Research article

Investigation of the strontium (Sr(II)) adsorption of an alginate microsphere as a low-cost adsorbent for removal and recovery from seawater

Hye-Jin Hong, Jungho Ryu, In-Su Park, Taegong Ryu, Kang-Sup Chung, Byuong-Gyu Kim*

Korea Institute of Geoscience and Mineral Resources, Gwanghang-no 92, Yuseong-gu, Daejeon, 305-350, Republic of Korea

Article info

Article history:
Received 20 July 2015
Received in revised form 24 September 2015
Accepted 26 September 2015

Keywords:
Seawater
Strontium
Alginate microsphere
Adsorption
Desorption

Abstract

In this paper, we investigated alginate microspheres as a low-cost adsorbent for strontium (Sr(II)) removal and recovery from seawater. Alginate microspheres have demonstrated a superior adsorption capacity for Sr(II) ions (~110 mg/g). A Freundlich isotherm model fits well with the Sr(II) adsorption of an alginate microsphere. The mechanism of Sr(II) adsorption is inferred as an ion exchange reaction with Ca(II) ions. The effects of the solution pH and co-existing ions in seawater are also investigated. Except for a pH of 1–2, Sr(II) adsorption capacity is not affected by pH. However, increasing the seawater concentration of metal cations seriously decreases Sr(II) uptake. In particular, highly concentrated (15,000 mg/L) Na(I) ions significantly interfere with Sr(II) adsorption. Sr(II) desorption was performed using 0.1 M HCl and CaCl₂. Both regenerants show an excellent desorption efficiency, but the FTIR spectrum reveals that the chemical structure of the microsphere is destroyed after repeated use of HCl. Conversely, CaCl₂ successfully desorbed Sr(II) without damage, and the Sr(II) adsorption capacity does not decrease after three repeated uses. The alginate microsphere was also applied to the adsorption of Sr(II) in a real seawater medium. Because of inhibition by co-existing ions, the Sr(II) adsorption capacity was decreased and the adsorption rate was retarded compared with D.I. water. Although the Sr(II) adsorption capacity was decreased, the alginate microsphere still exhibited 17.8 mg/g of Sr(II) uptake in the seawater medium. Considering its excellent Sr(II) uptake in seawater and its reusability, an alginate microsphere is an appropriate cost-effective adsorbent for the removal and recovery of Sr(II) from seawater.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Presently, seawater is considered to be an important source of minerals, considering the depletion of mineral ores on land. Seawater contains approximately $5 \times 10^{16}$ tons of mineral salts, and extraction from this large source is promising and beneficial compared with typical land mining (Bardi, 2010). However, the extraction cost of these metals is a practical problem. Because a large amount of seawater is treated during the extraction process, an economic system is an important key to demonstrating the feasibility of metal extraction from seawater.

In this study, we investigated a low-cost strontium (Sr(II)) adsorbent for removal and recovery from seawater. Sr(II) is a rare earth metal that is widely used in the ceramic and glass manufacturing industries, primarily in television face plate glass and secondarily in ceramic ferrite magnets and other ceramic and glass applications (Ober, 2004). Sr is one of the most abundant minerals in seawater, with an average concentration of 6–7 mg/L (Angino et al., 1966). Almost all Sr in seawater is non-radioactive Sr, and it exists as divalent (Sr(II)) or mono-valent (SrOH⁺) cations in aqueous solutions. Regardless of the abundance of minerals in seawater as well as their many industrial applications, research on the recovery of Sr(II) from seawater has received little attention. Only a few studies have been conducted to recover Sr(II) from seawater. Jeong et al. reported a Sr(II) extraction method from seawater using a liquid membrane (Jeong and Ju, 2002), and V.A. Avramenko recovered Sr from seawater using commercial resin type sorbents (Avramenko et al., 2001).

The Fukushima nuclear plant accident (2011) has led to serious seawater contamination by radioactive strontium (90Sr) (Katsumi...
Shozugawa, 2015; Nagaoka et al., 2015). $^{90}$Sr isotope is a beta-gamma emitter with a half-life of 29 years (Sachse et al., 2012). It genetically affects seawater organisms and eventually causes damage to humans. Thus, the demand for a $^{90}$Sr(II) removal technique from seawater is increasing.

Alginate is a polysaccharide from marine brown algae, and it has the following advantageous characteristics: it is an abundant resource with a low-cost and high bio-compatibility. Alginate is composed of anionic blocks of 1,4 linked $\alpha$-guluronic acid (G) and $\alpha$-mannuronic acid (M) (Sone et al., 2009). It is soluble in water, but it converts to insoluble hydrogel in the presence of certain multivalent cations, such as Ca, Ba and Sr. The gel formation mechanism is well known as an 'egg box model' (Li et al., 2007; Rees and Welsh, 1977). Insoluble alginate beads are widely used as bio-sorbents of various heavy metals due to the many carboxylic groups on the beads, which can react with metal cations (Deze et al., 2012; Lakouraj et al., 2014; Papageorgiou et al., 2006, 2008; Silva et al., 2008).

In addition, there are several studies examining the possibility of using alginate as a rare earth metal selective adsorbent. Song et al. discovered that alginate beads indicate high adsorption capacities for rare earth metals, including Sr(II) (Song et al., 2013). Wu et al. also discovered that alginate beads exhibit a high adsorption capacity for lanthanum (Wu et al., 2010). Also, Arne Haug et al. reported a strong ion binding affinity for Sr(II) in algic acid among alkaline earth metals (Haug and Smidsrod, 1970).

Herein, Sr(II) removal and recovery is investigated for seawater through a bio-sorption process using a low-cost alginate microsphere. Alginate microspheres are synthesized, and their characteristics are analyzed. Then, the Sr(II) adsorption capacity of the alginate microspheres is evaluated, and the chemical aspects of Sr(II) adsorption are discussed. The Sr(II) desorption conditions and reusability of alginate microspheres are also investigated. Finally, an alginate microsphere is applied in a real seawater medium for the adsorption of Sr(II).

2. Materials and Methods

2.1. Materials

To prepare alginate microspheres, sodium algic acid was obtained from Junsei (Japan), and calcium chloride (CaCl$_2$, Samcheon, Republic of Korea) was used for cross-linking the sodium algic acid. Strontium chloride hexahydrate (SrCl$_2$·6H$_2$O, Jinsei, Japan) was applied as a source of Sr(II) solution to evaluate the Sr(II) adsorption capacity of the alginate microspheres. To control the pH of the reaction, standard solutions of 1 and 0.1 M hydrochloric acid (HCl, Junsei, Japan) and sodium hydroxide (NaOH, Jinsei, Japan) were used. Sodium chloride (NaCl, Sigma–Aldrich, USA), Magnesium chloride hexahydrate (MgCl$_2$·6H$_2$O, Sigma–aldrich, USA) and calcium chloride dehydrate (CaCl$_2$·2H$_2$O) were applied to simulate seawater concentration minerals.

2.2. Synthesis of the alginate microspheres

Alginate microspheres were synthesized according to the following procedure. First, a 2 wt% sodium algic acid solution was prepared by solubilizing sodium algic acid in D.I. water, which became a yellow viscous solution. To synthesize the spherical adsorbent, a 2 wt% algic acid solution was supplied drop-wise by a peristaltic pump into a CaCl$_2$ solution under vigorous stirring. Silicon tubes (MasterFlex 96410-13) for supplying a sodium algic acid solution with an inner diameter of 0.8 mm were used to obtain 1–2 mm sized beads. An alginate microsphere gel was immediately formed when the sodium alginate drops contacted with the CaCl$_2$ solution, and the gel was kept in the CaCl$_2$ solution, with 24 h of stirring, to obtain a hardened alginate microsphere gel. The synthesized alginate microsphere gel was washed several times with D.I. water to remove free Ca(II) ions. Finally, alginate microspheres were dried at 60 °C to remove the moisture from the gel beads.

2.3. Characterization of the alginate microsphere

The physico–chemical characteristics of the synthesized alginate microspheres were analyzed. The morphology of the adsorbent was analyzed by scanning electron microscopy (SEM: JSM-6380LA, JEOL, Japan), and the chemical structural changes were characterized by Fourier-transform infrared spectroscopy (FTIR, Jasco).

2.4. Sr(II) adsorption-desorption experiments

A Sr(II) adsorption experiment was conducted using 100 mg/L of Sr(II) in D.I. water and seawater. The composition of Sr(II) spiked seawater is presented in Table 1. The initial Sr(II) concentration in seawater is approximately 6.1 mg/L; however, for the comparison of Sr(II) adsorption behavior in different mediums, Sr(II) was spiked in the seawater.

An aliquot of 0.2 g of the alginate microspheres was applied to 0.1 L of a Sr(II) solution or seawater for 24 h with magnetic stirring at 300 rpm. After the reaction, the solution was filtered using a 0.2-μm PVDF filter, and the Sr(II) concentration was analyzed.

In the pH effect experiment, 100 mg/L of the initial Sr(II) solution was used. The solution pH was controlled three times; before adsorption, in the middle of the reaction (12 h) and at the end of the reaction (24 h). In the co-existing ion effect experiment, the Sr(II) concentration was fixed at 100 mg/L and the seawater concentrations of the cations (Na(15,000 mg/L), Mg(1200 mg/L) and Ca(400 mg/L)) were added. Sr(II) adsorption was conducted in Sr/Na, Sr/Mg and Sr/Ca double component systems to determine the influence of different cations.

Sr(II) uptake by alginate microspheres was calculated by the following equation:

$$q_{e} = \frac{(C_0 - C_e) \times V}{m} \quad (1)$$

$q_e$ denotes Sr(II) uptake (mg/g) by the alginate microsphere and $C_0$ and $C_e$ indicate the initial and equilibrium Sr(II) concentrations (mg/L), respectively. $V$ denotes the solution volume (L), and $m$ is the amount of alginate microspheres (g).

Sr(II) desorption experiments were also conducted using 0.01–1.0 M CaCl$_2$ solutions and 0.1 M HCl as regenerants. Alginate microspheres, which previously adsorbed Sr(II), were washed and then dried at 60 °C. They were applied for desorption experiments. As with the Sr(II) adsorption experiment, 0.2 g of the alginate microsphere was applied to 0.1 L of the regeneration solution for 24 h, and then, the supernatant was filtered using 0.2-μm syringe filters for the Sr(II) concentration analysis. Desorbed amounts of Sr(II) ($q_d$, mg/g) and the desorption efficiency ($D$, %) are derived as follows:

$$q_d = \frac{C_d \times V}{m} \quad (2)$$

<table>
<thead>
<tr>
<th>Table 1 Composition of Sr(II) spiked seawater.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Element</td>
</tr>
<tr>
<td>----------------</td>
</tr>
<tr>
<td>Concentration (mg/L)</td>
</tr>
</tbody>
</table>
The Sr(II) concentration was analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES; Perkin and Elmer). All of the experiments were performed in duplicate.

3. Results and discussion

3.1. Synthesis of the alginate microspheres

The alginate microspheres were prepared as bio-sorbents to adsorb Sr(II) from seawater. Because the alginate microspheres are synthesized by a hardening process by cross-linking a drop of a sodium alginic acid solution with divalent Ca(II) ions, the concentration of CaCl$_2$ affects the shape and size of the adsorbent. SEM images of alginate microspheres are shown in Fig. 1 according to the CaCl$_2$ concentration.

Alginate microspheres synthesized at 0.01 and 0.05 M CaCl$_2$ do not form a spherical shape. If the Ca(II) concentration is not high enough, the sodium alginic acid does not become sufficiently cross-linked. Thus, these microspheres are larger in size compared with those synthesized at higher CaCl$_2$ concentrations and containing more moisture. Thus, they change shape after removing moisture during the drying process. From 0.1 M to 2 M CaCl$_2$, the alginate microspheres exhibit a completely spherical shape. Microspheres formed at 0.1 M CaCl$_2$ exhibited a crumpled surface due to the removal of moisture. Cracks were observed in alginate microspheres synthesized in 0.5–2.0 M CaCl$_2$. These cracks represent the inflexibility of the microsphere. At 0.1–2 M CaCl$_2$, 500–700 μm-sized spherical alginate microspheres were formed.

Fig. 2 shows the FTIR spectrums of the alginate microspheres. Sodium alginic acid has numerous peaks, which indicate various functional groups. A dominant peak at 3000–3500 cm$^{-1}$ indicates the existence of the −OH group. The absorption peaks at 1613 and 1417 cm$^{-1}$ represent the asymmetric and symmetric stretching vibrations of the carboxylate (−COOH) group, respectively (Bajpai and Sharma, 2004). Additionally, the 1027 cm$^{-1}$ and 1097 cm$^{-1}$ peaks indicate OC−OH (Song et al., 2013). After cross-linking with the Ca(II) ion, alginate microspheres show two new peaks at 3610 and 1670 cm$^{-1}$. These changes indicate that the hydroxyl (OH−) and carboxylate (−COO) groups of alginic acid are involved in the cross-linking of alginic acid and the Ca(II) ion. The carboxylic and hydroxyl groups of the guluronic acid part of alginic acid and the divalent Ca(II) ion interact with each other and form an insoluble alginate microsphere (Braccini and Pérez, 2001; Morris et al., 1978; Strand et al., 2003).

Alginate microspheres synthesized at 0.1 and 2 M CaCl$_2$ show clear new peaks at 3610 and 1670 cm$^{-1}$, which indicate the cross-linking of alginic acid. In contrast, alginate microspheres synthesized with 0.01 M CaCl$_2$ do not show these peaks, and the hydroxyl group (OH−, 3000–3500 cm$^{-1}$) is sharpened and shifted to the right side. It seems that the cross-linking reaction does not completely occur due to the low Ca(II) concentration, and the carboxylic groups are not yet involved in the reaction, as only hydroxyl groups reacted with Ca(II).

Considering the FTIR spectrum and SEM images, CaCl$_2$ concentrations higher than 0.1 M yield complete cross-linking of alginate microspheres and show a stable appearance. Thus, the 0.1 M CaCl$_2$ concentration was chosen for alginate microsphere preparation and was used for further study.

3.2. Sr(II) adsorption isotherm experiment

The Sr(II) adsorption isotherm of the alginate microsphere was investigated to evaluate the Sr(II) adsorption capacity. Fig. 3 (a) shows the adsorption isotherm of the Sr(II) of the alginate microsphere. The Sr(II) uptake of the alginate microsphere increases rapidly when the equilibrium concentration of Sr(II) is lower than 50 mg/L. After that concentration, Sr(II) uptake shows a gentle slope. However, the equilibrium does not reach a maximum and gradually increases according to the Sr(II) concentration. Finally, 110 mg/g of Sr(II) uptake is obtained when the equilibrium concentration is 270 mg/L.

Two isotherm models, Langmuir and Freundlich, are employed to analyze Sr(II) uptake of an alginate microsphere (Pérez-Rama et al., 2010). The Langmuir isotherm is given by

$$Q = \frac{k_b C_e}{1 + k_b C_e}$$

where $Q$ is the adsorbed Sr(II) (mg/g), $C_e$ is the equilibrium concentration (mg/L), $k$ is the Langmuir isotherm constant, and $b$ is the theoretical maximum monolayer adsorption capacity of Sr(II) (mg/L).
The Langmuir model assumes a monolayer adsorption and that the adsorption sites are uniformly distributed on the substrate. The Freundlich model is an empirical model in which the condition of the substrate is heterogeneous. The Freundlich model equation is as follows:

\[ Q = K_f C_e^{1/n} \]

where \( K_f \) is the Freundlich constant, which is related to the adsorption capacity, and \( n \) denotes the adsorption intensity.

Both the Langmuir and Freundlich models fit well with the Sr(II) adsorption isotherm. However, the Freundlich isotherm shows better linearity \( (R^2 = 0.984, \text{Fig. 3(a)}) \). This indicates that the Sr(II) adsorbed dominantly by the alginate microsphere formed multiple layers. The higher Freundlich coefficient \( (K_F = 11.3) \) indicates the high Sr(II) adsorption capacity of the alginate microspheres. Song et al. reported consistent results (Song et al., 2013). Song applied Ca-alginate beads to adsorb rare earth metals, such as Sr(II) and La(II) ions, and the adsorption isotherms of these metals fit well with the Freundlich model. The adsorption of divalent ions, such as Sr(II), by alginate base material is dominated by multilayer adsorption.

**3.3. Effect of pH on Sr(II) adsorption**

In this section, the effect of pH on Sr(II) adsorption is investigated. Fig. 4 shows Sr(II) uptake of an alginate microsphere at various pH values. At a pH of 1, Sr(II) is not adsorbed by the alginate microsphere. Ion exchange of Ca(II) and Sr(II) does not occur at this pH. Additionally, only a 16 mg/g of Sr(II) uptake is obtained at a pH of 2. This indicates that the Sr(II) adsorption capacity is decreased at low pH values. Under acidic conditions, the carboxylic \((-\text{COOH})\) and hydroxyl \((-\text{OH})\) groups of the alginate microsphere change to

![Figure 2. FTIR spectrum of alginate microsphere according to CaCl₂ concentration.](image)

![Figure 3. (a) Sr(II) adsorption isotherm on alginate microsphere [Adsorbent: 0.2 g; solution volume: 0.1 L; reaction time: 24 h; reaction temperature: 25°C, 300 rpm] Fig. 3(b) Released amount of Ca(II) from alginate microsphere according to Sr(II) uptake.](image)
the protonated form, and cross-linking ions (Ca(II)) are released to the solution (Lagoa and Rodrigues, 2007). Thus, the ion exchange reaction does not occur and the Sr(II) adsorption capacity is decreased.

At a pH of 4–8, the alginate microsphere shows a similar adsorption capacity (40 mg/g). Considering that seawater pH is approximately 7–8, the alginate microsphere adsorption of Sr(II) is not influenced by the solution pH.

### 3.4. Effect of ions in seawater on Sr(II) adsorption

The effect of co-existing ions in seawater on Sr(II) adsorption is investigated. Three major cations in seawater are Na(I), Mg(II) and Ca(II). Seawater composition shows some slight variance depending on the ocean, but the average Na(I), Mg(II) and Ca(II) concentrations are known as 15,000, 1200 and 400 mg/L, respectively. The Sr(II) adsorption capacity of alginate microspheres is evaluated using these concentrations of co-existing ions.

Fig. 5 shows the Sr(II) uptake of the alginate microsphere when the seawater concentration of Na(I), Mg(II) and Ca(II) is used in the solution. Highly concentrated Na(I) ions cause the highest inhibition of Sr(II) uptake. Only 17 mg/g of Sr(II) was adsorbed by the alginate microsphere. Na(I) is a mono-valent cation, which cannot be the cross-linking ion of the alginate microsphere. However, extremely high concentrations change the ionic strength, thus interfering with Sr(II) adsorption. Mg(II) and Ca(II) also cause Sr(II) uptake to decrease. 24 and 22 mg/g Sr(II) uptakes are obtained, respectively. These two ions can cross-link with the alginate, thereby competing with Sr(II) in the ion exchange reaction. Considering that the Mg(II) concentration (1200 mg/L) is 3 times higher than Ca(II) (400 mg/L), the Ca(II) ion shows a stronger inhibition effect than the Mg(II) ion of the Sr(II) adsorption reaction.

### 3.5. Sr(II) desorption and reusability experiment

For repeated use of an alginate microsphere, desorption of Sr(II) from alginate microspheres is also studied. Sr(II) desorption occurs via two different mechanisms. The first mechanism is Sr(II) desorption by reducing the pH. The carboxylic group (–COOH), which is an important functional group involving the adsorption of the Sr(II) ion in alginic acid, has a pKₐ value of 4.2 (Lagoa and Rodrigues, 2007). The binding sites in alginate microspheres convert to protonated forms at low pH, releasing the previously bound Sr(II) ions (Silva et al., 2008). The other mechanism is ion exchange with the Ca(II) ion and the adsorbed Sr(II) ion. Contact with the high concentration CaCl₂ solution causes ion exchange between the Ca(II) in the solution and the adsorbed Sr(II) ions on the alginate microsphere to match the equilibrium with Ca(II) ions.

Fig. 6 (a) shows the Sr(II) desorption efficiency with various concentrations of CaCl₂ and 0.1 M HCl. The Sr(II) desorption efficiency increases with the increasing CaCl₂ concentration, and reaches an 100% desorption efficiency with CaCl₂ concentrations higher than 0.5 M. It is considered that 0.5 M Ca(II) is sufficient for exchanging all of the bound Sr(II) ions in the alginate microsphere. HCl (0.1 M) also shows greater than an 87.0% desorption efficiency.

Fig. 6 (b) shows Sr(II) uptake of the alginate microsphere when it is repeatedly used for Sr(II) adsorption with different regeneration solutions. A fresh alginate microsphere has a Sr(II) adsorption capacity of 41.2 mg/g. In the second adsorption, all of the regeneration solutions show similar Sr(II) uptake compared with a fresh alginate microsphere. CaCl₂ solutions (0.01–0.05 M) also exhibit similar Sr(II) uptake to fresh alginate microspheres, despite the incomplete regeneration. Alginate microspheres have sufficient available Sr(II) adsorption sites, and thus, the Sr(II) adsorption capacity does not decrease until the second adsorption.

In the third adsorption, 0.01–0.05 M CaCl₂ treated adsorbent shows a 25% decreased Sr(II) sorption capacity. In the third adsorption, the Sr(II) binding sites on the alginate microspheres are fully occupied, and incomplete regeneration causes a decrease in the Sr(II) sorption capacity. CaCl₂ (0.1–1.0 M) shows the same or even higher Sr(II) uptake during 2–3 repeated uses. However, the 0.1 M HCl treated alginate microsphere shows decreased Sr(II) after reuse. In second and third use, the Sr(II) adsorption capacity decreased to 30 and 25 mg/g, respectively.

Fig. 7 shows the FTIR spectrums of the alginate microspheres after regeneration using 0.5 M CaCl₂ and 0.1 M HCl 3 times. The FTIR spectra of fresh alginate microspheres and regenerated microspheres with 0.5 M CaCl₂ are similar to each other. This indicates that 0.5 M CaCl₂ does not affect the chemical structure of the adsorbent after desorbing Sr(II). However, alginate microspheres treated with 0.1 M HCl show a significantly different spectrum. The 1670 cm⁻¹ peak completely disappears. Several peaks are newly
shown at 2500–3500 cm\(^{-1}\), which indicate the deformation of hydroxyl groups (–OH). Additionally, the intensities of the 1200 (C–O–C group) and 1300 (–COOH) peaks are changed and merged with each other. Desorption of Sr(II) by 0.1 M HCl destroys the chemical structure of the alginate microsphere. Thus, the 0.1 M HCl treated alginate microsphere shows a decreased capacity for Sr(II) uptake due to a resulting decrease in Sr(II) adsorption sites.

From this result, it is considered that the 0.5 M CaCl\(_2\) solution is an appropriate regeneration solution for the desorption of Sr(II) from an alginate microsphere without adsorbent damage and with complete desorption of Sr(II). Our results are consistent with those obtained in Chen et al. They regenerated plant root tissue is immobilized in alginate beads, which were used for Sr(II) adsorption with 0.1 M CaCl\(_2\) (Chen, 1997).

### 3.6. Sr(II) adsorption in the seawater medium

In this section, an alginate microsphere is applied for the adsorption of Sr(II) in real seawater medium to demonstrate the feasibility and investigate the adsorption behavior of the alginate microsphere in real seawater conditions. Fig. 8 shows the Sr(II) adsorption of the alginate microsphere according to the reaction time in D.I. water and the seawater medium. In D.I. water, Sr(II) is the only existing ion, except H\(^+\) and OH\(^-\). The alginate microsphere shows an excellent Sr(II) adsorption capacity of 41.0 mg/g. However, the Sr(II) adsorption capacity is decreased to approximately 17.8 mg/g in the seawater medium. Seawater consists of numerous mineral ions, including Na(I) (10,000 mg/L), Mg(II) (1200 mg/L) and Ca(II) (400 mg/L). These ions interfere with the ion exchange reaction between Sr(II) and Ca(II) ions in the alginate microsphere, thereby decreasing the adsorption capacity.

A pseudo-second order kinetic model and intra-particle diffusion model is applied to analyze the Sr(II) adsorption behavior of an alginate microsphere in real seawater. The kinetic models are expressed as follows:

\[
\text{Pseudo – second order model : } \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t, \quad h = k_2 q_e^2
\]

\[
\text{Intra – particle model : } q = x_i + k_pt^\frac{1}{2}
\]

where \(q_t\) and \(q_e\) denote the adsorbed amount of Sr(II) at time \(t\) and equilibrium, respectively, \(k_2\) (g/mg·hr) and \(k_p\) (g/mg·hr\(^{0.5}\)) are the reaction rate constants for the pseudo-second-order model and the
intra-particle diffusion model, respectively. $h$ (mg·hr/g) reflects the initial adsorption rate of the adsorbent.

Table 2 shows the pseudo-second order and intra-particle kinetic model constants and linear regression coefficients. The Sr(II) adsorption data of the alginate microsphere fit well with the pseudo-second order kinetic model in both mediums. The pseudo-second order kinetic model assumes that the adsorption rate of the solution is determined by the speed of the chemical mechanism (Vinhal et al., 2015). In this experiment, the chemical adsorption reaction is the ion exchange between Sr(II) and Ca(II). Regardless of the medium, the Sr(II) adsorption rate of the alginate microsphere depends on the Sr(II) and Ca(II) exchange rate; 43.5 and 18.4 mg/g hr of $h$ is obtained in D.I. water and seawater, respectively. This indicates that the ion exchange reaction between Sr(II) and Ca(II) is retarded in seawater. Divalent cations compete with Sr(II) ions for binding sites. Although the Sr(II) adsorption capacity and adsorption rate of the alginate microsphere is decreased in real seawater, the alginate microsphere still shows 17.8 mg/g of Sr(II) uptake.

The seawater used in this experiment shows a Sr(II) concentration of 6.1 mg/L. Without the addition of a Sr(II) source, the Sr(II) uptake of the alginate microsphere is 4.4 mg/g (Seawater: 0.1 L, alginate microsphere: 0.02 g, 24 h, 120 rpm, batch experiment). Considering the low initial Sr(II) concentration, the alginate microsphere exhibits a quite high potential as a Sr(II) sorbent in real seawater. In future studies, the Sr(II) adsorption/concentration process will be investigated in real seawater using continuous column operation.

4. Conclusions

In this study, an alginate microsphere is synthesized as a low-cost adsorbent and applied for strontium (Sr(II)) adsorption from seawater. To synthesize alginate microspheres, a sodium alginate acid solution was reacted drop wise with a CaCl$_2$ solution to form an insoluble alginate microsphere. Stable and fully cross-linked alginate microspheres were obtained with CaCl$_2$ concentrations higher than 0.1 M. The synthesized alginate microspheres exhibited an excellent Sr(II) adsorption capacity ($\approx$ 110 mg/g). The Sr(II) adsorption isotherm fit well with the Freundlich model, and the Sr(II) adsorption mechanism was ion exchange between the Ca(II) in the alginate microsphere and Sr(II) ions. The effect of pH and seawater concentrated metal cations were also investigated. At the pH of seawater (7–8), the alginate microsphere adsorbed Sr(II) without inhibition. However, concentrated seawater minerals interfered with the adsorption of Sr(II). In particular, Na(I) caused a significant decrease of Sr(II) uptake. Adsorbed Sr(II) by the alginate microsphere was desorbed using 0.1 M HCl and CaCl$_2$ solutions. However, repeated use of acid caused damage to the microsphere and decreased the Sr(II) adsorption capacity. Thus, a 0.5 M CaCl$_2$ solution was chosen as the regeneration solution. The alginate microsphere also adsorbed Sr(II) in real seawater. Although the Sr(II) adsorption capacity of the alginate microsphere was decreased in the seawater medium, it still showed a 17.8 mg/g Sr(II) adsorption capacity. From this result, it can be concluded that alginate microspheres are a feasible low-cost material for Sr(II) removal and recovery from seawater.

Acknowledgements

This research was supported by the Basic Research Project “Fundamental research for strontium recovery from seawater” (GP2015-007, 15-3224) of the Korea Institute of Geoscience and Mineral Resources (KIGAM) funded by the Ministry of Science, ICT and Future Planning of Korea.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jenvman.2015.09.040.

References


Lakouraj, M.M., Mojerlou, F., Zare, E.N., 2014. Nanogel and superparamagnetic nanocomposite based on sodium alginate for sorption of heavy metal ions.