Journal of Materials Science and Chemical Engineering, 2014, 2, 1-5
Published Online August 2014 in SciRes. http://www.scirp.org/journal/msce
http://dx.doi.org/10.4236/msce.2014.28001

Decrease in Cation Exchange Capacity of Zeolites at Neutral pH: Examples and Proposals of a Determination Method

Moses Wazingwa Munthali, Ponyadira Kabwadza-Corner, Erni Johan, Naoto Matsue

Laboratory of Applied Chemistry for Environmental Industry, Faculty of Agriculture, Ehime University, Matsuyama, Japan
Email: munthalimw@yahoo.co.uk

Received 26 May 2014; revised 20 June 2014; accepted 18 July 2014

Abstract

Cation exchange capacity (CEC) is an important characteristic of zeolites, especially when they are used as adsorbents in the aqueous system. However, no international standard method exists for the determination of CEC of zeolites. We determined CEC of Linde-type A and Na-P1 type zeolites at various pH (4 to 10) with a simple method, where Na^+-saturated zeolites were prepared, and then various amounts of HCl were added. CEC was simply calculated by subtracting the amount of Na^+ in the final supernatant from the content of Na^+ of the Na^+-saturated zeolites. CEC of the zeolites decreased with decreasing pH and with decreasing Na^+ concentration of the final supernatant. The concentration of Na^+ of the supernatant, CEC of the zeolites began to decrease at weakly alkaline or neutral pH, and that of the Linde-type A zeolite became about half at pH around 6. When CEC was plotted against pH-pNa; where pNa is negative logarithm of the activity of Na^+; CEC of each zeolite was expressed by a curve. It indicates that the CEC or the amount of Na^+ retention is univocally determined by the ratio of activities of Na^+ and proton.

Keywords

Cation Exchange Capacity, Na^+ Retention, pH Dependence, Linde-Type A Zeolite, Na-P1 Type Zeolite

---

1. Introduction

Various zeolite species have been utilized as adsorbents and catalysts usually in gases and organic solvents. Zeolites are also used in aqueous system to adsorb cations such as heavy metals and radioactive cesium, by uti-

How to cite this paper: Munthali, M.W., Kabwadza-Corner, P., Johan, E. and Matsue, N. (2014) Decrease in Cation Exchange Capacity of Zeolites at Neutral pH: Examples and Proposals of a Determination Method. *Journal of Materials Science and Chemical Engineering*, **2**, 1-5. http://dx.doi.org/10.4236/msce.2014.28001

lizing their high negative charge density and high selectivity toward some kinds of cations [1] [2]. When zeolites are used as adsorbent in aqueous system, cation exchange capacity (CEC) of zeolites is one of the important factors to estimate their ability, but no international standard method is available for the determination of CEC of zeolites. A possible reason for this is that CEC of zeolites have been considered to be same as the amount of isomorphous substitution. On one hand, CEC of soil clay minerals in aqueous system had been extensively studied with agricultural purposes: in this case, "cation" meant cations except for proton. Consequently, two types of negative charges, namely pH-dependent and pH-independent negative charges had been recognized in soil clay minerals [3]. The pH-dependent negative charge is due to the dissociation of Si-OH, Al-OH and Fe-OH groups of soil clays, and the pH-independent negative charge was ascribed to 2:1 type layer silicate clay minerals such as montmorillonite. Because origin of the negative charge of the 2:1 type layer silicate clay minerals is isomorphous substitution, negative charges derived from isomorphous substitution, including those of zeolites, had been thought to be independent of pH, at least under environmental pH of about 4 - 10 [4]. Some studies were carried out concerning pH-dependent adsorption of Ca^{2+} [5], Pb^{2+} [6], sulfa drugs [7], and phenol [8] on zeolites from acidic to alkaline pH range. However, detailed cation retention behavior of various zeolite species as affected by pH is not known, especially at neutral pH region. In this study, we found that the CEC (the amount of Na^+ retention) of Linde-type A and Na-P1 type zeolites decreased with decreasing pH, and the decrease began at pH around 7 to 9. We also proposed a simple method to determine the effect of pH and cation activity on the CEC of zeolites.

2. Materials and Methods

2.1. Sample Preparation

Two zeolite species were used in this study. Linde-type A zeolite was obtained from Wako Chemicals Ltd, and Na-P1 type zeolite was synthesized in this study. Linde-type A zeolite is a common zeolite species, and Na-P1 type zeolite is a main zeolite species when low price "artificial zeolite" is synthesized from coal fly ash. In a 250 mL centrifuge bottle, 10 g of the zeolite was washed five times with 150 mL of 1 M NaCl to saturate the zeolite with Na^+. Then the content was washed twice with 150 mL of water, washed once with 100 mL of acetone, air-dried, and used as a sample.

2.2. Determination of CEC

The Na^+ contained in the sample are retained exchangeable Na^+ and free Na^+ as NaCl. The sum of retained and free Na^+ contents of the sample (hereafter Na^+ content) was determined by washing 1 g of the sample with 30 mL of 1 M NH_4NO_3 in a 50 mL centrifuge bottle for seven times. Water content of the sample was determined by heating at 105˚C for 3 h. The content of Si and Al of the samples was determined after dissolution with hydrofluoric acid. The determination of CEC (the amount of Na^+ retention) of the samples was carried out with the following method, which was modified from a method proposed for soil clays [9]. One gram of a sample was put in a 250 mL centrifuge bottle, and 200 mL of 0 to 7.5 mM HCl solution was added. The mixture was shaken for 3 h at 25˚C ± 0.5˚C, centrifuged at 2000 *g*, and the concentration of Na^+ and pH of the supernatant were measured. Preliminary experiments indicated that the Na^+ concentration and pH of the supernatant became constant within 3 h, and the measured Na^+ concentration and pH are hereafter referred to as equilibrium Na^+ concentration and equilibrium pH, respectively. The CEC (the amount of Na^+ retention) of the sample was simply calculated from the difference between Na^+ content of the sample and the amount of Na^+ in the supernatant. Similar CEC determination as the above was carried out using 50 mL centrifuge bottle, 1 g of sample, 20 mL of solutions containing of 0 to 75 mM HCl and 83 mM NaCl, to estimate the effect of solution Na^+ concentration on CEC at a same equilibrium pH. The volume of 20 ml was used in order to increase the relative change of Na^+ concentration in the supernatant, and to increase the accuracy of Na^+ concentration determination. The concentration of Al and Si in the supernatant was measured to check the dissolution of the sample, and the measurement of Na, Al and Si was carried out using atomic absorption spectrophotometer (Hitachi Z-5000).

Powder X-ray diffraction pattern of the samples before and after the CEC determination was obtained with a Rigaku Ultima IV X-ray diffractometer with Cu-Kα radiation generated at 40 kV and 40 mA, between 3˚ - 60˚ of 2θ angles with a sampling width of 0.02˚ and a scanning rate of 2˚·min^{-1}.

3. Results and Discussions

Figure 1 shows change in CEC (the amount of Na^+ retention, $cmol \cdot kg^{-1}$, 105˚C oven dry basis) of the zeolite samples with change of equilibrium pH. Closed symbols in **Figure 1** show the results without NaCl background solution in total volume of 200 mL, and open symbols are the results with 83 mM NaCl in 20 mL. In the absence of NaCl, the concentrations of Na^+ in the supernatants were from 0.3 mM to 7.4 mM for Linde-type A zeolite, and 0.1 mM to 6.6 mM for Na-P1 type zeolite, with increasing the amount of addition of HCl. When 83 mM NaCl was added, they were 88 mM to 153 mM for Linde-type A zeolite, and 85 mM to 138 mM for Na-P1 type zeolite.

In the absence of the NaCl background solution (closed symbols in **Figure 1**), at higher pH region, CEC of the two samples were slightly affected by pH. With increasing the amount of HCl addition, equilibrium pH decreased, and CEC of the two zeolites decreased with the decrease of the equilibrium pH. The CEC of Na-P1 type zeolite began to decrease from pH about 7 (**Figure 1**, closed triangles), and that of Linde-type A zeolite began to decrease from pH about 9 (**Figure 1**, closed circles). The decrease of CEC indicates that the negative charge of zeolite was partly compensated by the adsorption of proton with the exchange with Na^+. The adsorption of proton onto the zeolites is due to greater selectivity of the zeolites toward proton, and **Figure 1** reveals that the adsorption of proton on the two zeolites occurred even at neutral pH region. In other words, CEC of the two zeolites is pH-dependent, and the zeolites are strong base like $Si\text{-}O^-$ of Si-OH group. Decrease in the retention of cations by zeolites with decrease in pH were also reported for Ca^{2+} on Linde-type A zeolite [5], and for Pb^{2+} on NKF-6 zeolite [6].

When 83 mM NaCl was added as a background solution (open symbols in **Figure 1**), CEC of the samples began to decrease from around pH 6 for Na-P1 type zeolite, and from around pH 8 for Linde-type A zeolite. As a result, at a same equilibrium pH in **Figure 1**, CEC of open symbols were greater than those of closed symbols, and the difference was greater at lower equilibrium pH. This means that not only pH, but also Na^+ concentration (more accurately, activity of Na^+) affected CEC or the amount of Na^+ retention of the zeolites. The effect of a monovalent cation (M^+) concentration on CEC was already reported for soils and soil clay minerals, and the effect of both pH and M^+ concentration was expressed by taking the abscissa as pH-pM or $\log\left\{\left(M^+\right)/\left(H^+\right)\right\}$ [10].

Then we re-plotted the data in **Figure 1** by taking the abscissa as pH-pNa, as shown in **Figure 2**. The figure shows that closed symbols and open symbols are nearly converged to a curve in both types of zeolites. This indicates that, in these experimental systems, CEC (the amount of Na^+ retention) is univocally determined by the ratio of activities of Na^+ and proton, similar to the case of soils and soil clay minerals [10]. **Figure 2** also indicates that the determination of CEC with the addition of NaCl in the HCl solution is not necessary. By plotting CEC against pH-pNa using the results with simple HCl solutions, CEC at a pH with higher Na^+ concentration is easily obtained. Here, Na^+ in aqueous solution is in hydrated form and weakly held or adsorbed onto zeolites [11]. In this case, the adsorption of proton on zeolite is more preferred than Na^+. Furthermore, specific Brönsted and Lewis acid-base sites exist in zeolite micropores [12] [13]. Considering the Lewis acid-base sites, after a proton is adsorbed through ion exchange with Na^+, the proton acts as a Lewis acid while the O between Si-O-Al acts as a Lewis base. Then the O gives lone pair electrons to the proton which results into a negative charge neutralization due to the formation of covalent bonding between the O and the proton [14]. The formed covalent bonding results into neutral charge and a loss of negative charge in zeolite. The covalent bonding is much stronger than the ionic bonding formed by Na^+ cation in balancing up the negative charge. The addition of HCl was from 0 to 150 cmol for 1 kg of zeolite. Within this range, the change in XRD pattern was not observed as shown in **Figure 3**, and the amount of dissolution of Si and Al was less than 0.5% and 0.1%, respectively. With more addition of HCl, it is clear that the zeolites are dissolved. When zeolites are used in aqueous systems, the dissolution of the zeolites should be taken into account.

In this study, two types of zeolites were used, and Na^+ was used as an index cation for the determination of CEC. In addition to pH and the activity of an index cation, CEC of a zeolite may change with index cation species and the amounts and species of coexistent ions. However, CEC data obtained with the method used in this study will give the basic information for the prediction of cation retention and solubility of a zeolite in more complicated aqueous systems.

4. Conclusion

In conclusion, CEC of Linde-type and Na-P1 type zeolites was strongly pH dependent even at weakly acidic

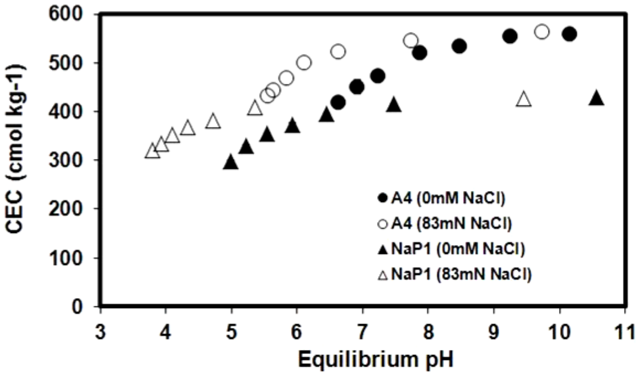


Figure 1. Changes in CEC of zeolites with equilibrium pH. Note: Linde-type A = 4A.

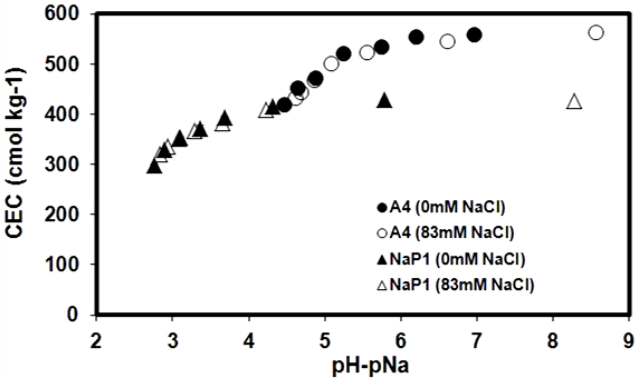


Figure 2. Changes in CEC of zeolites with pH-pNa. Note: Linde-type A = 4A.

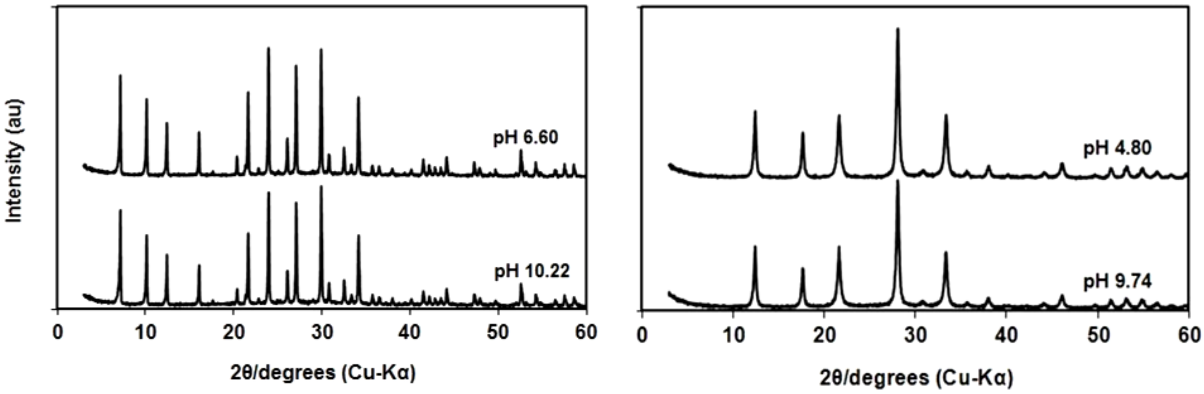


Figure 3. XRD patterns of Linde-type A zeolite (left) and Na-P1 zeolite (right) after CEC measurement without NaCl addition. pH values on each XRD pattern indicate equilibrium pH.

range. CEC of the zeolites was also affected by the activity of Na^+ in solution, and CEC was well expressed by pH-pNa. The method used in this study for the determination of CEC at various pH is simple, with minimal sample destruction. Outline of a method for the determination of CEC at various pH is proposed as follows: 1) Prepare air-dried Na^+-saturated sample, and contents of water and Na^+ are measured; 2) To 1 g of the sample, 200 mL of 0 to 7.5 mM HCl are added; 3) Shake for 3 h, centrifuge, and pH and Na^+ concentration of supernatant are measured; 4) Calculate CEC by subtracting the amount of Na^+ in the supernatant from Na^+ content of the sample; 5) Calculate activity of Na^+ for each supernatant, and plot CEC against pH-pNa. By adding known amount of NaOH, instead of HCl, CEC at higher pH-pNa is also obtained.

References

[1] Misaelides, P. (2011) Application of Natural Zeolites in Environmental Remediation: A Short Review. *Microporous and Mesoporous Materials*, **144**, 15-18. http://dx.doi.org/10.1016/j.micromeso.2011.03.024

[2] Wang, S. and Peng, Y. (2010) Natural Zeolites as Effective Adsorbents in Water and Wastewater Treatment. *Chemical Engineering Journal*, **156**, 11-24. http://dx.doi.org/10.1016/j.cej.2009.10.029

[3] McBride, M.B. (1989) Surface Chemistry of Soil Minerals. In: Dixon, J.B. and Weed, S.B., Eds., *Minerals in Soil Environments*, 2nd Edition, SSSA Book Series No. 1, Soil Science Society of America, Madison, 35-88.

[4] Ferreiro, E.A., Helmy, A.K. and de Bussetti, S.G. (1995) Interaction of Fe-Oxyhydroxide Colloidal Particles with Montmorillonite. *Clay Minerals*, **30**, 195-200. http://dx.doi.org/10.1180/claymin.1995.030.3.03

[5] Qin, C., Wang, R. and Ma, W. (2010) Characteristic of Calcium Adsorption by Ca-Selectivity Zeolite in Fixed-pH and in a Range of pH. *Chemical Engineering Journal*, **156**, 540-545. http://dx.doi.org/10.1016/j.cej.2009.04.006

[6] Yang, X., Yang, S., Yang, S., Hu, J., Tan, X. and Wng, X. (2011) Effect of pH, Ionic Strength and Temperature on Sorption of Pb(II) on NKF-6 Zeolite Studied by Batch Technique. *Chemical Engineering Journal*, **168**, 86-93. http://dx.doi.org/10.1016/j.cej.2010.12.039

[7] Fukahori, S., Fujiwara, T., Ito, R. and Funamizu, N. (2011) pH-Dependent Adsorption of Sulfa Drugs on High Silica Zeolite: Modelling and Kinetic Study. *Desalination*, **275**, 237-242. http://dx.doi.org/10.1016/j.desal.2011.03.006

[8] Yousef, R. and El-Eswed, B. (2009) The Effect of pH on the Adsorption of Phenol and Chlorophenols onto Natural Zeolite. *Colloids and Surfaces A*: *Physicochemical and Engineering Aspects*, **334**, 92-99. http://dx.doi.org/10.1016/j.colsurfa.2008.10.004

[9] Wada, S. (1983) pH- and Ionic Concentration-Dependence of Monovalent Cation Retention by Clays and Clay Minerals Expected in Soils. *Soil Science and Plant Nutrition*, **29**, 561-564. http://dx.doi.org/10.1080/00380768.1983.10434660

[10] Wada, S. and Kawabata, K. (1991) Ion Adsorption on Variable Charge Materials and Thermodynamics of Ion Exchange. *Soil Science Plant Nutrition*, **37**, 191-200. http://dx.doi.org/10.1080/00380768.1983.10434660

[11] Deka, R.C., Roy, R.K. and Hirao, K. (2004) Local Reactivity Descriptors to Predict the Strength of Lewis Acid Sites in Alkali Cation-Exchanged Zeolites. *Chemical Physics Letters*, **389**, 186-190. http://dx.doi.org/10.1016/j.cplett.2004.03.094

[12] Almutairi, M.T., Mezari, B., Filonenko, A., Magusin, P.C.M.M., Rigutto, M.S., Pidko, E.A. and Hensen, E.J.M. (2013) Influence of Extraframework Aluminum on the Brønsted Acidity and Catalytic Reactivity of Faujasite Zeolite. *ChemCatChem*, **5**, 452-456.

[13] Serykh, A.I. (2005) Nature of Cadmium Cationic Sites in Cadmium-Modified ZSM-5 Zeolite According to the Drift Studies of Molecular Hydrogen Adsorption. *Microporous and Mesoporous Material*, **80**, 321-326. http://dx.doi.org/10.1016/j.micromeso.2004.10.024

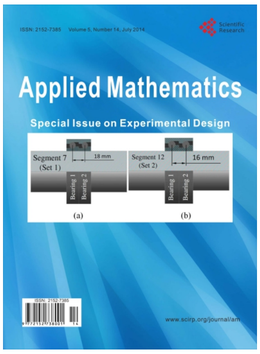
[14] Malik, A.S., Boyko, O., Aktar, N. and Young, W.F. (2009) A Comparative Study of MR Imaging Profile of Titanium Pedicle Screws. *Acta Radiologica*, **42**, 291-293. http://dx.doi.org/10.1080/028418501127346846


Advances in Bioscience and Biotechnology

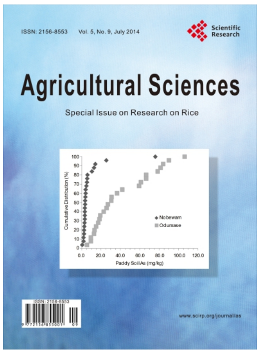

American Journal of Analytical Chemistry


American Journal of Plant Sciences

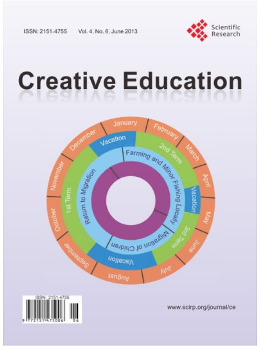
Special Issue on Photosynthesis

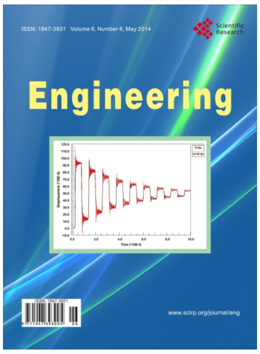

Applied Mathematics

Special Issue on Experimental Design

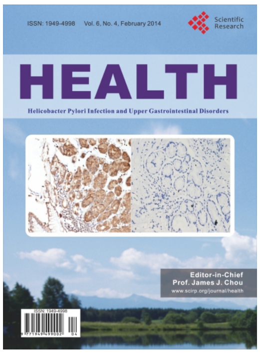

Agricultural Sciences

Special Issue on Research on Rice


Creative Education


Engineering


Food and Nutrition Sciences


HEALTH

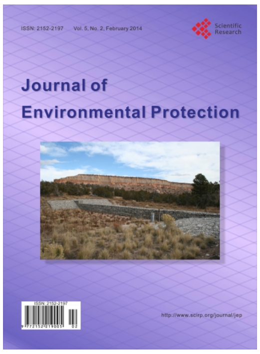
Helicobacter Pylori Infection and Upper Gastrointestinal Disorders

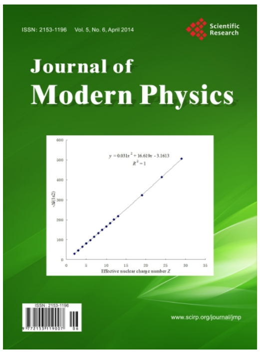
Editor-in-Chief Prof. James J. Chou


Journal of Computer and Communications

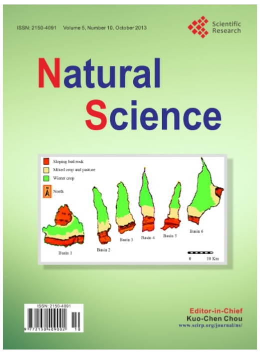

Journal of Cancer Therapy

Special Issue on Bone Tumor Research

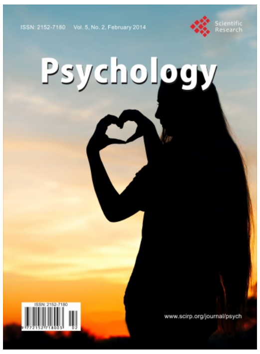

Journal of Environmental Protection


Journal of Modern Physics


Modern Economy


Natural Science

Editor-in-Chief Kuo-Chen Chou


Psychology