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DESALINATION OF SEAWATER USING NATURAL ZEOLITE FOR AGRICULTURAL UTILIZATION

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ABSTRACT: The aim of this study is to provide an agricultural cultivation solution from seawater with a simple process using natural zeolite. In the 21st century, the demand for food is increasing due to the global population growth, and securing farmland is one of the most important factors in food production. Approximately 20 % of farmland in the world is salt-damaged soil with unsuitable properties for agriculture by high salinity water, and simple desalination methods of high salinity water to improve salt-damaged soil is desired. Natural zeolite has a cation exchange ability and is available in large quantities at low cost. In this study, desalination of seawater, as high salinity water, using Japanese clinoptilolite zeolites with typical exchangeable cation, Na^+, K^+, NH_4^+, Mg^{2+}, and Ca^{2+}, were examined. Ca^{2+}-type zeolite indicates the highest reduction of NaCl from seawater among these ion-exchanged natural zeolites. The column experiment using Ca^{2+}-type natural zeolite shows that pH can be controlled to neutral and salinity can be reduced by the reaction between Ca^{2+} in zeolite and other ions in seawater. Although Radish sprouts did not grow in seawater, they could be grown in the solution treated with column process of Ca^{2+}-type natural zeolite.

Keywords: Seawater Desalination, Natural zeolite, Radish sprout growth, Ca-ion exchange

1. INTRODUCTION

In the 21st century, global environmental issues are very serious and effective utilization of energy and mineral resource and securing food and water are urgent problems. Production of a stable supply of food is essential to sustain human life. Securing agricultural water is one of the most important factors in food production. Due to the global population growth, the demand for water is increasing. Many countries of the Middle East and Africa are in a chronic shortage of water, and it is expected that half of the countries in the world will get into a water shortage in 2025 [1].

One of the ways to supply water resources is seawater desalination because seawater is the most abundant water resources on earth. The multi-stage flash (MSF) method and the reverse osmosis membrane method (RO) are well-known desalination technologies [2], but these technologies are expensive for agricultural use because they are producing high-quality fresh water for domestic or industrial use. However, the highest utilization of fresh water in the world is irrigation, and the percentage of irrigation utilization is 70% of the total freshwater utilization [3]. Agricultural water should contain elements for crops rather than be highly purified. Seawater contains the essential elements needed for plant growth, but its high concentration of NaCl causes salt damage that precludes its direct use. Irrigation water has no need to be high-quality fresh water and can be obtained by reducing the high content of NaCl in seawater.

The securing farmland is also one of the most important factors in food production. Approximately 20 % of farmland in the world is salt-damaged soil with unsuitable properties for agriculture by high salinity water. Furthermore, the cultivated lands in northeast Japan were damaged by the tsunami and became salted soil not to use for agriculture. Therefore, a simple and inexpensive technique is desirable for agricultural use to decrease the salinity of saline water or salted soil.

Natural zeolite occurs in natural deposits, generally associated with grassy volcanic rock, and is available in large quantities at low cost [4], especially Japan is a volcanic country with abundant natural zeolite deposits, such as clinoptilolite, mordenite and so on. Based on their high ion-exchange capacity, absorptivity, water retention, and low cost, natural zeolites have been used in agronomy, horticulture, and industry [5]. Therefore, natural zeolite has the possibility to be used to reduce NaCl in saline water at a low cost. There are some papers for seawater desalination using natural zeolites [6-8]. Little information is available, however, on the treatment of saline water with natural zeolite.

In this study, the ability of ion-exchanged Japanese natural zeolite for seawater desalination is investigated. Reduction of NaCl from seawater using Japanese clinoptilolite-type zeolites with typical exchangeable cation, Na^+, K^+, NH_4^+, Mg^{2+}, and Ca^{2+}, were examined, and column test using ion-exchanged natural zeolite was performed to produce the solution for agricultural utilization from seawater.

2. MATERIALS AND METHODS

2.1 Samples

Seawater used in this study was collected from the surface layer in Imari Bay, Saga Prefecture, Japan. Japanese clinoptilolite-type natural zeolite, which was obtained from the deposit of Koriyama, Kagoshima prefecture, Japan, was used in zeolite treatment.

2.2 Ion-exchanged Natural Zeolite Treatment

Five different ion-exchanged natural zeolites, Na^+-, K^+-, NH_4^+-, Mg^{2+}- and Ca^{2+}-zeolite, were prepared, and the NaCl reductions in seawater by these ion-exchanged zeolites were compared. Before the experiment, natural zeolites used in this experiment was grounded by the mill, sieved under 500 μm, and dried in drying oven at 80 ºC overnight.

Na^+- and NH_4^+-zeolites were prepared using the method reported in [9], and K^+-, Mg^{2+}- and Ca^{2+}-zeolites were prepared as follows. Na^+-zeolite (100 g) was put into 4 M KCl, 2 M $MgCl_2$ or 2 M $CaCl_2$ solution (500 mL) in 1 L vessel, and set in a drying oven at 80 ºC overnight. Then, the slurry was filtrated, and the solid was put into each fresh solution (500 mL) again. This procedure was repeated 3 times, then the obtained solid was washed with 80 % EtOH, and dried at 80 ºC overnight to obtain K^+-, Mg^{2+}- and Ca^{2+}-zeolite. It is noted that all exchangeable cation sites in natural zeolite were completely occupied by the objective cations.

The reduction of NaCl in seawater using ion-exchanged natural zeolites was examined as follows. 1.5 g of natural zeolite was added to 15 mL of seawater and stirred for 2 hours with a magnetic stirrer. After stirring, the slurry was filtered, and then fresh natural zeolite was added to the filtrate. This procedure was repeated 5 times. The concentrations of Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^- and SO_4^{2-} in seawater and the filtrate after each time of zeolite treatments were determined using ion chromatography (DX-120, Dionex).

2.3 Column Test using Ion-exchanged Natural Zeolite

Before the column test, Ca-exchanged natural zeolite packed column was prepared. Natural zeolite particles with the diameter of 1.0 mm (40 g) was packed into the glass column tube (inner diameter: 14 mm, height: 30 cm) sandwiched between layers of quartz wool, 1 M $Ca(NO_3)_2$ solution (100 mL) was then fed to the column from bottom to top at a flow rate of 10 mL/min using a ceramic pump, and the effluent was circulated to the column again for 2 hours. After circulation, distilled water (800 mL) was passed through the column to remove the excess $Ca(NO_3)_2$ in the column to prepare the Ca-exchanged natural zeolite column. Four these columns were prepared.

Seawater desalination experiment was done using Ca-exchanged natural zeolite column. Seawater (40 mL) was fed to the Ca-exchanged column from bottom to top at a flow rate of 4 mL/min using a ceramic pump, and the effluent was circulated to the column again for 2 hours. After circulation, the solution was completely passed through the column to collect the column treated seawater. This column treated seawater was fed to the fresh Ca-exchanged column, and done as the same procedure. This operation was repeated 4 times.

The pH, salinity and the concentrations of main elements, Na^+, K^+, Mg^{2+}, Ca2$^+$, Cl^- and SO_4^{2-}, in the solution after passing through the column was measured using pH meter (Horiba, F-72), salt meter (MK, YK-31SA) and ion chromatography (Tosho, IC-2010), respectively. The changes of each element on each step represent as the ratio of measured concentrations to the original concentrations in seawater (*R*) as follows;

$$R_M = \frac{C_M}{C_0} \quad (M\text{: } Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, SO_4^{2-}) \quad (1)$$

where C_0 and C_M are the initial concentration in original seawater and the measured concentration in the treated solution, respectively.

2.4 Growth Test

The solution after 4 times column treatment, tap water and seawater were applied to growth test using radish sprouts (*Raphanus sativus*). During this test, cultivation was conducted for 10 days at room temperature to investigate the possibility of using the obtained solutions for cultivation.

3. RESULTS AND DISCUSSION

3.1 Desalination Ability of Ion-exchanged Natural Zeolite

Figure 1 shows the change of (a) Na^+ and (b) Cl^- concentrations in seawater as a function of the number of zeolite treatment. Although the Na^+ content is almost constant using Na^+-type zeolite, other types of zeolites can decrease Na^+ content in seawater. The order of Na^+ reduction is $NH_4^+ \fallingdotseq K^+$

≒ Ca^{2+} > Mg^{2+} > Na^{+} ≒ 0, which is good accordance with adsorption affinity of clinoptilolite for cations [10]. On the other hands, Mg^{2+}- and Ca^{2+}-type zeolites, including divalent cations, can decrease Cl^{-} contents in seawater, while Cl^{-} contents are almost constant using Na^{+}-, NH_4^{+}- and K^{+}-type zeolites, including monovalent cations.

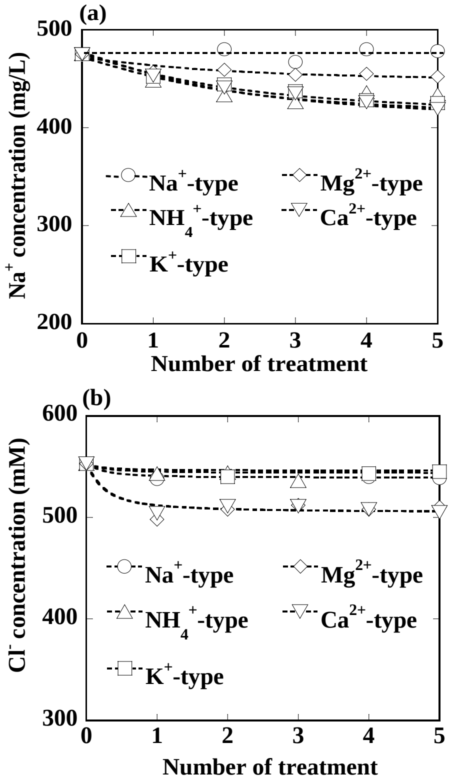

Fig. 1 Change of (a) Na^{+} and (b) Cl^{-} concentrations in seawater as a function of the number of zeolite treatment.

Table 1 shows the chemical compositions of seawater and the solution after 5-times treatment with ion-exchanged natural zeolites. It is noted that original seawater indicates typical chemical compositions of seawater [2], [11]. The cation including in each type-zeolite is high content in each solution, and the contents of K^{+} and Ca^{2+}, which are the cations with high adsorption affinity of clinoptilolite, decrease, except the solutions treated with K^{+}- and Ca^{2+}-type zeolite, respectively. It is considered that the exchangeable cations with high mobility (high affinity) can be exchanged with a high content of Na^{+} in seawater. SO_4^{2-} content is almost constant using all types zeolites. It is unclear why divalent-type zeolite can reduce only Cl^{-} content in seawater. Anion removal using zeolite may depend on surface adsorption because zeolite is cation exchanger. One of the reasons may be that the surface properties of divalent-type zeolite are different to monovalent-type, which indicates a higher affinity for Cl^{-} than SO_4^{2-}.

These results suggest that Ca^{2+}-type natural zeolite is the best for NaCl reduction from seawater.

Table 1 Chemical compositions of seawater (SW) and the solution after 5-times treatment with ion-exchanged natural zeolites (NZ).

	SW	Na^{+}-NZ	NH_4^{+}-NZ	K^{+}-NZ	Mg^{2+}-NZ	Ca^{2+}-NZ
Na^{+}	475	477	402	415	450	406
NH_4^{+}	0.0	0.0	66.5	0.0	0.0	0.0
K^{+}	10.3	0.3	0.9	59.8	5.7	3.1
Mg^{2+}	56.0	51.2	51.9	52.4	73.7	57.3
Ca^{2+}	11.7	6.8	9.3	10.1	10.4	51.1
Cl^{-}	553	541	562	548	507	506
SO_4^{2-}	27.8	28.0	27.6	27.5	27.2	27.1

Unit: mmol/L

3.2 Desalination Using Column

The pH and salinity of the solution after natural zeolite column treatment on each step are shown in Fig. 2. The pH of seawater is 7.76, and those of the solution after zeolite treatment is neutral (pH 6.5 - 7.5), which indicates the solution pH after natural zeolite treatment is neutral to be used for cultivation. The salinity of seawater is 3.40 %, and with increasing the number of treatment to four times, that of the solution gradually decreases to 0.66%, which is approximately one-fifth of the original salinity of seawater.

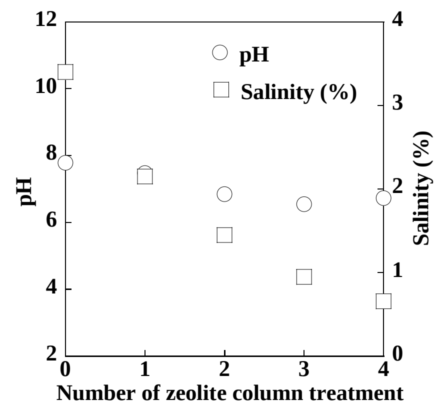

Fig. 2 pH and salinity of the solution treated with Ca-exchanged natural zeolite columns.

Changes of each element in the solution during each number of Ca-exchanged natural zeolite treatment are shown in Fig. 3. On each column treatment, behaviors of all elements are almost the same, and all contents increase and reach equilibrium within 30 minutes.

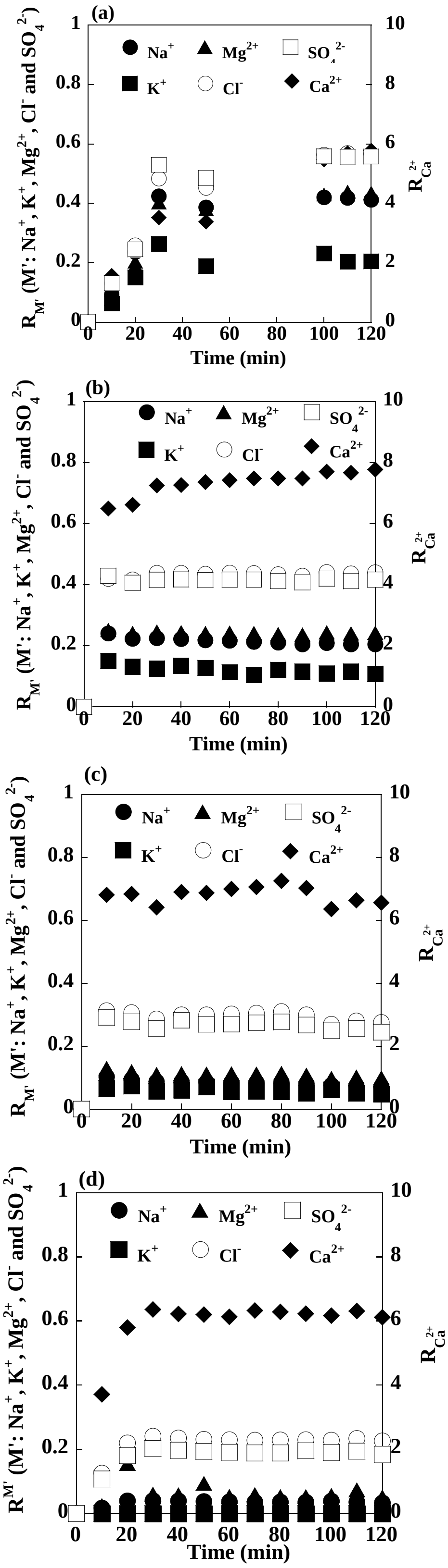

Fig. 3 Ratios of Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^- and SO_4^{2-} in seawater to those in the solution during (a) first, (b) second, (c) third and (d) fourth treatment with Ca-exchanged natural zeolite column.

Ratios of Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^- and SO_4^{2-} in seawater to those in the solution after each number of treatment with Ca-exchanged natural zeolite column are shown in Fig. 4. The contents of Na^+, K^+, Mg^{2+}, Cl^- and SO_4^{2-} drastically decreases on first zeolite treatment and then gradually decrease after second zeolite treatment, which is approximately below one-fifth of the original contents of seawater, while that of Ca^{2+} drastically increases and then be almost constant after second zeolite treatment.

Therefore, the decrease of salinity mainly depends on the decreases of all elements, except Ca^{2+}.

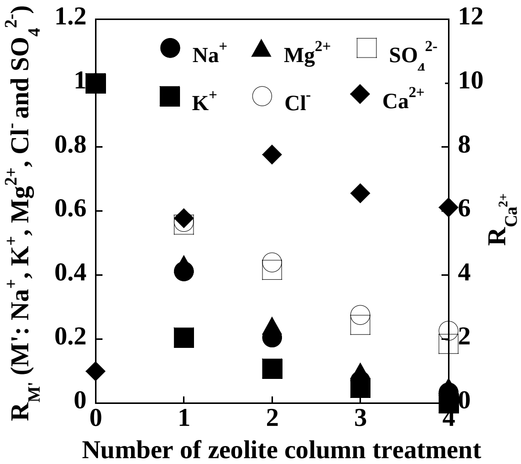

Fig. 4 Ratios of Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^- and SO_4^{2-} in seawater to those in the solution after each number of treatment with Ca-exchanged natural zeolite column.

Table 2 shows the chemical composition, salinity, and pH of seawater and the solutions after various times of natural zeolite treatment. Although seawater contains high amounts of Na^+ (12191 mg/L), Cl^- (21891 mg/L) and other elements and indicates high salinity (3.4 %) The solutions after zeolite treatment contain lower amounts of Na^+, Cl^-, K^+, Mg^{2+}, and SO_4^{2-} than seawater, except Ca^{2+}, and indicates lower salinity than seawater. It is noted that pH of the solution is neutral to be used for cultivation. The contents of Na^+, Cl^-, K^+, Mg^{2+}, SO_4^{2-} and Ca^{2+} in the solution after 4-times natural zeolite column treatments are 405 mg/L, 4959 mg/L, 0 mg/L, 70 mg/L, 504 mg/L and 2466 mg/L, respectively, which indicates that the solution contains low NaCl and minerals, Mg^{2+} and Ca^{2+}, and indicates low salinity (0.66 %) for plant growth.

Table 2 Chemical compositions, salinity, and pH of seawater (SW) and the solution after 1-4 times treatment with Ca-exchanged natural zeolite columns.

	SW	1-times	2-times	3-times	4-times
Contents (mg/L)					
Na^+	12191	5027	2501	857	405
K^+	682	140	74	33	0
Mg^{2+}	1360	592	330	135	70
Ca^{2+}	403	2330	3132	2644	2466
Cl^-	21891	12409	9643	6036	4959
SO_4^{2-}	2724	1520	1136	667	504
Salinity (%)	3.40	2.15	1.45	0.95	0.66
pH	7.79	7.48	6.85	6.55	6.73

Figure 5 shows the growth test of radish sprouts for 10 days at room temperature. Although we could not observe the germination of radish sprouts using seawater, we could confirm the growth of radish sprouts using the treated solution like using distilled water. These results suggested that it is possible to prepare the solution for agricultural cultivation from seawater using Ca-type natural zeolite treatment.

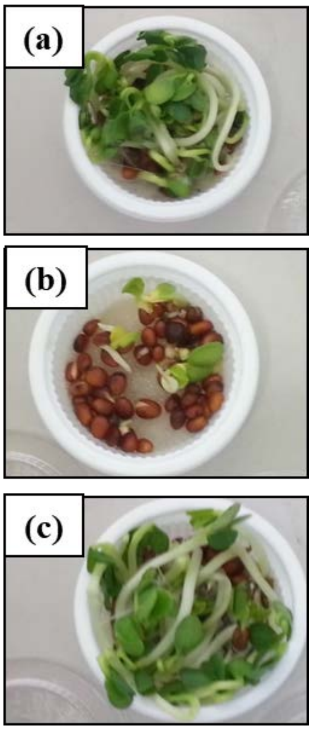

Fig. 5 Observation of *Raphanus sativus* after 10 days growing using (a) tap water, (b) seawater, and (c) the solution after 4 times zeolite treatment of seawater.

4. CONCLUSIONS

The desalination behaviors from seawater using Japanese clinoptilolite-type natural zeolite was investigated in order to be used as desalination agent for producing irrigation water from salty water. The ability of ion-exchanged clinoptilolite zeolite for NaCl reduction from seawater was examined. Among typical ion-exchanged zeolites, such as Na^+-, K^+, NH_4^+, Mg^{2+}- and Ca^{2+}-type natural zeolites, the Ca^{2+}-type zeolite is the best for reduction of NaCl from seawater. We could decrease the salinity of seawater using a simple Ca-exchanged natural zeolite column and can obtain the solution with neutral pH and low salinity to be used for cultivation. Although radish sprouts did not grow in seawater, they could be grown in the solution after zeolite treatment. These results suggested that it is possible to prepare a solution for agricultural cultivation from seawater using a simple Ca-exchanged natural zeolite treatment. I found that Ca-natural zeolite can desalinate seawater by removing both cations and anions. In future, Ca-exchanged natural zeolite will be applied to improve the salted soil to cultivate crops.

5. ACKNOWLEDGMENTS

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