Determination of Cation Exchange Capacity of Natural Zeolite : A Revisit

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ABSTRACT

Natural zeolite has been widely used as an ion exchanger since the 1950s. The purpose of this study was to quantify the cation exchange capacity (CEC) of natural zeolite from different locations (Bayah and Cikembar in West Java, Indonesia) based on particle sizes of 0.15 and 0.079 mm, using different displacement solutions of 0.5M cesium chloride (CsCl) and 0.5 M potassium chloride (KCl). Higher CEC was observed in Cikembar100 compared to Bayah100 due to its higher surface area (31%) and total pore volume (11%) compared to Bayah100. Cikembar100 had 11% higher clinoptilolite mineral content compared to Bayah 100. The low CEC measured for Bayah100 and Bayah200 may be due to the lower percentage purity of the clinoptilolite mineral content in those samples. The natural zeolite samples displaced with 0.5M CsCl had 6% higher CEC compared to 0.5M KCl, which means that Cs^+ had more strength compared to K+ in displacing NH_4^+ into the solution from the nanocavity site of the zeolitic framework into the solution. In both displacement solutions (0.5M CsCl and KCl), Cikembar100 had 10% more net negative charge compared to Bayah100 due to its isomorphous substitution properties in natural zeolite. Isomorphous substitution in natural zeolite affects its negative charge and the capacity to retain NH_4^+ in the zeolitic framework, thus increasing its CEC and making natural zeolite with the particle size of 0.079 mm (Cikembar100) a promising material for cation removal, particularly Cs from aqueous solution.

Keywords: Natural zeolite, Clinoptilolite, cesium chloride, potassium chloride, isomorphous substitution

INTRODUCTION

Clinoptilolite is one of the most abundant natural zeolites because it retains its residual mineral phases during weathering of volcanic parent materials (Ming and Dixon 1986). The fundamental building block of natural zeolite is a tetrahedron of four oxygen atoms surrounding silicon (Si^{4+}) or aluminium (Al^{3+}) atom. The physical structure of a zeolite is porous with interconnected cavities in which exchangeable cations (Na^+, K^+, Mg^{2+}, Ca^{2+}) and water molecules are present. The adsorption of counter cations contributes to the net negative charge of natural zeolites derived from isomorphous substitution of Si^{4+} by Al^{3+} (Dyer and White 1999). Natural zeolites are classified as low cost adsorbents and have been

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widely used in the management of radioactive wastes from nuclear reactors, gas purification, petroleum production and wastewater treatment (Ames 1961; Hor *et al*. 2016). One of the important properties of zeolite is its cation exchange. Among the factors that affect cation exchange of natural zeolite from aqueous solutions are washing frequency, chemical conditioning, contact time, type of displacement solution and the presence of soluble and competing ions in an aqueous solution. Based on the study by Ames (1960)(1961 in the ref list), the cation selectivity series in natural zeolite is described as cesium, Cs^+>ammonium, NH_4^+>potassium, K^+>sodium, Na^+>calcium, Ca^{2+} >magnesium, Mg^{2+}. The cation selectivity of natural zeolite is advantageous for the efficient storage of fission products Cs^{137}generated by a nuclear power plant. The 11th Malaysia Plan 2016-2020, calls for exploring the usage of nuclear power as an alternative energy resource (Khattak *et al.* 2016). Natural zeolite is abundant worldwide in huge deposits, readily available and inexpensive compared to synthetic zeolite. Natural zeolites have been widely used as an ion exchanger but this is often limited to countries having their own natural zeolite deposits such as the United States of America, Russia, China, Turkey and Indonesia. The purpose of this study was to quantify the cation exchange capacity (CEC) of natural zeolite from different locations (Bayah and Cikembar in West Java, Indonesia) based on particle sizes of 0.15 and 0.079 mm, using different displacement solutions of 0.5M cesium chloride (CsCl) and 0.5 M potassium chloride (KCl).

MATERIALS AND METHODS

Natural zeolite samples were selected from from two locations inWest Java, Indonesia (Bayah and Cikembar) with different particle sizes of 0.079 mm and 0.15 mm. X-Ray diffraction analysis was conducted to identify the clinoptilolite mineral at the Department of Land Management, Faculty of Agriculture, UPM. The pore structure, surface area (micropore and mesopore), total pore volume, and pore size of natural zeolite were measured using Brunauer-Emmett-Teller (BET) method (Brunauer *et al*.1938) at INFRA Laboratory, Universiti Malaya.

Particle Size
To determine the CEC of natural , the shaking method was conducted in four batches under laboratory conditions with a constant room temperature of 27^0C. A total of six experimental units comprising one location and one particle size with three replications were analysed per batch. In each batch, six samples were microwaved and washed with 50 mL of distilled water. Samples were shaken with an end-to-end shaker and then centrifuged. The supernatant was decanted for Na^+, K^+, Ca^{2+}, and Mg^{2+} determination using atomic absorption spectrophotometer (AAS).

Contact Time
Five g of samples with 50 mL of 0.5M NH_4Cl were shaken with an end-to-end shaker and left equilibrated for 24 h. After 24 h, the sample was mixed with

50 mL of 95% denatured alcohol and agitated using an end-to-end shaker and then centrifuged. Samples were decanted to determine exchangeable bases (Na^+, K^+, Ca^{2+}, Mg^{2+}) using AAS. A 50 mL of fresh solution of 0.5M NH_4Cl was then replaced every 24 h (Mackenzie 1951) for five consecutive days to imitate a dynamic system of ion exchange (Noda, 1980; Bain and Smith 1987).

Displacement Solution
Ammonium was then displaced using two displacement solutions of 0.5M CsCl and 0.5M KCl. Ammonium concentration in solution extract was analysed using an autoanalyser. The value of NH_4^+ concentration obtained in mg L^{-1} was then converted to cmolc kg^{-1}. The sensitivity of natural zeolite CEC with the F-ratio value in relation to experimental factors (location, displacement solution and particle size) was tested using analysis of variance model using the MIXED procedure with SLICE function. All respective experimental factors were included in the model as independent variables and CEC as the response variable. F-ratio from the model output was used to assess the relative magnitude of CEC sensitivity to the experimental factors at 99% confidence level.

RESULTS AND DISCUSSION

Washing with Distilled Water and Presence of Soluble Cations
One of the factors that affect cation selectivity is the presence of other cations (Na^+, K^+, Ca^{2+}, and Mg^{2+}) that could reduce the value of NH_4^+ adsorbed on the natural zeolite. In our study, across location and particle sizes, washing with distilled water prior to ionic saturation resulted in higher exchange of Na^+ (from 0.10 to 0.49 cmolc kg^{-1}; Table 4 compared to other cations in the solution. Sodium ions in zeolitic framework are held by weak electrostatic interaction and thus they can be replaced by other cations (Sprynskyy *et al*. 2005). An undetectable Ca^{2+} and low release of Mg^{2+} (Table 4) may suggest that much of Ca and Mg may be fixed in the natural zeolite framework (Kitsoupoulos1999).

Contact Time of Saturating Solution and Exchangeable Cations
Without any pre-treatment of chemical conditioning, the natural zeolites generally have low CEC and therefore are frequently treated by increasing contact time by saturating zeolite samples with an ionic solution. In our study, 93-96% of the exchangeable cations were released in the first three days of saturation with 0.5M NH_4Cl (data not shown), in comparison to five days (Kitsoupoulos, 1999; Noda, 1980; Sprynskyy *et al*. 2005) , where the values were within range of the study conducted by Kitsopoulos(1999) and Hulbert (1987). Ammonium adsorption into the zeolite nanocavities can be achieved with time due to the process of slow diffusion of NH_4^+ ions into the channels and central nanocavities of natural zeolite (Kithome *et al*. 1998).

Effects of Displacement Solution on the CEC of Natural Zeolite
Natural zeolite samples displaced with 0.5M CsCl had 6% higher CEC compared to 0.5M KCl (P<0.0001), which means that Cs^+ had more strength compared to K+ in displacing NH_4^+ from the nanocavity site of the zeolitic framework into the solution. Yoshida et al. (2013) reported that the ionic radius of Cs^+ (0.17 nm), NH_4^+ (0.14 nm), K^+ (0.13 nm) and Na^+ (0.10 nm) plays a functional role in cationic selectivity. An increase in ionic radius results in an increase in selectivity. Based on the lyotropic series, the cation selectivity series in natural zeolite is described as $Cs^+> NH_4^+> K^+> Na^+> Ca^{2+} > Mg^{2+}$ (Ames 1960).

Location
F-ratio from the ANOVA models represents the magnitude of the effect of the experimental factors (location, displacement solution and particle size) on the CEC of natural zeolite. Greater sensitivity is reflected by a larger F-ratio. In this study, location (Cikembar and Bayah) had a larger F-ratio than displacement solution and particle size (Table 2). In both the displacement solutions, Cikembar100 recorded significantly higher CEC compared to Bayah100, 21% and 11%, respectively (Table 3). The higher CEC observed in Cikembar100 compared to Bayah100 was due to its higher surface area (31%) and total pore volume (11%) (Table 1). The CEC of natural zeolite, particularly clinoptilolite is within the range of the value as reported by Ahmed *et al.* (2006) and Kithome *et al*. (1998).

Table numbers are not right. Should be in numerological order???

Purity of Clinoptilolite and Particle Size on CEC of Natural Zeolite
The composition and purity of natural zeolites depend on the amount of clinoptilolite minerals in the natural deposits. Cikembar100 had 11% higher clinoptilolite mineral compared to Bayah 100 (Table 1). The low CEC measured for Bayah100 and Bayah200 may be due to the lower percentage purity of the clinoptilolite mineral content in those samples (Table1). According to Ferguson and Pepper (1987), clinoptilolite zeolite is characterised by a rigid three dimensional lattice with tunnels nm in size and which contain internal exchange sites that have an affinity for NH_4^+. A 25% decrease in pore size of Cikembar100 compared to Bayah100 (Table 1) increased NH_4^+ retention in the zeolitic framework and resulted in significantly higher CEC in Cikembar100 compared to Bayah100 (Table 3).

Isomorphous substitution and Cation Exchange in Natural Zeolite
In both displacement solutions (0.5M CsCl and KCl), Cikembar100 had 10% more net negative charge compared to Bayah100 due to its isomorphous substitution properties in natural zeolite (Table 4). Isomorphous substitution in natural zeolite affects its negative charge and the capacity to retain NH_4^+ in the zeolitic framework. This thus increases its CEC and makes natural zeolite a promising material for cation removal from aqueous waste streams.

TABLE 1:
Key properties of natural zeolite from two different locations (Bayah and Cikembar) with different particle sizes (0.15 and 0.079 mm) in West Java, Indonesia.

Sample	Estimated Clinoptilolite mineral (%)	Particle size (mm)	Surface area (m^2/g)	Total pore volume (cm^3/g)	Pore size* (nm)
Bayah100	78	0.15	56.9	0.083	5.2
Cikembar100	89	0.15	82.2	0.093	3.9
Cikembar200	80	0.079	--	--	--
Bayah 200	71	0.079	--	--	--

*Classification by the International Union of Pure and Applied Chemistry. Width of pore size between 2 – 50 nm = Mesopores and < 2 nm = Micropores (Sing *et al*.,1985).

TABLE 2
The F-ratio and P-values of sources of variation from experimental factors at 99% confidence level (n=24).

Experimental Factors	F-ratio	P-value
Particle size	24.35	0.0001
Location	179.95	<0.0001
Displacement solution	31.70	<0.0001

TABLE 3
Comparison of cation exchange capacity (CEC) of natural zeolite using two displacement solutions (0.5M CsCl and 0.5M KCl) (n=24).

	Displacement Solution	
	0.5M CsCl	0.5M KCl
Sample	Mean ± Standard error	Mean ± Standard error
Cikembar100	107 a ± 0.2	95 a ± 0.6
Cikembar200	101 a ± 1.3	89 a ± 1.2
Bayah100	85 b ± 1.1	84 b ± 0.4
Bayah 200	80 b ± 0.4	77 b ± 0.9
MSD (99% level)	11	10

Means with different letters within column showed significant difference at 99% confidence level. Minimum significant difference (MSD) based on Tukey's Honestly Significant Difference (HSD) at 99% confidence level.

TABLE 4

Soluble cations from washing and isomorphous substitution of natural zeolite samples (n=24).

	--------------Soluble Cations ($cmol_c$ kg^{-1})--------------			
Element	Cikembar100	Cikembar200	Bayah100	Bayah200
Ca	ND[‡]	0.02 c	ND[‡]	ND[‡]
Mg	0.01 c	0.01 c	0.01 c	0.01 c
Na	0.41 a	0.37 a	0.49 a	0.14 a
K	0.05 b	0.04 b	0.06 b	0.06 b
	----------------Isomorphous Substitution (%)---------------			
Displacement Solution	(100 - Percent Base Saturation)			
0.5M CsCl	87	91	77	77
0.5M KCl	86	89	76	76

‡ND = Not Detected. Means with different letters within column showed significant difference at 99% confidence level. Minimum significant difference (MSD) based on Tukey's Honestly Significant Difference (HSD) at 99% confidence level.

CONCLUSION

Our study found d that the natural zeolite exchangeable cations, Na^+ adsorbed weakly at the edge of the clinoptilolite structure during washing prior to saturating with an ionic solution. Our results indicate that 0.5M CsCl is a more promising displacement solution for higher CEC determination of natural zeolite than 0.5M KCl. Due to its low cost and easily accessible raw materials from the neighbouring country, natural zeolite from Cikembar with a particle size of 0.079 mm (Cikembar100) from West Java has potential for cost-effective removal of Cs (including Cs^{137}) from aqueous solution.

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