

SIMPLE TWO-STEP PROCESS FOR MAKING AGRICULTURAL CULTIVATION SOLUTION FROM SEAWATER USING CALCINED HYDROTALCITE AND NATURAL ZEOLITE

TAKAAKI WAJIMA^{a,*}, TOMOE SHIMIZU^b, TAKEHIKO YAMATO^b and YASUYUKI IKEGAMI^c

^a *Department of Applied Chemistry, Faculty of Engineering and Resource Science, Akita University, 1-1, Tegata-gakuen cho, Akita 010-8502, Japan*

^b *Faculty of Science and Engineering, Saga University, 1-Honjo, Saga 840-8502, Japan*

^c *Institute of Ocean Energy, Saga University, 1-48, Kubara, Yamashiro-cho, Imari, Saga 849-4256, Japan*

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ABSTRACT

We attempted to make agricultural cultivation solution from seawater with a two-step process using calcined hydrotalcite and natural zeolite. Commercial calcined hydrotalcite was used in first step to reduce Cl⁻ content in seawater. Two types of Japanese natural zeolite, mordenite-type zeolite (Iizaka mine, Fukushima prefecture) and clinoptilolite-type zeolite (Koriyama mine, Kagoshima prefecture) were used in second step to reduce Na⁺ concentration. Cl⁻ in seawater can be reduced by calcined hydrotalcite to obtain anion-reduced solution; Na⁺ can be reduced by ion exchange with both types of natural zeolite. The obtained solution was neutral, and included the nutrients K⁺, Mg²⁺, and Ca²⁺, and low levels of Na⁺ and Cl⁻. Higher concentrations of K⁺, Mg²⁺ and Ca²⁺ in the solution can be obtained by mordenite-type Iizaka natural zeolite than those by clinoptilolite-type Koriyama natural zeolite. Radish sprouts did not grow in seawater and anion-reduced solution, but they grew in both solutions after zeolite treatment.

Key words: Agricultural cultivation solution, Calcined hydrotalcite, Natural zeolite, Radish sprout, Seawater

INTRODUCTION

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. Recent environmental problems such as soil desertification are major contributors to the decline in water resources for crops, and an increasing number of regions are having difficulty achieving a stable supply of food. During the twentieth century, the global human population increased fourfold, but the withdrawal of water from natural freshwater sources increased eightfold (Abdul, 2006).

Effective utilization of resources is an important issue in the twenty-first century (WWC, 2002). One of the ways to supply water resources is seawater desalination. The multi-stage flash (MSF) method and the reverse osmosis membrane method (RO) are well-known desalination technologies (Goto, 2000) in which almost all ions contained in seawater are removed, producing high-quality fresh water for domestic or

industrial use. However, the highest utilization of the fresh water in the world is irrigation, and the percentage of irrigation utilization is 70% of the total freshwater utilization (Tilzer, 2006). Agricultural water should contain elements for crops rather than be highly purified. The water produced by MSF or RO is expensive for agriculture. High-purity water requires the addition of fertilizer before application to the agricultural field. Seawater contains the essential elements needed for plant growth, but its high concentration of NaCl causes salt damage that precludes direct use. Producing irrigation water from seawater by reducing NaCl using a simple process would be extremely advantageous.

We attempted a new, simple two-step process to reduce the NaCl concentration in seawater using hydrotalcite-like compound (CHT) and natural zeolite. There has been no attempt to apply these materials for desalination. CHT is inorganic matter that can remove anions. It can be synthesized from dolomite (Kameda et al., 2001), or aluminum dross (Shibata et al., 2005). Zeolite occurs in natural deposits, is generally associated with grassy volcanic rock, and is available in large quantities at low cost (Tominaga, 2001). Based on their high ion-exchange capacity, absorption characteristics, water retention and low cost, natural zeolites have been used in agrono-

* Corresponding author: Takaaki Wajima, Department of Applied Chemistry, Faculty of Engineering and Resource Science, Akita University, 1-1, Tegata-gakuen cho, Akita 010-8502, Japan, e-mail: wajima@gipc.akita-u.ac.jp

my, horticulture and industry (Akgü et al., 2006). This process can be applied to seawater after its use as a coolant in electric power plants and chemical plants. For example, we expect this process to be useful for vegetation in arid areas (e.g., Saudi Arabia, Egypt).

We examined the reduction of Cl^- and Na^+ , other elemental contents of the solution, and pH of the solution during the process for producing agricultural cultivation solution from seawater. We then applied the prepared solution to the growth of an agricultural crop.

EXPERIMENTAL

Seawater and experimental procedure

Seawater was collected from the surface layer in Imari Bay, Saga Prefecture, Japan. Commercial CHT, KW-2000 (Kyowa Kagaku Kogyo Company Limited, Japan) was used in the first step. Two types of Japanese natural zeolite, Iizaka-zeolite (IZ; obtained from Fukushima prefecture) and Koriyama-zeolite (KZ; obtained from Kagoshima prefecture) were used in the second step.

We attempted to reduce NaCl from seawater using a two-step process (Fig. 1). The first step involved reducing the Cl^- content in seawater. CHT was added to seawater and stirred. This solution was filtered after stirring to obtain CHT-solution with about 10000 mg/L of Cl^- . The second step involved reducing Na^+ content in the CHT solution. Natural zeolite was added to CHT-solution, and the solution stirred for 1 h. After stirring, the solution was filtered, and fresh natural zeolite was added to the filtrate. It was then stirred for 1 h. This ion-exchange process was repeated to reduce Na^+ to obtain IZ-

solution and KZ-solution using IZ and KZ, respectively. IZ-solution and KZ-solution were applied as potential agricultural cultivation solutions.

Anion reduction process

We examined the effects of the amount of CHT addition and reaction time on Cl^- and SO_4^{2-} reduction from seawater.

To investigate the effect of the amount of addition, 0.05–2.5 g of CHT was added into 10 mL of seawater (5–250 g/L; the addition was 100 g/L, i.e., 0.1 g of CHT was added to 10 mL of seawater) and the slurry was shaken for 24 h with a reciprocal shaker. After agitation, the solution was separated by centrifugation to measure Cl^- and SO_4^{2-} contents, and pH of the solution.

To investigate the effect of reaction time, 50 g of CHT was added to 500 mL of seawater and stirred with a magnetic stirrer. During stirring, 3-mL aliquots of the slurry were removed at varying time intervals (every 1 h initially) to determine concentrations of Cl^- and SO_4^{2-} in seawater over 10 h.

Natural zeolite treatment

We examined the effect of the number of zeolite treatments on Na^+ reduction from CHT-solution, which was treated with CHT at a ratio of CHT to seawater (S/L) = 1/10 for 4 h.

Twenty grams of natural zeolite was added to 200 mL of CHT-solution and stirred for 1 h with a magnetic stirrer. After stirring, the slurry was filtered and fresh natural zeolite added to the filtrate. This procedure was repeated eight times. We determined the pH of the filtrate, and the concentrations of Na^+ , K^+ , Mg^{2+} and Ca^{2+} in the filtrate for each round of exposure to zeolite.

Cultivation estimation

We grew radish sprouts (*Raphanus sativus*) using the solution obtained during the process. Cultivation proceeded for 10 days at 25°C to investigate the possibility of using the solution.

Characterization

Chemical and mineralogical properties of samples were determined by X-ray fluorescence spectrometry (XRF, XRF-1700, Shimadzu) and X-ray diffraction (XRD) with a Rigaku RAD-C diffractometer using $\text{CuK}\alpha$ radiation, respectively. The pH of the filtrate was measured with a pH meter (MA-130, Mettler Toledo). Concentrations of Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- and SO_4^{2-} in the solution were determined using ion chromatography (DX-120, Japan Daionex). Exchangeable cations and cation exchange capacities of IZ and KZ were measured by the modified Schollenberger's method (DNUM, 1994).

RESULTS AND DISCUSSION

Anion reduction process for the production of CHT-solution

Figure 2 and Figure 3 show the change of pH, and the concentrations of Cl^- and SO_4^{2-} as a function of amount of addition of CHT, respectively. With increasing CHT addition, the pH of the seawater rapidly increased to 12 at < 50 g/L of CHT addition, and thereafter slowly increased. SO_4^{2-} concentration in the solution decreased rapidly at > 50 g/L of CHT addition,

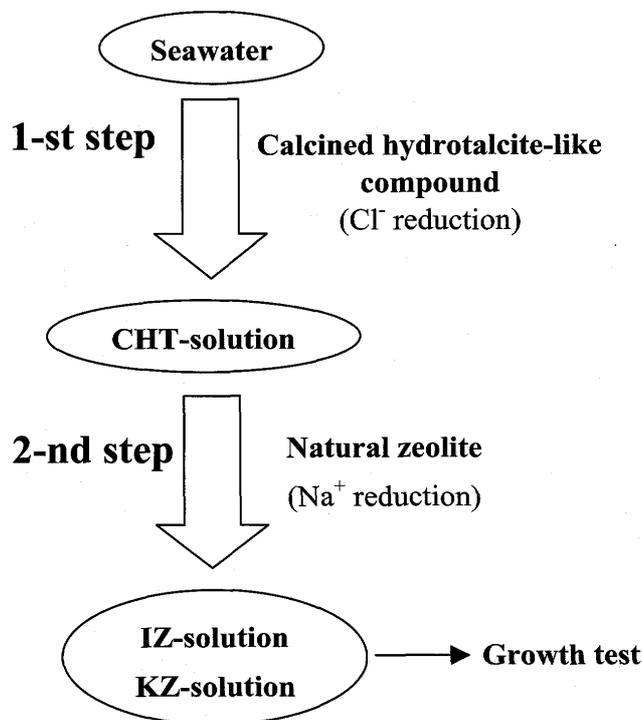


FIG. 1. Method of production of agricultural cultivation solution.

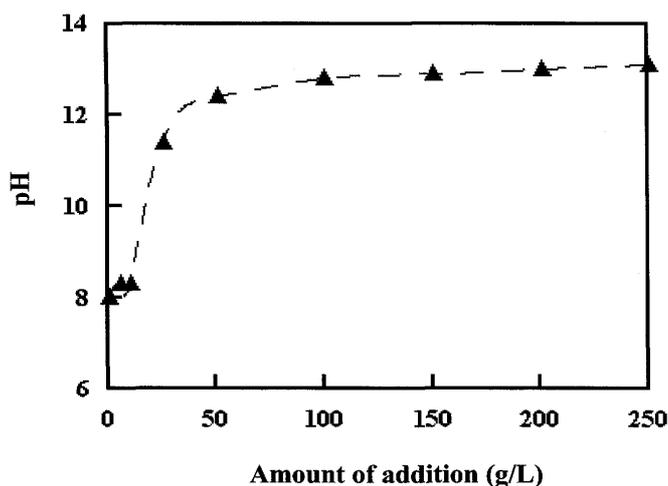


FIG. 2. Change in solution pH as a function of amount of CHT addition.

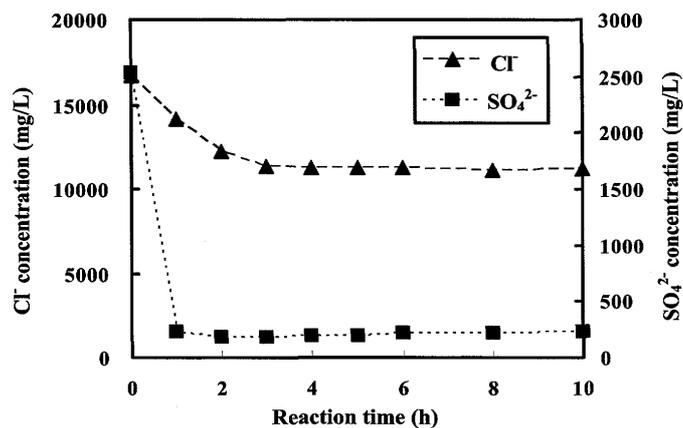


FIG. 4. Change of concentration of Cl^- and SO_4^{2-} with addition of CHT as a function of reaction time.

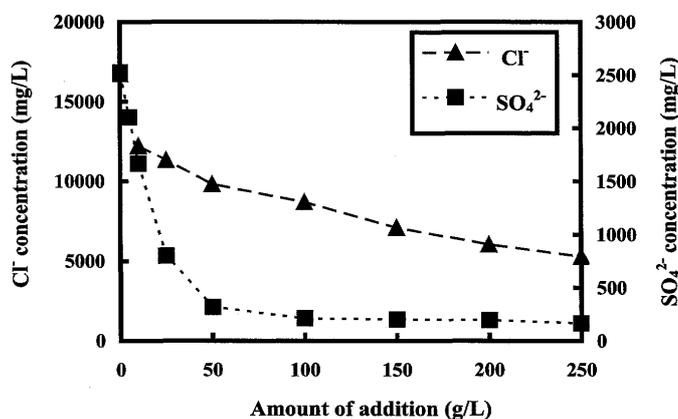


FIG. 3. Change of concentration of Cl^- and SO_4^{2-} as a function of amount of CHT addition.

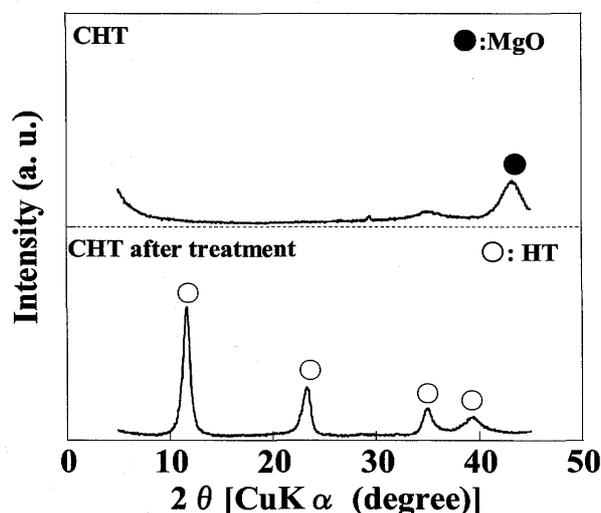


FIG. 5. X-ray diffraction patterns of CHT and CHT after treatment.

thereafter becoming almost constant, whereas Cl^- concentration in the solution decreased slowly due to the higher selective removal of SO_4^{2-} than that of Cl^- by CHT (Kameda et al., 2003). The tendencies of anion concentration ($\text{SO}_4^{2-} + \text{Cl}^-$) and pH were almost similar because CHT has the characteristic of fixing anions and releasing OH^- (Kameda et al., 2001). In our previous studies, it was sufficient to reduce about 10000 mg/L of Cl^- in seawater for making cultivation solution (Wajima et al., 2006a; Wajima et al., 2006b). From these results, the reduction of Cl^- content was sufficient with CHT addition of 100 g/L ($S/L = 1/10$).

Figure 4 shows the change in concentration of Cl^- and SO_4^{2-} during the reduction when 50 g of CHT was added to 500 mL of seawater. Cl^- concentration in seawater decreased initially, and become constant after 4 h of reaction; SO_4^{2-} concentration in seawater rapidly decreased below 1 h to become constant. We suggest that the reaction of SO_4^{2-} reduction is saturated faster than that of Cl^- reduction, and that the reaction of Cl^- reduction is saturated after 4 h.

CHT-solution can therefore be obtained to make agricultural cultivation solution by treatment of seawater with CHT at $S/L = 1/10$ for 4 h.

Figure 5 and Table 1 show the XRD patterns and chemical compositions of CHT and CHT after treatment, respectively. CHT contains Mg and Al, and the peaks of MgO, which originated from Mg–Al oxide, were confirmed in the XRD patterns of CHT. After treatment, the Mg–Al oxide intercalated anions (SO_4^{2-} , Cl^-) in seawater (Table 1) and the hydrotalcite (HT) structure was reconstructed (Figure 5). The produced HT contained SO_4^{2-} and Cl^- in interlayer, and can be used as an ion exchanger for the phosphate ion due to the selectivity of HT ($\text{PO}_4^{3-} > \text{SO}_4^{2-} > \text{Cl}^-$) to prevent eutrophication of surface water by an algae bloom (Ookubo et al., 1993; Shin et al., 1996; Kawamoto et al., 1999).

Ion-exchange treatment by natural zeolite

Figure 6 shows the XRD patterns of IZ and KZ. IZ is a mordenite-type zeolite, and KZ is a clinophilolite-type zeo-

TABLE 1. Chemical compositions of CHT and CHT after treatment.

	CHT	CHT after treatment
MgO	66.9	64.6
Al ₂ O ₃	32.9	33.1
CaO		0.4
SO ₃		1.5
Cl		0.2
Total	99.9	99.9

Unit: wt. %

TABLE 2. Chemical compositions of IZ and KZ.

	IZ	KZ
SiO ₂	76.5	73.0
Al ₂ O ₃	13.1	15.5
CaO	3.6	3.4
Fe ₂ O ₃	2.7	1.8
Na ₂ O	1.9	1.8
K ₂ O	1.5	2.5
MgO	0.4	1.2
TiO ₂	0.1	0.3
SO ₃		0.3
P ₂ O ₅		0.1
Total	99.8	99.9

Unit: wt. %

lite. These types of natural zeolites are typical natural zeolite structures found worldwide. Table 2 and Table 3 show the chemical compositions of IZ and KZ, and the exchangeable cations and cation exchange capacities of IZ and KZ, respectively. Although the occurrence and crystal structure of IZ and KZ are different, the chemical composition, the content of each exchangeable cation, and cation exchange capacity were almost identical.

Figure 7 shows the pH of the solution as a function of the number of zeolite treatments. The pH of the solution was almost initial pH (12.4) below two treatments, then decreased to pH 8; solutions become neutral above five treatments. The curves for pH in the treatment of IZ and KZ were very similar, but the decrease of pH from two treatments to five treatments with IZ was more rapid than that with KZ.

Figure 8 shows the change in concentrations of (a) Na⁺, (b) K⁺, (c) Mg²⁺ and (d) Ca²⁺ in the filtrate as a function of the number of zeolite treatments. The concentrations of Na⁺ and K⁺ in the solution decreased and those of Mg²⁺ and Ca²⁺ increased after treatment with both zeolites. The amount of decrease of Na⁺, those of increase of Mg²⁺ and Ca²⁺ by IZ are larger than those by KZ, while the amount of decrease of K⁺ by KZ is larger than that by IZ. The amount of exchangeable cations and the cation exchange capacities of IZ and KZ were almost identical (Table 3). It is thought that these differences are caused by properties in the crystal structures of IZ and KZ.

TABLE 3. Exchangeable cations and cation exchange capacities of IZ and KZ

	Exchangeable cation				Cation exchange capacity
	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	
IZ	0.56	0.21	0.03	0.44	1.67
KZ	0.58	0.28	0.02	0.4	1.51

Unit: mmol/g

The natural zeolite after treatment can also be used as an ion exchanger for NH₄⁺ to prevent the eutrophication of surface water (DNUM, 1994; Oomori et al., 1999).

The trends of the change of these elements in the solution treated with IZ and KZ were very similar. With increasing number of zeolite treatments, the change in the concentration of Na⁺ decreased linearly, and that of K⁺ decreased rapidly until two zeolite treatments, and then decreased slowly. The increase in the concentration of Mg²⁺ and Ca²⁺ started at three zeolite treatments. The "changing points" of the concentrations of Mg²⁺ and Ca²⁺ correlated with that of solution pH. During the first three exposures to zeolite, the adsorption process on the surface overwhelmed the ion-exchange process.

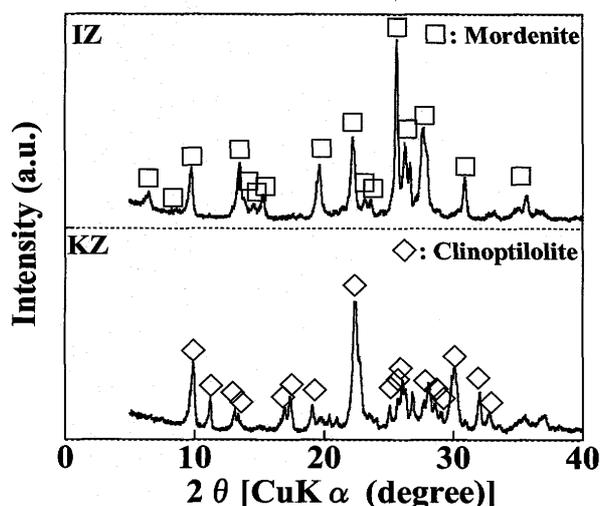


FIG. 6. X-ray diffraction patterns of IZ and KZ.

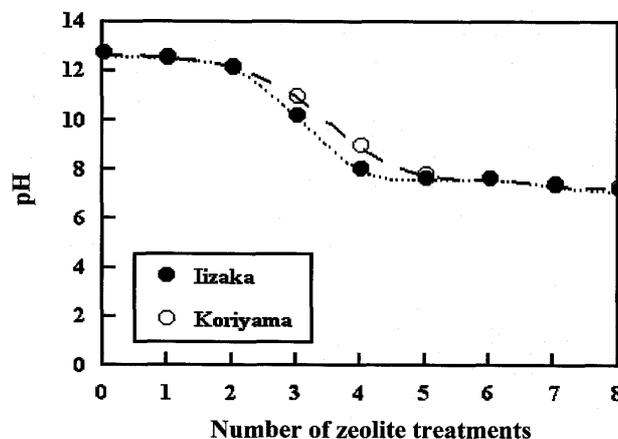


FIG. 7. Change of solution pH as a function of the number of zeolite treatments.

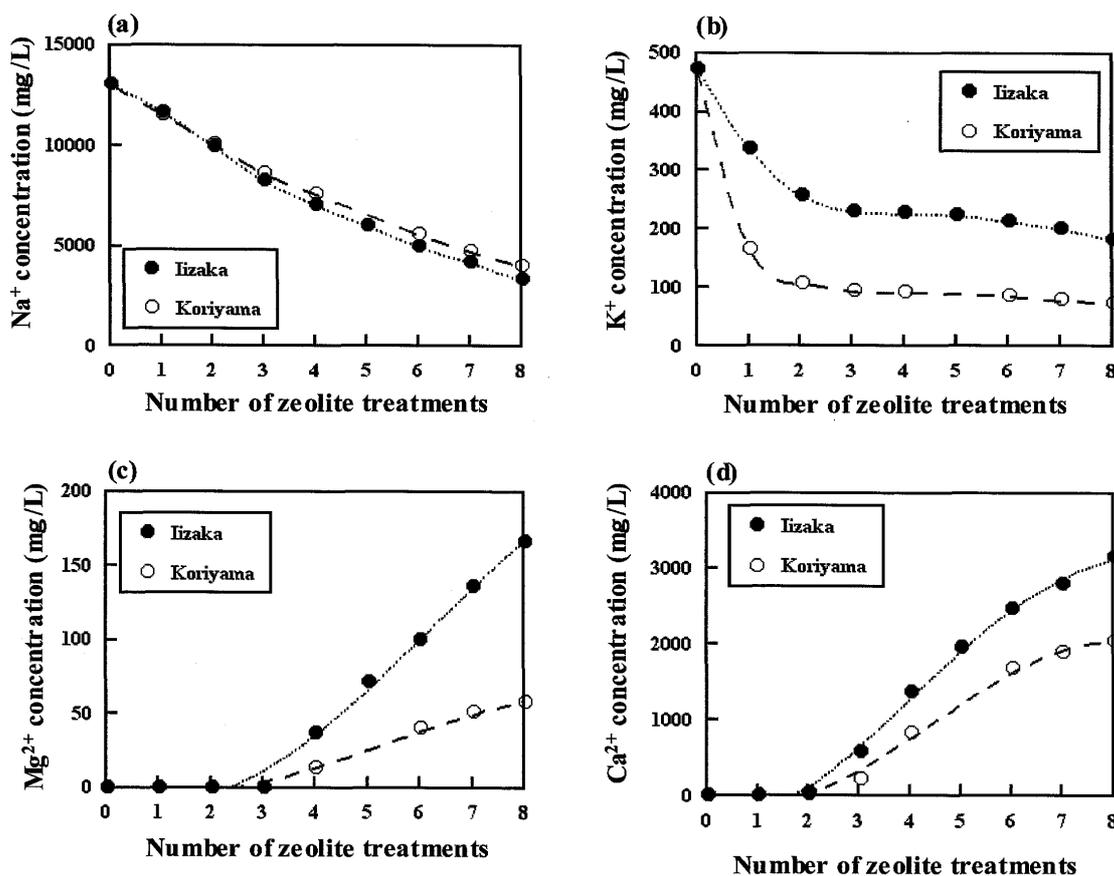


FIG. 8. Change of the concentrations of Na⁺, K⁺, Mg²⁺ and Ca²⁺ in the solution as a function of number of zeolite treatments.

Na⁺ and K⁺ exchanged with H⁺ on zeolite surface to decrease solution pH. The release of Mg²⁺ and Ca²⁺ into the solution was difficult due to the hydroxylation in the alkaline solution (Kragten, 1978). After three rounds of zeolite treatment, the ion-exchange process began to proceed faster than surface adsorption because the pH of the solution reached neutrality, and Mg²⁺ and Ca²⁺ could be released into the solution. The changing points of the concentrations of Mg²⁺ and Ca²⁺ therefore correlated with solution pH.

Cultivation

Radish sprouts were cultivated with seawater, CHT-solution, IZ solution and KZ solution.

Table 4 shows the chemical compositions and pH of seawater, CHT-solution, IZ-solution and KZ-solution. Seawater contained high concentrations of Na⁺ (10000 mg/L) and Cl⁻ (17000 mg/L). The concentrations of Cl⁻ and SO₄²⁻ were greatly reduced in CHT-solution, which was treated with CHT at S/L = 1/10 for 4 h, and the solution was alkaline (pH 12). The concentrations of Mg²⁺ and Ca²⁺ also decreased because the increasing pH caused Mg²⁺ and Ca²⁺ to hydroxylate and precipitate (Kragten, 1978). In IZ and KZ solutions, which were CHT-solutions treated eight times with IZ and KZ, solution pH became neutral, Na⁺ decreased, and Mg²⁺ and Ca²⁺ (which were lost in first step) increased because of ion exchange between the Mg²⁺ and Ca²⁺ in the natural zeolite and the Na⁺ in CHT-solution. Regardless of type of natural zeolite,

TABLE 4. Chemical composition and pH of seawater, CHT-solution, IZ-solution and KZ solution

	Chemical composition (mg/L)						pH
	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	Cl ⁻	SO ₄ ²⁻	
Seawater	10417	375	1262	375	17653	2591	7.9
CHT-solution	12494	444	0	0	11224	89	12.4
IZ-solution	3299	183	166	3161	11162	211	7.2
KZ-solution	3989	73	58	2042	9866	173	7.3

zeolite processing supplemented Mg²⁺ and Ca²⁺ to the solution and neutralized the solution, together with reduction of Na⁺.

Radish sprouts were grown in each solution for 10 days at 25°C (Figure 9). Radish sprouts could be cultivated in the product solutions, IZ and KZ solutions, through a two-step process (Fig. 8 (c), (d)), although they could not be cultivated in seawater and CHT-solution (Fig. 8 (a), (b)). The solution prepared in this process from seawater can be used as a cultivation solution.

CONCLUSION

We attempted to make a solution for agricultural cultivation from seawater with a two-step process using CHT and natural zeolite. We could decrease Cl⁻ in seawater with the addition of CHT at S/L = 1/10 for a 4-h reaction in the first step, and

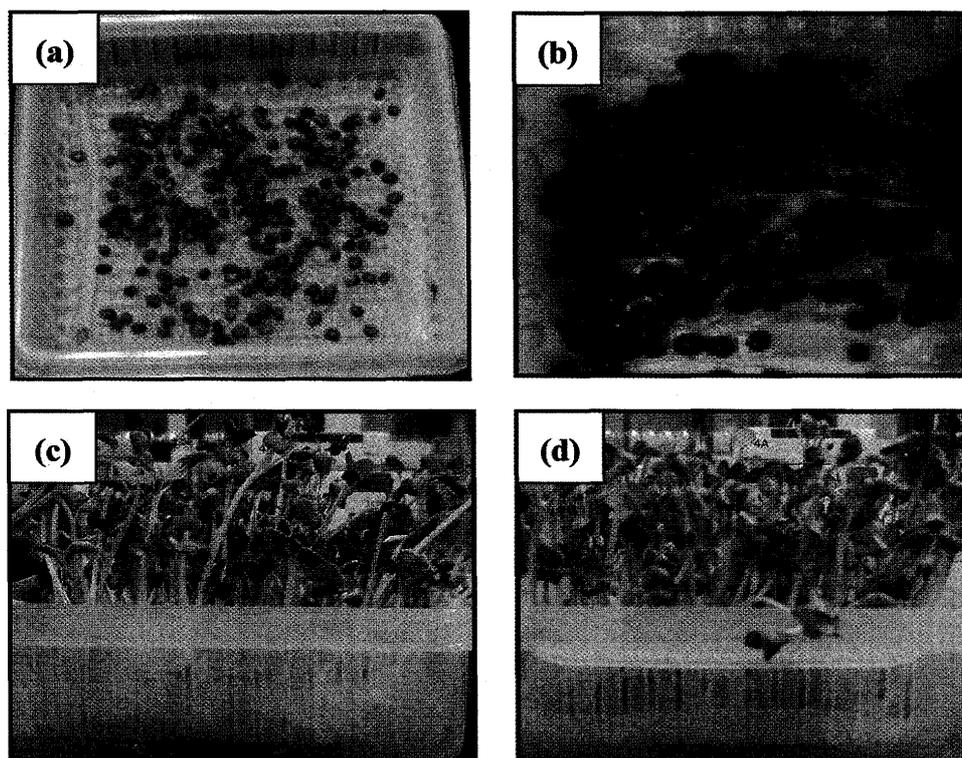


FIG. 9. *Raphanus sativus* after 10 days of growth using (a) seawater, (b) CHT-solution, (c) IZ-solution and (d) KZ-solution.

decrease Na^+ with eight times ion-exchange of natural zeolite. Regardless of type of natural zeolite, the obtained solution was neutral, and included the nutrients, K^+ , Mg^{2+} , and Ca^{2+} , and low levels of Na^+ and Cl^- , which is possible for use in cultivation. Radish sprouts were cultivated using the prepared solutions. Although they did not grow in seawater, they could be grown in the prepared solution. These results suggest that it is possible to prepare a solution for agricultural cultivation from seawater using this process.

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