Determination of lead biosorption properties by experimental and modeling simulation study

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Abstract

The Ca-alginate based ion exchange resin was applied in the lead removal from the synthesized waste streams in batch reactors. This study shows that the resin had both high removal capacities and rate at the optimum pH of 4 or higher. The Langmuir isotherm well described the equilibrium data in various cases. The maximum removal capacity (q_{max}) for lead ions was 3.24 mmol/g for the Ca- and Na-free solutions, which is much higher than regular adsorbents. The q_{max} values decreased to 1.12 and 2.49 mmol-Pb/g respectively in the presence of calcium and sodium, due to the competitions among the metals for the ion exchange sites. The removal was increased as the initial solution pH was increased.

A series of kinetic experiments was conducted with various conditions. It was found that the metal ions can quickly be removed. More of the metal can be removed within 20 min and the complete uptake was achieved in 90 min, which is much shorter than the most of adsorption processes. The presence of calcium and sodium ions played some roles in the uptake kinetics. It is found through experiments that the mass transfer was the controlling mechanism. A diffusion-controlled model was employed in the simulation. It was demonstrated that the model successfully described the uptake kinetics with such operational conditions as initial concentrations, stirring speeds, and presence of calcium and sodium ions.
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Keywords: Ca-alginate based ion exchange resin; Metal biosorption; Isotherm; Kinetics; Modeling

1. Introduction

Increasing toxic heavy metal contamination in aqueous environment is a common problem in many developing countries. For instance, severe lead poisoning can cause encephalopathy with permanent damage. Some studies indicate that moderate lead poisoning can result in neurobehavioral and intelligence deficits [1]. Both copper and zinc are important micronutrients for normal human growth and immune function when their concentrations are very low. Deficiencies of such metals are common in developing countries because the best sources of the micronutrients are in high protein food such as meat [2]. However, these metals become harmful to the environment as their concentrations reach a certain level. It is therefore regulated by many countries that the heavy metal ions must be treated to certain levels before their discharges into watercourses.

Among several available technologies, the metal biosorption by biopolymers extracted from the non-living organisms is quite promising [3]. Alginate is one of biopolymers for the metal ion removal from dilute aqueous solutions [4]. The commercial alginate commonly existing as sodium alginate in the form of powder has various organic functional groups [5]. The calcium alginate resins containing significant amount of water are usually prepared for the metal ion removal. An approach for preparation of the Ca-alginate based ion exchange resin (resins) was recently developed in our laboratory [6]. This material has been proved to have very high capacities for the metal ion removal.

In order to transfer the technologies from the laboratory studies to full-scale applications, it is necessary to develop mathematical models for the metal ion biosorption by the resins. The models should be helpful in interpreting the experimental data and predicting the treatment results when the conditions are changed.

Several equilibrium models were developed for the metal uptake processes by the alginate compounds. Jang et al. developed several extended Langmuir models for the metal

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ion removal by alginate gels in a batch loop fluidized bed reactor [7]. It was assumed that the metal ion uptake was due to a chemical reaction between the metal ion and the carboxyl group (binding site). A surface complexation model, on the other hand was employed to interpret the experimental observation by Chen et al. [4], whose assumption was the surface adsorption reactions between the functional groups and metal ions.

The reaction- and diffusion-controlled models were employed to describe the kinetics of the metal uptake. It was found that the mass resistance of the substrates with molecular weight lower than 2×10^4 was neglectable in the alginate beads [8]. Based on the observations, Konishi et al. assumed that the diffusion of metal ions was much faster than reactions and could be neglected [9]. They used a simple reaction-controlled model to describe the metal ion uptake by the alginate acid beads. On the other hand, Chen et al. found through experimental studies that diffusion was an important factor for copper ion removal by the calcium alginate beads, which led to a successful application of a diffusion-controlled model for calculating the biosorption kinetics [4].

In our earlier studies, it was showed that the resins we developed have both high removal capacity and rate [6]. A recent study by the authors showed that the removal process kinetics was suspected to be controlled by the mass transfer. However, the kinetic mechanisms of the removal using the resins still remain unclear. Because the fundamental mechanism of metal removal by the resins has been proved to be ion exchange, it needs to investigate that whether the mass transport or the ion exchange reaction is the determining factor in the kinetic behavior of the process. In this study, we first carried out a series of equilibrium and kinetic to find out the treatment capacities, optimum conditions and the controlling mechanisms. A diffusion-controlled model subsequently was used for representation of the experimental observations under such conditions as various initial metal concentrations, stirring speeds and presence of other metal ions.

2. Theoretical

As the diffusion-controlled mechanism was confirmed by changing the stirring speed in the kinetic experiments (see the discussion later), a diffusion model based on Fick's law was used. The following assumptions and simplifications were made:

(i) Since the specific surface of the resins is found to be low, the metal ions can be assumed to transfer through the surfaces of resins. Hence the process is controlled by the surface diffusion rather than the pore diffusion. The mass transfer of the metal ions in the resins is controlled by the Fick's law.

(ii) The diameters of resins vary within a narrow range according to our measurement. Swelling or shrinking of the resins during the metal uptake is negligible. The effect of the electric field gradient due to the metal biosorption does not change the physical properties of resins. Thus, the kinetic

parameters, physical parameters and equilibrium constants are assumed to be unchanged in the modeling calculation.

According to the above assumptions, the mathematical model can be formulated:

$$D_s \left(\frac{\partial^2 q}{\partial r^2} + \frac{2}{r} \frac{\partial q}{\partial r} \right) = \frac{\partial q}{\partial t}, \quad 0 \leq r \leq a_p, \ t > 0 \tag{1}$$

The initial and boundary conditions may be specified as

$$\frac{\partial q}{\partial r} = 0, \quad r = 0 \tag{2}$$

$$D_s \frac{\partial q}{\partial r} \rho_p = k_f(C - C*), \quad r = a_p \tag{3}$$

$$q = 0, \quad t = 0 \tag{4}$$

where C and q are the concentrations of the metal ions in bulk and in solid phases, respectively, $C*$ the aqueous phase concentration at the particle surface, in equilibrium with the corresponding concentration in the solid phase $q*$, D_s the surface diffusivity, ρ_p the particle density, and k_f is the external mass transfer coefficient. Eq. (1) with the initial and the boundary conditions can be solved by the method developed by Tien [10].

3. Materials and methods

Regular calcium alginate beads are prepared by dripping 1–3% sodium alginate solution into a stirred $CaCl_2$ solution [4]. The resins (see Fig. 1) used in this study were prepared by a different approach illustrated in our previous paper [6]. The diameter of the randomly selected particles was measured by a light microscope (Olympus Bxbo, Japan). The resins prepared in this study had an averaged diameter of 0.39 mm, smaller than that reported previously [6].

Lead nitrate, nitrate acid, and sodium hydroxide from Merck (Germany) were used; sodium alginate, calcium chloride dehydrate and sodium nitrate from Fulka (Switzerland) were used. All other chemicals were purchased from Sigma–Aldrich (Singapore). All chemicals are of analytical grades. Nitrate acid and sodium hydroxide solutions in various concentrations were used for pH adjustments. A series of equilibrium and kinetic experiments was carried out respectively to investigate the characteristics of biosorption processes. $Pb(NO_3)_2$ solutions with various initial pH and concentrations were prepared.

The equilibrium experiments aimed at studying effects of initial solution pH on the biosorption, and effects of calcium and sodium ions on the sorption isotherms. In the initial pH effect experiment, the resins were added into the conical flasks containing the Ca- and Na-free solutions of lead ions. The solution pH was adjusted ranging from 1 to 6. The flasks were placed in a shaking water bath with temperature controlled at 25 °C for 2 days. The final samples were analyzed by an inductively couple plasma emission spectroscopy (ICP-ES) (Perkin-Elmer Optima 3000, USA).
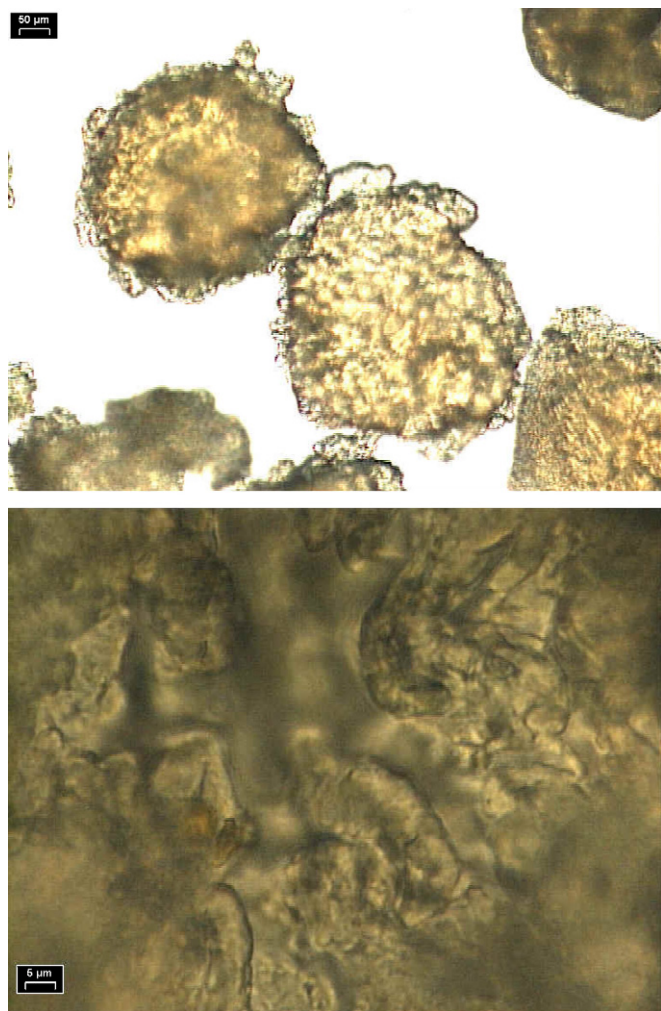
Fig. 1. Microscopic visualization of the Ca-alginate based ion exchange resin.

In the isotherm experiments, the solution pH was adjusted at 4–5. The lead solution with a concentration was prepared; the resins with various amounts were added into the solution. The calcium or the sodium ions were added into the lead solution. The flasks were placed in a shaking water bath with temperature controlled at 25 °C for 2 days. The final samples were analyzed by the ICP-ES.

Several kinetic experiments with various initial metal concentrations and initial solution pH of 4–5 were carried out. The resins were added to the solutions while being stirred with a speed of 180 rpm. The samples were taken at periodic time intervals and analyzed by the ICP-ES. The same procedures were repeated for the sorption system with the PbNO$_3$ and Ca(NO$_3$)$_2$ or NaNO$_3$, aiming at investigation of the effect of calcium or sodium (ionic strength) on the uptake rate.

In order to find out the controlling steps, two kinetic experiments with the different stirring speeds were conducted. The speed was set at 180 and 30 rpm for the so-called "normal stirring" and "slow stirring", respectively. In these experiments, two glass beakers were used instead of plastic ones. We observed that the speed in this "normal stirring" mode was slightly faster than that in the plastic beakers. Other procedures were the same as the above.

4. Results and discussion

4.1. Biosorption equilibrium

Equilibrium experimental studies at various initial pH values were carried out with the results shown in Fig. 2. The sharp increase in the metal uptake from 5 to almost 100% was observed between pH 1.2 and 4.0 and a plateau was formed when the pH was above 4.0. Similar findings of the metal removal by other biosorbents were reported [4,11]. The lead ion removal efficiency sharply increased as pH was increased from 2.0 to 4.0, and it remained unchanged with its highest value when pH was above 4.0.

The pH-dependence metal removal could be interpreted on the basis of ion exchange reaction(s). In the pH range in this study, lead ions are in the form of free lead ions (Pb^{2+}), which can be exchanged with calcium ions (Ca^{2+}) in the solid matrix according to Eq. (5):

$$M^{2+} + [Ca^{2+}R^{2-}] = Ca^{2+} + [M^{2+}R^{2-}] \tag{5}$$
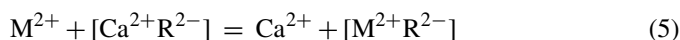
where M^{2+} is the free metal ion in the aqueous solution, R symbolizes the negatively charged network of the cation exchanger and M = Pb.

Since hydrogen ions are also positively charged, there is the similar ion exchange reaction between hydrogen and calcium ions. The pKs values of guluronic and mannuronic acids are 3.65 and 3.38, respectively [13]. Consequently, hydrogen ions competed with lead ions for exchange sites. When pH was lower, concentration of hydrogen ions was higher, reducing the exchange sites for lead ions. On the other hand, more exchange sites were available for lead ions when pH was higher. As a result, lead ion removal enhanced when pH was increased. It is concluded that the optimum metal ion removal can be achieved when initial pH is above 4.0.

A series of experiments for determination of the adsorption isotherms for the lead removal were then carried out in pH ranging from 4 to 5. The metal removal capacity (q, mg/g) is defined as the amount of metal removed (mg) per mass of the adsorbent
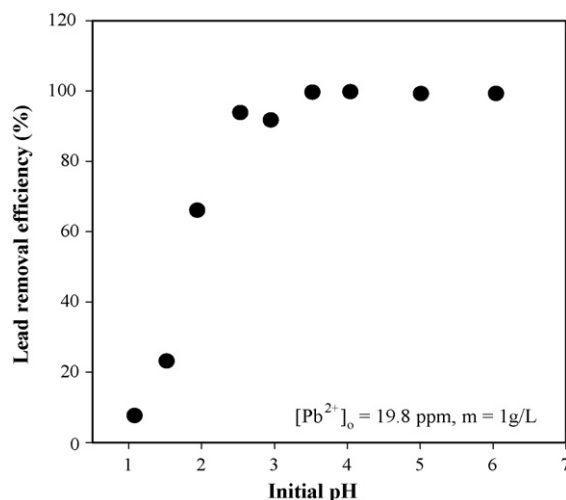

Fig. 2. Effect of initial pH on the lead removal.

applied (g), while C_e is the metal equilibrium concentration (mg/L). Our earlier study showed that Langmuir equation fitted the experimental data much better than the Freundlich Eq. (4). Hence, the Langmuir equation expressed as following was used:

$$q = \frac{q_{\max}bC_e}{1 + bC_e} \tag{6}$$

where $q_{\max}$ and b are the maximum metal removal capacity and the Langmuir constant, respectively. Eq. (6) was rewritten as

$$\frac{C_e}{q} = \frac{1}{q_{\max}b} + \frac{C_e}{q_{\max}} \tag{7}$$

C_e/q versus C_e for the lead removal under three different initial conditions was plotted in Fig. 3, by which $q_{\max}$ and b can be determined. In the following discussions, the solid points and the lines represent experimental data and modeling results, respectively.

As shown in Fig. 3a, the Langmuir equation fitted the lead removal experimental data (calcium and sodium free) very well. The $q_{\max}$ and b values were 670.2 mg-Pb/g (or 3.24 mmol-Pb/g) and $0.8730 \, (\text{mg-Pb/L})^{-1}$, respectively. The removal capacity here is much higher than that by the commercial granular activated carbons. According to our previous study [4], $q_{\max}$ for copper was 115.4 mg-Cu/g (1.82 mmol-Cu/g). Higher $q_{\max}$ value for lead ions suggested that lead is easier to be removed than copper. In addition, the $q_{\max}$ value here is higher than that we found previously for lead. In this study, a complete washing of the newly prepared resins was performed. The presence of calcium ions reduces the lead uptake as discussed later. The washing in the preparation resulted to removal of most of remaining calcium ions that was used in the preparation. As a result, the adsorption capacity of lead ions is enhanced.

Fig. 3b shows that the addition of Ca^{2+} of 4.34 ppm significantly affected the lead removal. When the Ca^{2+} with concentration of 4.34 ppm was added, the $q_{\max}$ and b values were 232.6 mg-Pb/g (or 1.12 mmol-Pb/g) and $0.6232 \, (\text{mg-Pb/L})^{-1}$, respectively. According to Eq. (5), the removal of lead ions reduced as the concentration of calcium ions was increased.

When the sodium ions of 20 ppm was added, the maximum lead removal capacity and the Langmuir constant were 516.3 mg-Pb/g (i.e. 2.49 mmol-Pb/g) and $0.8968 \, (\text{mg-Pb/L})^{-1}$ (see Fig. 3c). Sodium ions could be exchanged with calcium ions by a similar ion exchange reaction shown above, which resulted in the decrease in the $q_{\max}$ value. As sodium is a relatively weaker metal ion to be complexed with organics than calcium ion [12], its effect on the lead uptake is not obvious as illustrated in the figure. Similar effect from higher ionic strength (NaCl) was also reported by Chen et al. when the regular calcium alginate resins were used for the copper removal [6]. The presence of NaCl reduces the copper sorption by about 10%.

4.2. Biosorption kinetics

Metal ion removal kinetic experiments were performed with the results illustrated in Fig. 4. As shown, the lead can be removed at a significantly high rate. Concentrations of metal ions were reduced sharply within 20 min and no further removal
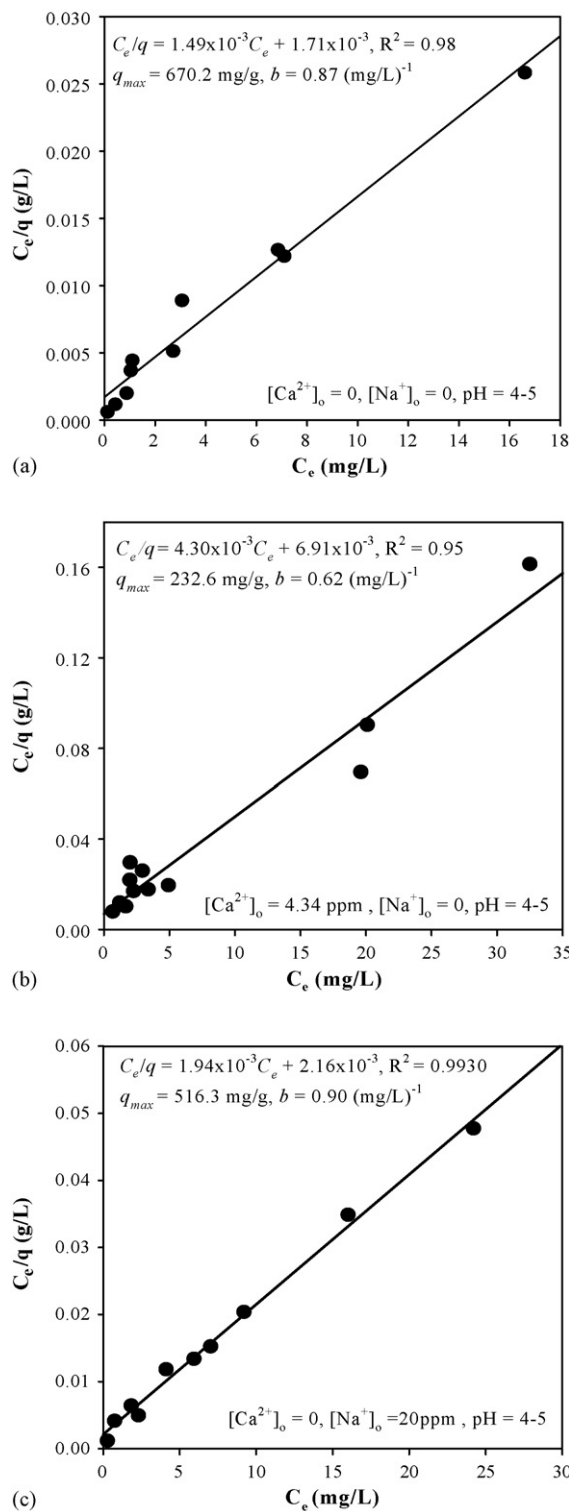

Fig. 3. Determination of the maximum metal removal capacity ($q_{\max}$) and the Langmuir constant (b): (a) Ca- and Na-free solution; (b) with calcium ions; (c) with sodium ions.

could be achieved after 90 min. The equilibrium time here is much shorter than that when most of activated carbons and biosorbents are used as sorbents [11,13]. Reed and Matsumoto used two types of activated carbon to remove cadmium and found that adsorption of the metal was completed in 6 h [13]. Chen
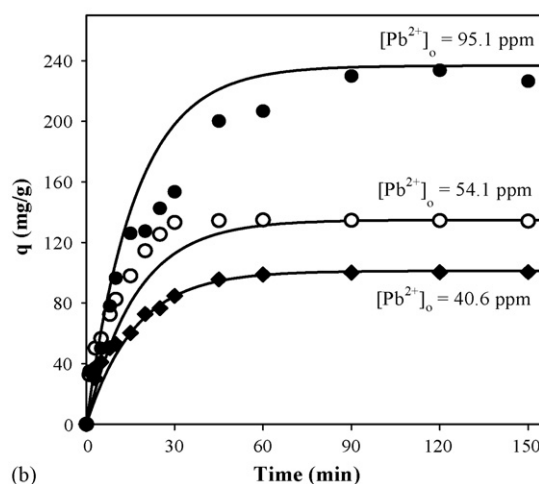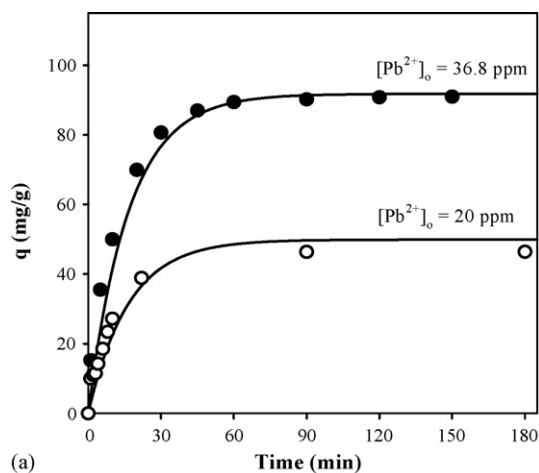
(a)

(b)

Fig. 4. Experimental observation and modeling results of the lead removal history: (a) $[Pb^{2+}]_0 = 20$ and 36.8 ppm; (b) $[Pb^{2+}]_0 = 40.6$, 54.1 and 95.1 ppm. pH = 4–5, $m = 0.4$ g/L, $D_s = 2.95 \times 10^{-11}$ m²/s, $k_f = 2.41 \times 10^{-4}$ m/s.

Fig. 5. Effect of stirring speed on the lead removal kinetics. $[Pb^{2+}]_0 = 39.3$ ppm, pH = 4–5, $m = 0.4$ g/L, $D_s = 2.95 \times 10^{-11}$ m²/s.

(a)

(b)
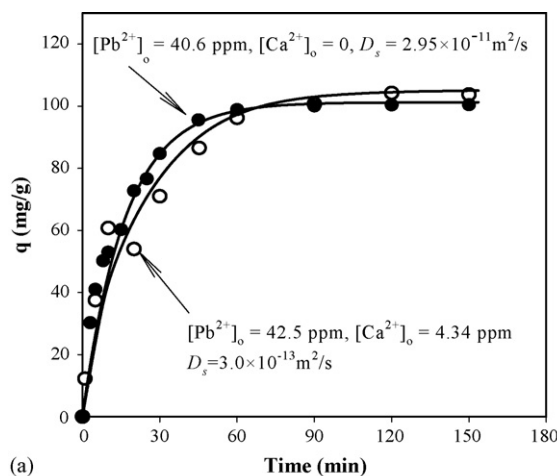
Fig. 6. Effect of other metal ions on the lead removal kinetics: (a) calcium: pH = 4–5, $[Na^+]_0 = 0$, $m = 0.4$ g/L, $k_f = 2.41 \times 10^{-4}$ m²/s; (b) sodium.

et al. reported that the removal of copper by calcium alginate occurred rapidly in the first hour, followed by a slow process that took about 15 h [4]. The shorter equilibration time observed in this study is due to the smaller sizes of the resins used, which essentially reduces the mass transfer resistance in the removal process.

Two kinetic experiments with the same initial concentration were carried out in order to find out the kinetic controlling mechanism(s). In the experiments, two different stirring speeds were used. As shown in Fig. 5, the uptake was faster when the fast stirring was applied. This observation clearly indicates that mass transfer (or diffusion) plays an important role in the lead removal process. Hence, the diffusion-controlled model discussed previously was used to describe the process.

The solution chemistry also can affect the removal process as illustrated in Fig. 6. The removal rate in the lead solution containing calcium ions was slightly slower than that for the calcium-free lead solutions (Fig. 6a) in the first phase (or first 60 min). Interestingly, presence of sodium ions, on the other hand, improved the kinetics as demonstrated in Fig. 6b.
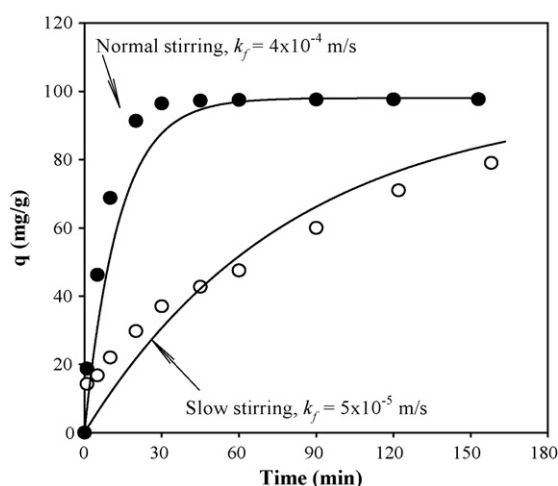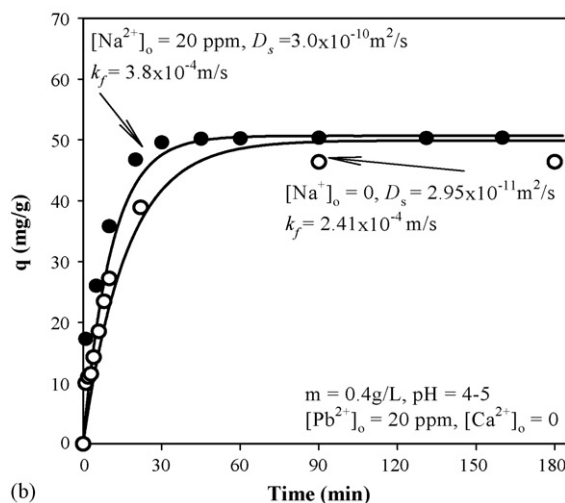
In the kinetic model discussed above, the surface diffusivity D_s and the external mass transfer coefficient k_f are two key kinetic parameters in determining the removal rate. It would be inaccurate to obtain the two parameters simultaneously by fitting the model results with the kinetic experimental data. In order to find the D_s, which results from the properties of this new adsorbent, k_f value was first estimated by a theoretical equation.

A method to calculate k_f (m/s) for ion exchange resins was used [14]:

$$\frac{k_f d}{D} = 2 + 0.44 \left(\frac{\rho d U_L}{\mu} \right)^{0.5} \left(\frac{\mu}{\rho D} \right)^{0.38} \tag{8}$$

where D is the ion diffusivity in the bulk solution (m^2/s), U_L the superficial liquid velocity, d the particle diameter (m), ρ the liquid density (kg/m^3) and μ is liquid viscosity (kg/m s).

The typical value of bivalence metal ion diffusivity in the solutions is about 1×10^{-9} m^2/s [15]. Accordingly, this value was used in our calculation. U_L was calculated directly from the stirring speed. The influence of the density difference between the liquid and the solids on the U_L could be ignored [14]. The normal stirring speed in the kinetic experiments under various conditions was 180 rpm. As the scale of our experiments was small, we could assume that the liquid in the cylinder tank was moving at the angle speed of 180 rpm around the symmetric axle of the tank. The averaged thread speed along the radius of the tank was therefore regarded as U_L. The U_L used in this calculation was 0.565 m/s. Therefore, the calculated value of k_f by Eq. (8) was 2.41×10^{-4} m/s.

D_s can be found by fitting the modeling results with the experimental data once the k_f value was found. D_s in this removal process was found to be 2.95×10^{-11} m^2/s. The comparisons between the calculated q values and the experimental data were summarized in Fig. 4. As shown, the kinetic model gave very good representations of the experimental observations. In other words, the uptake process is controlled by the diffusion, instead of reactions. Furthermore one set of kinetic parameters (i.e. D_s and k_f) can exactly describe the process with five different initial concentrations.

An equation to estimate D_s value ($D_{s,\text{theory}}$) was proposed in the literature [14], which related the ion diffusivity in the particles ($D_{s,\text{theory}}$) with that in bulk solutions (D) and the particle porosity (ε):

$$D_{s,\text{theory}} = D \left[\frac{\varepsilon}{2 - \varepsilon} \right]^2 \tag{9}$$

The typical value of D is 1×10^{-9} m^2/s [15]. ε can be estimated by replacing the actual fractional void volume with the weight fraction of the imbibed solvent. The value of ε measured by this way was 0.48. Thus the $D_{s,\text{theory}}$ calculated was 9.97×10^{-11} m^2/s. By comparing the $D_{s,\text{theory}}$ with the D_s of 2.95×10^{-11} m^2/s used in the modeling, we can know that these two values are quite close to each other. Comparing the kinetic parameters obtained here with the literature showed that the values here are within the ranges reported [16–18]. The D_s and k_f for the adsorption of Cd^{2+} onto aluminum oxide with an averaged diameter of 60 μm were 1.5×10^{-11} m^2/s and 1.7×10^{-3} m/s

[17]. For the recycled iron material, the D_s and k_f values were 1.5×10^{-14} and 1.5×10^{-4} m/s (60 × 80 mesh) and 1.5×10^{-11} and 1.7×10^{-3} m/s (30 × 40 mesh), respectively as reported by Smith and Amini [18].

Modeling of the lead removal history under two different stirring speeds was subsequently performed as illustrated in Fig. 5. In the modeling, the diffusivity (D_s) was maintained the same as that used in the previous cases (see Fig. 4). As the stirring speed values were increased or decreased significantly, two different values of k_f were therefore used. As demonstrated, the kinetic model gives a good description of the removal process. The k_f value in the slow stirring case was lower than that in the normal cases (Fig. 4). Meanwhile the k_f in the fast stirring case was larger than that in the normal, due to the slightly faster speed in the glass beakers. The results from these two cases (Fig. 5) show that the stirring speed essentially controls the external mass transfer (or k_f), while it is less important in the mass diffusion within the particles.

The presence of calcium and sodium on the removal was studied by using the kinetic model as illustrated in Fig. 6. The removal histories in the absence and presence of calcium ions were first modeled, which assumed the same value of the k_f for both cases. The respective equilibrium model's parameters of q_{max} and b for these two cases were used (see Fig. 3a and b). The value of the D_s in the presence of calcium ions was decreased significantly from 2.95×10^{-11} to 3.0×10^{-13} m^2/s, indicating the dramatic increase in the mass transfer resistance inside of the particles. By using the kinetic parameters, it is shown that the model gives a good description of the removal history as one can see in Fig. 6a.

The influence of sodium's existence was described by the kinetic model as shown in Fig. 6b. The removal history in the absence of sodium ions was also plotted in the figure. Te respective equilibrium model's parameters of q_{max} and b for these two cases were used (see Fig. 3a and c). The comparison of the modeling results and experimental observations shows that the model did a good job in the representation of the data. The D_s for this case was increased from 2.95×10^{-11} to 3.0×10^{-10} m^2/s, demonstrating the enhancement of the diffusion inside of the particles. The k_f value for the case of the sodium presence was slightly increased.

5. Conclusions

The Ca-alginate based ion exchange resin was applied in the removal of lead ions from the synthesized waste streams in batch reactors. It was found that higher initial pH would cause higher metal removal. The optimum pH was found to be 4.0 or higher. The Langmuir equation well described the equilibrium data in various cases. The maximum removal capacity (q_{max}) for lead ions was 3.25 mmol-Pb/g for the solutions free of calcium and sodium ions. However, the q_{max} values decreased to 1.12 and 2.49 mmol-Pb/g for the solutions containing calcium and sodium, respectively. The competitions among the metal ions for the ion exchange sites were the reason causing the reduction.

The kinetic experiments were conducted with various conditions. It was found that the metal ions can be removed at a

significantly high rate. More of metal can be removed within 20 min and the equilibrium was achieved in 90 min, which is much shorter than most of adsorption processes by activated carbons and biosorbents. The presence of calcium and sodium ions can alter the uptake kinetics. Calcium ions reduced the removal rate, while sodium ion can improved it. The experiments illustrated that the mass transfer was the controlling mechanism for this process. It is therefore that a diffusion-controlled model was employed in the simulation.

It was demonstrated that the diffusion-controlled model successfully described the uptake kinetics with various operational conditions. The removal histories with five different initial concentrations were described by using a set of kinetic parameters of diffusivity and external mass transfer coefficient. Through the simulations, we also found that the presence of calcium ions reduced the diffusion in the resins, while that of sodium enhanced it.

Acknowledgements

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