Development of a Fixed-Bed Column with Cellulose/Chitin Beads to Remove Heavy-Metal Ions

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ABSTRACT: Environmental friendly cellulose/chitin beads, having relatively high mechanical properties, were successfully prepared from a blend of cellulose and chitin in 6 wt % NaOH/5 wt % thiourea aqueous solution by coagulating with 5% H_2SO_4 aqueous solution. The ability of the beads to adsorb Pb^{2+} in an aqueous solution was measured with a fixed-bed column. The effects of important parameters, to design an adsorption column of the cellulose/chitin beads for fixed-bed columns, were investigated. The breakthrough curves for the adsorption behavior indicated that the column performance was improved with decreasing initial lead concentration, ionic strength, flow velocity or bead size, as well as increasing pH dependence and bed height. Column studies showed that constants, calculated from the experimental data, and the Bed Depth Service Time (BDST) model had a good correlation. The columns were easily regenerated by treating with 0.1 mol/L HCl aqueous solution after the adsorption of metals, providing a simple and economical method for removal and recovery of heavy metals. After four adsorption–desorption cycles, the efficiency of column for the removal of lead was not significantly reduced (not more than 5%). It is shown that heavy-metal biosorption processes in fixed-bed columns could give a broad range of potential industrial applications. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 94: 684–691, 2004

Key words: cellulose; chitin; bead; adsorption; lead; column

INTRODUCTION

Heavy-metal contamination in aqueous wastewater from industries is a serious problem, because the heavy metals are not biodegradable and tend to accumulate in living organisms, causing various diseases and disorders.[1] Biosorption is potentially an attractive technology for treatment of industrial wastewaters for the separation and recovery of heavy-metal ions.[2] Traditional treatment methods such as ion exchange, chemical precipitation, and membrane separation are often ineffective and/or very expensive when they are used for the removal of heavy-metal ions in very low concentrations.[3] Many inexpensive biosorbents such as algae, fungi, bacteria, yeast, chitin, chitosan, moss, and modified wool, etc. have been extensively studied for the adsorption of various heavy metals.[4–11] Some natural polymers not only have excellent adsorbability of heavy metals, but also have biocompatibility, biodegradability, and nontoxicity. Therefore, they can be

expected to exhibit the potential of creating suitable functional materials.[12] Chitin is the second most abundant resource (next to cellulose) in nature and is found in the exoskeletons of crabs and other arthropods and in the cell walls of some fungi. Chitin in crab shell is also a waste product of the crabmeat canning industry. It is estimated that more than 40,000 tons of chitin is annually available.[13] Both chitin and chitosan, the *N*-deacetylated derivative of chitin, are recognized as excellent metal ligands, forming stable complexes with heavy-metal ions. The formation of a coordination complex between the metal and the *N*-acetyl group in chitin has been reported.[14] Usually, the adsorption ability of chitosan is much higher than that of chitin. However, Gyliene et al.[15] pointed out that some metal ions, such as Fe^{3+} and Pb^{2+}, are adsorbed much better on chitin than chitosan. Moreover, chitosan is soluble in dilute acidic solutions while chitin is resistant to the action of acids, so that metal ions cannot be removed by acids from chitosan, but they can be easily separated from chitin. It is well known that chitin is insoluble in many solvents and is very brittle, causing a limitation in its reactivity and processibility for utilization. Recently, in our lab, a novel solvent, aqueous 6 wt % NaOH/5 wt % thiourea,[16] and a new method, which can dissolve cellulose and chitin to obtain a homogeneous solution, and blend membranes having relatively high mechanical properties and a simple

process were developed for the cellulose and chitin solution.[17]

In most wastewater flowing systems, as the contact time is not sufficiently long for the attainment of equilibrium, the data obtained under batch conditions are generally not adequate. Hence, it is required to perform equilibrium studies by using columns. We therefore were interested in preparing a column filled with beads prepared by simple blending of cellulose and chitin in the NaOH/thiourea aqueous solution, to study the adsorption of heavy-metal ions in the column. Pb^{2+} was chosen as a representative heavy metal as one of the most widespread serious environmental pollutants, whose world production has exceeded 3 million tons per year.[18] Thousands of tons of lead are discharged annually from industrial wastewaters (e.g., from mine drainage, plating plants, paint and ink formulation, porcelain enameling). Besides, as described above, Pb^{2+} is adsorbed very well on chitin. In our previous study, we have already investigated adsorption of Pb^{2+} on cellulose/chitin beads and found that the ability of adsorption Pb^{2+} on cellulose/chitin beads was higher than that of pure chitin flakes because of the network and hydrophilic skeleton of cellulose. In this study, important parameters to design a column packed with cellulose/chitin beads such as bead size, column bed height, flow rate of metal solution into the column, initial concentration of metal solution, and regeneration have been investigated. The breakthrough curves for the adsorption of metals were analyzed using Bed Depth Service Time (BDST) models.[19] The column was regenerated and reused after adsorption of heavy-metal ions in a number of cycle operations.

EXPERIMENTAL

Materials

Cellulose (cotton linters) was supplied by Hubei Chemical Fiber Group, Ltd. Its viscosity-average molecular weight (M_η) was determined to be 1.03×10^5 by viscometry in cadoxen at 25°C according to $[\eta] = 3.85 \times 10^{-2} M_w^{0.76}$ (mL/g).[20] Chitin was supplied by Zhengjiang Yuhuan Co., Ltd. (China). The intrinsic viscosity ($[\eta]$) of the chitin sample was measured in N,N-dimethylacetamide (DMAc) containing 5 wt % LiCl at 25°C and the M_η was calculated to be 1.4×10^6 according to $[\eta] = 2.4 \times 10^{-2} M_\eta^{0.69}$ (mL/g).[21] Its degree of acetylation (DA) was calculated to be 73% from the nitrogen content according to DA = 1 $- [(W_C/W_N - 5.14)/1.72] \times 100\%$,[22] where W_C/W_N is the ratio of carbon to nitrogen. All the reagents used were of analytical grade and were purchased from Shanghai Chemical Reagent Co., Ltd. (Shanghai, China). The Pb^{2+} used for the study was prepared in distilled water with lead nitrate. The pH adjustments

were made by using either 1 mol/L HNO_3 or 1 mol/L NaOH solution.

Preparation of beads

The beads were prepared by coagulating a mixture of 4 wt % cellulose solution and 2 wt % chitin solution in 6 wt % NaOH/5 wt % thiourea aqueous according to our previous procedure.[23,24] Eight grams of cellulose was dissolved in 6 wt % NaOH/5 wt % thiourea aqueous solution and was kept below 0°C for 8 h. Then, it was stirred vigorously for 1 h to obtain 4 wt % cellulose solution (I). Four grams of chitin was immersed in 16 mL 46 wt % NaOH in an ice bath for 6 h, and 103.8 g ice pieces was added to obtain 2 wt % chitin solution (II). A mixture of I and II, at a weight ratio of 3 : 1 (w/w), was stirred, filtered, degassed, and injected into a cylinder to extrude a wire in a 5% H_2SO_4 aqueous solution. In this way, a fiber with a diameter of 0.3 mm was coagulated. The cellulose/chitin fibers were cut to small beads with a suitable length (0.3–2.0 mm), then washed by distilled water, and deaerated prior to the adsorption test, by ultrasonics.

Characterization of adsorption

The colored complexes of Pb^{2+} ions with 4-(2-pyridylazo)resorcinol (PAR) was measured by using a UV–visible recording spectrophotometer (UV-160 Shimadzu, Japan). To calculate the concentration of free heavy-metal ions in the aqueous solution, calibration between ions concentration (c) and absorbency (A) was employed.[25]

The cellulose/chitin beads were packed into a glass column, 1-m-long, 2.5-cm internal diameter and 0.2-cm wall thickness. To minimize possible wall and axial dispersion effects in the fixed-bed column, the bed length-to-particle diameter ratio (L/d_p) must be greater than 20.[26] The cellulose/chitin beads bed height varied in the range from 40 to 60 cm and the diameter of beads was 0.3–2.0 mm, so the bed length-to-particle diameter ratio (L/d_p) was greater than 20 in all experiments. The influents containing Pb^{2+} were passed downward through the column with the desired flow rates in the range of 2–6 mL/min. The concentration of Pb^{2+} in the influents was controlled in the range of 10–20 mg/L. Packed bed experiments were carried out at room temperature. The metal solutions at the desired concentration were fed by a peristaltic pump at a fixed flow rate to the column filled with a certain bed height of adsorbents. The solutions containing metal from the downstream of the column were collected by means of a fraction collector, and the ion concentration was determined spectrophotometrically. Usually, breakthrough and exhaustion were defined as the phenomenon when the
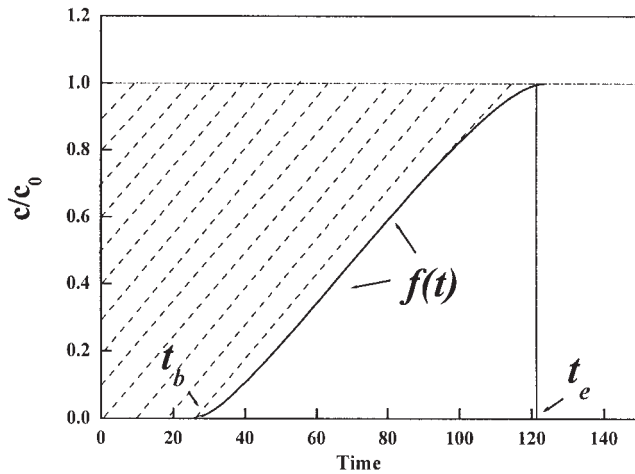
Figure 1 Typical breakthrough curve in fixed-bed column.

effluent and the influent concentrations were about 3–5 and 90%, respectively. The number of bed volumes (BV) was defined as[27]

$$BV = \frac{\text{Volume of solution treated}}{\text{Volume of cellulose/chitin beads}}$$

$$= \frac{\text{operation time}}{\text{empty-bed contact time}} \quad (1)$$

The amount of metal ions adsorbed per unit weight of adsorbents (q, mg/g) can be calculated by the equation

$$q = \frac{(t_e - \int_{t_b}^{t_e} f(t)dt)Qc_0}{W} \quad (2)$$

where Q, c_0, and W represent volumetric flow rate (ml/min), influent concentration (mg/mL), and dry weight of adsorbent applied (g), respectively. $(t_e - \int_{t_b}^{t_e} f(t)dt)$ represents the area of the shadow in Figure 1 and can be estimated through integration. The $f(t)$, t_b, and t_e are functions representing effluent curve obtained from fixed bed, time to breakthrough (min), and time at exhaustion (min), respectively.

Operation of the column was stopped when the ratio of effluent-to-influent concentration exceeded a value of 0.9. After the column reached exhaustion, the column saturated with metal ions was regenerated with 0.1M HCl solutions by passing it in down-flow operation of the column. The samples were collected at regular time intervals to study the metal elution. After acid elution, distilled water was used to rinse the beads until the pH value in the wash effluent exceeded 6.5. Then, the column was fed again with a metal solution for the second cycle of operation to investigate the potential of reusing the cellulose/chitin beads for removal of heavy metal. After adsorption, the col-

umn was again regenerated and subjected to further adsorption. The cycle of adsorption–desorption was repeated at least four times.

Column modeling

Several models were applied to simulate the breakthrough curves to predict the scaling-up of a unit plant. BDST is a simple model for predicting the relationship between bed depth (Z) and service time (t) in terms of process concentrations and adsorption parameters given by eq. (3)[19] as

$$\ln\left(\frac{c_0}{c} - 1\right) = \ln(e^{K_a N_0 Z/F} - 1) - K_a c_0 t \quad (3)$$

where c_0 is the initial concentration of metal ions in the liquid phase (mg/L); c is the effluent concentration metal ions in the liquid phase (mg/L); F is the flow rate (m/h); N_0 is the amount of metal ions adsorbed onto the unit amount of the adsorbent (mg/L); K_a is the rate constant in BDST model (L/mg h); t is the service time (h); and Z is the bed depth of the column (m).

Hutchins[28] proposed a linear relationship between bed depth and service time given by eq. (4)

$$t = \frac{N_0}{c_0 F} Z - \frac{1}{K_a c_0} \ln\left(\frac{c_0}{c} - 1\right) \quad (4)$$

The critical bed depth (Z_0) is the theoretical depth of adsorbent sufficient to prevent the adsorbate concentration from exceeding a predefined breakthrough value at $t = 0$. By letting $t = 0$, Z_0 is obtained from eq. (4) by solving for Z.

Equation (4) indicates the linear relationship between t and Z as

$$t = m_x Z - c_x \quad (5)$$

where m_x is the slope of the BDST line and the intercept of this equation represents

$$c_x = \frac{1}{K_a c_0} \ln\left(\frac{c_0}{c} - 1\right) \quad (6)$$

The slope of the BDST line, m_x, represents the time required for the adsorption zone to travel a unit length through the adsorbent and is used to predict the performance of the bed. If there is a change in the initial metal ions concentration c_0 to a new value of initial metal ions concentration c_0^1, The new slope (m_x^1) can be written as

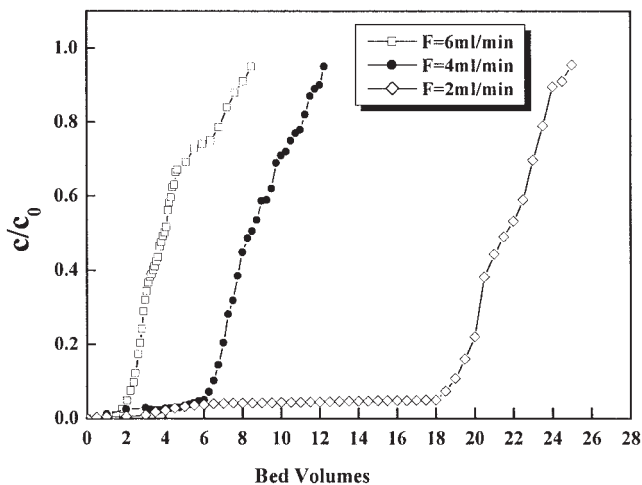$$m_x^1 = m_x\left(\frac{c_0}{c_0^1}\right) \quad (7)$$

Figure 2 Effect of flow rate (F) on the breakthrough curves for adsorption of Pb^{2+} (c_0 = 20 mg/L, pH_0 = 5.3, h = 60 cm).

Figure 3 Effect of bed height (h) on the breakthrough curves for adsorption of Pb^{2+} (c_0 = 20 mg/L, pH_0 = 5.3, F = 2 mL/min).

and the new intercept can be written as

$$c_x^1 = c_x \left(\frac{c_0}{c_0^1}\right) \frac{\ln(c_0^1/c - 1)}{\ln(c_0/c - 1)} \tag{8}$$

If the designed data are required for a change in flow rate of metal ions to the adsorption system, the intercept remains unchanged and the new slope (m_x^2) can be written as[29]

$$m_x^2 = m_x \left(\frac{F}{F^1}\right) \tag{9}$$

RESULTS AND DISCUSSION

Effect of flow velocity and bed height

To investigate the effect of flow rate on the adsorption of Pb^{2+} ions into cellulose/chitin beads, both the metal concentration in the feed solution and the bed height were kept constant at 20 mg/L and 60 cm, respectively, whereas the flow rate was changed from 2.0 to 6.0 mL/min. The results are given in Figure 2, where the uptake of Pb^{2+} decreased with an increase in flow rate. Breakthrough, for flow velocities of 6.0, 4.0, and 2.0 mL/min, occurred at 2.0, 6.0, and 18 BV, respectively. The adsorption amounts were estimated to be 16.2, 30.6, and 75.6 mg, and the corresponding adsorption efficiencies against total influent amounts were 47.6, 61.2, and 74.1%, respectively. Obviously, the beads saturated early at higher flow rate (6.0 mL/min). This is because the time required to reach an equilibrium state between cellulose/chitin beads and heavy-metal solutions is much longer (about 4–6 h).[30] Therefore, increasing the flow velocity causes a shorter retention time, which may cause a negative effect on the mass transfer efficiency of the adsorbate.
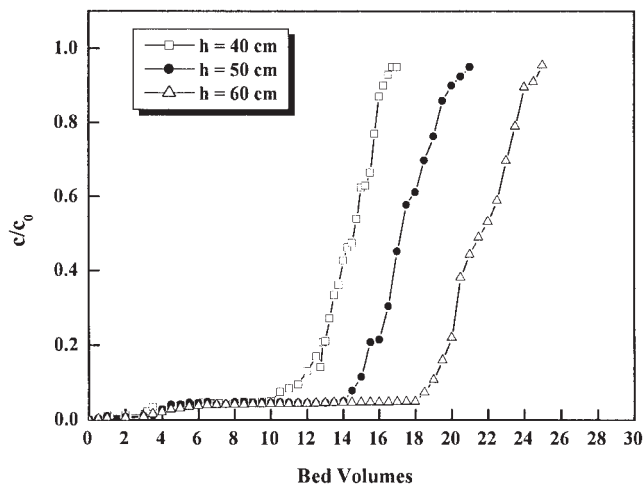
For Pb^{2+} ion adsorption on cellulose/chitin beads, the maximum adsorption efficiency was obtained at a flow rate of 2 mL/min. Figure 3 represents the breakthrough curves of Pb^{2+} adsorption for different bed heights at a constant flow rate of 2 mL/min. As we expected, increasing the depth of the bed produces an increase in the uptake of Pb^{2+} and the breakthrough volumes. This may be due to an increase of the surface area of adsorbent that provided more binding sites for adsorption in a column with a longer bed height and the efficiency of the bed is increased by allowing sufficient time for the adsorbate to diffuse into the whole mass of the adsorbent.

Effect of beads size

The influence of the bead size on the breakthrough curves for adsorption of Pb^{2+} is illustrated in Figure 4.
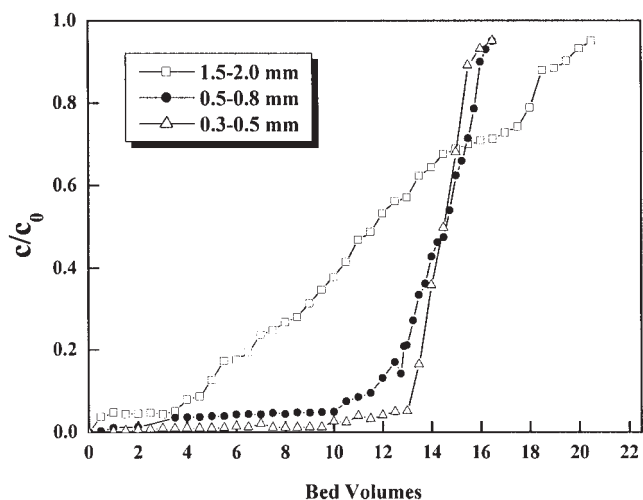

Figure 4 Effect of beads size on the breakthrough curves for adsorption of Pb^{2+} (c_0 = 20 mg/L, pH_0 = 5.3, h = 40 cm).

This indicated that increasing beads size led to a decrease in breakthrough, and the breakthrough for beads size 0.35 ± 0.2, 0.65 ± 0.2, and 1.7 ± 0.3 mm occurred at 13.1, 10.1, and 3.8 *BV*. Clearly, the breakthrough curves of smaller sized beads are much steeper than that of large-sized beads. This demonstrates that the surface area of the beads is related to the removal efficiency, and the diffusion rate in the pore could dominate the Pb^{2+} adsorption process during the early stages of the operation. Therefore, faster Pb^{2+} removal was observed for the smaller sized beads. Smaller sized beads are more favorable for heavy-metal adsorption but the pressure drop increases with a decrease in the bead's size. For application of the process at an industrial scale, an intermediary bead size is preferable.

Effect of initial Pb^{2+} ion concentration

Figure 5 shows the breakthrough curves for the adsorption of Pb^{2+} ions at different initial concentrations. The breakthrough, for initial concentrations 20, 15, and 10 mg/L, occurred at 10, 13.3, and 20 *BV*, respectively. For influent concentrations of 20 and 15 mg/L Pb^{2+} ions, the *BV* prior to the breakthrough decreased by 33.5 and 50%, respectively, as compared with those for influent concentration of 10 mg/L: the higher the initial Pb^{2+} concentration was set, the earlier the breakthrough occurred. On the one hand, increasing molecular size, induced by hydrolysis, resulted in less diffusing species: the saturation of the adsorbent takes a much longer time, and exhaustion is reached before all the adsorbing sites are occupied and all the metal ions are able to diffuse through the polymer.[31] On the other hand, the total amount of sites available for ion adsorption may be finite; therefore,
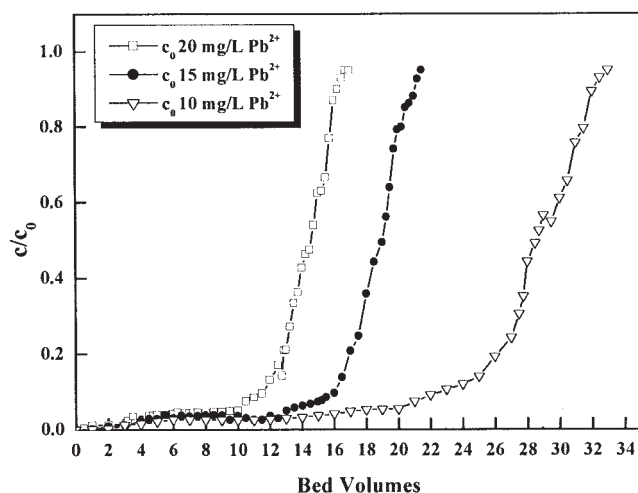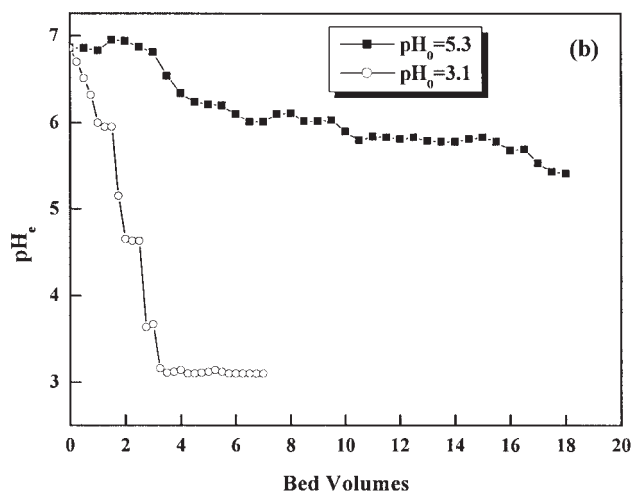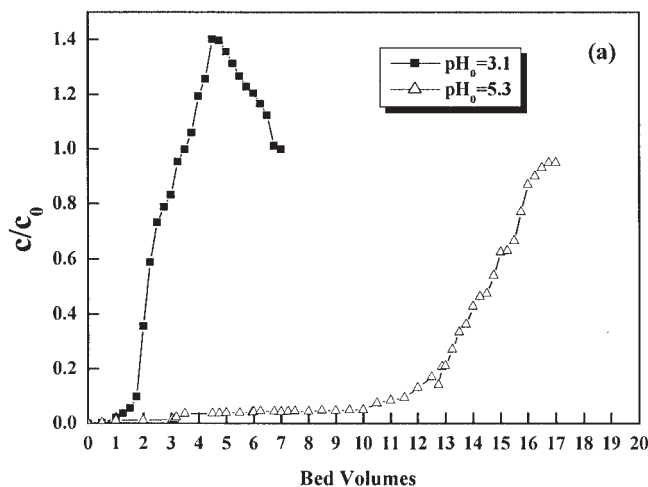

Figure 6 Effect of pH on Pb^{2+} adsorption in fixed-bed columns: (a) breakthrough curves; (b) effluent pH_e curves (c_0 = 20 mg/L, F = 2 mL/min, h = 40 cm).

Figure 5 Effect of influent concentration on the breakthrough curves for adsorption of Pb^{2+} (F = 2 mL/min, pH_0 = 5.3, h = 40 cm).

by increasing metal ion concentration, the adsorption of metal ion decreases. In addition, the higher surface coverage, resulting from the increase of metal concentration, enhances the activation energy for the adsorption reactions, thereby making it more difficult for the surface to bind metal ions.[32] These results suggest that the biosorption process can be applied to the treatment of dilute effluents.

pH dependence

pH of the solution is an important factor in adsorption equilibrium and kinetics of metal ion. The breakthrough curves for the adsorption of Pb^{2+} ions at different initial pH values and the curves of effluent pH versus *BV* are shown in Figure 6. Figure 6(a) shows that breakthrough occurred at 2 and 10 *BV* for initial pH 3.1 and 5.3, respectively: the respective es-
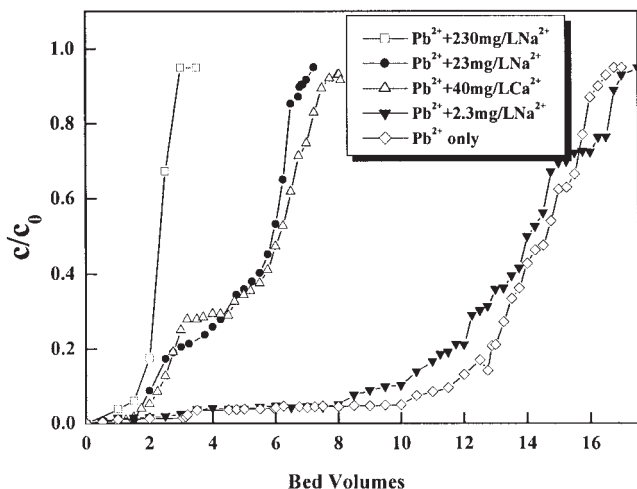
Figure 7 Effect of ionic strength on the breakthrough curves for adsorption of Pb^{2+} (c_0 = 20 mg/L, pH_0 = 5.3, F = 2 mL/min, h = 40 cm).

timated adsorption amounts were 7.2 and 52 mg. As the pH increased, the breakthrough bed volumes increased. Interestingly, a slight overshoot in the effluent concentration was observed in the experiment with pH 3.1. Namely, the c/c_0 value increased to 1.4 and then decreased to 1.0. We can see that the pH variation inside the column plays an important role in this overshoot.[26] At beginning effluent, pH increased to 6.5; when the influent solution with pH 3.1 continued flowing into the column, the solution pH inside the column decreased slowly to the influent pH value, causing desorption of Pb^{2+} from the surface–metal complexes and thus the occurrence of the overshoot. In addition to precipitation of lead in the pores of the biosorbents, so-called surface precipitation may be a
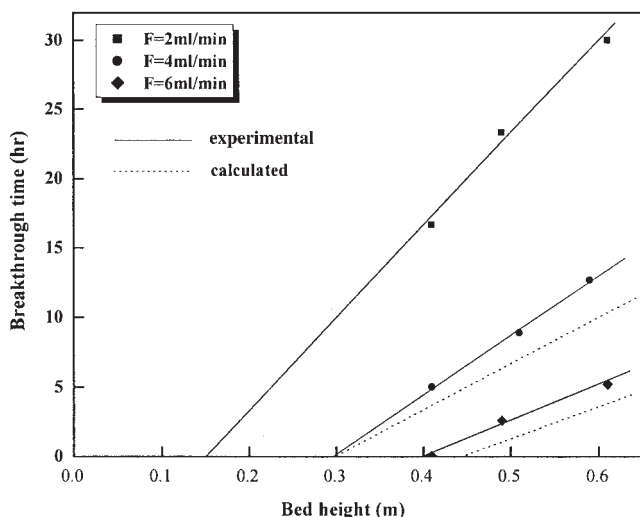
factor for its removal according to our previous experiments. In the early period of the fixed-bed operation of the present study, the pH was higher; similarly, surface precipitation effects may occur in the pores of the beads. As the lower pH influent flowed into the column, the reverse reaction of precipitation took place, which may cause the overshoot. Figure 6(b) shows the variation of effluent pH. For the influent pH 3.1 and 5.3, the effluent pH increased to 6.5 and 6.7 at first and then decreased slowly to 3.1 and 5.6. This indicates that the beads could adsorb hydrogen ions, which essentially cause the pH to increase and subsequently facilitates metal ion adsorption.

Influence of other ionic strength

Ionic strength of other ions present except Pb^{2+} is another important factor for heavy-metal ion adsorption. Experiments with such ionic strength with other ions were set at 0, 0.1, 1.0, and 10 mM and pH 5.3 were performed, and the results are shown in Figure 7. It indicates that the removal efficiency of Pb^{2+} decreased as the ionic strength increased, especially for solutions of ionic strength of 1 and 10 mM, but for the solution of ionic strength of 0.1 mM, the removal efficiency did not change significantly as compared with the solution without other ions such as Ca^{2+} or Na^+. Breakthrough for ionic strengths 0, 0.1, 1, and 10 mM occurred at 10, 9.9, 2, and 1 BV, and the removal efficiencies were 78.1, 77.9, 56.2, and 56.1%, respectively. Higher ionic strength impedes adsorption on beads, whereas lower ionic strength does not influence adsorption of metal significantly.

TABLE I
Experimental and Calculated Bed Depth Service Time (BDST) Equation Constants for Adsorption of Pb^{2+} (C_0 = 20 mg/L)

Flow rate (mL/min)	Analysis	Slope m_x (h/m)	Intercept c_x (h)	Correlation index
2	Experimental	66.5	−9.91	0.998
4	Experimental	38.5	−10.38	0.997
6	Experimental	25.8	−10.29	0.997
4	Calculated	33.25	−9.91	1
6	Calculated	22.17	−9.91	1

Figure 8 Effect of flow rate on experimental and calculated BDST model for adsorption of Pb^{2+}.

TABLE II
Bed Depth Service Time (BDST) Parameters for Adsorption of Pb^{2+}

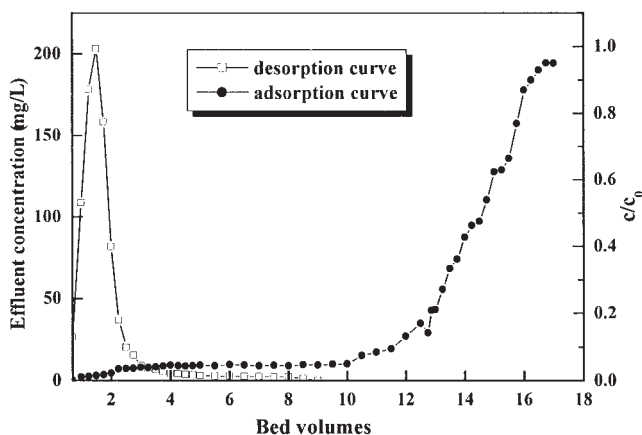| Flow rate (mL/min)	Linear flow rate (m/h)	N_0 (10^3 mg/L)	$K_a \times 10^2$ (L/mg h)	Z_0 (m)
2	0.244	0.325	1.108	0.15
4	0.488	0.375	1.058	0.27
6	0.733	0.378	1.067	0.40

Figure 9 Desorption/adsorption curve of Pb^{2+} through a packed bed of cellulose/chitin beads ($c_0 = 20$ mg/L, $F = 2$ mL/min, $h = 40$ cm, for desorption 0.1M HCl as effluents).

Application of BDST models on the adsorption of lead ions by the cellulose/chitin beads

The breakthrough times against bed height at two different flow rates of 2 and 4 mL/min for the adsorption of Pb^{2+} are shown in Figure 8. The plots exhibit a linear relationship, indicating the BDST model can be applied to a fixed-bed column of cellulose/chitin beads in this study. The BDST model can be applied to predicate a model slope at other flow rates once the slope at a given flow rate is determined. Table I shows the experimental and calculated BDST model constants for adsorption Pb^{2+} at different flow rates: the calculated and experimental values of slopes and intercepts are in good agreement. It is the advantage of the BDST model that any experimental test can be reliably scaled up for other flow rates without further experimental data and analyses. To obtain higher accuracy, more data should be obtained to check any deviation in the slope of a straight line. Table II shows the BDST model parameters: adsorption capacity (N_0), rate constant (K_a), and critical bed depth (Z_0) were calculated from slope and intercept of BDST by using eq. (4). It can be seen that the critical bead depth (Z_0) and rate constant (K_a) increased with increasing flow rate. However, calculated values of adsorption capacity (N_0) decreased with increasing flow rate. This indicates that to achieve a longer service time in a column, flow rates should be lower. Therefore, the BDST model can be used to design fixed-bed biosorption columns.

Regeneration

Once the beads were saturated with Pb^{2+}, it was important to regenerate beads for the reuse of biosorbent for biosorption. Figure 9 shows the desorption and adsorption curves of Pb^{2+}. The results exhibit a sharp increase of Pb^{2+} concentration at the beginning of acid elution, with the maximum concentration of 200 mg/L, which is 10-fold the feeding Pb^{2+} concentration in the adsorption operation. About 98% of adsorbed Pb^{2+} ions were recovered after being regenerated with 0.1M HCl solutions for only 2.5 BV, in contrast to about 16 BV feeding of 20 mg/L Pb^{2+} solution to fully saturate the column. That is, the adsorbed metal ions can be easily desorbed from the cellulose/chitin beads in the column and the recovery ratio (ratio between feeding volume and recovery volume) is 16 : 2.5. The adsorption/desorption (A/D) cycle was repeated four times to justify the reusability of the column and the results are shown in Table III. It is clear that the adsorption efficiency of Pb^{2+} was maintained (not more than 5%) and the regeneration efficiency was nearly the same. The regeneration and subsequent use of the cellulose/chitin beads offer a simple and economical method for removal and recovery of heavy metals from industrial wastewater. Furthermore, these beads are biodegradable and fit sustainable development goals.

CONCLUSION

The cellulose/chitin beads were found to be an effective biosorbent for the removal of heavy metals such as Pb^{2+}. With an increase in influent pH, the bed volumes increased. An overshoot of the effluent concentration was observed at influent pH 3.1. This is the result of the Pb^{2+} desorption from the surface–metal complexes. The effluent pH increased at the beginning of experiments, then dropped, and approached a constant value. Higher influent concentration, beads size, flow rate, and lower bed height could result in lower bed volumes. When ionic strength was less than 0.1

TABLE III
Effects of Adsorption/Desorption Cycles on Pb^{2+} Adsorption Characteristics

	Adsorption efficiency (%)	Regeneration efficiency (%)		Adsorption efficiency (%)	Regeneration efficiency (%)
Cycle 1	78.1	99.2	Cycle 1	78.1	99.1
Cycle 2	76.5	99.1	Cycle 2	75.8	99
Cycle 3	75.6	99.2	Cycle 3	74.2	99.2
Cycle 4	74.1	99.1	Cycle 3	73.5	99.1

mM, the uptakes of Pb^{2+} were not changed. However, the column performance could be lower as ionic strength was larger than 1 mM. The BDST model was successfully used to analyze column performance and evaluate the model parameters. These cellulose/chitin beads can be regenerated easily and efficiently by treating with $0.1M$ HCl and used several times. It shows that the biosorption process can be used in an industry wastewater treatment for removal and recovery of heavy metals.

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