Enhanced adsorption of cesium on PVA-alginate encapsulated Prussian blue-graphene oxide hydrogel beads in a fixed-bed column system

Jiseon Jang, Dae Sung Lee

Department of Environmental Engineering, Kyungpook National University, 80 Daehak-ro, Buk-gu, Daegu 41566, Republic of Korea

Highlights

- PVA-alginate encapsulated PB-GO hydrogel bead were synthesized.
- A fixed-bed column reactor packed with PB-GO hydrogel beads was used for cesium removal.
- The effects of the operating parameters on the breakthrough curves were investigated.
- The Yoon–Nelson model gave the best fit to the experimental data.

Graphical Abstract

Continuous fixed-bed column reactor

The effect of initial cesium concentration

Abstract

A continuous fixed-bed column study was performed using PVA-alginate encapsulated Prussian blue-graphene oxide (PB-GO) hydrogel beads as a novel adsorbent for the removal of cesium from aqueous solutions. The effects of different operating parameters, such as initial cesium concentration, pH, bed height, flow rate, and bead size, were investigated. The maximum adsorption capacity of the PB-GO hydrogel beads was 164.5 mg/g at an initial cesium concentration of 5 mM, bed height of 20 cm, and flow rate of 0.83 mL/min at pH 7. The Thomas, Adams–Bohart, and Yoon–Nelson models were applied to the experimental data to predict the breakthrough curves using non-linear regression. Although both the Thomas and Yoon–Nelson models showed good agreement with the experimental data, the Yoon–Nelson model was found to provide the best representation for cesium adsorption on the adsorbent, based on the $\chi^2$ analysis.

1. Introduction

The effective and safe management of liquid wastes is a primary requirement in the nuclear industry. These wastes arise at every stage of the nuclear fuel cycle and must be treated to ensure compliance with stringent regulatory standards before final disposal into the environment. In particular, the need to accommodate wastes arising from the decommissioning of nuclear installations has gradually increased over the past two decades. Among the main fission products in nuclear waste solutions, $^{137}\text{Cs}$ and $^{134}\text{Cs}$ are of special concern due to their long half-life (30 years), high fission yield (6.09%), high activity, and high water solubility. These properties enable the migration of cesium through ground water to the biosphere, and this cesium poses a serious threat to the environment and human health (Ding and Kanatzidis, 2007).

Several physico–chemical methods have been investigated for the removal of radioactive cesium from wastewater, including solvent extraction, chemical precipitation, membrane processes, coagulation, electrodeionization, and ion-exchange (Iwanade et al.,...
and activated carbon, have been used to remove radioactive elements. A variety of adsorbents, such as clays, zeolites, biopolymers, metal oxides, and activated carbon, have been used to remove radioactive cesium from contaminated water (Chakraborty et al., 2007; Ding et al., 2013). However, these adsorbents are either expensive or inefficient for practical application. Therefore, it is necessary to develop efficient and inexpensive adsorbents with high removal capacity for cesium.

Prussian blue (PB), a class of cyano-bridge coordination polymers based on hexacyanometallates and transition metal ions, has been used as an adsorbent in the separation of cesium because of its high affinity for cesium. It was used to treat cesium exposure after the Chernobyl nuclear reactor disaster and the Goiânia accident in Brazil (Melo et al., 1997). However, PB obtained by chemical precipitation is intrinsically a very fine powder, and it is quite unfeasible to separate the used adsorbent from the treated solution using either centrifugation or filtration. Therefore, anchoring PB to graphene oxide (GO) could be a very effective method to improve its hydrodynamic characteristics. There are many oxygen-containing functional groups at the GO surface, such as hydroxyl, epoxide, carbonyl, and carboxy. This makes GO water soluble and improves the accessibility and affinity of GO to the adsorbates (Zhao et al., 2012).

Alginate, a naturally occurring anionic polymer typically obtained from brown seaweed and bacteria, has been widely used for entrapment of adsorbents in the environmental applications due to its capability to hydrogels with multivalent cations (Kuen and David, 2012). However, alginate hydrogel beads typically give poor chemical resistance and mechanical strength. To improve these properties, alginate can be blended with poly vinyl alcohol (PVA), which possesses desirable properties such as non-toxicity, high elasticity, and mechanical strength. In addition, the immobilization of nanomaterials in spherical polymeric matrices is promising for improvement of adsorption efficiency, especially in large-scale applications.

In this study, PVA-alginate encapsulated Prussian blue-graphene oxide (PB-GO) hydrogel beads were synthesized to remove cesium from aqueous solutions. The PB-GO composites were prepared as PB nanoparticles attached to the surface of multi-layered GO sheets. The chemical and physical characterization of the synthesized composites was conducted by scanning electron microscopy (SEM), Brunauer–Emmett–Teller (BET) analysis, X-ray photoelectron spectroscopy (XPS), Fourier transform infrared/near infrared (FT-IR/NIR) spectroscopy, and Raman spectroscopy. The PVA-alginate hydrogel beads with PB-GO on their cross-linked structure were prepared and packed in a fixed-bed column system. The fixed-bed operation has a number of advantages, such as easy operation, low cost, and relatively easy scale up from a laboratory procedure. The effect of various parameters, such as initial cesium concentration, flow rate, bed height, and adsorbent size, on the removal of cesium in the fixed-bed column system was investigated. Furthermore, the Thomas, Adams–Bohart, and Yoon–Nelson models were used to analyze the breakthrough curves using non-linear regression methods.

2. Materials and methods

2.1. Preparation of PVA-alginate encapsulated PB-GO hydrogel beads

The graphene oxide sheets were synthesized from purified natural graphite by the modified Hummer’s method (Hummers and Offeman, 1958). To prepare the PB nanocomposites, 5 mL of K$_4$[Fe(CN)$_6$]·3H$_2$O solution (157 mg/mL) was slowly dropped into a 100 mL FeCl$_3$·6H$_2$O solution (92 mg/mL) under sonication at 30 °C. The reaction mixture was kept at room temperature overnight. Then, the precipitated product was washed several times with distilled water until the solution became colorless. The synthesized PB nanocomposites were dried in an oven at 60 °C for 24 h. The PB nanoparticles (0.3 g) were immersed in 20 mL of GO suspension (0.3 mg/mL) in sonication fluid for 6 h. The PB-GO composite was dried in a vacuum oven at 30 °C for 24 h.

PVA-alginate encapsulated PB-GO hydrogel beads were formed by crosslinking the PVA with saturated boric acid using the drop method. The PB-GO suspensions were combined with a mixed solution of 80 mL of PVA (12% w/v) and sodium alginate (1% w/v). Sodium alginate provided a spherical skeleton for the PVA hydrogel beads while they cured (Hui et al., 2014). The mixture was dropped into a 500 mL solution of boric acid (5% w/v) and calcium chloride (2% w/v) using a syringe to form the hydrogel beads and stirred for 1 h. The hydrogel beads were stored at room temperature for 24 h. The beads were washed and stirred several times with distilled water until pH 7 was reached. Fig. 1 shows a schematic diagram of the synthesis of the PVA-alginate encapsulated PB-GO hydrogel beads. The beads had a reasonably good spherical shape with diameters of 2.1 ± 0.3 mm, determined by measuring 50 beads with a vernier caliper. A drying test indicated that the hydrogel beads had a water content of 90%.

2.2. Characterization of PVA-alginate encapsulated PB-GO hydrogel beads

Field emission transmission electron microscopy (FE-TEM, Titan G2 ChemiSTEM Cs Probe, FEI Company, Netherlands) was used to identify the morphology of the PB-GO composite and the presence of trace elements. Surface and vertical cross sectional images of the PB-GO hydrogel beads were obtained using field emission scanning electron microscopy with energy dispersive X-ray spectroscopy (FESEM-EDX, SU8220, Hitachi, Japan). The pore size distribution, pore volume, and pore diameter were determined according to the Barrett–Joyner–Halenda sorption model using a specific surface area analyzer (Autosorb-iQ & Quadrasorb SI, USA). The specific surface area was determined from the N$_2$ sorption/desorption isotherm fitted by the BET model. A variety of oxygenated functional groups of the GO and PB-GO hydrogel beads were determined by FT-IR/NIR spectroscopy (Spectrum 100, PerkinElmer, USA). The surface chemical composition and functional groups of the graphene oxide were identified by XPS using an AXIS Ultra spectrometer with a high-performance Al monochromatic source operated at 15 kV. Raman spectra were recorded using a Renishaw System 1000 with a 50 mM He-Ne laser operating at 514 nm and a CCD detector.

2.3. Continuous fixed-bed column studies

Fig. 2 shows a schematic diagram of a fixed-bed column system. The fixed-bed column reactor was designed using glass tubes with a 1.5 cm internal diameter and maximum 20 cm bed height. The PB-GO hydrogel beads with different average diameters (2, 3, or 5 mm) were packed into the column to yield the desired bed height for the adsorbent (5, 10, or 20 cm) between two supporting layers of glass wool. A cesium solution (1, 3, 5, or 10 mM) at neutral pH was passed through the up-flow column reactor at a specified flow rate (0.83, 1.67, or 2.49 mL/min) using a Masterflex L/S digital pump. In addition, the influence of pH on the adsorption of cesium onto the PB-GO hydrogel beads was investigated (in the range of pH 1–9). All of the experiments were performed at room temperature (20 ± 1 °C). The effluent was collected at regular time intervals
from the top of the column and was then analyzed by inductively coupled plasma mass spectrometry (Optima 2100 DV, PerkinElmer Co., USA). All adsorption experiments were carried out in triplicate and the mean values were used in the data analysis.

2.4. Fixed-bed adsorption process analysis

The loading behavior of the PB-GO hydrogel beads into the fixed-bed column is expressed in terms of the normalized concentration \(C/C_0\) (where \(C\) and \(C_0\) are the inlet and outlet cesium concentrations, respectively) as a function of time \((t)\) for a given bed height, giving a breakthrough curve. The time for breakthrough appearance and the shape of the breakthrough curve are very important characteristics for determining the operation and the dynamic response of the fixed-bed column (Rao and Viraraghavan, 2002). The effluent volume \((V_{eff})\) can be calculated from:

\[
V_{eff} = Q t_{total}
\]

where \(t_{total}\) and \(Q\) are the time of exhaustion (min) and volumetric flow rate (mL/min), respectively. For a given feed concentration and flow rate, the area under the breakthrough curve can be obtained by integrating the adsorbed concentration \(C_{ad}\) (mg/L) versus \(t\) (min) plot and used to find the total adsorbed cesium capacity, \(q_{total}\) (mg):

\[
q_{total} = \frac{Q}{1000} \int_{t=0}^{t_{total}} C_{ad} dt
\]

The equilibrium uptake \(q_{eq}\) (mg/g) of the column is calculated from:

\[
q_{eq} = \frac{q_{total}}{x}
\]

where \(x\) (g) is the total dry weight of the adsorbent in the fixed-bed column. The total amount of cesium added into the column, \(W_{total}\) (mg), is determined from:

\[
W_{total} = \frac{C_0 Q t_{total}}{1000}
\]

The removal percentage of cesium for the fixed-bed column (at saturation) is calculated from:

\[
R(\%) = \frac{q_{total}}{W_{total}} \times 100
\]

The breakthrough adsorption capacity for cesium can be determined from the following equation:

\[
q_b = \left( \frac{C_i - C_b}{m} \right) b_v
\]

where \(C_i\) and \(C_b\) are the initial and breakthrough concentrations (ppm) of cesium ion, respectively; \(b_v\) is the breakthrough volume of cesium solution in liters and \(m\) is the mass of the adsorbent used (g).

3. Results and discussion

3.1. Characterization of PB-GO composites

Fig. S1(a) shows a Raman spectrum of the GO sheets, where the disorder band (D band) is at 1339.22 nm and the in-phase vibra-
tion (G band) is at 1567.04 nm. The spectrum of the GO sheet agrees with the reference spectrum (Paredes et al., 2008). C1s XPS was used to further study the surface composition of the GO sheet. Fig. S1(b) clearly shows a high level of oxidation in the GO sheet. The four chemical binding energy peaks are attributed to the carbon groups in the non-oxygenated ring. These peaks have an effective area much higher than the non-oxygenated signal at 284.8 eV, confirming the high oxidation level of the synthesized GO sheet (Bosch-Navarro et al., 2012). FT-IR spectroscopy was employed to investigate the bonding interactions in the GO sheets and PB-GO composite (Fig. S1(c)). The intense bands at 3450 and 1250 cm$^{-1}$ are associated with stretching vibrations of the O–H and CO–H bonds. The band at 1700 cm$^{-1}$ is attributed to stretching of the C=O bond of carboxyl groups. The band present at 1100 cm$^{-1}$ is assigned to deformation of the C–O bond. Furthermore, three other peaks around 2080, 602, and 498 cm$^{-1}$ are also present in the spectrum for PB. They can be ascribed to the CN metal–carbon–nitrogen bending modes of PB (Farah et al., 2012; Yue et al., 2015), which confirms that the nanoparticles on the surface of the GO sheet (in Fig. S1(c)) are PB.

The TEM image in Fig. S2(b) clearly shows that the uniform PB nanoparticles were embedded in multi-layered GO sheets (3–8 layers) with an interlayer distance of 0.37 nm (Chen et al., 2012). SEM images of the vacuum dried PB-GO composite show that the full-sized beads were spherical with an average diameter of 1.0 mm (Fig. S2(c)). Fig. S2(d) reveals that the vertical cross section of the beads contains several porous channels.

3.2. Fixed-bed column studies

3.2.1. Effect of pH

The effect of pH on the adsorption capacity of the PVA-alginate encapsulated PB-GO hydrogel beads in the fixed-bed column was investigated. The adsorption experiments were carried out at an initial cesium concentration of 1 mM, flow rate of 0.83 mL/min, and bed height of 5 cm. Fig. 3 shows the breakthrough profile of cesium adsorption at different initial pH values, ranging from 1 to 9. With an increase of the pH from 1 to 7, the breakthrough curves shifted from left to right, which indicated that more cesium was removed, and less time was required to reach the saturation point. These results indicated that the adsorption capacities increased with increasing pH. This occurred because some of the PB on the hydrogel beads may dissolve under acidic conditions (Yang et al., 2014). However, as the pH was increased further from 7 to 9, a significant negative effect of the alkaline pH on the adsorption capacity was observed, similar to what was previously reported (Nilchi et al., 2011). This low stability was due to the strong interaction between ferric ions and hydroxyl ions at an alkaline pH, which results in Fe–CN–Fe bond cleavage in PB (Ricci et al., 2003). It was also observed that maximum adsorption capacity of PVA-alginate encapsulated PB-GO hydrogel beads was obtained at pH 7, and thus all further adsorption experiments in this work were conducted at an initial pH of 7.

3.2.2. Effect of initial cesium concentration

The effect of initial cesium concentration (1, 3, or 5 mM) on the adsorption in the fixed-bed column was studied, while flow rate and bed height were held constant at 0.83 mL/min and 20 cm, respectively. As can be seen in Fig. 4(a), the breakthrough time decreased with increasing influent cesium concentration. At lower initial cesium concentrations, the breakthrough curves were dispersed and the breakthrough rate was slower. An increased initial cesium concentration gave the steeper slope of breakthrough curves because of the faster mass-transfer flux from the bulk solution to the particle surface due to increased diffusion coefficient. Higher initial cesium concentration resulted in better column performance with the increase of driving force and decrease in the adsorption zone length for adsorption process (Chen et al., 2011; Uddin et al., 2009). These results indicated that the concentration gradient change affected the saturation rate and breakthrough time (Goel et al., 2005). Furthermore, with an increase in initial cesium concentration from 1 to 5 mM, the adsorption capacity of the PB-GO hydrogel beads increased from 141.6 to 163.1 mg/g (Table 1).

3.2.3. Effect of flow rate

The breakthrough curves for different flow rates (0.83, 1.67, and 2.49 mL/min) at a constant initial cesium concentration (1 mM) and at a fixed-bed height of 20 cm are shown in Fig. 4(b). The breakthrough curves were steeper at the higher flow rates because cesium ions did not have enough time to make contact with the PB-GO hydrogel beads. Both the breakthrough time and saturation time decreased with an increased flow rate (Table 1). An increase in flow rate might decrease the opportunity of the contact between the binding sites and cesium ions. In addition, the decrease in the saturation adsorption capacity of the column was observed with an increase of the flow rate. At higher flow rate, the residence time of solute in the column is insufficient for adsorption equilibrium to be reached (Maiti et al., 2009).

3.2.4. Effect of bed height

The effect of bed height (5, 10, or 20 cm) on the breakthrough curve at a constant initial cesium concentration (1 mM) and flow rate (0.83 mL/min) is shown in Fig. 4(c). Both breakthrough time and saturation time increased with an increase of the bed height. Since an increase in the total amount of the adsorbent provided more adsorption binding sites, a longer time was required to reach the breakthrough and saturation points. Fig. 4(c) shows that the slope of the breakthrough curve is lower for a higher bed height, indicating a slow attainment of the saturation point after achieving breakthrough at a higher bed height. Similar to the breakthrough and saturation times, an increase in bed height from 5 to 20 cm led to an increase of the adsorption capacity of the PB-GO hydrogel beads from 141.6 to 163.1 mg/g (Table 1). This adsorption capacity increase could be attributed to the long residence times for cesium...
ions in the adsorption region, which provide sufficient time for the solute to further diffuse into the adsorbent bed. The breakthrough time also increased with increase in bed height.

3.2.5. Effect of adsorbent size

The influence of particle size on the adsorption capacity of the PB-GO hydrogel beads was studied with respect to average particle size. The results indicated that adsorption capacity decreased with increasing particle size. This is likely due to the decrease in surface area available for adsorption with larger particle sizes.

![Graphs showing the influence of operational parameters on the cesium adsorption breakthrough curves using PB-GO hydrogel beads.](image)

Fig. 4. The influence of operational parameters on the cesium adsorption breakthrough curves using PB-GO hydrogel beads: (a) influent cesium concentrations, (b) flow rate, (c) bed height, and (d) adsorbent size.

Table 1

Parameters in the fixed-bed column for cesium adsorption by the PVA-alginate encapsulated PB-GO hydrogel beads.

<table>
<thead>
<tr>
<th>Experimental conditions</th>
<th>Experimental parameters of breakthrough curve</th>
</tr>
</thead>
<tbody>
<tr>
<td>C0 (mM) F (mL/min) H (cm)</td>
<td>t_b (h) t_s (h) V_eff (mL) q_b (mg/g) q_s (mg/g) R (%)</td>
</tr>
<tr>
<td>1 0.83 20</td>
<td>2 15 747 141.1 161.1 99.0</td>
</tr>
<tr>
<td>3 0.83 20</td>
<td>1.5 12 597.6 142.6 162.6 95.0</td>
</tr>
<tr>
<td>5 0.83 20</td>
<td>1 10 498 144.5 164.5 91.1</td>
</tr>
<tr>
<td>1 0.83 5</td>
<td>1 10 747 134.8 154.8 84.6</td>
</tr>
<tr>
<td>1 1.67 20</td>
<td>1 11 747 137.1 157.1 96.3</td>
</tr>
<tr>
<td>1 2.49 20</td>
<td>0.5 10 597.6 134.5 154.5 88.6</td>
</tr>
</tbody>
</table>

C0 (mM) = influent concentration (mg/L), F = flow rate (mL/min), H = bed height (cm), t_b = breakthrough time (h), t_s = saturation time (h), V_eff = effluent volume (mL), q_b = adsorption at breakthrough (mg/g), q_s = adsorption at saturation (mg/g), R = total cesium removal at saturation (%).
size (in the range of 2–5 mm). Increasing the adsorbent particle size increased the breakthrough time (Fig. 4(d)). The adsorption capacity decreased from 161.1 to 130.96 mg/g as the average particle size increased from 2 to 5 mm. Smaller particles have a shorter diffusion path, thus allowing cesium ions to penetrate deeper and more quickly into the adsorbent. In addition, the total external surface area per unit volume is larger for the smaller size of the adsorbent material inside the column (Malkoc et al., 2006).

3.3. Dynamic modeling of the breakthrough curves

Successful design and operation of a fixed-bed column system requires the prediction of the breakthrough curve for the effluent. Therefore, the breakthrough curves for the adsorption of the PB-GO hydrogel beads were analyzed using the Adams–Bohart, Thomas, and Yoon–Nelson models to determine the dynamic behaviors in the column. The experimental results were fitted to the models through non-linear regression using Matlab 7.8. The fitness of the breakthrough model equations was evaluated by Chi-square ($\chi^2$) and average percentage errors (APE) (Ho and Wang, 2004; Subramaniam and Das, 2009).

\[
\chi^2 = \sum \frac{\left(\left(C/C_0\right)_{\text{calc}} - \left(C/C_0\right)_{\text{exp}}\right)^2}{\left(C/C_0\right)_{\text{exp}}} \tag{7}
\]

\[
\text{APE} = \frac{100}{n} \sum \left| \frac{\left(\left(C/C_0\right)_{\text{calc}} - \left(C/C_0\right)_{\text{exp}}\right)}{\left(C/C_0\right)_{\text{exp}}} \right| \tag{8}
\]

where $n$ is the number of experiments, and $(C/C_0)_{\text{calc}}$ and $(C/C_0)_{\text{exp}}$ are the observed and estimated values, respectively.

3.3.1. The Thomas model

The Thomas model is one of the most widely used breakthrough models in fixed-bed column performance theory. It assumes Langmuir kinetics for adsorption and desorption with no axial dispersion. The model expression can be expressed as (Thomas, 1994):

\[
\frac{C}{C_0} = \frac{1}{1 + \exp\left(k_n q_0 x/v - k_n C_0 t\right)} \tag{9}
\]

where $k_n$ (mL/min/mg) is the Thomas rate constant, $q_0$ (mg/g) is the adsorption capacity, $x$ (g) is the amount of adsorbent in the column, and $v$ (mL/min) is the volumetric flow rate.

The Thomas rate constant and adsorption capacity of the PB-GO hydrogel beads were obtained using non-linear regression according to Eq. (8), and the results are presented in Table 2. It is clear from Table 2 that the Thomas model’s correlation coefficients are high ($R^2 = 0.991–0.998$) and its corresponding $\chi^2$ and APE values are low, which indicates that the model is able to describe the dynamic behaviors in the fixed-bed column. With an increase of initial cesium concentration, the value of $k_n$ decreased. This is because the driving force for adsorption is the concentration difference between the cesium on the hydrogel beads and in the solution (Chen et al., 2012). As the flow rate increased, the unavailability of reaction sites caused a decrease in the value of $q_0$. With an increased bed height, the value of $k_n$ decreased. Thus, the higher flow rate, lower initial cesium concentration, and lower bed height would decrease the adsorption of cesium on the fixed-bed column. The predicted and experimental breakthrough curves with respect to initial cesium concentration, flow rate, bed height, and adsorbent size are shown in Fig. 4. As can be observed, the Thomas model describes well the breakthrough curves for all the process variables.

3.3.2. The Adams–Bohart model

The Adams–Bohart model is typically used for describing the initial part of the breakthrough curve and is expressed as follows (Bohart and Adams, 1920):

\[
C/C_0 = \exp \left(k_n C_0 t - k_n N_0 Z\right) \tag{10}
\]

where $k_n$ is the kinetic constant (L/mg/min), $N_0$ is the saturation concentration (mg/L), $Z$ is the bed height of the fixed-bed column (cm), and $U_0$ is the superficial velocity (cm/min). The non-linear regression results showed that $k_n$ decreased with an increase of the flow rate, but increased with an increase of both the flow rate and bed height (Table 2). This is attributed to a dominance of external mass transfer activities during adsorption in the column at the initial stages (Auta and Hameed, 2014). The adsorption capacity of the bed ($N_0$) increased with increasing initial cesium concentration and bed height, but decreased with increasing flow rate. However, both low $R^2$ and high $\chi^2$ and APE values indicate that the Adams–Bohart model is less satisfactory than the Thomas model in describing adsorption dynamics. In addition, as can be observed in Fig. 4, the experimental breakthrough curves are not close to those predicted by the Adams–Bohart model.

3.3.3. The Yoon–Nelson model

The Yoon–Nelson model requires no detailed data about the characteristics of the adsorbent physical properties in the fixed-bed column (Yoon and Nelson, 1984). The Yoon–Nelson model is expressed as:

\[
\frac{C}{C_0} = \frac{\exp\left(k_n t - \tau_k\right)}{1 + \exp\left(k_n t - \tau_k\right)} \tag{11}
\]

where $\tau_0$ is the time required for 50% adsorbate breakthrough (min) and $\tau_k$ is a rate constant that depends on the diffusion characteristics of the mass transfer zone (min$^{-1}$). The values of $\tau_k$ and $\tau_0$ decreased and increased, respectively, with increasing bed height and vice versa (Table 2). An increase of both the flow rate and initial cesium concentration led to an increase of $\tau_k$ and $\tau_0$ as the column saturation reached more quickly at a higher initial cesium concentration and flow rate. Table 2 shows that the Thomas model and the Yoon–Nelson model have almost the same $R^2$ values at different experimental conditions, but the Yoon–Nelson model might be a

<table>
<thead>
<tr>
<th>$C_0$ (mM)</th>
<th>$F$ (mL/min)</th>
<th>$H$ (cm)</th>
<th>(a) Thomas model</th>
<th>(b) Adams–Bohart model</th>
<th>(c) Yoon–Nelson model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$k_n$ (L/t)</td>
<td>$q_{max}$ (mg/g)</td>
<td>$\chi^2$</td>
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<td>156.88</td>
<td>25.78</td>
<td>0.995</td>
</tr>
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</table>
better prediction model because of the lower $\chi^2$ and APE values. Furthermore, as can be observed in Fig. 4, the Yoon–Nelson model is satisfactory predictors for the breakthrough curves. Therefore, the Yoon–Nelson model could be used to describe the adsorption behavior of cesium ions in a fixed-bed column under different experimental conditions.

4. Conclusions

PVA-alginate encapsulated PB-GO hydrogel beads were successfully prepared and used for adsorption of cesium in the fixed-bed column system. The adsorption process performed better at lower initial cesium concentration and flow rate, and higher bed height. The Thomas, Adams–Bohart, and Yoon–Nelson models were applied to experimental data to predict the breakthrough curves using non-linear regression. The Yoon–Nelson model was most appropriate for the description of the entire breakthrough curves under different operating conditions. Overall, PB-GO hydrogel beads have a strong potential as an efficient adsorbent for the treatment of wastewater polluted with cesium in continuous operation mode.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.biotech.2016.06.100.

References


