International Journal of Farming and Allied Sciences
Available online at www.ijfas.com
©2015 IJFAS Journal-2015-4-1/50-54/ 31 January, 2015
ISSN 2322-4134 ©2015 IJFAS

Removal of Nacl from aqueous solutions by using clinoptilolite

F Shokrian[1*], K Solaimani[2], GH Nematzadeh[3] and P Biparva[4]

1.Ph.D. student of watershed management, Sari Agricultural Sciences and Natural Resources University
2.Professor, Sari Agricultural Sciences and Natural Resources University
3.Professor, Sari University of Genetic& Agricultural Biotechnology Research Institute (GABIT)
4.Assistant professor, Department of Basic Sciences, Sari Agricultural Sciences and Natural Resources University

Corresponding author: F Shokrian

ABSTRACT: This study focuses on the absorption of sodium chloride via clinoptiolite. The effect of different parameters is investigated like concentration, adsorbent dosage and particle size. The results showed that, by decreasing the particle size, sodium chloride removal percentage increases. Also by increasing the adsorbent dosage, more absorption will increase. Equilibrium data followed the freundlich and Langmuir isotherm model. The result indicated that, Sodium Chloride absorption shows a better fit ($R^2 = 0.96$) from freundlich model.

Keywords**:** Adsorbent, Clinoptiolite, Equilibrium isotherm, Freundlich, Langmouir

INTRODUCTION

A shortage of fresh water is one of the acute challenges facing the world today. An energy-efficient approach to converting sea water into fresh water could be of substantial benefit, but current desalination methods require high power consumption and operating costs or large-scale infrastructures, which make them difficult to implement in resource-limited settings or in disaster scenarios (kim ., 2010).

Continuous population growth, rising standards of living, industrialization, urbanization and climate changes have increased water demand significantly (Pearce, 2008).

Desalination is hailed as the panacea to alleviate the problems of fresh water shortage in many water stressed countries (Ng ., 2013).

A number of seawater desalination technologies have been developed during the last several decades to augment the supply of water in arid regions of the world. Due to the constraints of high desalination costs, many countries are unable to afford these technologies as a fresh water resource. However, the steady increasing usage of seawater desalination has demonstrated that seawater desalination is a feasible water resource free from the variations in rainfall (Khawaji ., 2008).

Adsorption is considered as an attractive one when the effective, low-cost materials are used as adsorbents. zeolite is recognized to be an attractive one for its high ion-exchange capacity, selectivity and compatibility with the natural environment. In this paper, natural zeolite was used as a low-cost adsorbent to evaluate its ability to removal Sodium Chloride from aqueous solution (Sea water). Zeolites are microporous aluminosilicate minerals which could be used as ion exchanger in domestic and commercial water purification, softening and other applications (Singer ., 2005). Substitution of silicon by aluminum atoms in the crystal framework leads to extra negative charge to be balanced by surrounding counter ions (such as Na^+, K^+, Ca^{2+}, and Mg^{2+}), and these counter ions are easily exchanged by other surrounding cations in a contact solution (Tsitsishvili ., 1992). Additionally, the high ion exchange capacity

(IEC) (Kithome ., 1998), large reserves of zeolite-rich rock, shortage of competing minerals and the relatively low market price prefer the use of zeolites in large scales.

There are more than 50 species of zeolites, such as clinoptilolite, heulandite, mordenite, erionite, and others (Tsitsishvili ., 1992) use of clinoptilolite in industry and academia mainly focuses on its ion exchange properties (Metropoulos ., 1993).

Natural zeolites are abundant and low cost resources, which are crystalline hydrated aluminosilicates with a framework structure containing pores occupied by water, alkali and alkaline earth cations. Due to their high cation-exchange ability as well as to the molecular sieve properties, natural zeolites have been widely used as adsorbents in separation and purification processes in the past decades (wang and peng, 2010).

Due to the shortage of water and its role for sustainable development, an extensive attempt has been bellowed by different researchers in the world regarding to the sea water desalination. Some attempts are; nano threads for desalination (Subramanian and Seeram 2013), carbon tube (Goh ., 2013) semi permeable membrane (Adham ., 2013), polyamide membranes (La ., 2013) hybrid forward osmosis–nanofiltration system for brackish water desalination (Zhao ., 2012) indirect frozen of Persian Gulf water desalination (Mahdavi ., 2010), Also for desalination of sea water *Zeolite* used as a suitable material (Zhu ., 2013; Wajima, 2013).

The main aim of this study is to determine the ability of the natural zeolite (clinoptiolite) to get the best results for the adsorption.

Characterization of study area

The salinity of the Caspian Sea changes from the north to the south from 1 to 13.5‰. This difference is concentrated in the north due to the freshwater supplied by the Volga River. In other areas, the average water salinity is ~12.5‰ (Dumont, 1998).

Figure 1. The location of study area

Experimental

Natural zeolite was obtained from a mine in Semnan Province, I.R. Iran. This adsorbent was washed with distilled water several times, and then put them in oven (Tegh Fan of D-H, Iran) at 60ºC for 24 h for drying. After drying the product was sieved to (841-74µ) mesh before utilizing. The surface morphology of this adsorbent was observed by scanning electron microscope (SEM, Philips-XL30 Electron Microscope, Netherland).

The adsorption of Sodium Chloride into clinoptilolite was studied by a series of batch adsorption experiments. The efficiency of zeolite as an adsorbent for the removal of sodium chloride ions from aqueous solutions has been determined at the different initial concentration (25-10000 mg/l), adsorbent dosage (0.5-2 g), particle size (841-74µ), fixed agitation speed (200 rpm), pH (6.5-7) and temperature (25° c). For each batch adsorption experiment, firstly 0.5 g of zeolite was added into the flask containing 50 ml of sodium chloride solution. Then the flask was shaking at fixed agitation speed. Silver nitrate ($AgNo_3$) was used to chloride titration obtained from Merck (Darmstadt, Germany). Finally the suspension was centrifuged and analyzed.

RESULTS AND DISCUSSION

Adsorbent characterization

Characterization of adsorbent sample was analyzed by scanning electron microscope. There are many natural zeolites identified in the world. Among the zeolites, Clinoptilolite is the most abundant natural zeolite and is widely used in the world and in this study. The SEM and bulk photographs are displayed in Fig. 2. Structural properties of Clinoptilolite is $(K_2, Na_2, Ca)_3Al_6Si_{30}O_{72}21H_2O$. Chemical composition (%) of Iranian Clinoptilolite includes: 70(SiO_2), 10.46(Al_2O_3), 0.46(Fe_2O_3), 0.2(CaO), 0 (MgO), 2.86(Na_2O), 4.92(K_2O), 0.02(TiO_2) [33].

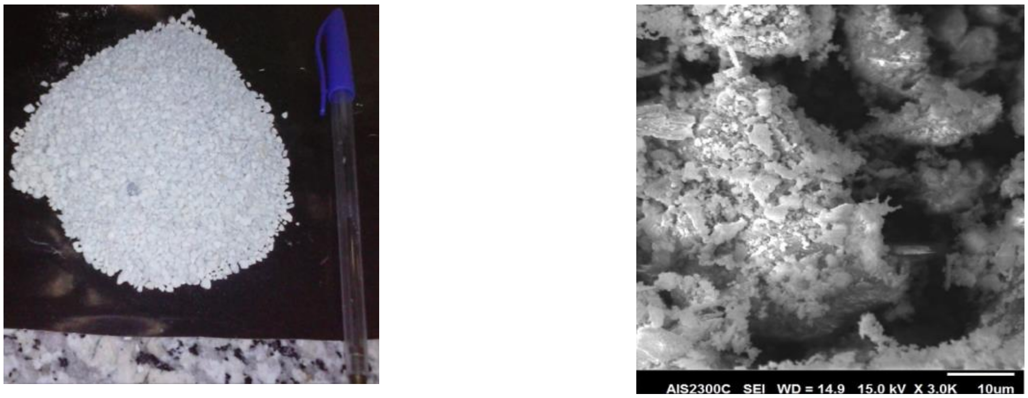


Figure 2. Photographs of *Zeolite*: (a) bulk zeolite, (b) SEM image of *zeolite*

Adsorption isotherms

To understand the mechanisms of sodium chloride adsorption by zeolite, The Langmuir and Freundlich isotherms were used for fitting sorption equilibrium data (Fig. 3-4). Langmuir and Freundlich model were evaluated as follows:

Langmuir model is based on the assumption that each active site can only hold one adsorbate molecule(Alshameri, 2013). The linear form of Langmuir model is expressed as:

(1)

$$\frac{Ce}{qe} = \frac{1}{qmax KL} + \frac{Ce}{qmax}$$

Freundlich model endorses the heterogeneity of the surface and assumes that the adsorption occurs at sites with different energy of adsorption (Alshameri, 2013). It is illustrated as:

$$\log q_e = \log K_f + 1/n \log C_e \qquad (2)$$

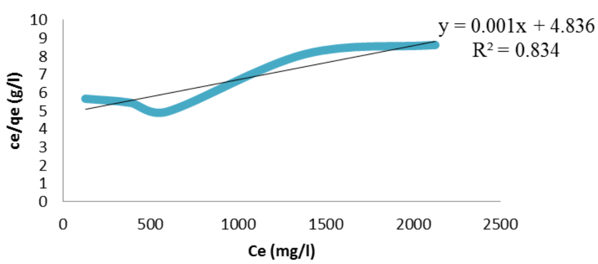


Figure 3. Langmuir adsorption isotherm for sodium chloride

The results were provided strong support for the Sodium Chloride adsorption of into clinoptilolite and which were observed to fit sufficient by the Freundlich isotherm in the most of case. K_f is also indicating the absorption capacity of adsorbent allocated large amount to indicate that adsorbent is a high tendency to adsorb (Tab.1).

Table 1. Adsorption parameter based on Langmuir and Freundlich model

Langmuir model			
q_{max}	K_L	R^2	Equation
1000	0.0002	0.834	y = 0.001x + 4.836
Freundlich model			
n	k_f	R^2	Equation
1.2	53.29	0.969	y = 0.829x - 3.976

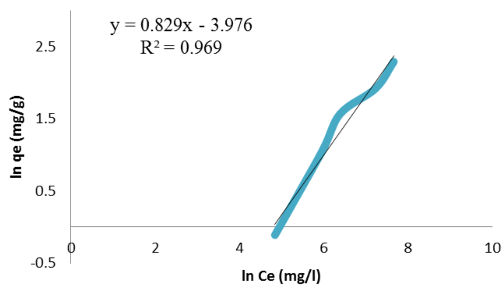
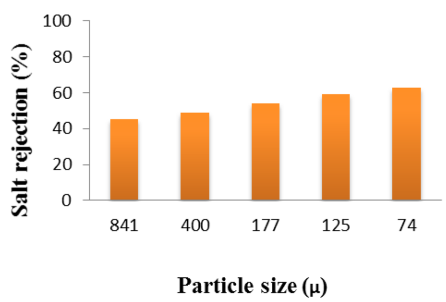


Figure 4. Freundlich adsorption isotherm for sodium chloride

Effect of particle size

To investigate the effect of particle size (841-74µ) was used ASTM sieving. The results showed that with decreasing particle size, surface area and salt rejection increase.



Adsorbent dosage

Result about adsorbent dosage indicated that the removal efficiency of Nacl ions by zeolite increases with increasing amount of zeolite. According Nemr; (2009) this effect can be attributed to an increased surface area and number of adsorption sites

REFERENCES

Adham S, Hussain A, Matar J M, Dores R and Janson A. 2013. Application of Membrane Distillation for desalting brines from thermal desalination plants. Desalination. 314:101–108

Al-Anbera M and Al-Anberb ZA. 2008. Utilization of natural zeolite as ion-exchange and sorbent material in the removal of iron. Desalination. 225: 70–81

Alshameri A, Yan C, Al-Ani Y, Salman Dawood A, Ibrahim, A Zhou C and Wang H. 2014. An investigation into the adsorption removal of ammonium by salt activated Chinese (Hulaodu) natural zeolite: Kinetics, isotherms, and thermodynamics. J. Taiwan Inst. Chem Eng. 2: 554–564

Dumont HJ. 1998. The Caspian Lake: history, biota, structure, and function. Lim& Ocean. 43 (1): 44-52

Goh PS, Ismail AF and Ng BC. 2013. Carbon nanotubes for desalination: Performance evaluation and current hurdles. Desalination. 308:2–14

Khawaji AD, Kutubkhanah IK and Wie JM. 2008. Advances in seawater desalination technologies. Desalination. 221: 47–69

Kim SJ, Ko SH, Kang KH and Han J. 2010. Direct seawater desalination by ion concentration polarization. Nat. Nanotec. 5: 297 – 301

Kithome M, Paul JW, Lavkulich LM and Bomke AA. 1998. Kinetics of ammonium adsorption and desorption by the natural zeolite clinoptilolite, Soil Sci. Soc. Am. J. 62:622–629

La YH, Diep J, Al-Rasheed R, Miller D, Krupp L, Geise GM, Vora A, Davis B, Nassar, Freeman BD, McNei M and Dubois G. 2013. Enhanced desalination performance of polyamide bi-layer membranes prepared by sequential inter facial polymerization. J. Membrane Sci. 437:33–39

Liu Y, Guo Y, Gao W, Wang Z, Ma Y and Wang Z. 2012. Simultaneous preparation of silica and activated carbon from rice husk ash. J Clean Produc. 32 : 204-209

Mahdavi M, Naseri S, Yunesian M, Mahvi AH and Alimohaadi M. 2011. Investigation of Indirect Contact Freezing Process in Desalination of Boshehr Beach's SalineWater. Iran. J. Health & Environ. 4(3): 363-374

Metropoulos K, Maliou E, Loizidou M and Spyrellis N. 1993. Comparative-studies between synthetic and natural zeolites ammonium uptake. Subst. Environ. Eng. 28 :1507–1518

Nemr AE, Abdelwahab O, El-Sikaily A and Khaled A. 2009. Removal of direct blue-86 from aqueous solution by new activated carbon developed from orange peel. J. Hazard Mater. 161:102–10

Ng KC, Thu K, Kim Y, Chakraborty A and Amy G. 2013. Adsorption desalination: An emerging low-cost thermal desalination method. Desalination. 308:161–179

Pearce GK. 2008. UF/MF pre-treatment to RO in seawater and wastewater reuse applications: a comparison of energy costs. Desalination. 222: 66–73

Singer PA, Salamanca-Buentello F and Daar AS. 2005. Harnessing nanotechnology to improve global equity, Issues. Sci. Technol. 21: 57–64

Subramanian S, Seeram R. 2013. New directions in nanofiltration applications- Are nanofibers the right materials as membranes in desalination?Desalination. 308:198–208

Tsitsishvili GV, Andronikashvili TG, Kirov GN and Filizova LD. 1992. Natural zeolites. Ellis Horwood, New York

Wajima T, 2013. Ion Exchange Properties of Japanese Natural Zeolites in Seawater. Anal sci Jan. 29:139-141

Wang S and Peng Y. 2010.Natural zeolites as effective adsorbents in water and wastewater treatment. Chem. Eng. J .156:11–24

Zhao S, Zou L and Mulcahy D. 2012. Brackish water desalination by a hybrid forward osmosis–nanofiltration system using divalent draw solute. Desalination. 284:175–181

Zhu B, Doherty CM, Hu X, Hill AJ, Zou L, Lin YS and Duke M. 2013. Designing hierarchical porous features of ZSM-5 zeolites via Si/Al ratio and their dynamic behavior in seawater ion complexes. Micro & Meso Mat 173:78–85