

Characterization and Improvement of Ion Exchange Capacities of Mexican Clinoptilolite-rich Tuffs

M.C. DÍAZ-NAVA^{1,2}, M.T. OLGUÍN^{1,*}, M. SOLACHE-RÍOS¹, M.T. ALARCÓN-HERRE-
RA² and A. AGUILAR-ELGUEZABAL²

¹Departamento de Química, Instituto Nacional de Investigaciones Nucleares, A.P. 18-1027, Col. Escandón, Delegación Miguel Hidalgo, C.P. 11801 México, D.F., México; ²Centro de Investigaciones en Materiales Avanzados CIMAV, S. C, Miguel de Cervantes 120, Complejo Industrial Chihuahua, C.P. 31109 Chihuahua, Chih. México

(Received: 29 March 2004; in final form: 24 November 2004)

Key words: clinoptilolite, cation exchange capacity, zeolitic tuffs

Abstract

Clinoptilolite-rich tuffs from the states of Chihuahua and Oaxaca in Mexico were modified with NaCl solutions to improve their ion exchange properties using different conditioning processes. First, the elemental and sodium compositions were identified by both induced coupled plasma atomic emission spectroscopy and neutron activation, respectively. The clinoptilolite-rich tuffs were characterized by scanning electron microscopy and X-ray diffraction and the surface areas were also determined in both tuffs. Effective, internal and external cation exchange capacities were determined. It was found that the elemental composition was different in both zeolitic rocks. A sodium treatment using a 0.1 M NaCl solution and reflux thus, improves effective cation exchange capacities of the Mexican clinoptilolite-rich tuffs. The external and internal cation exchange capacities depend on the size of the particle, as well as the source of the zeolitic rocks. The quaternary ammonium salt (HDTMABr or BCDMACl) considered is important in those determinations.

Introduction

Zeolite tuffs have generated worldwide interest for their use in a broad range of applications due to their geographically widespread abundance, and their low-cost [1]. Here to mention its use in ion exchange, adsorption or molecular sieves to remove several toxic substances including heavy metals or hydrocarbons (such as phenols) from waste waters [2, 3].

A significant number of studies have suggested that a pre-treatment of zeolitic rocks may enhance their ion exchange abilities. Zeolites normally provide a number of different intra-crystalline environments for cations in the crystalline network [4]. These cations then have different exchange properties for each environment and this is why pre-treatment is recommended in order to reach a final homoionic or near homoionic state of the zeolites thus improving their effective exchange capacities (EfCEC) to therefore enhance performance in ion exchange applications.

Bowman *et al.* [5] shows that, by treating clinoptilolite-rich tuffs with cationic surfactants, their surface chemistry becomes dramatically altered. Large organic cations exchange is essentially irreversible with native cations such as Na⁺, K⁺ or Ca²⁺, located on the

material's surface. This is why it is vital to determine the external ion exchange capacities of these materials.

There are several methods for evaluating the cation exchange capacities for zeolites. Ming *et al.* [6] has proposed a method for determining effective cation exchange capacities in clinoptilolites.

The difference between total and effective cation exchange capacities is due to several factors such as, low mobility and strong bonding forces within the material's structure and as a result, these can restrain the cations from being easily removed from the zeolites [7].

Initially, the external cation exchange capacity (ECEC) in zeolites was determined by using *tert*-butylammonium chloride solutions according to the Ming and Dixon [8] methodology. Later on, modifications of this procedure using different quaternary ammonium compounds such as tetramethylammonium bromide [9, 10] or hexadecyltrimethylammonium bromide [11, 12] have been used.

In order to improve EfCEC, many pre-treatment procedures for the preparation of homoionic ion exchangers have been employed. However, NaCl salt is the most widely used for this purpose [13–17] and many authors overlook giving details about sodium treatment conditions.

Zeolitic rocks' composition, as well as its chemical and physical treatments [18, 19] play an important role

*Author for correspondence. E-mail: mog@nuclear.inin.mx

on ion exchange behavior. Therefore, the aim of this paper was to compare different treatment conditions, such as temperature and sodium chloride concentrations to prepare homoionic materials (clinoptilolite type), and consequently, improve the cation exchange properties which were measured considering the effective cation exchange capacities as well as the internal and external cation exchange capacities. The latter was determined by using a modified Ming and Dixon [8] procedure, hexadecyltrimethylammonium or benzylcetyldimethylammonium ions were used instead of *tert*-butyl ammonium ions because of future applications of these materials for removing organic water pollutants. The zeolitic rocks' particle size and source were two key parameters considered in this investigation. The characterization of zeolitic rocks from the states of Oaxaca and Chihuahua, Mexico are also included in this paper.

Experimental

Materials

The clinoptilolite-rich tuffs used in this study were from 'Cerro Prieto ejido San Miguel de los Anchondo', located 7 km from Parral, Chihuahua (106°9' West longitude and 28°17' North latitude) and Etna, located 15 km from Oaxaca City (97°13' West longitude and 17°14' North latitude), Mexico. These materials from Chihuahua and Oaxaca will be called CLICHI and CLIO respectively.

The minerals were grinded in an agate mortar and sieved to different size ranges (Table 1).

Elemental composition determination

Induced coupled plasma atomic emission spectroscopy (ICP).

Al, Si, Ca, Na, Mg, K and Fe in the zeolitic rocks were determined by induced coupled plasma analysis (ICP) with a spectrometer Thermo Jarrell Ash, Model Iris/AP Duo.

Samples of 200 mg of each zeolitic rock were treated with a mixture of hydrofluoric, hydrochloric and perchloric acids (1:1:1). The digestions were carried out in a closed atmosphere, using a microwave oven Mars 5, model CEM (each sample was analyzed in triplicate).

Neutron activation analysis

The sodium content in the untreated and treated zeolitic materials was determined by neutron activation analy-

sis. The samples, together with a reference, were irradiated in a nuclear reactor TRIGA MARK III (neutron flux about 10^{13} n cm⁻² s⁻¹) for 30 s. The energy gamma of 1369 keV from ²⁴Na was measured for sodium analysis.

Characterization techniques

X-ray diffraction

Powder diffractograms of the zeolitic samples were obtained with a Siemens D500 diffractometer coupled to a copper-anode X-ray tube. Conventional diffractograms were used to identify the compounds and to verify crystallinity.

Scanning electron microscopy

The natural zeolitic samples were mounted directly onto the holders and then observed at 10 and 20 kV in a Philips XL 30 electron microscope for scanning electron micrographs. The microanalysis was done with a DX-4 probe.

N₂ Adsorption and surface area (BET)

The nitrogen adsorption isotherms were measured at 77 K and the BET surface areas were determined by standard multipoint techniques of nitrogen adsorption, using a Micromeritics ASAP 2000 instrument. The untreated and sodium treated (with 0.1 M NaCl and reflux) zeolitic samples were heated at 373 K for 24 h before specific surface areas were measured.

Sodium zeolitic rocks treatments

Two different means were used to treat the natural zeolitic materials with NaCl solutions to obtain a homoionic material: First, in a batch type treatment with 5 M NaCl solution at room temperature for 8 days and the second, in reflux (358 K) with 0.01 or 0.1 M NaCl solutions for 3 or 18 h, then the phases were separated and the zeolites were once more placed in a reflux in the same conditions with fresh solutions. The materials were washed until Cl⁻ free, using a silver nitrate solution as an indicator.

Cation exchange capacities

Effective cation exchange capacities

Effective cation exchange capacities were determined in the untreated and the sodium zeolitic materials by using a technique reported by Ming *et al.* [6]. The materials were treated with a 1 M sodium acetate buffered solution of pH 5 to eliminate the carbonate coating on the zeolitic rocks, then they were treated with a 1 M potassium chloride solution and finally, with a 0.2 M cesium chloride solution.

The effective cation exchange capacities were calculated by the quantity of potassium removed per gram from the zeolitic rock and expressed in meq/g. Potassium was determined in the solutions by atomic

Table 1. Grain size of the zeolitic rocks from Chihuahua and Oaxaca

Zeolitic samples	Mesh	Diameter (mm)
CLICHI12, CLIO12	8–12	1.700
CLICHI30, CLIO30	20–30	0.600
CLICHI40, CLIO40	30–40	0.425

absorption spectroscopy (Atomic absorption spectrometer GBS 932 Plus with a potassium hollow cathode lamp, wavelength 404.4 nm).

External cation exchange capacities

The external cation exchange capacities of the clinoptilolite-rich tuffs were determined by using the Ming and Dixon [8] technique and the surfactants HDTMABr and BCDMACl were used instead of *tert*-butylammonium chloride.

Different particle size samples of sodium zeolitic rock were placed into contact with a buffer 1 N sodium acetate solution of pH 5 for 18 h at room temperature. The solids were then separated and left at room temperature for 24 h. Again they were mixed with a 0.1 M of surfactant (HDTMABr or BCTMACl) solution and left for another 48 h at 30 °C. The samples were then separated and washed twice with 5 ml of surfactant solution.

The surfactants retained in the zeolitic rocks were determined as follows: the solids were dried at 25 °C for 12 h, then they were milled and carbon was determined in each sample by using an elemental analyzer CHNS-O, CE-Instrument, model EA-1110. The quantities of surfactants retained on the zeolitic materials were calculated from the carbon determined in the samples. The external cation exchange capacity was calculated in meq of surfactants retained in each gram of clinoptilolite-rich tuff.

Internal ion exchange capacities

The internal cation exchange capacities were determined as follows: the zeolitic samples treated with the surfactants mentioned above were washed five times with distilled water and they were put into contact and shook in a 1 N ammonium acetate solution for 18 hours at room temperature. Then, the phases were separated and sodium was determined in the aqueous phases. The internal cation exchange capacities were calculated as meq NH_4^+ /g in the clinoptilolite-rich tuff.

Results and Discussion

Elemental composition

Ion exchange studies on zeolitic-rich tuffs present special difficulties due to their composition. Natural zeolites used in ion exchange processes are usually zeolitized volcanic tuff specimens and their composition commonly includes minerals such as quartz, feldspar, etc.

Although the elemental composition of the clinoptilolite-rich tuffs from Chihuahua and Oaxaca are alike, the differences in their cation composition can be observed. The main cations found in the samples were sodium, potassium and iron. The natural materials contain different cations depending on their geographic source. Ming and Dixon [8], have reported that the main cations are Na^+ , K^+ and Ca^{2+} . Iron has been

associated with impurities present in zeolitic tuffs such as iron oxides. The iron found in the clinoptilolite-rich tuff samples varies from 0.05 to 0.2 meq/g.

Different compositions have been reported for zeolitic tuffs with different grain size from the same location [19], the elemental compositions of the untreated zeolitic rocks studied in this work have confirmed these results.

The highest contents of sodium, potassium and manganese were found in the samples CLIO12, CLIO30 and CLICHI40, respectively.

The Si/Al ratio values determined in the zeolitic rocks were from 4.8 to 6.3. The majority were higher than the value reported by Tsitsishvili *et al.* [20], for clinoptilolite (about 4), which provides evidence of other mineral components present in the zeolitic samples studied.

Characterization

X-ray diffraction

The components found by X-ray diffraction were similar in both zeolitic materials CLICHI and CLIO. Clinoptilolite was found in both materials, JCPDS card 39-1383 ($\text{Na}_{1.4}\text{Ca}_{0.1}\text{K}_{0.3}\text{Mg}_{0.05}\text{Al}_2\text{O}_4(\text{SiO}_2)_9 \cdot 6.5\text{H}_2\text{O}$). Mordenite, quartz and sodium anorthite (JCPDS cards 06-0239, 33-1161 and 20-0528, respectively) were also found in both rocks.

Zeolitic materials from both Chihuahua and Oaxaca showed a heterogeneous composition (grains of different colors). The zeolitic rock from Chihuahua showed clear, black and brown grains and the zeolitic rock from Oaxaca showed clear, black and green grains. The grains were separated and their X-ray diffraction patterns indicated the presence of clinoptilolite. Quartz was better observed in the clear grain than in the brown grain in the clinoptilolite-rich tuff from Chihuahua.

The black grains were identified as Fe_2O_3 (JCPDS 39-1346 card) in both minerals (Figure 1). The zeolitic rocks samples did not show any significant changes after they were treated with NaCl solutions.

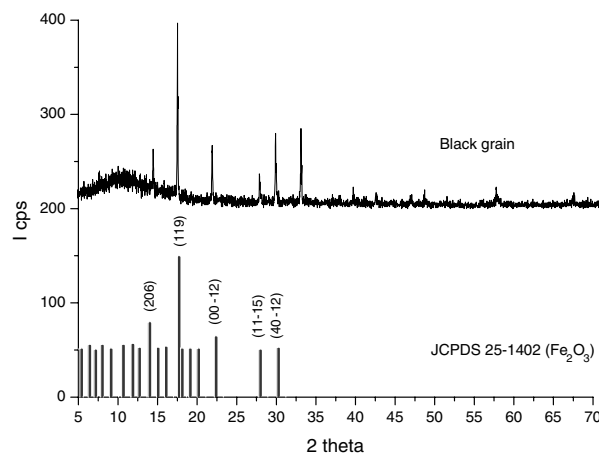


Figure 1. XRD patterns of black grains present in both zeolitic rocks (Chihuahua and Oaxaca).

Electron microscopy

SEM images and EDS analysis showed that the morphology and chemical composition of the different color grains in both clinoptilolite-rich tuffs were not the same.

Most of the clinoptilolite crystals analyzed displayed a typical morphology of sedimentary clinoptilolites [21], coffin- and cubic-like crystals were observed in the clear grains and, cubic-like crystals in the brown grains of the zeolitic rock from Chihuahua (Figure 2). The black grains presented different morphologies. The micro-analysis of the samples by EDS showed that the highest concentration of sodium was found in the clear grains and the highest concentrations of iron, magnesium and titanium were found in the black grains. Sodium and calcium were not found in the last sample.

As mentioned earlier, the clear and green grains of the zeolitic material from Oaxaca showed coffin- and cubic-like crystals, which have typical clinoptilolite morphology, and look similar in all cases. The black grains showed different morphologies similar to those observed in the Chihuahua zeolitic sample.

The elemental analysis of the Oaxaca clinoptilolite-rich tuff using EDS showed that the white and green grains' sodium content was higher than that of calcium. However, these elements were not detected in the black grains. The black grains are not of zeolitic material; their composition is principally Fe and O. The X-ray diffraction observations confirm these results (Figure 1).

Several morphological changes on the clinoptilolite's crystal surfaces in the Chihuahua samples were observed after the reflux treatment. In every case, small fragments adhered to the surfaces of the clinoptilolite were

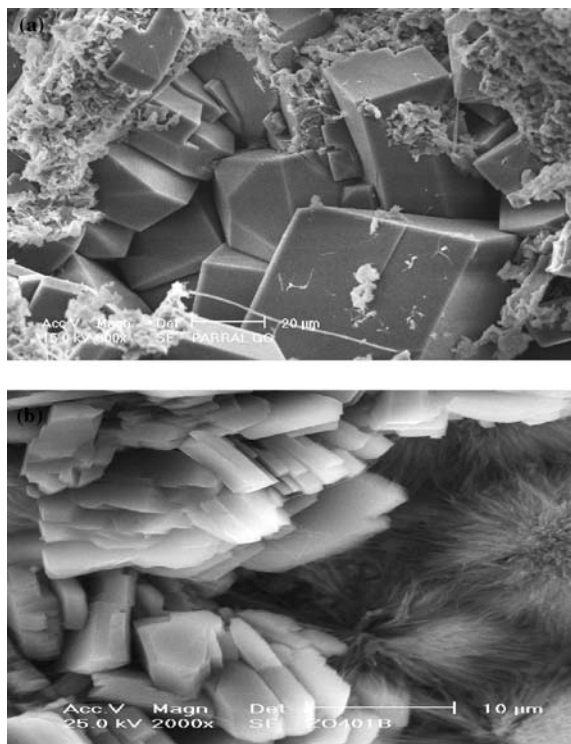


Figure 2. SEM images of zeolitic minerals from (a) Chihuahua and (b) Oaxaca.

observed before and after NaCl treatment, possibly a result from the mineral's mechanical breakage.

N_2 adsorption and surface area (BET)

The adsorbed volumes of N_2 for the samples were 1, 1.8, 1, 24, 10 and 50 cm^3/g for CLICHI40, CLICHI30, CLICHI12, CLIO40, CLIO30 and CLIO12 respectively, at a lower partial pressure ($p/p_0 = 0.03$). According to Dong *et al.* [22], all zeolitic rocks contain small amounts of micro-pores in their framework. On the other hand, the isotherms' hysteresis loops in the samples (except CLIO12) at a higher partial pressure are typical of type H3 in the IUPAC classification [22] and therefore, demonstrates that the samples are aggregates of plate-like or needle-like particles giving rise to slit-shaped pores, whereas, the isotherm of the CLIO12 sample is Type I reversible isotherm obtained from micro-porous materials having a high surface area.

The surface areas determined for the Oaxaca clinoptilolite-rich tuff samples were higher than those from Chihuahua (12, 30 and 40 mesh). The areas in the Chihuahua samples increased slightly after they were treated with sodium chloride solutions (Table 2) and, the behavior was different in the Oaxaca zeolitic rock samples. It is worth mentioning that there were differences in the surface areas between the samples CLIO40-CLIO12 and CLIO30-CLIO12. This may be due to zeolitic components present in each grain size fraction as was mentioned earlier. The surface areas increased as the zeolitic rock grain size decreased in the CLICHI samples and this behavior could be due to the composition of the zeolitic rocks.

The surface area values of the Chihuahua and Oaxaca clinoptilolite-rich tuffs are in the reported range by using different techniques for other zeolitic rocks [10, 23, 24].

Sodium clinoptilolite-rich tuffs

The ion exchange of the cations from the zeolitic rocks with sodium ions from the solution was the lowest when the samples were treated with a 0.01 M NaCl reflux solution compared with those treated in 0.1 M NaCl reflux solutions.

The samples CLICHI40, CLICHI30 and CLICHI12 treated with a 0.1 M NaCl reflux solution, revealed that the quantities of sodium increased up to a hundred percent compared to the untreated zeolitic rock. This effect was not observed when the samples were placed in a 5 M NaCl solution at room temperature. Temperature and concentration play an important role in cation exchange processes of zeolitic rocks (Figure 3).

The samples CLIO40 and CLIO30 exhibited an increase of sodium of about a hundred percent when they were placed in a 5 M sodium chloride solution at room temperature and displayed an increase of about two hundred percent when they were placed in a 0.1 M NaCl reflux solution. However, in the sample CLIO12, the sodium quantities remained constant after the

Table 2. CLICHI and CLIO surface areas

Diameter of the grain (mm)	Area (m ² /g)			
	CLICHI untreated	CLICHI 0.1 M NaCl treated	CLIO untreated	CLIO 0.1 M NaCl treated
0.425	5.44	6.95	72.11	59.56
0.600	5.33	6.85	34.1	51.24
1.700	5.15	6.72	151.9	149.12

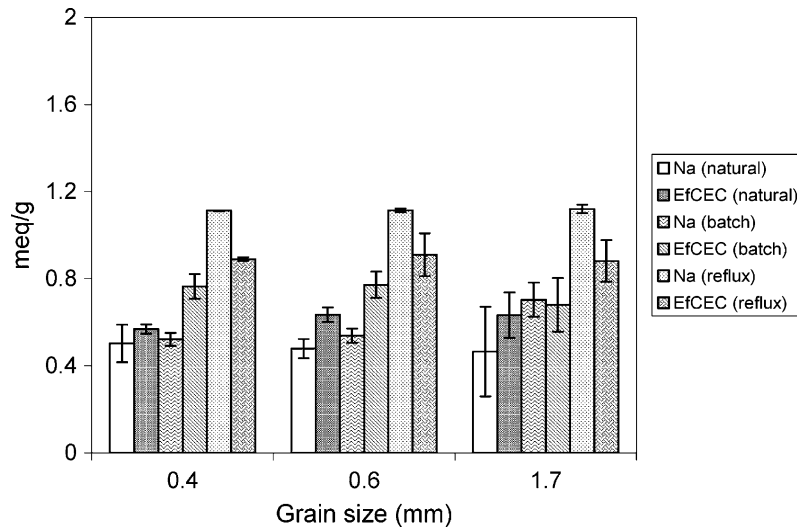


Figure 3. Sodium content and EfCEC of the untreated and treated CLICHI with 0.1 M NaCl solution (reflux) and 5 M NaCl solution (batch).

sodium treatments (Figure 4). This behavior could be due to the composition and distribution of the mineral components after the samples were sieved.

After the 0.1 M NaCl reflux solution treatment, the sodium amount in CLIO was approx. 1.5 times higher than in CLICHI in all particle sizes. It is expected that

the effective cation exchange capacity will have the same behavior.

Curkovic *et al.* [25] have stated that three of the most important parameters that can influence the ion-exchange behavior of zeolitic rocks are; the chemical composition of the zeolitic material, the temperature at

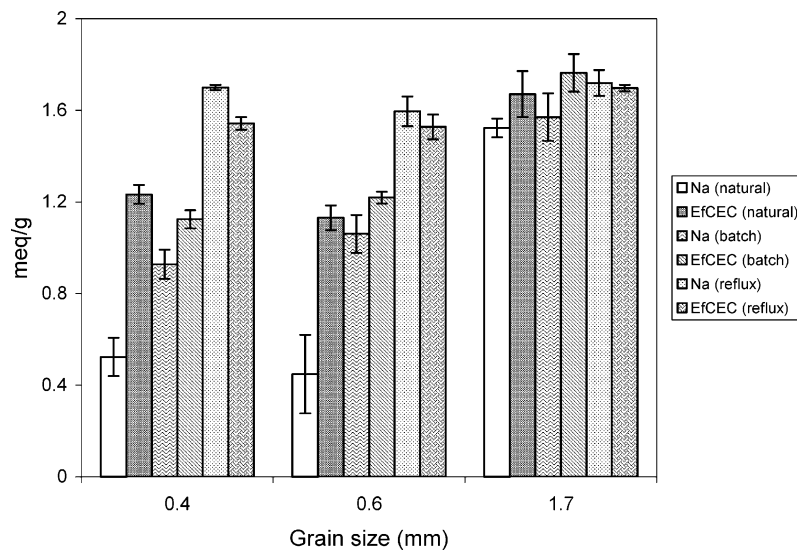


Figure 4. Sodium content and EfCEC of the untreated and treated CLIO with 0.1 M NaCl solution (reflux) and 5 M NaCl solution (batch).

which the ion exchange takes place and, its conversion to a single ionic form.

Cation exchange capacities

Effective cation exchange capacity

When the zeolitic rock samples from Chihuahua were treated with a 5 M NaCl solution (Figure 3), a slight increase of the EfCEC was observed for samples CLICHI30 and CLICHI40, however, an increase was not observed for sample CLICHI12. The EfCEC for CLIO remained about the same in every case for the untreated and treated zeolitic rocks with a 5 M NaCl solution (Figure 4).

The EfCEC increased about 50% in the Chihuahua zeolitic samples treated with 0.1 M NaCl in comparison to the untreated zeolitic rock (samples CLICHI30 and CLICHI40). In the case of sample CLICHI12, the EfCEC in the untreated and 0.1 M NaCl treated were slightly different, considering the error bar (Figure 3). In the same treatment conditions, the EfCEC increased around 1.3 times for samples CLIO30 and CLIO40 after they were treated with a 0.1 M NaCl solution, but in sample CLIO12 no changes were observed after the treatment (Figure 4).

It is important to point out that the EfCEC obtained from the Oaxaca zeolitic rock treated with 0.1 M NaCl was higher than the value attained from the treated Chihuahua zeolitic rock (approximately 1.6 and 0.9 meq/g, respectively) in the three particle sizes (0.4, 0.6 and 1.7 mm) within similar conditions. These results were comparable to those reported for other materials [6, 8, 26].

In every case, the treatment improved the ion exchange capacities compared to the untreated zeolitic rock samples. The amount of sodium in the Chihuahua zeolitic rock after the 0.1 M NaCl solution treatment was higher than the effective ion exchange capacities. In the Oaxaca samples, this behavior was only observed in the CLIO40 sample (Figure 4). Pabalan and Bertetti [27], Inglezakis *et al.* [15], and Curkovic *et al.* [25] had observed this effect. These authors had revealed that potassium and calcium ions were stronger held onto clinoptilolite than sodium. Therefore, extensive exposure to high sodium concentration was required to exchange these ions from the zeolite network. Temperature and sodium concentrations improve the sodium ion exchange in the zeolitic rocks. Within these conditions, the sodium content in the zeolite increases, mainly due to the potassium and calcium exchange [25]. It has also been suggested that part of the calcium and potassium ions are not exchangeable since a few are associated with impurities in the zeolitic materials.

Semmens and Martin [17] reported similar cation exchange capacities for clinoptilolite samples treated in different ways. It is likely that the differences found in the EfCEC values were due to the composition of the

samples after sieving. Kitsopoulos [19] along with attributing the variations of the CEC values in clinoptilolite-rich zeolitic materials to the variability of the clinoptilolite content as well as to the chemical composition of the samples.

When working with natural materials, the determined EfCEC values are in general, different to the total exchange capacities and the differences can be acknowledged mainly to the following; first, clinoptilolite's ratio to the rest of the minerals [26] and secondly, to the cations compositions, which only a fraction in a zeolitic rock are exchangeable according to the sites occupied in the zeolite network. It has also been reported, that the EfCEC in zeolitic rocks depends on the material's particle size [19] although this behavior was not observed in the Chihuahua zeolitic rock. However, in Oaxaca's zeolitic rock, this behavior was observed in the samples CLIO12–CLIO30 and CLIO12–CLIO40 but was not observed for samples CLIO30–CLIO40. These results show that the nature of the zeolitic rocks also plays an important role in the EfCEC (Figures 3 and 4).

Klieve and Semmens [18] have showed how the capacity of zeolitic rocks depends significantly on the pre-treatments the zeolites have received. The results revealed that the cation exchange capacities of the Oaxaca and Chihuahua rocks depends on treatment conditions, the exchangeable cations present in the material and, the zeolitic rocks' source.

External cation exchange capacity

The ECEC were 3.5 and 2.7 times higher for Oaxaca zeolitic samples than for Chihuahua zeolitic samples in all grain sizes considering HDTMABr and BCDMACl, respectively (Figures 5).

The ECEC for CLICHI40, CLICHI30 and CLICHI12 were similar when the same ammonium quaternary salt (HDTMABr or BCDMACl) was used. However, according to these results, the particle size did not play an important role on the external cation exchange capacity, although a slight difference (about 15%, taking into account the error bar) in the ECEC were observed for the same grain size but conditioning with a different surfactant. Therefore, it is important to consider the effect of the surfactant adsorbed on the zeolitic rock in the ECEC determinations. Similar results were observed for the Oaxaca zeolitic rock.

The ECEC values obtained by other authors for clinoptilolite-rich tuffs varied from 0.01 to 0.37 meq/g as they can be seen in Table 3. The value of the ECEC for the CLICHI and CLIO (mean values from the 12, 30 and 40 mesh samples) are 0.031 ± 0.001 and 0.105 ± 0.003 meq/g, respectively.

Internal cation exchange capacity

The internal cation exchange capacities for CLICHI40, CLICHI30 and CLICHI12 were similar when the ammonium quaternary salt (HDTMABr or BCDMACl) was the same, so the particle size does not play an

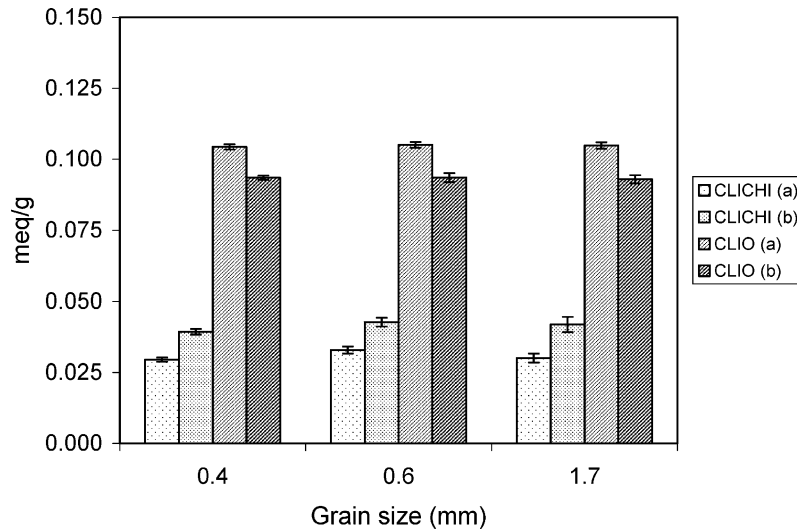


Figure 5. ECEC of CLIOCHI and CLIO determined with (a) HDTMABr or (b) BCDMACl.

important role on the internal cation exchange capacity. Important differences (around 40%) were observed when different surfactants were used for the same grain size of CLIOCHI samples. Therefore, it is important to consider the effect of the surfactant adsorbed on the zeolitic rock in ICEC determinations (Figure 6) as was mentioned before for ECEC, although the zeolitic rock from Oaxaca did not show this behavior. In this case, no difference in the ICEC values were found using both surfactants for samples CLIO40 and CLIO30, but an important difference (around 50%) in ICEC of sample CLIO12 was observed when HDTMABr or BCDMACl were used for the determinations (Figure 6). It is important to note that the ICEC is similar in all cases when HDTMABr was used for the determinations.

The ICEC for zeolitic samples from Chihuahua are similar to those from Oaxaca for all grain sizes using HDTMABr for the determinations.

There is a difference between the EfCEC obtained by the Ming *et al.* [6] method compared to the sum of the ECEC and ICEC for both zeolitic rocks as seen in Figures 7 and 8. This difference is attributed to the quaternary ammonium salt used (HDTMABr or BCDMACl) in the determinations of both the ECEC and the ICEC.

The ICEC in Table 4 shows values for different clinoptilolite-rich tuffs. In this work, 1.09 ± 0.01 meq/g for CLIOCHI and 1.02 ± 0.03 for CLIO mean values from the 12, 30 and 40 mesh samples were obtained.

It is important to mention that it depends on the zeolites' surfactant modification, which will enable them to sorb neutral molecules and anionic metals while retaining their ability to exchange heavy metal cations, subsequently, the zeolitic rocks modified with surfactants simultaneously will remove organics, inorganic

Table 3. ECEC for clinoptilolite-rich tuffs from different regions

Author and [reference]	Year	Method	ECEC (meq/g)	Observations (Clinoptilolite)
Ming and Dixon [8]	1987	Ming and Dixon	0.10	Webb Country, Texas purified 100% 2 mm
Haggerty and Bowman [11]	1994	Ming and Dixon modified HDTMABr	0.15	St. Cloud, New Mexico 0.42–0.83 mm
Cadena and Cazares [10]	1995	Ming and Dixon modified TMA	0.20	Crisman Hill, Oregon 0.45–1.05 mm
			0.15	Winston, New Mexico 0.12–1.20 mm
Sullivan <i>et al.</i> [23]	1997	Ming and Dixon	0.30	Tilden, Texas 0.28–0.75 mm
			0.07–0.09	St. Cloud, New Mexico Not specified
Li and Bowman [12]	1997	Ming and Dixon	0.09	St. Cloud, New Mexico 0.42–0.83 mm
		Ming and Dixon modified HDTMA	0.11	St. Cloud, New Mexico 0.15–2.0 mm
Kitsopoulos [28]	1997	MBA method (methylene blue absorption)	0.01–0.12	Polyegos, Greece μm
			0.07–0.37	Santorini, Greece μm
Li and Bowman [29]	1998	Ming and Dixon and Ming and Dixon modified HDTMA	0.09–0.11	St. Cloud, New Mexico 0.42–0.83 mm
Sullivan <i>et al.</i> [30]	1998	Ming and Dixon modified	0.07–0.09	St. Cloud, New Mexico Not specified
Li [31]	1999	Ming and Dixon modified	0.10	St. Cloud, New Mexico 0.4–1.4 mm
Li <i>et al.</i> [32]	2000	Ming and Dixon modified	0.09–0.11	St. Cloud, New Mexico 0.4–1.4 mm
Salinas <i>et al.</i> [33]	2001	Ming and Dixon modified BTBA	0.06	Oaxaca 1.7 mm
		Ming and Dixon modified HDTMA	0.01	Oaxaca 1.7 mm

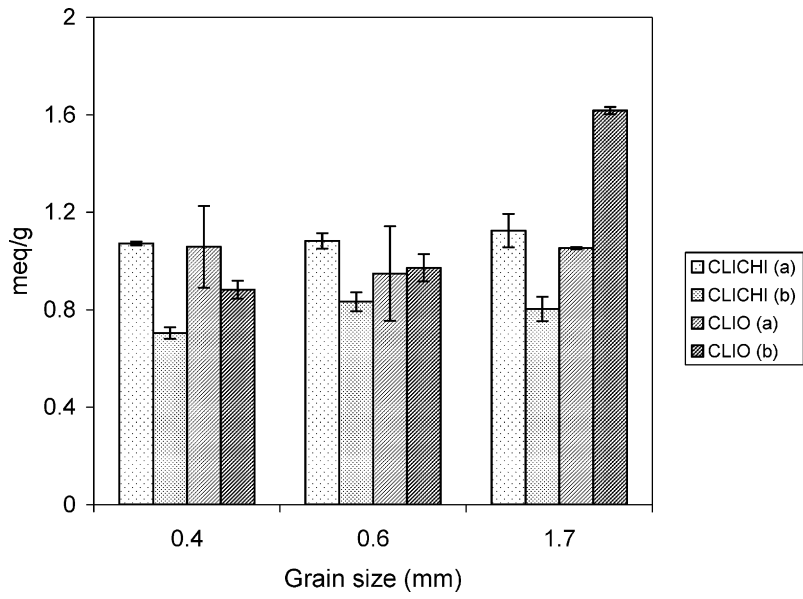


Figure 6. ICEC of CLIOCHI and CLIO determined with (a) HDTMABr or (b) BCDMACl.

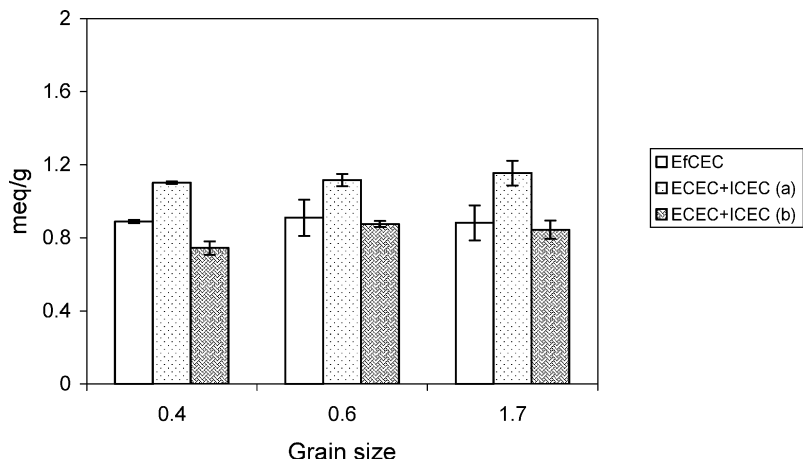


Figure 7. EfCEC and ECEC plus ICEC of CLIOCHI determined with (a) HDTMABr or (b) BCDMACl.

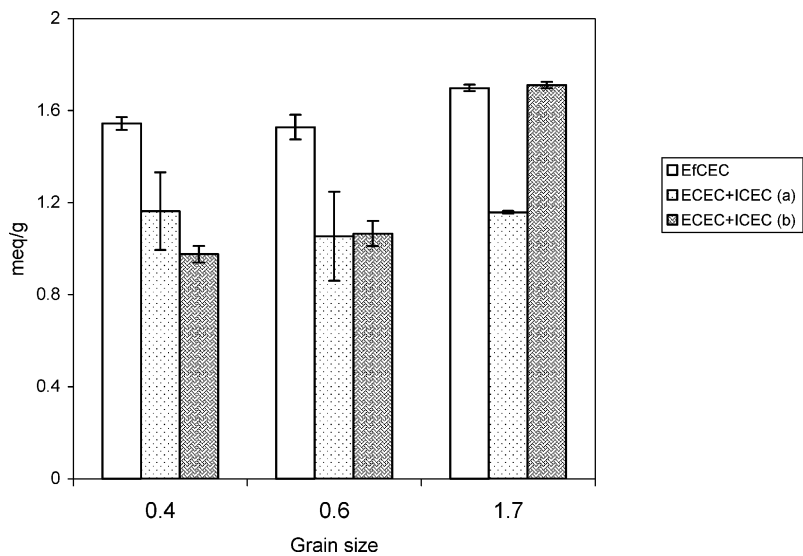


Figure 8. EfCEC and ECEC plus ICEC of CLIO determined with (a) HDTMABr or (b) BCDMACl.

Table 4. ICEC for clinoptilolite-rich tuffs from different regions

Author and references	Year	Method	ICEC (meq/g)	Observations (clinoptilolite)
Ming and Dixon [2]	1987	Ming and Dixon	1.65	Webb Country, Texas purified 100% 2 mm
Li <i>et al.</i> [32]	2000	Ming and Dixon modified	0.80	St. Cloud, New Mexico 0.4–1.4 mm
Salinas <i>et al.</i> [33]	2001	Ming and Dixon modified BTBA	1.06	Oaxaca 1.7 mm
		Ming and Dixon modified HDTMA	0.63	Oaxaca 1.7 mm

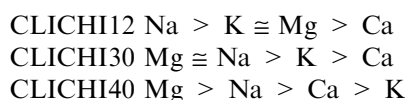
cations and inorganic anions from contaminated water and will also depend on both the external (ECEC) and internal ion exchange capacities (ICEC) of each zeolitic rock (Figure 9).

Conclusions

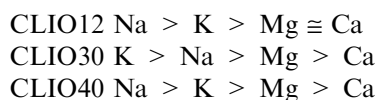
The Oaxaca zeolitic rock is a sodium–potassium material and the zeolitic rock from Chihuahua is a magnesium–sodium material.

Depending on the particle size, the milliequivalents of Na, K, Ca and Mg in the studied zeolitic minerals have the following order:

Zeolitic rock from Chihuahua:



Zeolitic rock from Oaxaca:



The Fe found in the zeolitic rocks is present as Fe_2O_3 .

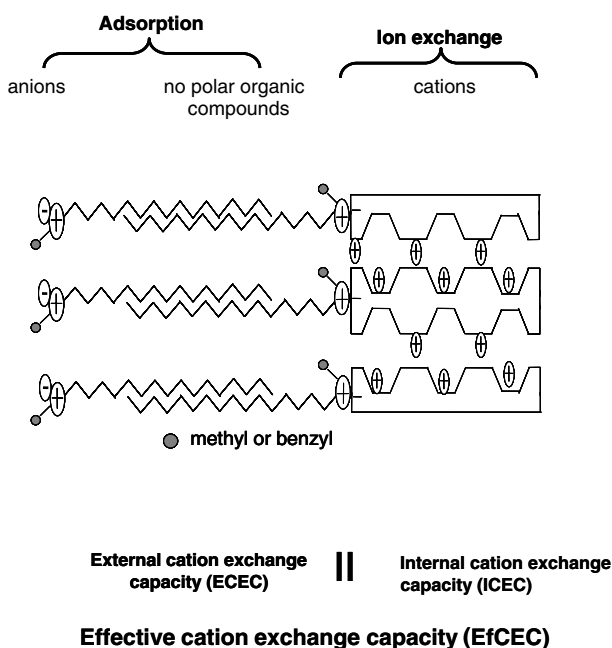


Figure 9. Representation of the ion exchange and adsorption properties of the modified zeolite (hexadecyltrimethylammonium bromide or benzylcetyldimethylammonium chloride).

The zeolitic rock components and the particle size are important parameters to be considered on the N_2 adsorption/desorption behavior, adsorbed volumes of N_2 and surface areas.

Sodium treatments improve the effective cation exchange capacities of the zeolitic rocks. The method that produce the best results is the treatment with the 0.1 M NaCl solution and reflux, the effective cation exchange capacities are higher (about 1.8 times) for the Oaxaca zeolitic rocks than for the Chihuahua zeolitic rocks.

The grain sizes as well as the source of the zeolitic rocks also play an important role on their cation exchange capacities (effective, external and internal).

It is important to consider that the type of surfactant adsorbed on the zeolitic rock has an important role on the external and internal cation exchange capacities determinations.

Acknowledgements

The authors acknowledge financial support provided by CONACYT (Project 35322-E) and are grateful to Geologist Enrique Torres Moye for the Chihuahua mineral collection.

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