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# Removal of cesium ion in aqueous solution using immobilized sericite beads

**Choong Jeon*,†, Jong-Oh Kim**, and Seung-Mok Lee*****

*Department of Biochemical Engineering, Gangneung-Wonju National University,
Jukhen-gil 7, Gangneung-si, Gangwon-do 210-702, Korea
**Department of Civil and Environmental Engineering, Hanyang University,
222, Wangsimni-ro, Seongdong-gu, Seoul 133-791, Korea
***Department of Environmental Engineering, Kwandong University, Gangneung-si, Gangwon-do 210-701, Korea
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**Abstract**−To apply sericite effectively in the adsorption process, it was immobilized by entrapment method using sodium alginate. Since the immobilized sericite beads have excellent mechanical strength and swelling characteristics, channeling of flow and the increase of pressure drop were not observed through column operations. In addition, it was also stable under pH 10 and 45 °C of cesium solution. The maximum adsorption capacity and Langmuir adsorption constant was 1.430 mg/g and 2.329 L/mg, respectively, at initial pH 5 of cesium solution in batch type and the Langmuir model with higher correlation coefficient of 0.997 fits experimental data better than Freundlich model. The break-through point emerged around 15 (1.0 mL/min) and 20 bed volumes (0.5 mL/min), and the cesium ions bound to the immobilized sericite beads were readily released and quantitatively recovered by a few bed volumes of 1.0 M of $HNO_3$ solution. Furthermore, bed volumes of cesium ions for firstly reused sericite beads can be still maintained as 18, which shows good regeneration ability.

Keywords: Sericite, Cesium Ion, Adsorption, Packed-bed Column, Immobilization

## INTRODUCTION

The concern on removal of radioactive elements such as cesium, strontium and selenium has sharply increased since many radioactive substances leaked into the ocean, soil and air due to the big nuclear accident at Fukushima, Japan in 2011. Among them, several isotopes of cesium ions are well known as being poisonous because of destructive effects on the environment due to their long half-lives which have $^{135}Cs$ ($t_{1/2}$=3,000,000 years) and $^{137}Cs$ ($t_{1/2}$=30.17 years) [1]. Especially, the $^{137}Cs$ is extremely toxic as it causes thyroid cancer through contaminated food and water, and it can be easily incorporated into terrestrial and aquatic organisms because of its similar chemical characteristics to potassium [2,3].

To separate and sequester cesium ions from water and wastewater, many efforts have been made to find effective and low cost methods. In general, several physical-chemical processes such as precipitation, reverse osmosis, solvent extraction, membrane filtration, ion-exchange, and adsorption have been successfully applied to the treatment system [4-7]. Among them, adsorption is quite attractive in terms of its high efficiency and adsorbent-selectivity of removal from dilute solutions [8]. Adsorption has the additional advantages of suitability for using batch and continuous processes, ease of operation, little sludge generation, and possibility of regeneration and reuse [9]. Recently, several kinds of low cost and easily available adsorbents such as sawdust, crab shells and rice hulls have been applied to the removal of heavy metals [10,11]. Walnut shell which is a kind of agricultural residue was used to adsorb cesium ions from aqueous solution by Tang et al. [12].

Among cost-effective adsorbents, the use of sericite for the recovery of valuable metals or the removal of toxic metals has been studied [13]. Sericite, which is a kind of clay, is a layered silicate mineral, generally recognized as white fine powder of muscovite in form, with nanosized layer structure, interlayer spacing of (002) plane of 10 Å, and generally widely used in the alkali flux and cosmetics [14]. In our previous work, we reported that sericite can be sufficiently applied to remove cesium ions from aqueous solution as a novel adsorbent [15].

In such applications, sericite is not rigid enough to be used in an up and/or down flow packed-bed column operation and furthermore presents an unacceptable pressure drop to flow [16]. Hence, for sericite to be effectively used, it needs to be immobilized in a bead form that preserves the adsorptive properties well and provides physical characteristics similar to those of conventional adsorbent particles, such as activated carbon or ion exchange resins. Many workers have investigated methods of immobilization and their application to water and wastewater treatment system [16,17]. Among immobilization methods, entrapment has been generally used because of easy operation and low cost. Agar, polyacrylamide, sodium alginate and k-carrageenan have been used as chemicals for immobilization. Especially, alginates are good matrix materials because the gel-forming property of alginates has led to their extensive application in biomedicine and biotechnology to immobilize or encapsulate enzymes and living cells [18]. Until now, unfortunately, there has been no study on cesium ion removal using immobilized sericite bead with alginate.

Therefore, we immobilized sericite by entrapment method using sodium alginate, which has many advantages such as ease of operation, excellent mechanical strength and low cost. And, the immobi-

†To whom correspondence should be addressed.
E-mail: metaljeon@gwnu.ac.kr

lized sericite beads were applied to the sequential adsorption process using packed-bed column for the removal of cesium ions. The physical properties for immobilized beads were also investigated.

## MATERIALS AND METHODS

Sericite used in this study was kindly provided by the SG mining industry located in the city of Gangneung in Korea, and preparation methods and chemical compositions were already presented in our previous work [15]. All of the chemicals used in the experiment were of analytical grade (Sigma Aldrich, U.S.A); distilled water was used to prepare all of solutions.

The optimal immobilization method of sericite using sodium alginate was as follows: 2.33 g of sericite, 1 g of sodium alginate, and 50 mL of distilled water were mixed to get a uniform mixture under 60 °C for 2 hr. This mixture was dropped into a gently stirred 4% of $CaCl_2$ solution to get gel beads. After overnight aging, the gel beads were separated from the $CaCl_2$ solution, washed with deionized water, and then dried at room temperature. The dried sericite beads were used for the adsorption experiments to remove cesium ions by using a packed-bed column.

Surface area for the beads was measured by BET analysis with nitrogen gas as adsorbate, and average diameter and stability to temperature and pH were investigated. To look into mechanical strength of sericite beads, the experiment presented by Khoo et al. was done as follows: 1 g of sericite beads was stirred in 500 mL of deionized water for 90 hr at 700 rpm in a stirred reactor with six evenly spaced baffles [19]. The swelling characteristics such as distention index and swelling ratio were measured from the weights and the volumes of dried and swollen sericite beads over time and the values were calculated by Eqs. (1) and (2):

$$\text{Distention index}=V_s/W_d \quad (1)$$

$$\text{Swelling ratio}=(W_s-W_d)/W_d \quad (2)$$

where $V_s$ is the volume of the swollen beads, $W_s$ and $W_d$ are the weight of the swollen and dry beads, respectively. Each sample was examined four times.

The experiment for the removal efficiency of cesium ions according to the content of sericite in immobilized beads was performed. To do so, various beads with different ratio between sodium alginate and sericite in beads were made and the beads were used by batch-type 100 mL in a shaking incubator (JEIO TECH, SI-600R, Korea). Cesium solutions were prepared by cesium chloride (CsCl, FW: 168.36) and the concentration was varied from 2 to 20 mg/L. The initial pH of cesium solution was controlled as 5.0 by NaOH and HCl. After 2 hr of adsorption time which was studied, in our previous work, to get an equilibrium state the solution was centrifuged at 4,000 rpm for 30 min to remove suspending sericite by centrifuge (Gyrozen, Gyro 1236 MG, Korea); then the concentration of cesium ion in supernatant was analyzed by ICP (Inductively coupled plasma spectroscopy, Perkin-Elmer, UK). The removal efficiency and adsorption capacity of cesium ions for immobilized sericite bead were calculated as Eqs. (3) and (4), respectively:

$$\text{Removal efficiency (\%)}=(C_i-C_f)/C_i \quad (3)$$

$$\text{Adsorption capacity (mg/g)}=(C_i\times V_i-C_f\times V_f)/m \quad (4)$$

where $C_i$ is the initial concentration of cesium ions (mg/L), $V_i$ is the initial solution volume (L), $C_f$ is the final concentration of cesium ions (mg/L), $V_f$ is the final solution volume (L), and m is the initial loading of immobilized sericite bead (g). Also, SEM (Scanning electron microscopy, Hitachi model S-4100, Japan) and EDX (Energy dispersive X-ray spectroscopy, U.S.A) for before and after adsorption of cesium ions were examined to confirm surface condition and existence of cesium ions on immobilized sericite bead, respectively.

Sequential adsorption experiments using borosilicate glass column with 1.0 cm of diameter were done at room temperature. Column was packed with 1.5 g of immobilized sericite beads and the initial cesium solutions with 20 mg/L were constantly run under 5.0 of influent pH of solution. Flow direction was up-flow, as is the case in most column operations, and rate was controlled as 0.5 (retention time: 2.4 min) and 1.0 mL/min (retention time: 1.2 min) using Acuflow Series II high-pressure liquid chromatograph (U.S.A). Effluent samples were automatically collected by Spectra/Chrom CF-1 fraction collectors. The influent and effluent concentration of cesium ions was also measured by ICP.

## RESULTS AND DISCUSSION

### 1. Decision on the Optimal Mixing Ratio between Sodium Alginate and Sericite for Manufacture of Immobilized Sericite Beads

Generally, the adsorption capacity of metals for immobilized adsorbent decreased, as compared to the natural adsorbent because functional groups which can combine metals decreased due to the

**Table 1. Manufacture of immobilized beads with different mixing ratio between sodium alginate and sericite (Distilled water: 50 mL, Sodium alginate: 1.0 g)**

| Mixing ratio (sodium alginate : sericite) | Contents of sericite (g) | Manufacture of beads |
|---|---|---|
| 10 : 0 | - | Possible (easy) |
| 9 : 1 | 0.11 | Possible (easy) |
| 7 : 3 | 0.43 | Possible (easy) |
| 5 : 5 | 1.0 | Possible (easy) |
| **3 : 7** | **2.33** | **Possible (easy)** |
| 1 : 9 | 9.0 | Possible (difficult) |

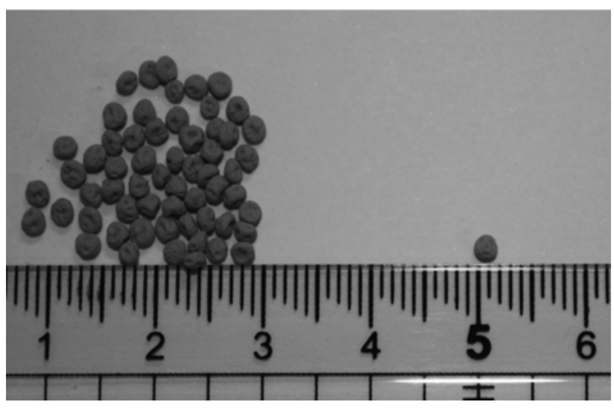



**Fig. 1. The picture of immobilized sericite beads with 3 : 7 (sodium alginate : sericite) of mixing ratio.**

use of functional groups to immobilize adsorbent in immobilizing solution [20]. Therefore, the study on increasing content of adsorbents in immobilized beads was needed. In this study, the content of sericite was varied under fixing the quantity of sodium alginate in 50 mL of distilled water. Table 1 shows the result of manufacture for immobilized beads with different mixing ratio between sodium

**Table 2. Physical property of immobilized sericite bead with 3 : 7 (sodium alginate : sericite) of mixing ratio**

| Physical property | Characteristic value |
|---|---|
| Diameter | 2.0±0.1 (mm) |
| Surface area using BET | 7.1±0.2 ($m^2$/g) |
| Temperature | Stable to ~45±5 (°C) |
| pH | Stable to ~10±0.05 |
| Mechanical strength | No cracking (700 rpm, 120 hr) |

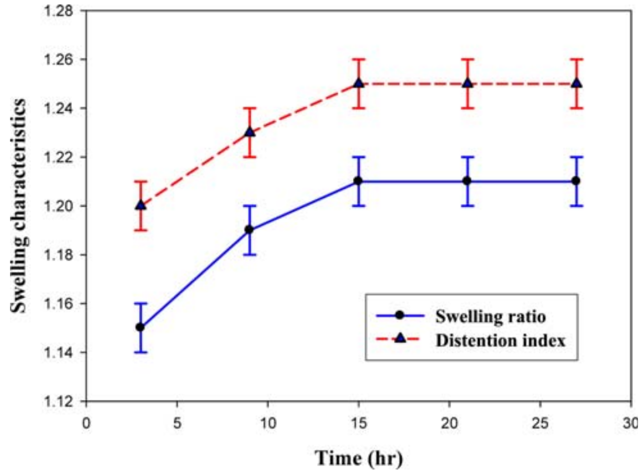
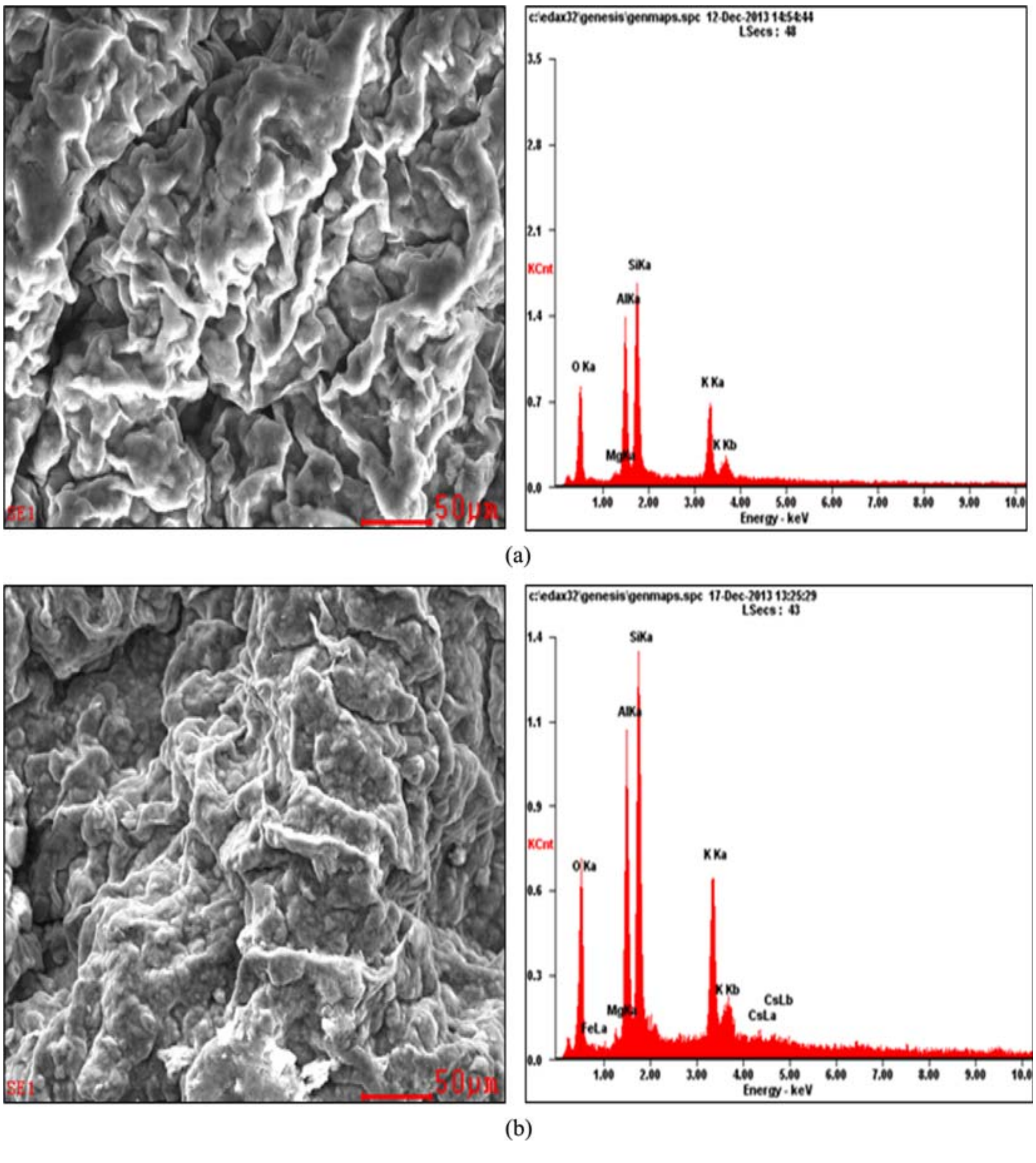



**Fig. 2. Swelling characteristics of immobilized sericite beads.**




(a)

(b)

**Fig. 3. SEM images and EDX spectra of immobilized sericite beads.**
(a) Before adsorption of cesium ions, (b) After adsorption of cesium ions

alginate and sericite. The sericite could be immobilized as the bead shape when the mixing ratio of sodium alginate and sericite was 1 : 9. However, each bead did not have a uniform shape; furthermore, it was very difficult to make beads in terms of manufacturing. Hence, the 3 : 7 (sodium alginate : sericite) of mixing ratio was chosen as the optimal condition for immobilization and the beads were applied to all the batch and sequential adsorption experiments.

**2. Physical and Swelling Characteristics for Immobilized Sericite Beads**

As shown in Fig. 1 and Table 2, the diameter and surface area of the beads was measured as about 2.0 mm and 7.1 $m^2$/g, respectively. In case of surface area, the value was higher than the 6.25 $m^2$/g reported for immobilized fungal beads using sodium alginate [19]. The bead was also stable to ~45 °C and ~pH 11 of aqueous solution without untangling. Especially, the beads did not crack under the condition of 120 hr and 700 rpm in batch operation. For reference, Khoo et al. used milder condition of 70 hr and 500 rpm than that of this study to investigate cracking of the fungal beads [19]. On the other hand, it was reported that the fracture strength for calcium-alginate cylinders with 3.8 mm of diameter and 15 mm long was 2.25 N by Remmers and Vorlop [21]. To examine swelling characteristics of the immobilized sericite beads, the swelling ratio and distention index were calculated by Eqs. (1) and (2), as mentioned above. As shown in Fig. 2, swelling phenomenon of the beads slightly increased up to 15 hr and then the beads were not swelled any more with further time. From the physical and swelling characteristics, it was concluded that the immobilized sericite beads had excellent mechanical strength to apply to the actual water and wastewater treatment process.

**3. Adsorption Characteristics of Immobilized Sericite Bead for Cesium Ion**

The SEM images and EDX spectra of immobilized sericite beads before and after adsorption of cesium ions are shown in Fig. 3. The SEM image of the beads before adsorption shows that there are cavities, which mean the porous nature of the immobilized sericite beads, while that of the beads after adsorption shows the electron dense part on the surface of immobilized sericite beads. It means reducing of pores, which was thought as mainly due to adsorption of cesium ions. The EDX spectrum of the beads after adsorption of cesium ions shows clear cesium peak, as compared with that of the beads before adsorption of cesium ions.

The removal efficiency of cesium ions using various immobilized sericite beads with different mixing ratio between sodium alginate and sericite was investigated. As shown in Fig. 4, the removal efficiency of cesium ions increased as the content of sericite increased and the highest removal efficiency was achieved as about 50% at the 1 : 9 (sodium alginate : sericite) of mixing ratio. However, the optimal immobilized sericite beads with 3 : 7 (sodium alginate : sericite) of mixing ratio, as mentioned in Table 1, had about 40% of removal efficiency and the value was reduced as about 50%, as compared with 80% of powdered sericite. It can be explained as the reducing of functional groups which can remove cesium ions in aqueous solution due to the use of sodium alginate for immobilization of sericite [20]. Also, when cesium ions were moved to sericite, transfer resistance may have happened due to the characteristics of the entrapment method [16]. The adsorption mechanism between sericite and cesium ions can be explained as two different surface-

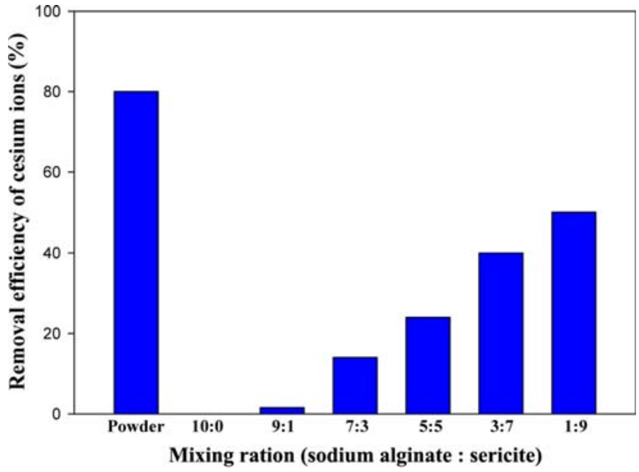



**Fig. 4. Removal efficiency of cesium ions according to the contents of sericite in immobilized bead (initial concentration of cesium ions: 20 mg/L, sericite concentration: 6.0 g/L, initial pH of cesium solution: 5.0).**

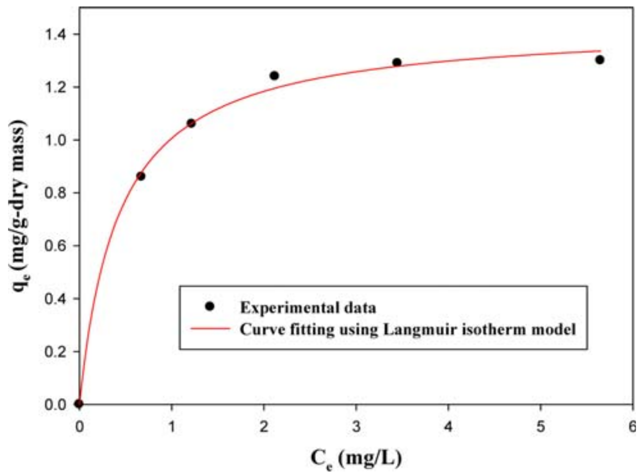



**Fig. 5. Isothermal adsorption curve for cesium ions of immobilized sericite using Langmuir model (initial pH of cesium solution: 5.0, working volume: 100 mL).**

active groups such as silanol and aluminol groups, as described in our previous work [15]. It was also reported that sodium alginate has the ability to remove metals such as lead, copper and cadmium [20]. However, immobilized beads including sodium alginate only could not remove cesium at all. It means sodium alginate has no affinity to cesium ions.

Figs. 5 and 6 show the isothermal adsorption curves of immobilized sericite beads for cesium ions using Langmuir and Freundlich model, respectively, at initial pH 5.0 and 25 °C of solution. Langmuir model Eq. (5) is described as follows:

$$1/q_e=1/q_m+(1/q_mK_L)1/C_e \quad (5)$$

where $q_e$, $q_m$ and $K_L$ are adsorption capacity (mg/g) corresponding to metal ion concentration ($C_e$), maximum adsorption capacity of metal ions (mg/g) and Langmuir adsorption constant (L/mg), respectively. The obtained $q_m$ and $K_L$ parameters for cesium ions were 1.430 and 2.329, respectively, and the regression curve fit well with the

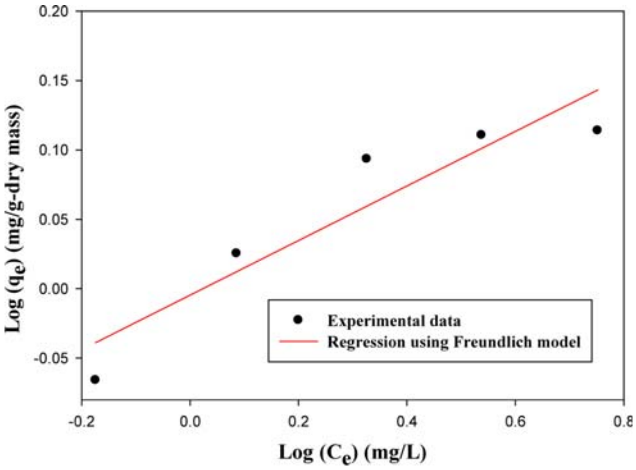



**Fig. 6. Isothermal adsorption curve for cesium ions of immobilized sericite bead using Freundlich model (initial pH of cesium solution: 5.0, working volume: 100 mL).**

**Table 3. Isotherm adsorption model parameters of immobilized sericite beads for cesium ions**

| Langmuir isotherm model | | | Freundlich isotherm model | | |
|---|---|---|---|---|---|
| $q_m$ (mg/g) | $K_L$ (L/mg) | $r^2$ | 1/n | $K_f$ (L/g) | $r^2$ |
| 1.430 | 2.329 | 0.997 | 0.197 | 0.989 | 0.873 |

experimental data together with the 0.997 of correlation coefficients ($r^2$), as shown in Table 3.

The Freundlich model was also applied to the sorption phenomena and the equation in linear form is given as follows:

$$\text{Log } q_e = \text{Log } K_f + (1/n) \text{ Log } C_e \quad (6)$$

where $k_f$ is a constant related to the adsorption capacity and 1/n is an empirical parameter related to the adsorption intensity which varies with the heterogeneity of material [22]. The isothermal adsorption fitting and parameters using Freundlich model are as shown in Fig. 6 and Table 3. The values of 1/n and $K_f$ for cesium ions were 0.197 and 0.989, respectively, and correlation coefficient ($r^2$) was 0.873. From the determined isotherm constants, we concluded that the Langmuir model with higher correlation coefficient fits experimental data better than Freundlich model.

Fig. 7 shows the effect of flow rate on breakthrough curve of the column packed with immobilized sericite bead. As shown, the breakthrough point, which is generally defined as 10% of the feed concentration [23], emerged around 15 (1.0 mL/min) and 20 bed volumes (0.5 mL/min). It means that the cesium ions were removed with more than 90% up to 15 and 20 bed volumes for each flow rate using immobilized sericite beads. The effect of flow rate can be explained as contact time between adsorbent and flowing metal solution. That is, the more flow rate was slow, the more contact time increased; therefore, the higher adsorption was achieved. Also, adsorption capacity of cesium ions on immobilized sericite beads was calculated as about 0.62 mg/g at 0.5 mL/min. The value was lower than that of batch test (1.43 mg/g); the difference can be explained as the basis that insufficient time of contact was given for the ion exchange of cesium ions on the sericite beads surface under the dynamic conditions [24].

As shown in Fig. 8, the cesium ions bound to the immobilized sericite beads were readily released and quantitatively recovered by a few bed volumes of 1.0 M of $HNO_3$ solution, whose efficiency had previously been determined in batch experiments as the optimum concentration. To achieve a desorption efficiency of about 95%, about three bed volumes of solution were required; the maximum concentration of cesium ions was obtained as about 300 mg/L at two bed volumes.

It is essential to describe regeneration aspects of the process in order to improve its cost-effectiveness by recycling the adsorbent for reuse in multiple cycles. To investigate the regeneration ability for immobilized sericite beads, sequential adsorption-desorption cycles were repeated three times by the means of the same adsorbent by packed-bed column. 1.0 M of $HNO_3$ was used as desorbing agent. As shown in Table 4, bed volumes of cesium ions for

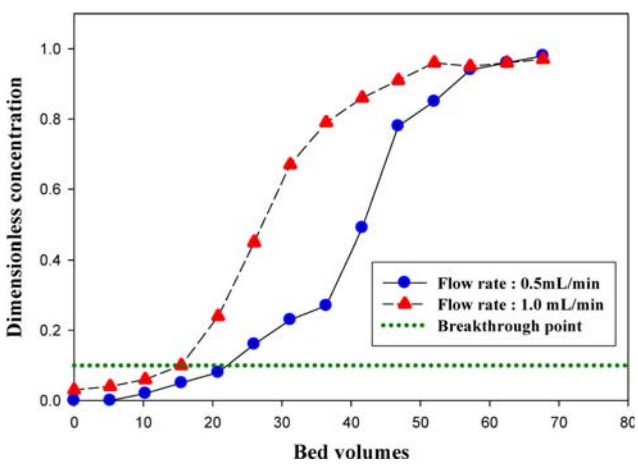



**Fig. 7. Effect of flow rate on breakthrough curve of cesium ions using immobilized sericite bead (one bed volume: 1.2 ml, influent concentration: 20 ppm, immobilized sericite bead: 1.5 g, influent pH of cesium ion solution: 5.0, break through point: 0.1).**

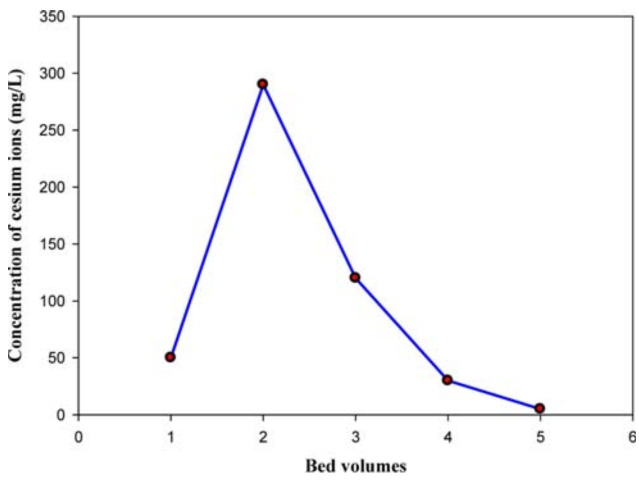



**Fig. 8. Development of desorption of cesium ions using 1.0 M of $HNO_3$ solution (amount of pre-loading with indium ions: 530 mg/L, one bed volume: 1.2 mL, flow rate: 0.5 mL/min).**

**Table 4. Breakthrough throughputs from sequential adsorption and desorption cycle (flow rate: 0.5 mL/min, initial concentration of cesium ions: 20 mg/L, breakthrough point: 2.0 mg/L, one bed volume: 1.2 mL, influent pH of cesium solution: 5.0)**

| Cycle number | Bed volumes |
|---|---|
| 1 | 18 |
| 2 | 14 |
| 3 | 8 |

firstly reused sericite beads can still be maintained as 18; however, the values quickly decreased due to incomplete desorption of sericite beads for cesium ions at the second cycle. The result shows that immobilized sericite beads have regeneration ability for cesium ions, to some extent. Therefore, it could be concluded that the immobilized sericite beads, which have excellent mechanical strength, swelling characteristics and good regeneration capacity, can be sufficiently applied for the removal of cesium ion using sequential adsorption process with packed-bed column.

## CONCLUSIONS

Sericite was successfully immobilized by entrapment method using sodium aginate, and the optimal mixing ratio was 3 : 7 (sodium alginate : sericite) to make sericite bead form. The immobilized sericite beads have excellent mechanical strength and swelling characteristics. They were also stable under pH 10 and 45 °C of cesium solution, and the surface condition and the existence of cesium ions on the immobilized sericite beads was confirmed by the SEM and EDX instrument analyses. The maximum adsorption capacity was 1.430 mg/g at initial pH 5 of cesium solution in batch type; the Langmuir model with higher correlation coefficient fit experimental data better than Freundlich model. The breakthrough point emerged around 15 (1.0 mL/min) and 20 bed volumes (0.5 mL/min), and bed volumes of cesium ions for firstly reused sericite beads can be still maintained as 18, which shows good regeneration ability. Consequently, immobilized sericite beads can be sufficiently applied to the removal of cesium ion using sequential adsorption process with packed-bed column.

## ACKNOWLEDGEMENTS

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