

DESALINATION BEHAVIOR OF NATURAL ZEOLITE IN SEAWATER

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ABSTRACT: In recent years, it has been considered to secure water and food using seawater desalination technology, and a new simple desalination material for reducing high concentration sodium chloride in seawater is required. In this study, desalting agents were prepared from natural zeolite with addition of calcined Ca-Fe type layered double hydroxide (LDH) to desalinate seawater for agricultural use. Mordenite type natural zeolite from Fukushima, Japan was used. The salinity and pH of seawater used in this study were 3.61% and 8.0, respectively. When more than 250 g/L of natural zeolite was added, the salinity decreased from about 3.56% to about 2.92% (reduction : about 18.0%) after stirring for 1 h. With higher dosage of calcined Ca-Fe LDH, the reduction time of salinity and the increase of pH became faster, while the reduction rate of salinity was almost same and pH value increased. When the mixture was used at the mixing ratio of natural zeolite and calcined Ca-Fe LDH was 5:4, the salinity decreased to 1.0% (reduction : about 70.0%) after stirring for 1 h, and the pH of the solution increased to 9.0 - 9.7. Radish sprouts could be harvested using seawater treated with a mixture of natural zeolite and calcined Ca-Fe LDH (5 : 4), while it was not possible to harvest using seawater and seawater treated with natural zeolite with lower addition of calcined Ca-Fe LDH.

Keywords: Natural Zeolite, Calcined Ca-Fe LDH, Desalination, Radish Sprouts

1. INTRODUCTION

In recent years, the demand for water has been increasing due to the increase of the world population, the improvement of economy and living standard. The total amount of water resources on the earth is about 1.3 billion km³. In water resources, seawater is about 97.5%, freshwater is about 2.5%, and human beings can only use about 0.01% of the total water resources due to the most freshwater present as glacier, cloud, vapor and so on. About 70% of fresh water for utilization of human being is used for agriculture. Therefore, the development of technology for obtaining agricultural water from high-salinity water, such as seawater, is under consideration to secure food. The main seawater desalination technologies are the multi-stage flash evaporation method and the reverse osmosis membrane method, which are methods for producing high-purity water used for securing drinking water or industrial water. Therefore, the production of agricultural water using these methods is expensive, and a simple new desalination method is desired [1, 2]. In previous studies, seawater was treated with calcined Mg-Al layered double hydroxide (LDH) and natural zeolite in two steps to obtain a solution that can be used for germination of radish sprouts from seawater [3 - 6] and we have succeeded in cultivating radish sprouts using seawater shaken for 5 h with a mixture of mordenite-type natural zeolite (produced in Iizaka, Fukushima Prefecture, Japan) and calcined Ca-Fe

LDH (calcination at 500 °C) (mixing ratio of zeolite to LDH = 5 : 4) [7]. There is a possibility to develop a new desalination material that reduces the high concentration of sodium chloride in seawater, causing salt damage to a level where crops can grow, using natural zeolite with calcined LDH. However, little information can be available on the desalination behaviors of natural zeolite with calcined Ca-Fe LDH.

In this study, the desalination behaviors of natural zeolite, calcined Ca-Fe LDH and the mixture of these treatment liquid were examined to produce the solution for plant growth from seawater.

2. EXPERIMENTAL

2.1 Samples

Mordenite-type natural zeolite obtained from Iizaka mine, Fukushima Prefecture, Japan was used as a natural zeolite sample. The exchangeable cations (ECs) and cation exchange capacity (CEC) of natural zeolite were shown in Table 1 [5, 6].

Table 1 Exchangeable cations and cation exchange capacity of natural zeolite

CEs (mmol/g)				CEC (mmol/g)
Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	
0.50	0.20	0.02	0.19	1.82

The calcined Ca-Fe LDH was prepared as follows. A mixed solution of Ca^{2+} and Fe^{3+} ($\text{Ca}/\text{Fe} = 2$) (200 mL) was prepared from 0.2 M CaCl_2 solution and 0.1 M FeCl_3 solution, and dropwise to 0.3 M NaCl solution (100 mL) at 4 mL/min. The stirring was carried out for 1 h while bubbling nitrogen gas, and the pH of the NaCl solution was maintained at 12.5 by dropping NaOH solution during the stirring. After stirring, the mixture was filtered, dried, and calcined in an electric furnace at 500°C for 1 h to obtain calcined Ca-Fe LDH [8]. The mineralogical compositions of natural zeolite and calcined Ca-Fe LDH were shown in Fig.1.

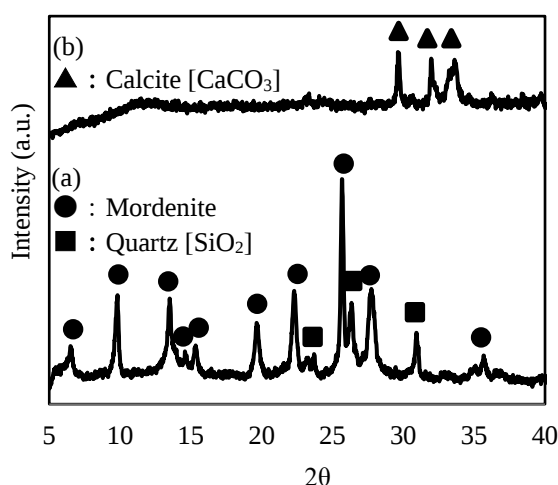


Fig. 1 XRD pattern of (a) natural zeolite and (b) calcined Ca-Fe LDH

Seawater used in this study was collected from the surface layer of Imari Bay, Saga prefecture, Japan. Chemical composition, salinity and pH of seawater were shown in Table 2.

Table 2 Chemical composition, salinity and pH of seawater

	Value
Content (mmol/L)	
SO_4^{2-}	34
Cl^-	805
Na^+	475
K^+	11
Mg^{2+}	71
Ca^{2+}	10
Fe^{3+}	0
Salinity (%)	3.46
pH	8.0

2.2 Desalination Ability

The desalting ability was evaluated as follows. Raw natural zeolite was added to 40 mL of seawater,

and stirred for 0 - 2 h. Calcined Ca-Fe LDH was added to 40 mL of seawater, and shaken for 0 - 2 h. The mixtures of natural zeolite (15 g) and calcined Ca-Fe LDH (1, 6, 12 g) were added to 40 mL of seawater, and stirring for 0 - 24 h. After stirring or shaking, the solution is filtered, the pH of the filtrate is measured by pH meter (Horiba, F-72), salinity is measured by salinity meter (LAQUAact, ES-71), the concentrations of SO_4^{2-} , Cl^- , Na^+ , K^+ , Mg^{2+} and Ca^{2+} in the filtrate were measured with an ion chromatograph (Tosho, IC-2010) and Fe^{3+} content in the filtrate was determined using an atomic absorption spectrophotometer (Perkin Elmer, AAnalyst 200). The reduction rate of each ion in seawater after treatment was calculated using equation (1).

$$R = \frac{C_0 - C}{C_0} \times 100 \quad (1)$$

where R is reduction rate (%), C_0 is each ion concentration in initial solution (mg/L), and C is each ion concentration in the solution after treatment (mg/L). The residue was dried, and the structure was confirmed by a powder X-ray diffraction apparatus (Rigaku, MiniFlex 600).

2.3 Growth Test

Radish sprouts (30 seeds) were used for 10 days growth test. Seawater or seawater treated with the mixtures of natural zeolite and calcined Ca-Fe LDH (5 : 2, 5 : 4) was given by a spray every day, and germinations of radish sprouts were observed [9].

3. RESULT AND DISCUSSION

3.1 Seawater Desalination with Natural Zeolites

Figure 2 shows the salinity and pH of seawater during natural zeolite treatment with various dosages. When 250 - 500 g/L of natural zeolite was added, the salinity rapidly decreased within 15 minutes, and then be almost constant to about 3.0 % (R : about 15.5 - 19.1%). When 50 - 125 g/L of natural zeolite was added, the salinity gradually decreased to 3.11 - 3.16% for 60 minutes, and then be almost constant (R : 11.2 - 12.6%). The pH decreased from 8.0 of seawater to 5.0 - 7.5 in 60 minutes, and became almost constant. With increasing the dosage of natural zeolite, the decrease of pH was larger.

From the above results, when more than 250 g/L of natural zeolite was added, the reduction of salinity was almost same after stirring for 1 h. Therefore, 375 g/L of natural zeolite was used for the subsequent experimental condition.

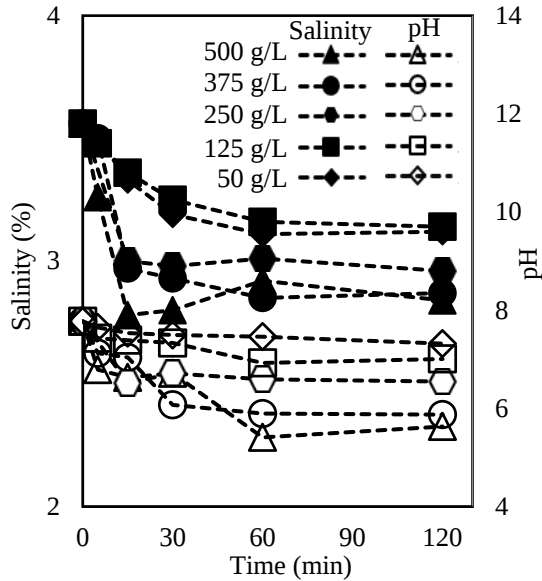


Fig. 2 Salinity and pH of seawater after treatment of natural zeolite

Figure 3 shows amounts of each ion in seawater during natural zeolite treatment. For 30 minutes-stirring, the Na^+ concentration decreased from 475 mmol/L to 274 mmol/L, and then became almost constant (R : about 40%), while the Ca^{2+} concentration increased from 10 mmol/L to 71 mmol/L for 30-minutes stirring. For 60-minutes stirring, Cl^- decreased from 805 mmol/L to 500 mmol/L, and then be almost constant (R : about 27%). The decrease of SO_4^{2-} , K^+ , and Mg^{2+} concentration and the increase of Fe^{3+} concentration were confirmed, and those amounts were very small compared with those of Cl^- , Na^+ and Ca^{2+} concentration. The reduction of SO_4^{2-} , K^+ and Mg^{2+} were 37%, 50% and 37%, respectively.

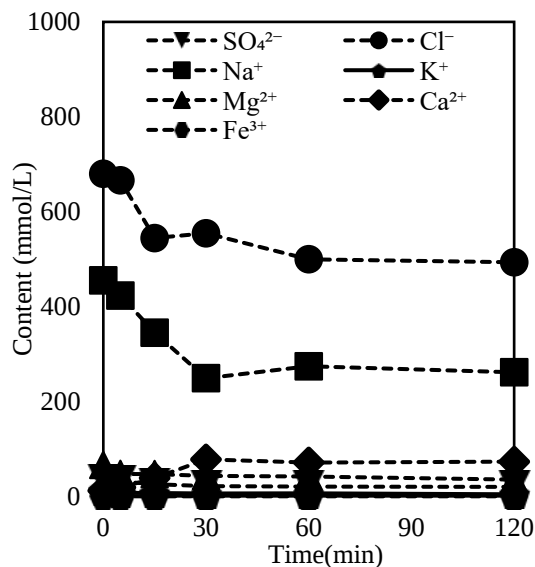


Fig. 3 Concentrations of each content in seawater after treatment of natural zeolite

3.2 Seawater Desalination with Calcined Ca-Fe LDH

Figure 4 shows the salinity and pH of seawater after calcined Ca-Fe LDH treatment. When 300 g/L of calcined Ca-Fe LDH was added, the salinity rapidly decreased from 3.61% to 3.26% (R : about 10%) in 10 minutes, then gradually increased to 3.49%, the pH increased from 8.0 to 10 in 5 minutes and then be almost constant. When 30 g/L of calcined Ca-Fe LDH was added, the salinity decreased to 3.2% after 30 minutes, then gradually increased, the pH increased from 8.0 to 8.8 in 30 minutes and then be almost constant. With higher dosage, the reduction time of salinity decreased and increase of pH became faster, while the reduction rate of salinity was almost same and pH value increased.

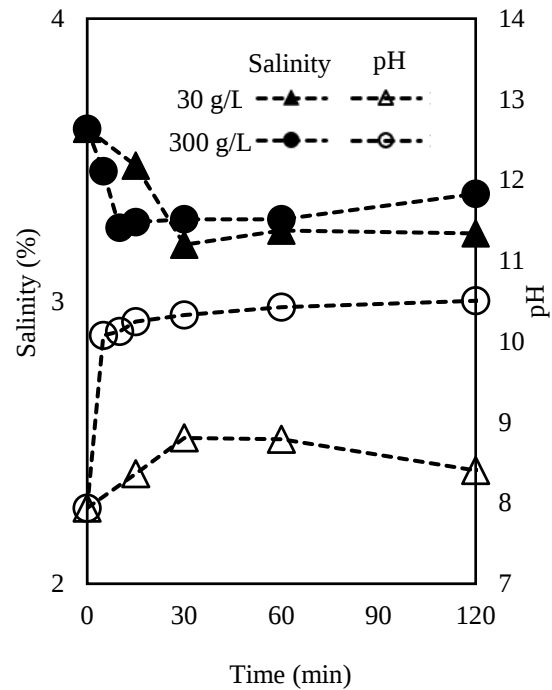


Fig. 4 Salinity and pH of seawater after treatment of calcined Ca-Fe LDH

Figure 5 shows amounts of each ion in seawater during treatment at 300 g/L dosage. The Na^+ concentration decreased from 475 mmol/L to 365 mmol/L in 10 minutes (R : about 23%), and became constant. The Cl^- concentration decreased from 805 mmol/L to 644 mmol/L in 10 minutes (R : about 9%), then was almost constant for 1 h and increased after 1 h. It is considered that Cl^- was captured in the calcined Ca-Fe LDH due to the reconstruction of Ca-Fe LDH (checked by XRD) and Ca-Fe LDH released the captured Cl^- as weak anion by ion exchange reaction of other anions, such as carbonate ion in the solution. The reduction rates of

SO_4^{2-} , Mg^{2+} and K^+ in the solution were about 26%, 24% and 17%, respectively. The Ca^{2+} concentration increased from 10 mmol/L to 333 mmol/L after 1-h treatment, and then became constant. The concentration of Fe^{3+} increased to 0.6 mmol/L within 1-h stirring. It is considered that Ca^{2+} and Fe^{3+} forming calcined Ca-Fe LDH were dissolved into seawater within 1 h.

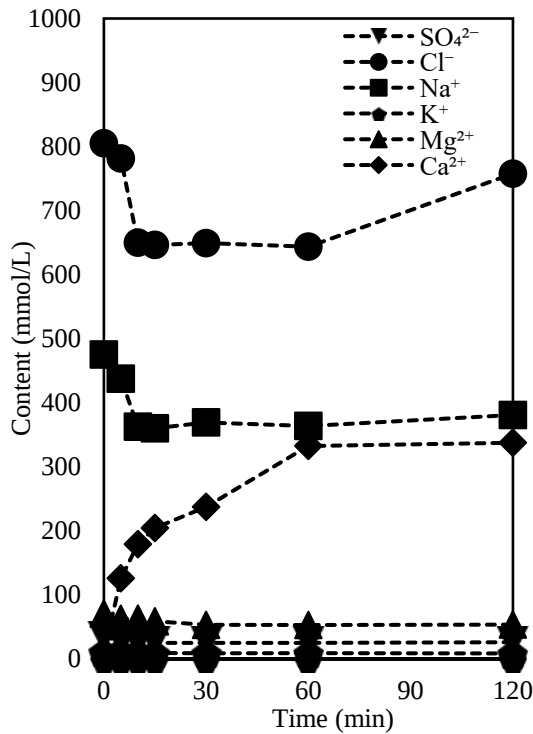


Fig. 5 Concentrations of each content in seawater after treatment of calcined Ca-Fe LDH

3.3 Seawater of Desalination with a Mixture of Natural Zeolite and Calcined Ca-Fe LDH

In order to determine the effect of adding ratio of calcined Ca-Fe LDH to natural zeolite on seawater desalination, the mixtures of natural zeolite (15 g) and calcined Ca-Fe LDH (1, 6, 12 g) were prepared, and their desalination behaviors were investigated.

Figure 6 shows the salinity and pH of seawater during the treatment by each mixture. For all mixtures the salinity reduced within 1 h, and then be almost constant. The mixture of natural zeolite and calcined Ca-Fe LDH (1 g) reduced the salinity to about 2.46% (R : about 32%) and pH became 8.1 after 1-h treatment. The mixture of natural zeolite and calcined Ca-Fe LDH (6 g) reduced the salinity to about 2.1% (R : about 42%) and pH became 9.3 after 1-h treatment. When a mixture of natural zeolite and calcined Ca-Fe LDH (12 g) was added, the salinity decreased to about 1.0% (R : about 70%) after 1 h treatment, then remained constant thereafter, and the pH after the treatment was 9.7. From these results, the salinity was reduced to less

than 1 % at which the plant could be cultivated using the mixture of natural zeolite and calcined Ca-Fe LDH at the mixing ratio of natural zeolite to LDH = 5 : 4.

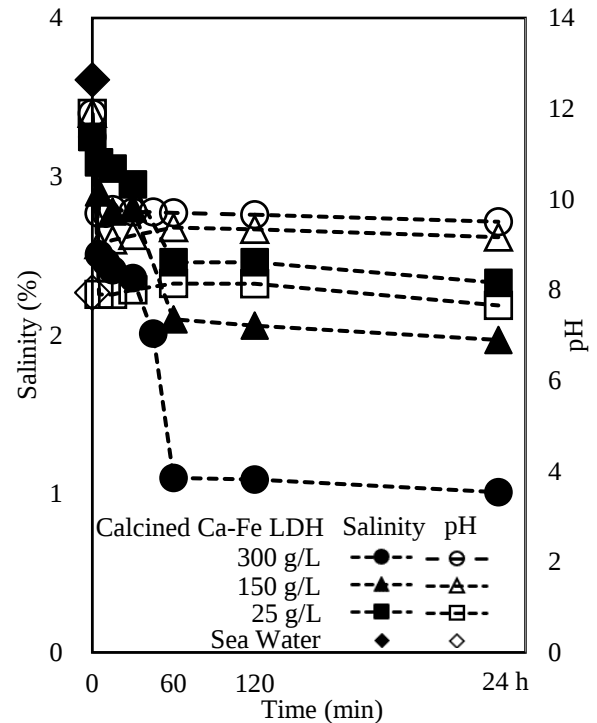


Fig. 6 Salinity and pH of seawater after treatment of the mixture of natural zeolite and calcined Ca-Fe LDH

Concentrations SO_4^{2-} , Cl^- , Na^+ , K^+ , Mg^{2+} , Ca^{2+} and Fe^{3+} in seawater after treatment with a mixture of 15 g of natural zeolite and various amounts of calcined Ca-Fe LDH were examined. The addition amount of calcined Ca-Fe LDH to seawater is (a) 1.0 g, (b) 6.0 g, and (c) 12.0 g.

Figure 7 shows amounts of each ion in seawater during the treatment using each mixture. In all cases, Cl^- and Na^+ were significantly reduced, SO_4^{2-} , K^+ and Mg^{2+} , which were much lower concentrations in seawater than Cl^- and Na^+ , were also reduced, and Ca^{2+} and Fe^{3+} increased. The concentrations of all ions became constant after 1 h stirring regardless of mixing ratio.

In the case of 1.0 g and 6.0 g, Na^+ and Cl^- decreased rapidly for 5 minutes and gradually decreased for 1 h. After 1 h, the concentrations of Cl^- and Na^+ were 441 mmol/L and 280 mmol/L at 1.0 g, and those were 366 mmol/L and 181 mmol/L at 6.0 g, respectively. At 12.0 g, the Cl^- and Na^+ concentrations decreased sharply for 5 minutes, and then gradually decreased to 226 mmol/L and 60 mmol/L, respectively. The concentration of Ca^{2+} in the solution after 1-h increased with increasing the LDH addition.

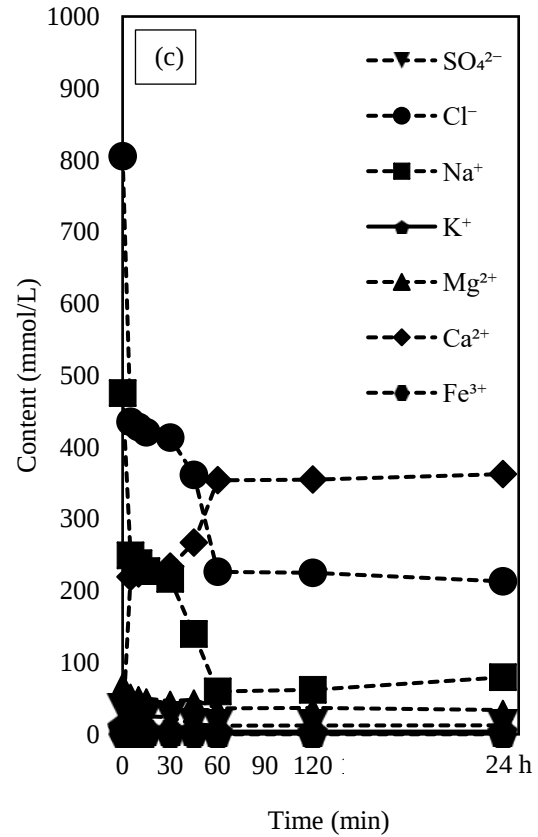
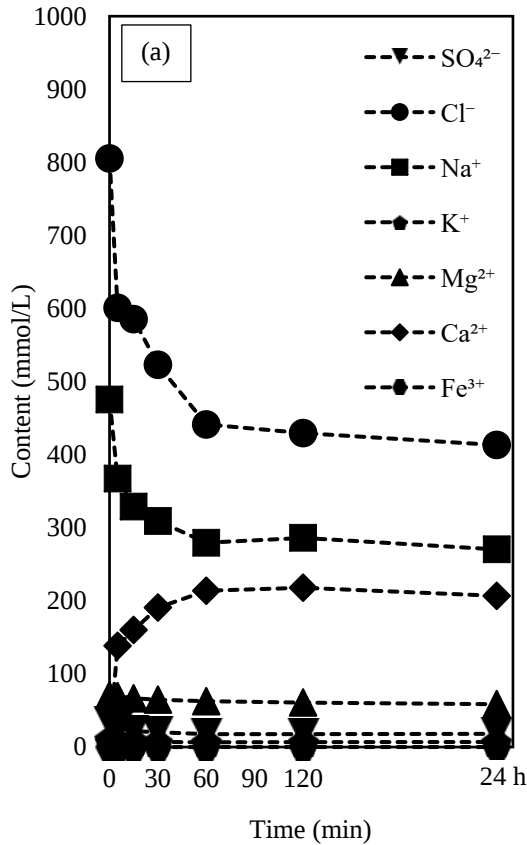
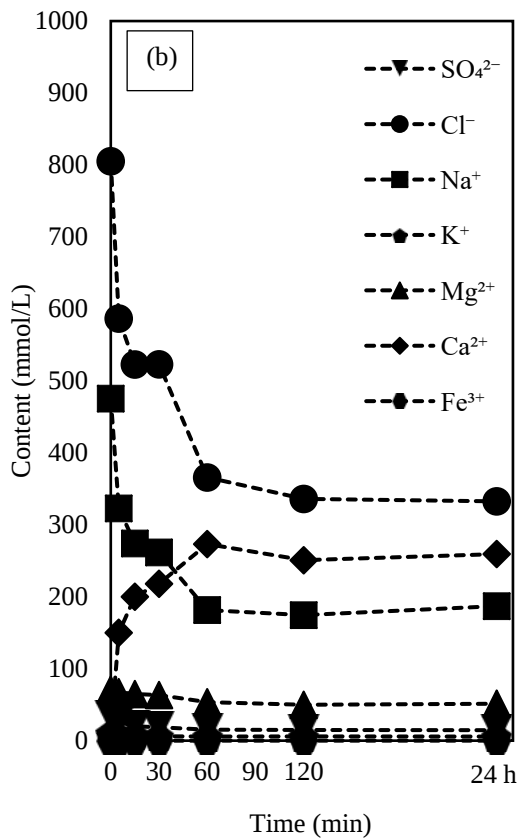


Fig. 7 Concentrations of each content in seawater after treatment of the mixture of natural zeolite and calcined Ca-Fe LDH of (a) 1.0 g, (b) 6.0 g and (c) 12.0g



When desalting seawater with natural zeolite and calcined Ca-Fe LDH, the concentrations of SO_4^{2-} , Cl^- , Na^+ , K^+ , Mg^{2+} decreased, and Ca^{2+} and Fe^{3+} increased. With increasing the LDH addition, these change is larger and the salinity of seawater decreases.

3.3 Cultivation of Radish Sprouts

Table 3 shows the ion contents, salinity and pH of (a) seawater, (b) seawater treated with the mixture of natural zeolite (15 g) and calcined Ca-Fe LDH (6 g) and (c) seawater treated with the mixture of natural zeolite (15 g) and calcined Ca-Fe LDH (12 g). It is noted that treatment time is 1 h.

By desalting with a mixture of natural zeolite and calcined Ca-Fe LDH, Cl^- and Na^+ were significantly reduced from seawater concentrations. In addition, the decrease rate increased as the amount of calcined Ca-Fe LDH added increased. The concentration of Ca^{2+} in the treated seawater increased as the amount of calcined Ca-Fe LDH added increased. Other SO_4^{2-} , K^+ and Mg^{2+} were much smaller than those of Cl^- and Na^+ , and with increasing calcined Ca-Fe LDH addition these

contents decreased. Fe^{3+} concentration were zero regardless of the treatment.

Table 3 Each ion concentration, salinity and pH of (a) the seawater and (b) the seawater after treatment of the mixture of natural zeolite (15 g) and Calcined Ca-Fe LDH (6 g) and (c) the seawater after treatment of the mixture of natural zeolite (15 g) and calcined Ca-Fe LDH (12 g)

Sample	(a)	(b)	(c)
Content (mmol/L)			
SO_4^{2-}	34	15	12
Cl^-	805	333	226
Na^+	475	187	60
K^+	11	6	4
Mg^{2+}	71	51	36
Ca^{2+}	10	259	354
Fe^{3+}	0	0	0
Salinity(%)	3.61	2.10	1.10
pH	8.0	9.3	9.7

Figure 8 shows observation of radish sprouts after 10 day growth using (a) seawater, (b) the seawater treated with the mixture of natural zeolite (15 g) and calcined Ca-Fe LDH (6 g), and (c) the seawater treated with the mixture of natural zeolite (15 g) and calcined Ca-Fe LDH (12 g). The germination of radish sprouts could be confirmed in seawater treated with a mixture of natural zeolite (15 g) and calcined Ca-Fe LDH (12 g), while radish sprouts cannot be germinated in seawater and seawater treated with a mixture of natural zeolite (15 g) and calcined Ca-Fe LDH (6 g).

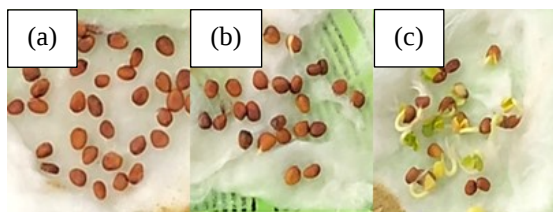


Fig. 8 Observation of radish sprouts after 10 day growth using (a) seawater, and (b) the seawater treated with the mixture of natural zeolite (15 g) and calcined Ca-Fe LDH (6 g) and (c) the seawater treated with the mixture of natural zeolite (15 g) and calcined Ca-Fe LDH (12 g)

4. CONCLUSION

Mordenite type natural zeolite mixed with calcined Ca-Fe LDH were used for desalination of seawater. By investigating the desalination behavior of these, we attempted to develop

desalination materials to obtain the solution for agriculture from seawater in order to stably supply agriculture water resources.

When 250 - 500 g/L of natural zeolite was added, the salinity rapidly decreased within 15 minutes to about 3.0% (R : about 15.5-19.1%). When 300 g/L of calcined Ca-Fe LDH was added, the salinity rapidly decreased from 3.61% to 3.26% (R : about 10%) in 10 minutes, then gradually increased to 3.49%, the pH increased from 8.0 to 10 in 5 minutes and then almost constant. With higher dosage, the reduction time of salinity and increase of pH became faster while the reduction rate of salinity was almost same and pH value increased. When a mixture of natural zeolite (375 g/L) and calcined Ca-Fe LDH (300 g/L) was added, the salinity decreased to about 1.0% (R : about 70%) after 1 h treatment, then remained constant thereafter, and the pH after the treatment was 9.7. Germination of radish sprouts was confirmed in seawater treated with a mixture of mordenite type natural zeolite (375 g/L) and calcined Ca-Fe LDH (300 g/L) for 1-h. From these results, the salinity was reduced to less than 1 % at which the plant could be cultivated using the mixture of natural zeolite and calcined Ca-Fe LDH.

5. REFERENCES

- [1] Wajima T., Shimizu T., and Ikegami Y., New simple proceed of making agricultural cultivation solution from seawater, Bull. Soc. Sea Water Sci. Jpn., Vol. 60, 2006, pp. 201-202.
- [2] Wajima T., Shimizu T., and Ikegami Y., Ion exchange properties of natural zeolite in the preparation of an agricultural cultivation solution from seawater, J. Ion. Exch., Vol. 18, 2007, pp. 201-202.
- [3] Wajima T., Shimizu T., and Yamato T., Removal of NaCl from seawater using natural zeolite, Int. J. Toxicol. and Environ. Chem., Vol. 91, Issue 1, 2010, pp. 21-26.
- [4] Wajima T., Ion exchange properties of Japanese natural zeolite in seawater, Anal. Sci., Vol. 29, 2013, pp. 139-141.
- [5] Wajima T., Shimizu T., Yamamoto T., and Ikegami Y., Simple two-step process for making agricultural cultivation solution from seawater using calcined hydrotalcite and natural zeolite, Clay Sci., Vol. 14, 2008, pp. 7-12.
- [6] Wajima T., Desalination behavior of calcined hydrotalcite from seawater for preparation of agricultural cultivation solution using natural zeolite, Energy Environ. Res, Vol. 4, 2014, pp. 3-10.

- [7] Sekihata F., and Wajima T., Desalination behavior of natural zeolite in seawater, Int. J. GEOMATE, Vol. 19, 2020, pp. 123-129.
- [8] Tsutsui D., and Wajima T., Desalination property of various calcined layered double hydroxides from seawater, Int. J. Environ. Agri. Res., Vol. 4, Issue 11, 2018, pp. 15-21.
- [9] Wajima T., Desalination of seawater using natural zeolite for agricultural utilization, Int. J. GEOMATE, Vol. 16, 2019, pp. 21-26.

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