

Removal Efficiency of Cesium and Strontium in Seawater by Zeolite Fixed-Bed Columns

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Abstract

It is documented that the Chernobyl nuclear meltdown released large amounts of Cs-137, Cs-134 and Sr-90 (100, 50 and 8 PBq, respectively). The accident had a devastating impact on the marine environment. The main aim of this research was to study the removal of cesium and strontium in seawater by natural zeolite. Experiments using fixed bed column with different bed depths, pH levels, and flow rates of seawater were conducted. The salinity of experimental seawater was adjusted to 35 ppt.; and concentrations of cesium and strontium were 80 and 20 mg/l. Natural zeolite treated with NaCl was found appropriate for use in this experiment. Zeolite could remove cesium but not strontium from the marine environment. The zeolite removal efficiency of cesium was compared at seawater pH values of 4, 7, and 9. Zeolite efficiency was significantly greater at a pH of 9 than at a pH of 4 ($P < 0.05$). Efficiency removal by zeolite was significantly better at a bed depth of 6 cm. (18.84 cm^3) than at only 3 cm. depth (9.42 cm^3) ($P < 0.05$). However, different flow rates of 3 and 6 ml/min. during zeolite removal did not significantly affect cesium levels ($P > 0.05$).

Keywords: Cesium, Strontium, Removal, Zeolite

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1. Introduction

It is documented that the Chernobyl nuclear meltdown released large amounts of Cs-137, Cs-134 and Sr-90 (100, 50 and 8 PBq, respectively) (Holm, 1997). The accident had a devastating impact on the marine environment. These radionuclides arise from the burning of uranium fuel in a nuclear reactor (high-level waste), which pose a great risk to human health. Radioactive uptake pathways are quite variable according to species and their habitats. Fish in nature normally encounter different uptake routes for radionuclides present in the environment. Radioactivity will enter the organism via contaminated food or will be accumulated directly from the surrounding water through drinking, by absorption across the gills, and to a minor extent by absorption through the total surface of the fish. Humans also experience radionuclide uptake through fish consumption.

Different techniques such as chemical precipitation, evaporation, and ion exchange have been used for the treatment of aqueous waste solutions containing these radioactive wastes. Ion exchange technique has become one of the most commonly used treatment methods for such aqueous streams due to its simplicity, selectivity and efficiency. Ion exchange resins are insoluble granular substances which have in their molecular structure acidic or basic radicals that can be exchanged. The positive or negative ions fixed on these radicals are replaced by ions of the same sign in solution in the liquid in contact with them (Lenntech, 2013).

The ion exchange property is one of the main features that zeolites exhibit (Rodriguez-Iznag, Petranovskii, & Rodriguez-Fuentes, 2014); Zeolite can be used for cation exchange. Zeolites are used in process water softening and water treatment for the removal of lead, mercury, cadmium and silver ions. Moreover, zeolites are absorbent materials that can separate a mixture of gases and vapors such as ammonia, hydrogen, oxygen, nitrogen, carbon dioxide and sulfur dioxide.

The main aim of this research was to study the removal of cesium and strontium in seawater by natural zeolite.

2. Experimental Design

An experiment was designed using zeolite fixed bed columns with different bed depths of zeolite, and several pH levels and flow rates of seawater. The salinity of experimental seawater was adjusted to 35 ppt.; CsCl and SrCl were used to represent Cs and Sr ions in the seawater and the concentrations of Cs and Sr ions were 80 and 20 mg/l, respectively.

2.1 Materials

2.1.1 Preparation of zeolite particles as adsorbents

Three types of natural zeolite were purchased: Classica Zeolite, Hi Filter Zeolite and MA Zeolite. The natural zeolite was sent for analysis at the Department of Geology, Faculty of Science, Chulalongkorn University. Prior to the experiment, the zeolite sample must be analyzed for crystal structures and chemical composition of the

zeolite sample. The ion exchange characteristics of any zeolite are dependent on its crystal structures and chemical composition. Crystal structures were identified from X-ray diffraction (XRD) and chemical composition analyzed by X-Ray Fluorescence Spectrometer (XRF) at Chulalongkorn University (CU, 2014).

Table 1
Chemical composition of the zeolite sample

<u>Element</u>	<u>Classica Zeolite(%wt)</u>	<u>Hi Filter Zeolite(%wt)</u>	<u>MA Zeolite(%wt)</u>
SiO ₂	78.00	76.50	73.60
Al ₂ O ₃	12.60	12.70	13.60
CaO	3.50	0.24	4.27
K ₂ O	3.11	5.39	2.87
Fe ₂ O ₃	1.32	0.90	2.21
MgO	0.73	-	0.88
Na ₂ O	0.38	3.99	1.82
TiO ₂	0.19	0.15	0.33
BaO	-	-	0.14
SrO	-	-	0.12

Table 2
Crystal structures of the zeolite sample

<u>Zeolite name</u>	<u>Mineral compositions</u>
Classica Zeolite	- Calcium Aluminum Silicate Hydrate - Potassium Aluminum Silicate Hydrate - Sodium Calcium Aluminum Iodide Silicate
Hi Filter Zeolite	- Calcium Aluminum Silicate - Potassium Sodium Aluminum Silicate Hydrate - Sodium Calcium Aluminum Iodide Silicate - Sanidine
MA Zeolite	- Calcium Aluminum Silicate Hydrate - Sodium Calcium Aluminum Iodide Silicate - Barium Aluminum Chloride Silicate Hydrate - Strontium Aluminum Silicate Hydrate

The result shown in Table 1 and Table 2 indicated that Classica Zeolite has the least chemical composition. Therefore, Classica Zeolite was used in all experiments.

Natural zeolite was washed with deionized water and dried at 103°C for 3 hours. Then, the required particle size of 850-1000 µm was obtained from the natural zeolite using sediment sieving with different mesh sizes ranging from 850-1000 µm.

2.1.2 Natural zeolite treated by sodium chloride

The zeolite was crushed to a size of 850-1000 µm.; 3.0 g of zeolite was continuously refluxed with 100 mL of 1.0 M NaCl at room temperature (R.T) for 24 hours. The mixture was filtered and the zeolite was, then, washed with 300 mL of deionized water. The zeolite was activated by mechanical shaking with 25 mL of methanol twice for 60 minutes. The zeolite was filtered and dried at 50°C for 3 hours.

2.1.3 Preparation of synthetic seawater

Synthetic seawater was prepared by adding commercial sea salt into demineralized water. An appropriate amount of the commercial sea salt was added to demineralized water to obtain the salinity of 35 ppt. The salinity was measured by a digital salinity probe. At the pilot study, four liters of synthetic seawater was used for each set of experiments; and appropriately 160 grams of commercial sea salt was added into this amount of demineralized water. The pH of synthetic seawater was adjusted to be 4, 7 and 9.

2.1.4 Chemical preparation

A solution of cesium and strontium in synthetic seawater at the concentration of 80 and 20 mg/l was prepared by dissolving 0.1014 g. and 0.0609 g. of cesium chloride and strontium chloride in 1000 ml of the synthetic seawater. The synthetic seawater, which was prepared in the previous step, with salinity of 35 ppt., was adjusted to pH levels of 4, 7 and 9.

2.2 Experimental Procedures

A set of pilot experiments was conducted to determine the feasibility of the study. The study of Cesium and Strontium removal efficiency consisted of the following steps:

1. A 2 cm-diameter column was filled with ten grams and five grams of the sieved natural zeolite to reach the height of 3 cm. and 6 cm, respectively. An amount of fiberglass was placed at the bottom of the column with thickness of 1 cm.
2. One liter of solution containing cesium and strontium and salinities of 35 ppt. was poured into the zeolite-packed columns with controlled flow rate continuously through the column. The flow rates were 3 ml/min and 6 ml/min.
3. After the continuous flow, every 100 ml of the outlet solution was collected for cesium and strontium concentration analysis using ICP-MS.
4. The process from Steps 1, 2 and 3 was repeated for natural zeolite treated by sodium chloride.
5. Experiments using natural zeolite and treated natural zeolite were conducted three times to obtain mean values as results.

2.3 Data record

The distribution coefficient (K_d) in radionuclide removal: The efficiency of an ion exchange is often measured by distribution coefficient K_d of radionuclides with the percent removal ($E\%$) and percent cesium and strontium remaining in solutions $R\%$ as well as amount of metal ion adsorbed onto the zeolite materials were calculated from the following equations (Borai, Harjulab, Malinenb, & Paajanenb, 2009):

$$E (\%) = \frac{A_o - A_e}{A_o} \times 100 \quad (1)$$

$$R (\%) = (A_e \div A_o) \times 100 \quad (2)$$

$$K_d = \frac{A_o - A_e}{A_e} \times \frac{V}{m} \quad (\text{ml/g}) \quad (3)$$

Where A_0 and A_e are the initial and equilibrium activities per unit volume for the corresponding radionuclide, respectively; V is the volume of the aqueous phase (ml), and m is the weight of the zeolite material (g).

3. Results and discussion

Initial results revealed that zeolite treated with NaCl was appropriate for use in this experiment. Zeolite could remove cesium and strontium from the deionized water (Figure 1.), but not strontium from synthetic seawater at all pH levels (Figure 2.). Results of chemical composition analyzed by X-Ray Fluorescence Spectrometer (XRF) revealed that Strontium in the structure of the zeolite sample only increased by 0.01%wt (Table 3).

Analysis shows that the zeolite could not remove strontium from synthetic seawater at all pH levels. At higher salinity levels in seawater, various positive ions were present in the solution competing with strontium. The ion exchange process could have been disrupted by various ions in seawater (Borai et al., 2009).

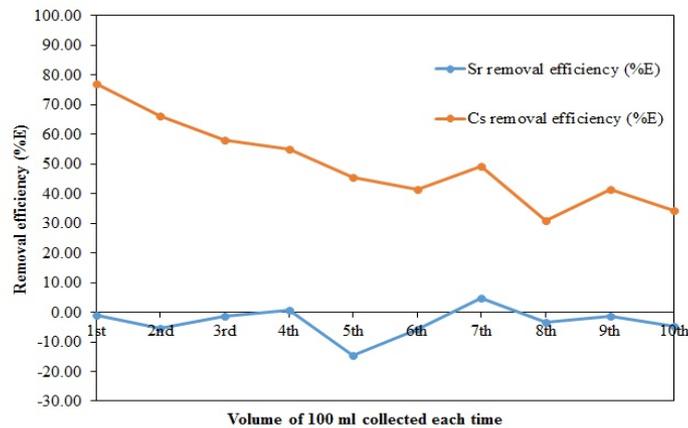


Figure 1. Removal efficiency of cesium and strontium in seawater

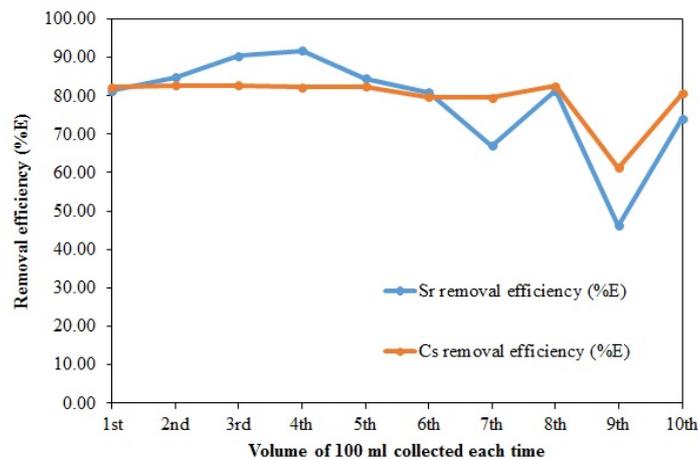


Figure 2. Removal efficiency of cesium and strontium in DI water

Table 3			
<i>Chemical composition of the zeolite sample</i>			
Element	Non-treat (%wt)	Treat (Before) (%wt)	Treat (After) (%wt)
SiO ₂	78.00	77.40	76.00
Al ₂ O ₃	12.60	13.00	12.80
CaO	3.50	1.33	1.14
K ₂ O	3.11	3.08	4.55
Fe ₂ O ₃	1.32	1.40	1.45
MgO	0.73	0.75	0.81
Na ₂ O	0.38	2.68	1.92
TiO ₂	0.19	0.25	0.25
BaO	-	-	-
SrO	-	0.05	0.06
Cs ₂ O	-	0<LLD (0)	0.84
ZrO ₂	-	0.04	0.04
MnO	-	0.03	0.04

Note: Non-treat is natural zeolite
Treat (Before) is natural zeolite treated by sodium chloride that before used in the process
Treat (After) is natural zeolite treated by sodium chloride that after used in the process

3.1 Bed depth effects

Zeolite packed columns were used at heights of 6 cm. and 3 cm. (18.84 and 9.42 cm³). The study involved an experiment with seawater salinity at 35 ppt., the concentration of cesium at 80 mg/l and, pH levels of seawater of 4, 7, 9, and flow rates of 3 and 6 ml/min. Results revealed that the cesium removal efficiency (%E) decreased with increasing time at all flow rates of seawater and bed depths. At a bed depth of 6 cm (18.84 cm³), Zeolite efficiency is greater than at a bed depth of 3 cm. (9.42 cm³) (Figures 3 and 4). The efficiency of removal by zeolite was significantly better at a bed depth of 6 cm. (18.84 cm³) than with only a 3 cm. depth (9.42 cm³) (P<0.05). The increase in the ion sorption with bed depth was due to the increase in the sorption doses in a larger bed, which provided greater sorption sites for cesium ions (El-Kamash, 2008.) Therefore, a bed depth of 6 cm. is appropriate for use in this experiment.

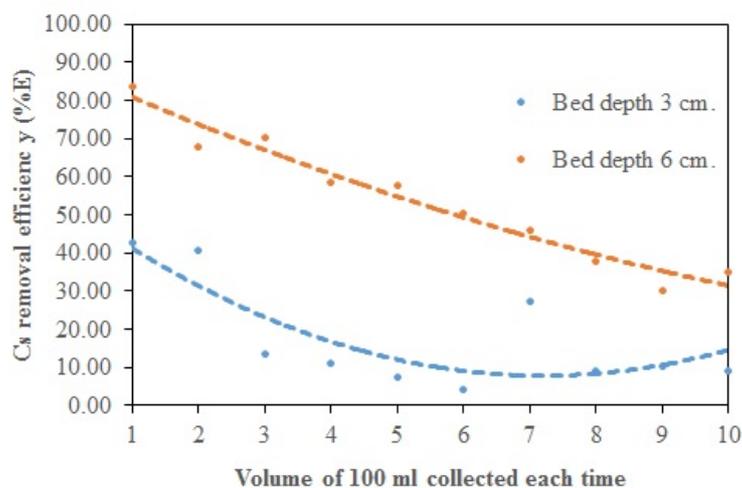


Figure 3. Removal efficiency of cesium in seawater at flow rate 3 ml/min

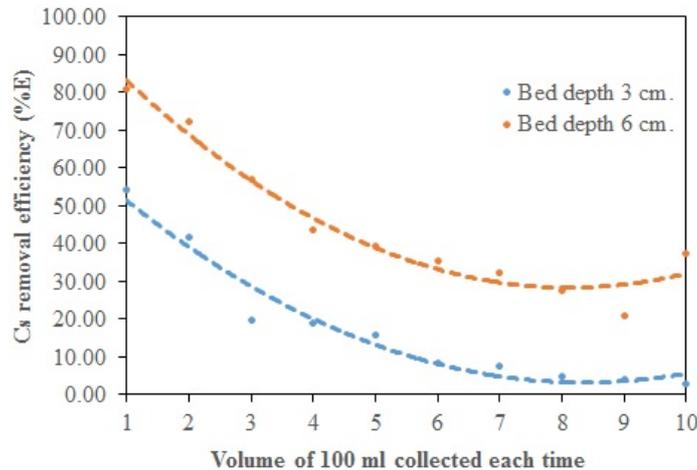


Figure 4. Removal efficiency of cesium in seawater at flow rate 6 ml/min

3.2 pH effects at different flow rates

In this part of the study, a bed depth was selected at 6 cm., while seawater salinity at 35 ppt., and concentration of cesium at 80 mg/l with various pH levels, 4, 7, and 9.

3.2.1 Flow rate of 3 ml/min

The effect of pH on the removal efficiency of cesium in seawater by zeolite fixed-bed columns at a flow rate of 3 ml/min was tested under different pH levels. Results revealed that the zeolite removal efficiency of cesium decreases from the 1st-100 ml collected to the 10th-100 ml collected of the outlet solution. The highest zeolite removal efficiency (%E) of cesium of 59.70, 70.70, and 83.50 of the mixed solution (pH of 4, 7, and 9) was at the 2nd-100 ml, 1st-100 ml, and 1st-100 ml, respectively (Figure 5). The maximum removal efficiency of cesium was observed at pH of 9. The zeolite removal efficiencies of cesium were compared at seawater pH values of 4, 7, and 9. Zeolite efficiency was significantly greater at pH of 9 than at pH of 4 ($P < 0.05$) (Figure 5). At lower pH values, the metal ion uptake was inhibited in the acidic medium which can be attributed to the presence of H^+ ions competing with the Cesium ions (El-Kamash, 2008).

Remaining cesium increases from each consecutive batch from the 1st-100 ml collected to the 10th-100 ml collected (Figure 6).

The highest distribution coefficient (K_d) of 15.45, 34.32, and 51.51 of the mixed solution (pH of 4, 7, and 9) was observed at the 2nd-100 ml, 1st-100 ml, and 1st-100 ml, respectively (Figure 7).

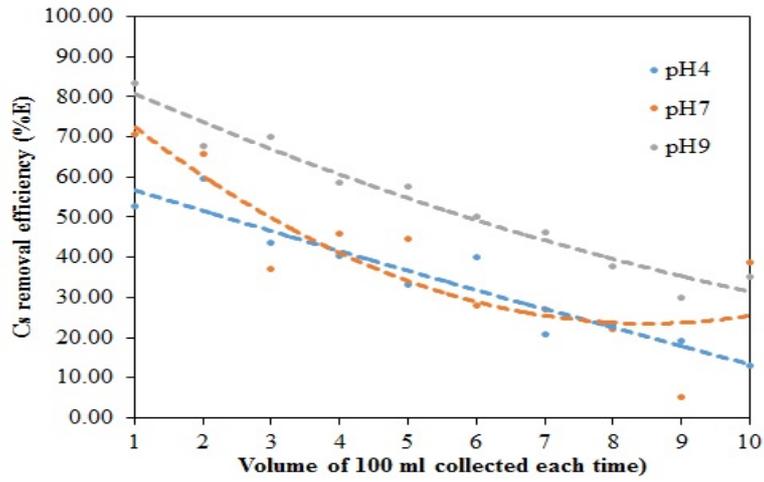


Figure 5. Cesium removal efficiency (%E)

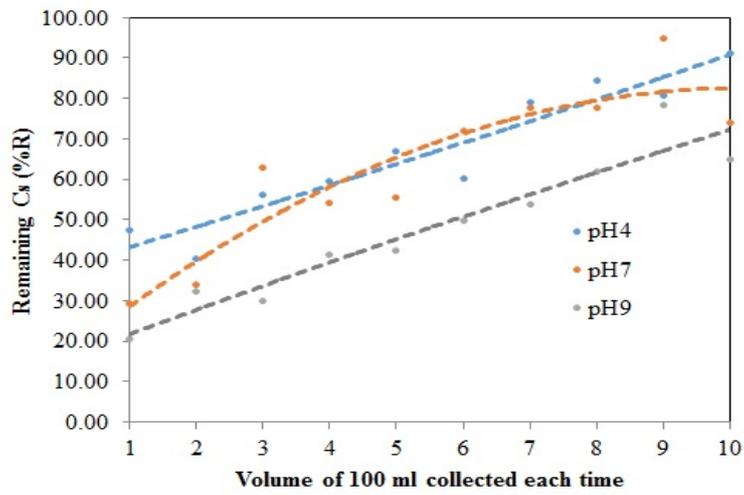


Figure 6. Remaining Cesium (%R)

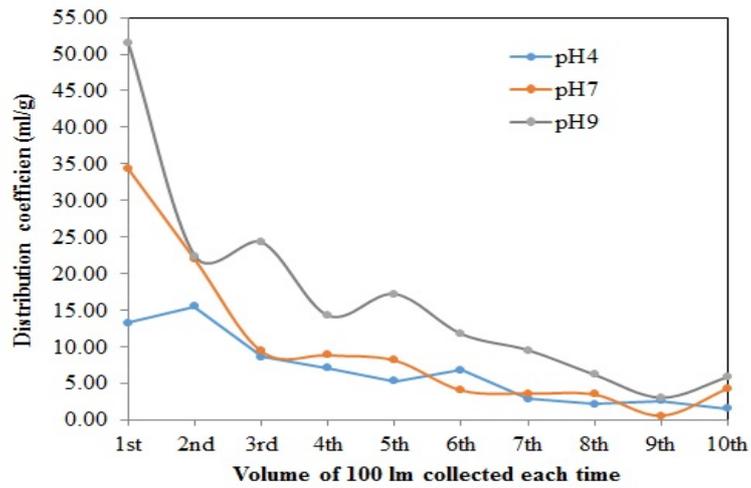


Figure 7. Distribution coefficient (ml/g)

3.2.2 Flow rate of 6 ml/min

At a flow rate of 6 ml/min, similar results to those at 3 ml/min were obtained. Zeolite removal efficiency of cesium decreases from the 1st-100 ml collected to the 10th-100 ml. The greatest zeolite removal efficiency (%E) of cesium of 66.67, 78.47, and 81.08 of the mixed solution (pH of 4,7, and9) was at the 1st-100 ml for all three pH values(Fig 8). The maximum removal efficiency of cesium was observed at pH of 9. The zeolite removal efficiencies of cesium were compared at seawater pH values of 4, 7, and 9. Zeolite efficiency was significantly greater at pH of 9 than at pH of 4 ($P < 0.05$) (Figure 8). At lower pH values, the metal ion uptake was inhibited in the acidic medium which can be attributed to the presence of H^+ ions competing with the Cesium ions (El-Kamash, 2008).

Similarly, the increase of remaining cesium occurred from the 1st-100 ml collected to the 10th-100 ml collected (Figure 9).

The highest distribution coefficient (K_d) of 23.62, 36.52, and 50.92 of the mixed solution (pH of 4, 7, and 9) was at the 1st-100 ml (Figure 10).

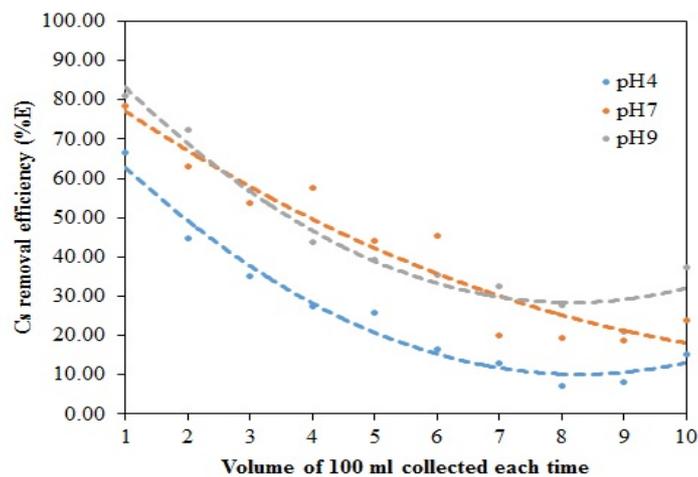


Figure 8. Cesium removal efficiency (%E)

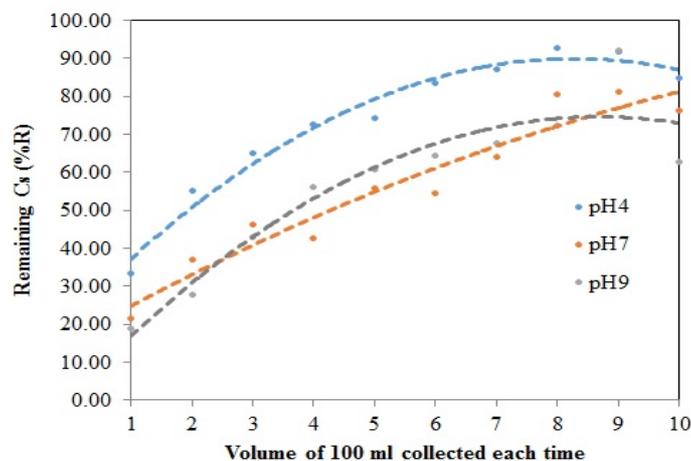


Figure 9. Remaining Cesium (%R)

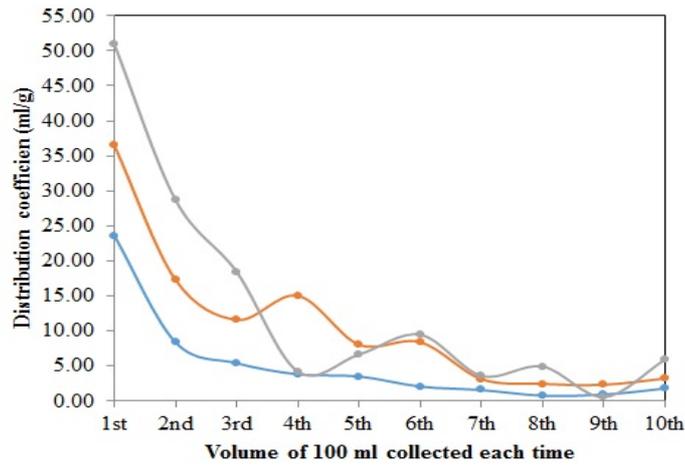


Figure 10. Distribution coefficient (ml/g)

3.3 Flow rate effects

We tested the effect of flow rate of seawater on the removal efficiency of cesium in seawater by zeolite fixed-bed columns. Results revealed that the flow rates of 3 and 6 ml/min. did not show any significant differences in zeolite efficiencies for removing cesium at any pH levels ($P > 0.05$).

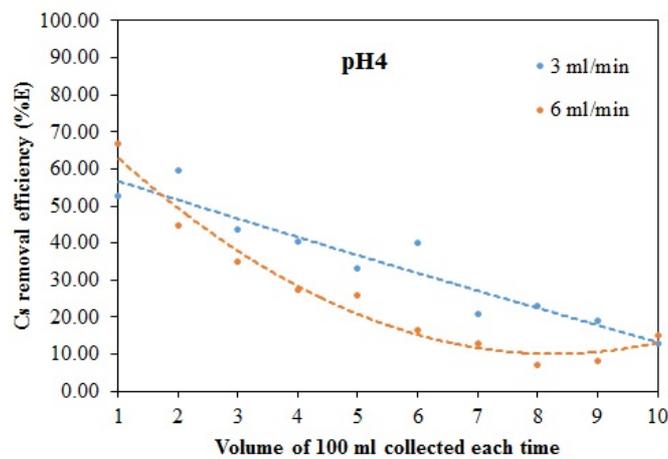


Figure 11. Cesium removal efficiency (%E) at pH4

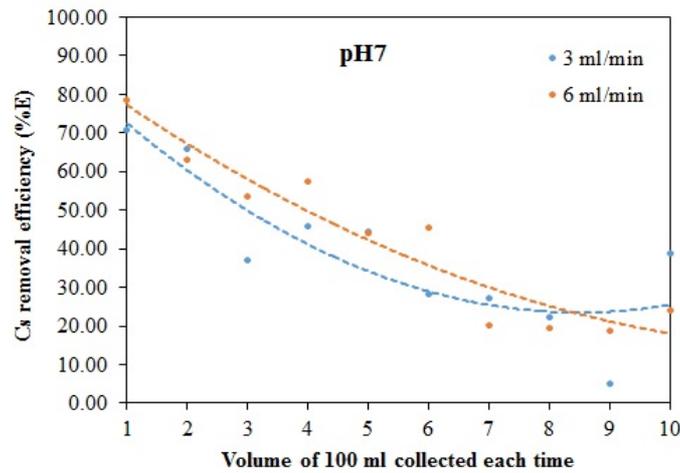


Figure 12. Cesium removal efficiency (%E) at pH7

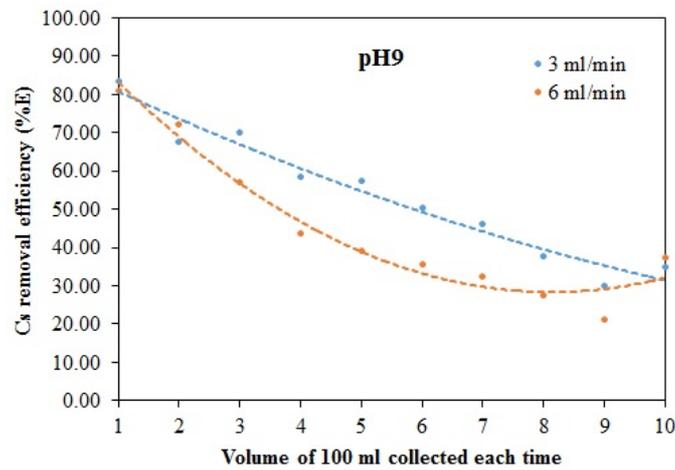


Figure 13. Cesium removal efficiency (%E) at pH9

4. Conclusion

The study was conducted to determine the efficiency of natural zeolite for the removal of cesium and strontium in synthetic seawater by zeolite-fixed bed column. The initial concentration of cesium and strontium was set at 80 and 20 mg/l respectively as cesium chloride and strontium chloride in seawater. Seawater adjusted salinity was 35 ppt. Several variables were considered in the study such as preparation of zeolite (Natural zeolite and natural zeolite treated by sodium chloride), bed depth, pH of seawater and flow rate. Results revealed that natural zeolite treated with NaCl was appropriate for use in this experiment. Zeolite could remove cesium but not strontium from the marine environment. The zeolite removal efficiencies of cesium were compared at seawater pH values of 4, 7, and 9. Zeolite efficiency was significantly greater at a pH of 9 than at a pH of 4 ($P < 0.05$). Efficiency of removal by zeolite was significantly better at a bed depth of 6 cm. (18.84 cm^3) than at only a 3 cm. depth (9.42 cm^3) ($P < 0.05$). However, different flow rates of 3 and 6 ml/min. during zeolite removal did not significantly affect cesium levels ($P > 0.05$).

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