Pb(II) removal using dried biomass of *Hydrilla* in a fixed-bed column. The maximum adsorption percentage of $65 \pm 1\%$ (82 $\pm 1 \text{ mg g}^{-1}$) was obtained at a 5.0 ml min⁻¹ flow rate. The flow rate was inversely related to Pb(II) adsorption onto the biosorbent surface, and the bed height of the biosorbent column was directly related to adsorption of Pb(II). The Thomas model and the Belter model showed good agreement with the experimental data and can be used to predict the behaviors of the adsorption system. The adsorption process followed second-order reversible kinetics. The BDST model fitted the laboratory-scale experimental data. Hence, the Thomas model can be used to predict the fixed-bed column parameters and breakthrough curves. The BDST model can be used to design a practical adsorbent for other flow rates and eluent. For the implemented adsorption column (flow rate 7.0 ml min^{-1} , bed height 5.0 cm, eluent concentration 10 mg L^{-1}) at $C_t/C_0 = 0.02$, the predicted breakthrough time was 1978 min (33 h). FT-IR spectroscopic data showed that the H⁺ of bonded O-H groups and carboxylic groups were replaced by Pb(II) to form a complex during the adsorption process. A 0.50 mol L^{-1} solution of Na₂CO₃ completely desorbed the Pb(II) from the H. verticillata biosorbent.

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