Research article

Development of the Saturated Ion-Exchangeable Mordenite for Desalinization Technology in Agricultural Fields

YUKIKO HARUTA*
Graduate School of Agriculture, Ehime University, Japan
Email: ahaharuta@gmail.com

CHULEEMAS BOONTHAI IWAI
Faculty of Agriculture, Khon Kaen University, Khon Kaen, Thailand

TAKASHI KUME
Graduate School of Agriculture, Ehime University, Japan

SHINSUKE HARUTA
Graduate School of Agriculture, Ehime University, Japan

Received 25 January 2017 Accepted 5 November 2017 (*Corresponding Author)

Abstract Soil salinization has being occurred not only in arid and semiarid region but in humid region under saline and shallow groundwater condition in the world. In Northeast Thailand, approximately 17% of land is salt- affected and it appears even in paddy fields in dry season. It is not easy to develop water resources in the region because of uneven rainfall patterns and geological formation such as unevenness of terrain. Rainfall in monsoon season charges soil water and groundwater, and it could be used as irrigation water resources. However, the water is salinized, and it needs treatment of desalinization process for the use of irrigation. In preliminary study, we developed artificially saturated mordenite with hydrogen ion for the first step of the development of the technology, and we found high rate of ion-exchange of the mordenite, sodium adsorption and hydrogen desorption, in test solution which was formed by one monovalent cation of sodium. However, soil and groundwater in salinized agricultural fields are not formed by one cation, containing various cations and pH is high, so that we need to reveal ion-exchange ability of the mordenite in such a complicate ion mixed conditions. Therefore, the objective of this study is to develop the saturated mordenites as ion-exchangeable materials for desalinization and to reveal ion-exchange ability of it by batch test. Batch test was conducted using the saturated mordenite and groundwater taken from the salt-affected field in Khon Kaen Province, Northeast Thailand. As a result, we found that sodium ion of the groundwater which contains various cations was adsorbed selectively by saturated mordenite. It is also revealed that alkalization is solved since pH decreased by desorption of hydrogen ion from saturated mordenite to groundwater. Hence, we concluded that the saturated mordenite can be utilized as ion-exchangeable material for desalinization of saline soil and groundwater in the experimental field.

Keywords salinization, saturated mordenite, desalinization of groundwater, ion exchange reaction, developing water resources

INTRODUCTION

In Northeast Thailand, approximately 17% of land is salt-affected and high salinity effects on crop growth (Land Development Department, 1991). Northeast Thailand belongs to tropical wet and dry climate and it distinguish clearly between dry season and monsoon season. Origin of the salt is rock salt in a stratum that called Mahasarakham formed during the Tertiary period, and eluted salts to groundwater is carried to soil surface by evapotranspiration in dry season at location because of high groundwater level. Total area of paddy in Northeast Thailand is approximately 6,070,000 ha and it accounts for 58 % of paddy fields in Thailand. However, productivity of crops is low due to soil degradation and salinization of irrigation water (Kimura et al., 1990). In addition, it is less suitable to construct extensive irrigation facilities in the region because of uneven rainfall patterns and geological formation such as unevenness of terrain (Fuji et al., 2012). Leaching is most popular way to solve salt-affected fields, however, it is not easy to apply it in Northeast Thailand because of less water resources and entailing high costs for development of irrigation and drainage channels.

On the other hand, there are rich amount of shallow groundwater derived from monsoon rainfall in the fields of Khon Kaen, Northeast Thailand. If it can be utilized for irrigation, it may help water resources development for dry season cultivation. Mordenite is a variety of natural zeolite and it has cation adsorb ability and it has been utilized as soil improvement material in various fields (Yoshida et al., 1971). In preliminary study, we have developed three types of saturated mordenite, type-K, type-KH and type-H, these are saturated by potassium ion, potassium ion: hydrogen ion =1:1, and hydrogen ion, respectively. We revealed that three types of saturated mordenite have ability of sodium adsorption, and type-K can supply K^+ to soil, type-H reduce alkalization of soil water and type-KH has both functions. Especially, type-H has high ability to adsorb sodium ion when using test solution of one monovalent sodium cation (Umakoshi, 2016). However, soil water and groundwater in salinized agricultural fields are not formed by one cation, containing various cations and pH is high, so that we need to reveal ion-exchange ability of the mordenite in complicate ion mixed conditions.

OBJECTIVE

The objective of this study is to examine ability of the saturated mordenites as ion-exchangeable materials for desalinization by batch test using saline groundwater in Khon Kaen Province, Northeast Thailand.

MATERIALS AND METHODS

1. Production of Saturated Mordenite Type-H

In this study, we produced saturated mordenite type-H (saturated mordenite) which has highest adsorbed ability of sodium in preceding study (Umakoshi, 2016). Procedure of the production is described below.

Equipment: Following equipments were used in this study: natural mordenite, potassium chloride aqueous solution (1 mol L^{-1}), nitric acid solution (100 mmol L^{-1}), deionized water, ethanol solution, acetone solution, centrifugal tubes (50 mL), weighting machine, shaking machine, centrifugal machine and ventilator.

Test procedure: The test procedures were summarized as follows.

(1) Put 2 g of natural mordenite and 20 mL of potassium chloride aqueous solution (1 mol L^{-1}) in a centrifugal tube then shake it for one hour by shaking machine. Thereafter centrifuge it for ten minutes by centrifugal machine then discard the supernatant liquid.

(2) Put 20 mL of 1 mol L^{-1} potassium chloride aqueous solution in the centrifugal tubes of (1) again then shake it for ten minutes and centrifuge them for 10 minutes and then discard the supernatant liquid. Repeat this process twice.

(3) Change solute in order, 100 mmol L^{-1} Nitric acid solution, Deionized water, Ethanol solution, Acetone solution and then shake them for 10 minutes and centrifuge them for 10 minutes and do same procedure as (2).

(4) Dry mordenite for 24 hours.

2. Groundwater Sampling

We took groundwater from agricultural field in Ban Phai, Khon Kaen Province, Northeast Thailand on 2nd December 2016.

3. Cation Analysis

Cations of the groundwater were analyzed using atomic adsorption spectrophotometer, novAA 350 (Analytik Jena AG) at Khon Kaen University.

4. Batch Test

We conducted batch test to examine quantitative analysis of sodium adsorption by saturated mordenite. Test method and equipment are shown below.
Equipment: The equipments used in this test are as follows: saturated mordenite, pH meter, EC meter, centrifugal tubes (50 mL), shaking machine, centrifugal, machine, atomic adsorption spectrophotometry, deionized water and weighting machine.
Test procedure: The test procedures were indicated as follows.
(1) Analyze cations, Na^{+}, $Ca2^{+}$, K^{+} and $Mg2^{+}$, of groundwater and measure EC and pH.
(2) Put 20 mL of groundwater and 1 g of saturated mordenite type-H (M:GW=1:20), 40 mL of groundwater and 1 g of saturated mordenite (M:GW=1:40), 40 mL of groundwater and 0.5 g of saturated mordenite type-H (M:GW=1:80) in tubes respectively and then shaking them for one hour and centrifuge them for ten minutes.
(3) Analyze the cations of the supernatant liquid and measure EC and pH.

RESULTS AND DISCUSSION

1. Result of Groundwater Analysis

Figure 1 shows result of cation analysis of the groundwater, and EC and pH of the groundwater were 2.3 mS cm^{-1} and 8.0, respectively. Concentration of sodium was 274.5 ppm. It shows that sodium was dominant ion of the groundwater and it was 72% of the total of four cations. CEC of natural mordenite is 2 mmol g^{-1}, therefore it could be estimated that 1 g of saturated mordenite can adsorb sodium ion of 0.17 L of the groundwater.

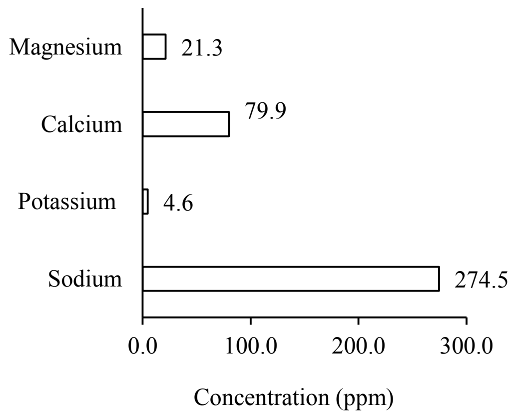


Fig. 1 Cation composition of groundwater

2. Batch Test Using Saturated Mordenite and Groundwater

Table 1 shows changes in concentrations of cations, sodium, potassium, calcium and magnesium, before and after the bath test. Decreasing of the concentrations was due to cations adsorption by saturated mordenite. Sodium concentration after batch test in M:GW=1:80 didn't decrease as much as M:GW=1:20 and M:GW=1:40. It could be due to adsorption of other ions such as ammonium ion which was supplied by fertilizer application in the research field.

Figure 2 shows amounts of adsorbed cations after batch test. Amounts of sodium, calcium and magnesium increased along with increasing the ratios of mordenite to groundwater. It clearly showed that amount of sodium was adsorbed much more than other cations. It means that sodium ion was adsorbed selectively by saturated mordenite. Concentration of potassium after batch test increased. Particle surface of saturated mordenite should be saturated by hydrogen ion and there should be no potassium ion on the surface, so that potassium ion after batch test cannot be increased. So, this should be a measurement error of the equipment.

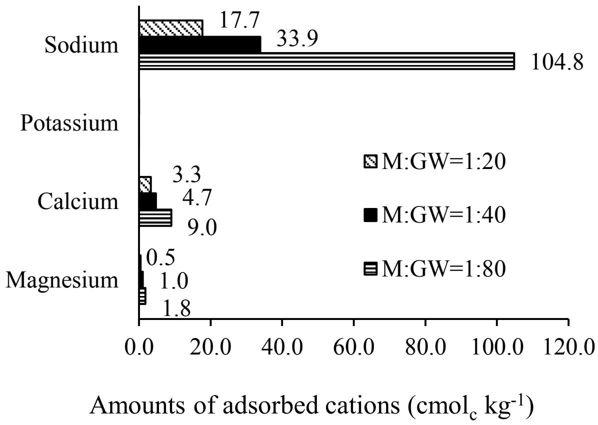


Fig. 2 Amounts of adsorbed or desorbed cations by saturated mordenite

3. Changes in EC and pH before and after Batch Test

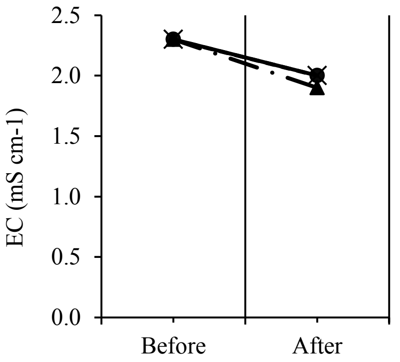
EC and pH decreased after batch test as shown in Figs. 3 and 4. EC didn't decrease as expected because of existing of other cations such as ammonium ion applied by fertilizer and anions. Decreasing of pH was due to ion exchange, sodium adsorption and hydrogen desorption, of particle surface of saturated mordenite. It means that alkalization was reduced since pH decreased by desorption of hydrogen ion from saturated mordenite to groundwater.

Table 1 Changes in ion concentration before and after batch test

Cations		M:GW=1:20	M:GW=1:40	M:GW=1:80
Sodium (mmol L^{-1})	Before	11.9	11.9	11.9
	After	3.1	3.5	5.4
Potassium (mmol L^{-1})	Before	0.1	0.1	0.1
	After	0.1	0.1	0.1
Calcium (mmol L^{-1})	Before	2.0	2.0	2.0
	After	0.4	0.8	1.4
Magnesium (mmol L^{-1})	Before	0.9	0.9	0.9
	After	0.7	0.6	0.9

4. Estimation Cost of Implementation of Saturated Mordenite in Actual Saline Field

Mordenite can be purchased about US$2 per kilo in Japan, so that the amount of mordenite are needed 8.4 kg if we could apply saturated mordenite as sheets on agricultural field which has an area of 1a using the data of groundwater as well as this study. Therefore, the costs were estimated about US$170 considering only costs of mordenite (Haruta, 2018).



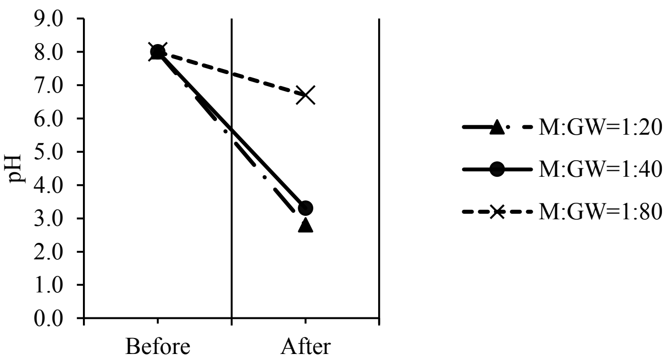


Fig. 3 Changes in EC before and after the batch test

Fig. 4 Changes in pH before and after batch test

CONCLUSION

Sodium ion of the groundwater which contained various cations was adsorbed by saturated mordenite selectively. It is also revealed that alkalization is reduced since pH decreased by desorption of hydrogen ion from saturated mordenite to groundwater. We could reveal ion-exchange ability of saturated mordenite in ion mixed conditions compared to the previous study using test solution (Umakoshi, 2016). Hence, we concluded that the saturated mordenite can be utilized for desalinization of saline soil and groundwater in the experimental field.

Estimated costs for applying saturated mordenite in actual fields were less than US$200 per 1a. There exists shallow groundwater in the field and it goes up to root zone by capillary rise during dry season. Applying saturate mordenite in soil layer in a proper way, it can work as desalinization material and pH adjuster.

ACKNOWLEDGEMENTS

The authors would like to thank the members who belong to, Integrated Water Resource Management Research and Development Center in Northeast Thailand, Khon Kaen University, Thailand. This work is supported by Japan Public-Private Partnership Student Study Abroad Program TOBITATE! Young Ambassador Program.

REFERENCES

Fuji, H., Nongluck, S., Ono, M. and Fujiwara, Y. 2012. Impact of on-farm pond on agricultural diversification in rainfed agricultural area in northeast Thailand. Irrigation, Drainage and Rural Engineering Journal, 277, 73-78.

Kimura, M. and Takai, Y. 1990. Coastal and inland salt-affected soils in Thailand, Their characteristics and improvement, Japan's oversea research activities. 6, Japanese Society of Soil Science and Plant Nutrition, 61 (5), 538-544.

Land Development Department. 1991. Distribution of salt affected soil in the northeast region 1: 100,000 map. Department of Land Development, Bangkok, Thailand.

Umakoshi, M. 2016. Development of groundwater desalinization technology in soil layer using mordenite sheet under evaporation process using mordenite sheet. Bachelor Thesis at Department of Rural Engineering, Faculty of Agriculture, Ehime University, Japan.

Yoshida, M., Nakao, Y. and Miyara, E. 1971. Cation adsorption characteristics of zeolite in relation to CEC determination. Clay Science, 11 (1), 31-35.

Haruta, Y. 2018. Basic study about applying ion-exchange material for improvement of salinization soil in Northeast Thailand. Professional Education Course in Rural Engineering. Master thesis at Graduate School of Agriculture, Ehime University, Japan.