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WATER DEFLUORIDATION BY MEXICAN HEULANDITE–CLINOPTILOLITE

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ABSTRACT

Fluorosis is caused by excess ingestion of fluoride. In this work, a natural Mexican zeolite (heulandite–clinoptilolite from Sonora) was evaluated for the sorption of fluoride ions from aqueous solutions and well-water. The effects of sodium, calcium, lanthanum, and europium in the crystalline network of this aluminosilicate, as well as, the effects of pH and particle size of the zeolite on the fluoride sorption were determined. It was found by x-ray diffraction, electronic microscopy, and IR that the structure of the material does not change after the retention of fluoride ions, and fluoride retention is not substantially affected by the cations (Na, Ca, La, and Eu) in the zeolite, the initial pH, or the particle size of the material studied. The K_d values obtained from the zeolitic mineral treated with La and Eu are slightly different

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from those obtained from both the untreated zeolitic mineral and the material treated with Na and Ca.

Key Words: Fluoride ions; Sorption; Mexican heulandite–clinoptilolite

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INTRODUCTION

Many studies on the adverse effects of fluoride ions on human health have been published.[1–5] Fluorosis caused by excess ingestion of fluoride ions has no treatment or cure but it can be easily prevented, provided the disease is diagnosed at an early stage of affliction.[2] It has been reported that any fluoride concentration level higher than 1.5 mg/L does not decrease significantly dental caries, but it increases the probability and severity of fluorosis. It has been recommended that the concentration of fluoride in water should be 1 mg/L, it has been reported that with this concentration the incidences of dental caries were reduced and the appearance of fluorosis was not observed.[5] The World Health Organization has specified the fluoride content for drinking water between 1.0 and 1.5 mg/L.[6]

Various methods have been studied for the removal of fluoride from water with higher fluoride concentrations; these methods can be broadly classified into two groups: chemical precipitation and sorption by different materials. Some mechanisms for the sorption of fluoride in various materials have been proposed; these include occlusion and adsorption.

Occlusion in the Cavities of the Materials

Zeolites have a large pore volume that is usually occupied by water molecules and cations. The entrapped water can be replaced by certain salts, depending upon the species in the zeolite.[7] Park and Komarneni[8] reported the capacity of a natural zeolite to occlude ammonium nitrate and potassium nitrate by molten salt treatment, and the salt-occluded zeolites were characterized.

Despite the fact that zeolites are cation-exchangers, it has been suggested that occlusion of anions can take place and depends on the size of the guest anion. Fluoride anion with a diameter of 2.66 Å is therefore easily occluded in the zeolite cavity due to the Donnan exclusion which depends on the fluoride salt in the solution.[9,10]

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Adsorption

The ionic radius of the fluoride ion (1.36 Å) is similar to that of the hydroxyl ion (1.40 Å) and they can be easily exchanged between the zeolite and aqueous solutions.[11]

The mechanism considered for the adsorption of F^- ions on hydrous oxides and yttrium-loaded poly(hydroxamic acid) resin adsorbents is ion exchange.[12]

For the aluminum form of the aminomethylphosphonic acid-type ion exchanger, it has been suggested that the uptake of fluoride ions can not be performed by regular anion exchange. The only other explanation for the uptake of fluoride ions is a complex formation with Al^{3+} on the resin matrix.[6] The selective removal of fluoride ions is very sensitive to the pH of the medium. Below pH 2.6 and above pH 6.9 the fluoride uptake deteriorates. At lower pH, Al^{3+} starts leaking and hence fluoride uptake is adversely affected. It has been found that approximately 10% of the total Al^{3+} loaded is leached from the resin column with 1 *M* hydrochloric acid under dynamic conditions. At higher pH, it has been stated[13] that deprotonation of the coordinated water takes place leaving an increased negative charge around the metal ion which repels F^- ions.[6]

The mechanism for fluoride removal when using activated alumina is generally considered to be a combination of ion-exchange and physical adsorption.[13] It has been suggested as well that at low pH, the retention of fluoride in alumina probably is caused by the formation of aluminum-fluoride complexes rather than by specific adsorption on the alumina surface.[14]

Anion adsorption sites on minerals as gibbsite, alumina, serpentine, and clay minerals are aqua groups (—M—OH_2^+) and hydroxo groups (—M—OH). The surface chemistry of an oxide in contact with an aqueous solution is determined to a large extent by deprotonation or a hydroxyl ion association reaction.

Metal oxides that are hydrolyzable in aqueous solutions have been considered as well, they develop a negative and positive charges on the surface depending on the pH of the solutions.[15]

Some of the materials studied for the separation of fluoride ions from aqueous solutions are: zeolites, polymeric resins, hydrous oxides, clays, coal, and activated alumina. These materials each present advantages and disadvantages. For example, the ion exchanger materials, generally require a complicated preparation and they usually need acid conditions for the optimum defluoridation. Some oxides, like cerium oxide, supported on ion exchange resins[12] have been studied as well; however, the defluoridation media should be an acid, which makes it difficult to use in the real problem of interest here.

For practical applications, the best results reported have been those obtained with zeolites. Although the optimum pH for defluoridation process could be in the acid range; in neutral or in basic media the defluoridation process

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is satisfactory. It is not clear how the cation (sodium or calcium) in the zeolite may influence the retention of fluoride.[9] Other materials have been studied that contain elements such as lanthanum, cerium, praseodymium, and yttrium, supported on different resins.[16,17] These elements confer acid properties to zeolites. Therefore the aim of this work was to evaluate the sorption of fluoride by a natural Mexican zeolite (clinoptilolite–heulandite) and to determine the effect on the sorption by the presence of sodium, calcium, lanthanum, and europium in the crystalline network of this aluminosilicate, as well as, the influence of pH and the particle size of the zeolite.

EXPERIMENTAL METHODS

Materials

Natural Mexican heulandite–clinoptilolite from Sonora, Mexico was ground to particle sizes of $12 < X < 20$ and $24 < X < 30$ mesh.

Treated Materials

The material samples were left in contact with 5 M NaCl or $CaCl_2$ solutions for 22 days; then the phases were separated; and the zeolite samples were washed with water until chloride ions were not detected in the aqueous phases with silver nitrate solution. Other zeolite samples were treated with lanthanum or europium; they were left for 22 days in 0.01 M lanthanide nitrate solutions. The phases were then separated by centrifugation; the zeolite samples were washed three times with water; and finally all materials were dried at 80°C. In order to have the same conditions in the experiments, the materials were left for at least 7 days in a humid medium to reach the same content of water in the zeolitic mineral before the sorption experiments were performed.

The samples treated with NaCl, $CaCl_2$, $La(NO_3)_3$, and $Eu(NO_3)_3$ are referred to in this article as HEUCLI-Na, HEUCLI-Ca, HEUCLI-La, and HEUCLI-Eu, respectively.

Thermogravimetric Analyses

Water content measurements in the natural zeolite was carried out with a TGA 51 TA Thermogravimetric Analyzer, which was operated in a nitrogen atmosphere, at a heating rate of 10K/min from 293 to 573K.

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X-Ray Diffraction

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

IR Spectrometry

The IR spectra of KBr pellets in the range $4000-400\,\mathrm{cm}^{-1}$ were recorded on an FTIR Nicolet Magna IR™ 550 spectrometer.

Electron Microscopy

For scanning electron micrographs, the samples were mounted directly on the holders and then observed at 10 and 20 kV in a Philips XL 30 electron microscope. The microanalyses were done using a DX-4 sonde.

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Sampling

Water samples were collected from two wells of Hermosillo City, Mexico, they were chosen because of their fluoride ion concentration. The depth of both wells was about 300 m, and the pH and fluoride concentrations were determined about 2 hr after sampling. The water samples were collected in plastic bottles which had been treated previously with "extran" from Merck and nitric acid at 70°C and rinsed several times with distilled water.

Sorption of Fluoride Ions

Samples of the zeolitic mineral (150 mg) were left in contact with fluoride solutions (15 mL) containing 5 mg F/L and shaken for 0.25, 0.50, 1, 8, 12, and 24 hr or with water (15 mL) from the two wells of Hermosillo, Sonora Mexico (containing 6.86 and 5.9 mg F/L) for 6 hr, then the phases were separated by centrifugation. Fluoride ion concentrations were measured in the aqueous phases, and the solid phases were characterized by x-ray diffraction, IR, and electron microscopy.

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The retention percentage was calculated as follows:

$$\text{Retention percentage}_{\text{HEUCLI}} = \frac{[\text{F}^-]_{\text{is}} - [\text{F}^-]_{\text{fs}}}{[\text{F}^-]_{\text{is}}} \times 100$$

where HEUCLI corresponds to the zeolitic mineral, i the initial fluoride concentration, f denotes the final fluoride concentration, and s refer to the solution.

The distribution coefficients after equilibration were calculated using the following equation:

$$K_{\text{d}} = \frac{[\text{F}^- \,(\text{mmol})]_{\text{HEUCLI}}}{[\text{F}^- \,(\text{mmol})]_{\text{S}}} \times \frac{\text{volume}\,(100\,\text{mL})_{\text{S}}}{\text{mass}\,(\text{g})_{\text{HEUCLI}}}$$

where HEUCLI corresponds to the zeolitic mineral and s to the solution.

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F^- Potentiometric Determinations

The concentration of fluoride ions in the solutions was determined using a selective electrode for fluoride ions (ORION) which measures concentrations from $10^{-6} M$ to saturated solutions. TISAB II (Total Ionic Strength Adjustment Buffer) with CDTA from ORION was added to the solutions to reduce the variation in the ionic strength of the samples. This buffer contains a chelate that forms complexes with other ions such as iron and aluminum that could interfere with the determinations.

A calibration curve was obtained using NaF standard solutions with different fluoride concentrations. The results were plotted as fluoride concentration (mg/L) vs. the potential (mV).

RESULTS AND DISCUSSION

Chemical Composition of the Zeolitic Mineral

The chemical composition of the zeolitic mineral from Sonora, Mexico, is shown in Table 1. As can be observed from Table 1, the content of calcium, potassium and sodium decreases in the following order: $\text{Ca} \gg \text{K} > \text{Na}$, according to this composition, the material is in the calcium form with $\text{CaO} > \text{Na}_2\text{O} + \text{K}_2\text{O}$.[17]

The $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of the zeolite is 5.4. This ratio is similar to those reported for heulandite and clinoptilolite rocks from various deposits, among them Patagonia, CA, Trancapatia/Russia, Redopes/Bulgaria, and Las Villas/Cuba which have ratios between 5 and 6.[18]

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Table 1. Chemical Composition of the Zeolitic Mineral from Sonora, Mexico

Composition	%
SiO_2	61.07
Al_2O_3	11.25
Fe_2O_3	7.52
MgO	1.53
CaO	4.48
Na_2O	0.24
K_2O	0.65
MnO_2	0.07
H_2O	16.00

Treated Mineral

Table 2 shows the content of sodium, calcium, lanthanum, and europium in the zeolitic mineral samples after treatment with the different solutions. Sodium increased in the zeolite four fold when it was treated with sodium chloride. When the zeolite was treated with calcium chloride, the content of calcium did not change at all. Clinoptilolite shows a higher preference for sodium than for calcium ions, this behavior has been reported elsewhere;[18–20] the affinity sequence of clinoptilolite for some cations has been determined elsewhere[21] as $K^+ > NH_4^+ > Na^+ > Ca^{2+}$. It was observed, in this work, that the content of calcium decreased when the material was treated with europium or lanthanum solutions, which indicates that calcium ions are exchanged by both elements. Either, two or three valent cations like $2Ln^{3+}$ exchange for $3Ca^{2+}$ cations in close neighborhood or more likely the cations exchange in the form of hydroxo-cations $(Ln(OH)_2)^+$ from aqueous solutions.

Table 2. Content of Sodium, Calcium, Lanthanum and Europium in the Zeolite Samples: HEUCLI, HEUCLI-Na, HEUCLI-Ca, HEUCLI-La, and HEUCLI-Eu

Material	Na (wt%)	Ca (wt%)	La (wt%)	Eu (wt%)
HEUCLI[a]	0.27 ± 0.02	3.20 ± 0.02	—	—
HEUCLI-Na	1.07 ± 0.07	2.20 ± 0.20	—	—
HEUCLI-Ca	0.27 ± 0.02	2.90 ± 0.30	—	—
HEUCLI-La	0.27 ± 0.02	2.00 ± 0.20	0.32 ± 0.01	
HEUCLI-Eu	0.27 ± 0.02	2.30 ± 0.20		1.49 ± 0.01

[a] HEUCLI refers to the untreated zeolitic mineral.

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X-Ray Diffraction

The composition of clinoptilolite–heulandite zeolite samples depends on their origin.[18] In this work the components of the zeolite mineral found by x-ray diffraction were: estilbite, cristobalite, clinoptilolite, mordenite, analcime, quartz, calcite, and heulandite, but the highest content corresponded to heulandite and clinoptilolite (Joint Committee of Powder Diffraction Standard (JCPDS) cards 25-0144 and 25-1349, respectively). The x-ray diffraction patterns were compared with those of other minerals such as albite, estilbite, cristobalite, moganite, mordenite, and biotite; however, they were not found in the composition of this mineral.

It is well known that thermal stabilities for heulandite and clinoptilolite are different. Heulandite is completely destroyed when it is heated at 400°C for 3 or 4 hr and clinoptilolite is stable up to 750–800°C.[18]

To determine the quantities of clinoptilolite and heulandite in the Mexican zeolitic mineral, a sample was heated at 400°C for 24 hr. Figure 1 shows the diffraction patterns of the Mexican zeolitic mineral before and after thermal treatment. The intensity of the reflection at 10° disappears after heating. This indicates that heulandite is the principal component of the zeolitic mineral from Sonora. The presence of metaheulandite was also observed after heating (JCPDS card 19-0209).

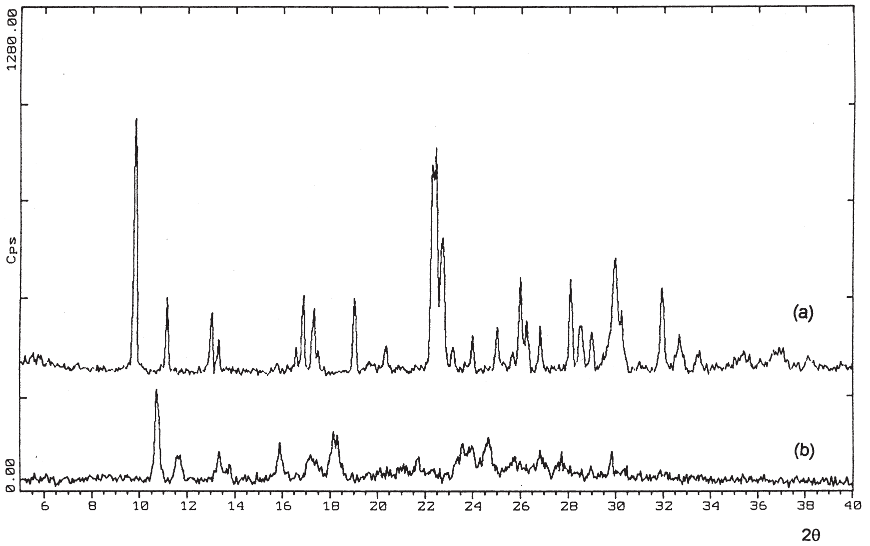

Figure 1. The x-ray diffraction patterns: (a) zeolitic mineral, (b) zeolitic mineral heated at 400°C.

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Important changes were not observed in the x-ray diffraction diagrams of the zeolitic mineral samples after they were exchanged with calcium, sodium, europium, or lanthanum or in the samples being in contact with fluoride solutions or well-water, probably due to the low concentrations of the fluoride ions retained by the zeolite samples.

Infrared Spectroscopy

Figures 2 and 3 show the IR spectra of the original and treated zeolite mineral samples with Na, Ca, La, and Eu solutions. The shifts in the framework vibrations are attributed to the interaction between cations and zeolite framework. Most of the spectra did not change after treatment. According to Rodríguez-Fuentes et al.,[22] some bands are affected by cation exchange. It has been reported that there is a 1035 cm^{-1} band for heulandite and a 1074 cm^{-1} band for clinoptilolite,[18] we found a 1053 cm^{-1} band which could be due to the presence of heulandite as it was found by x-ray diffraction. For a better evaluation of the acquired data, the ratio of the transmission 1053 cm^{-1} band assigned to

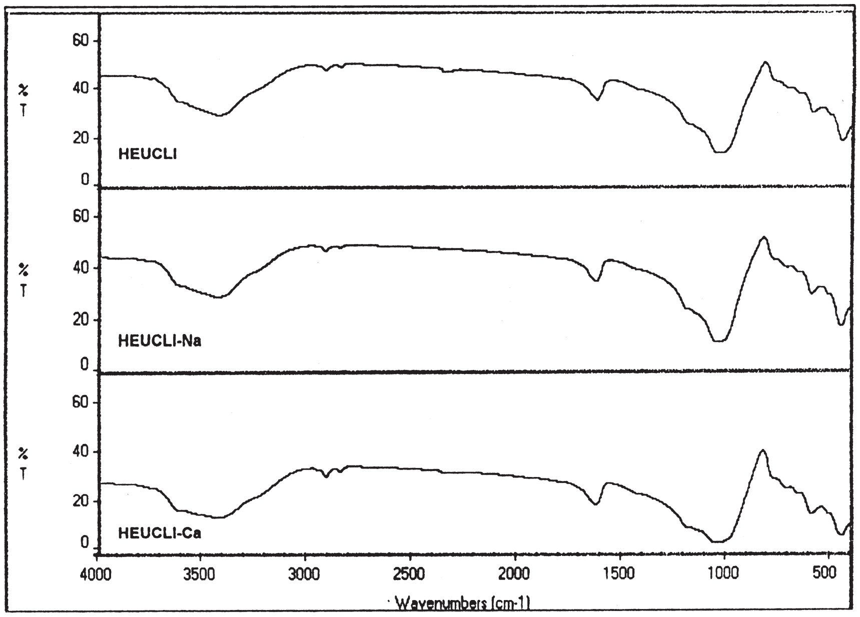

Figure 2. IR spectra: untreated zeolitic mineral (HEUCLI), sodium zeolitic mineral (HEUCLI-Na), calcium zeolitic mineral (HEUCLI-Ca).

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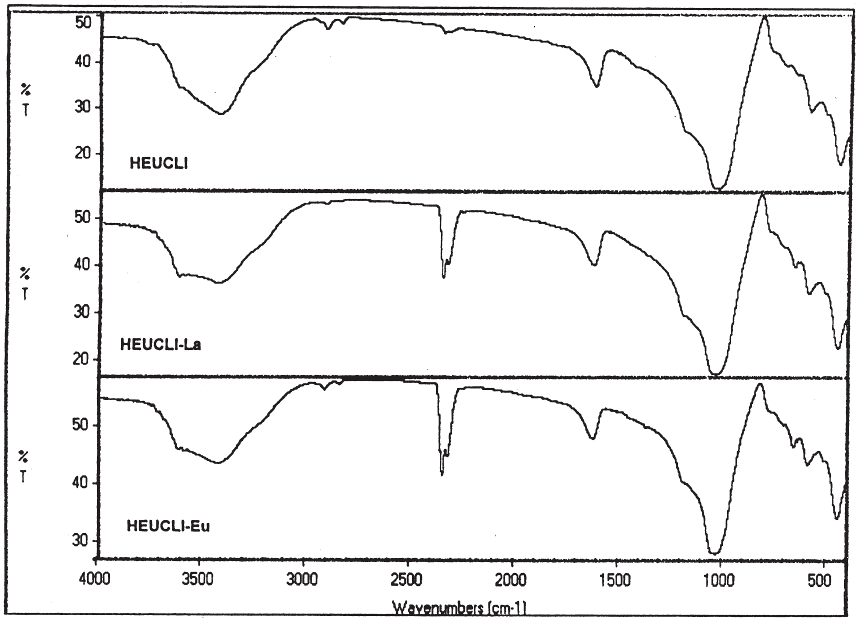

Figure 3. IR spectra: untreated zeolitic mineral (HEUCLI), lanthanum zeolitic mineral (HEUCLI-La) and europium zeolitic mineral (HEUCLI-Eu).

asymmetric stretching vibration of the external tetrahedral linkage in the zeolite framework, to the transmission of the 455 cm^{-1} band corresponding to the internal tetrahedral bending was calculated. Small differences in the values were observed for the materials treated with sodium and europium and they can be attributed to the nature of the ions in the zeolitic mineral. In some samples a band around 2300 cm^{-1} was observed which can be attributed to the presence of CO_2.

Electron Microscopy

Although, the elemental analysis of the sample is given above, electric dispersive amplitude x-ray energy (EDAX) analyses were done as well. The qualitative elemental composition of the material was the same as that found by EDAX. However, the quantitative analysis was different, this could be due to the characteristics of the EDAX analysis which is performed in a small particle. Therefore, it is not representative for the elemental composition of the whole sample. The elements found in the samples were oxygen, magnesium, aluminum,

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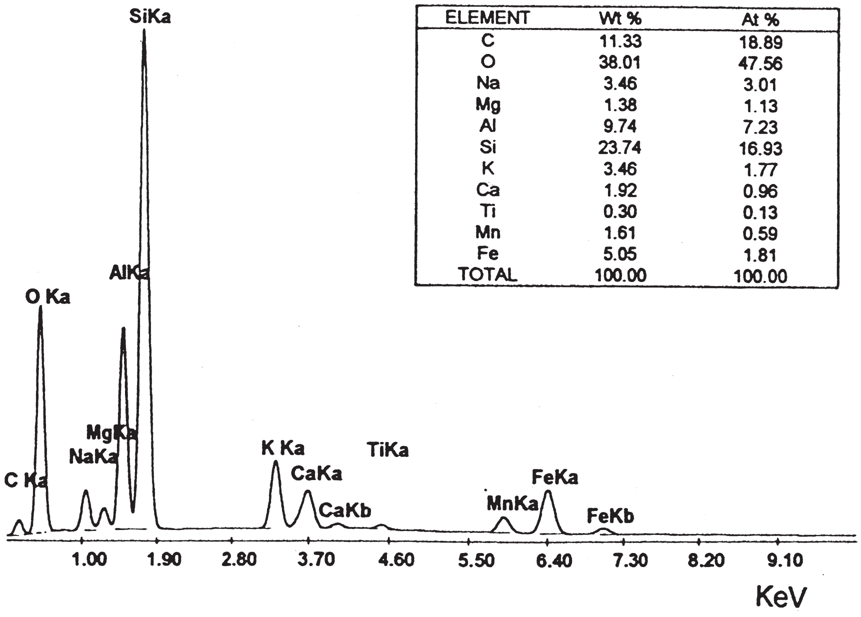
silicon, potassium, calcium, sodium, iron, barium, magnesium and carbon, this last element could be from the tape used as a sample holder.

The zeolite mineral showed black and yellow particles and their elemental composition was different as shown in Figs. 4 and 5. Sodium was not observed in the black particles and the content of magnesium, iron, barium, and potassium was higher than that found in the yellow particles.

Figure 6 shows the SEM images of the zeolitic minerals from Sonora with particles size from 200 to 400 μm. When the image was increased (Fig. 6b), it was observed that the morphology was the same as that reported by Mumpton and Ormsby.[23] The crystals show monoclinic symmetry which is characteristic of the heulandite group. Some crystals are observed in the form of coffin-shaped, slab and criss-cross plates. The morphology of the samples did not change after treatments.

Fluoride Content in the Well-Water

Table 3 shows the fluoride ions concentration and the pH of the well-water determined during sampling. Then 12 days after sampling, the fluoride ions were



ELEMENT	Wt %	At %
C	11.33	18.89
O	38.01	47.56
Na	3.46	3.01
Mg	1.38	1.13
Al	9.74	7.23
Si	23.74	16.93
K	3.46	1.77
Ca	1.92	0.96
Ti	0.30	0.13
Mn	1.61	0.59
Fe	5.05	1.81
TOTAL	100.00	100.00

Figure 4. Black zeolitic mineral grains elemental micro analysis.

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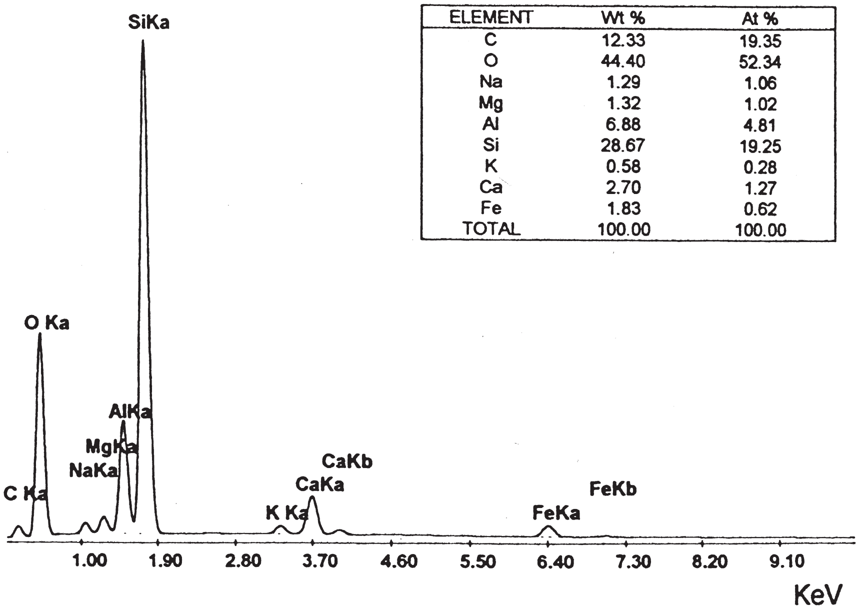

ELEMENT	Wt %	At %
C	12.33	19.35
O	44.40	52.34
Na	1.29	1.06
Mg	1.32	1.02
Al	6.88	4.81
Si	28.67	19.25
K	0.58	0.28
Ca	2.70	1.27
Fe	1.83	0.62
TOTAL	100.00	100.00

Figure 5. Yellow zeolitic mineral grains elemental micro analysis.

determined again by both colorimetric and potentiometric techniques, and the results were similar. Therefore the changes in temperature, transport, and storage of the water samples did not affect the fluoride composition of the samples.

Fluoride Ions Retention

The concentrations of fluoride ions in the aqueous solutions after being in contact with the different materials at initial pH 5, 7, and 9 are shown in Figs. 7–9. The pH of the solutions, after the adsorption process, was seven for the three cases, the final pH was independent of the initial pH of the solutions. This behavior indicates the buffering of the zeolitic mineral. Legoux et al.[24] have reported that the solid phases may consume H^+ or OH^- depending on the medium conditions.

For the retention experiments at initial pH 5 using the zeolitic mineral treated with lanthanum, it was observed after 15 min contact time that 56% of the fluoride ions from the solution were retained by the material, the rest of the samples removed about 55% of the initial fluoride concentration. After 30 min most of the materials removed about 53% and the samples exchanged with

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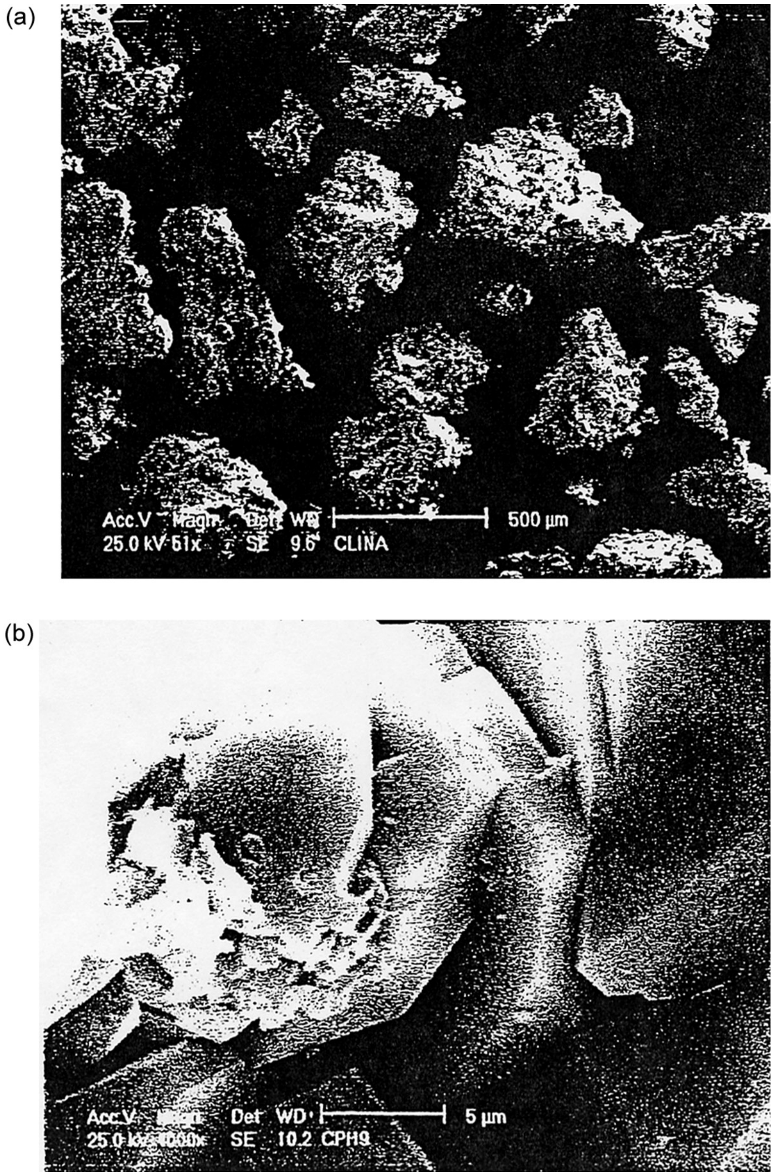

Figure 6. Zeolitic mineral SEM micrograph: (a) 50× and (b) 4000×.

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Table 3. Fluoride Concentration Determined In Situ and pH of the Wells Water Studied in the Present Work

Well Name	F (mg/L)	pH
Tronconal	6.8 ± 0.2	8.4
Well 14	5.9 ± 0.3	8.5

lanthanum and europium removed 57%, perhaps a slight improvement. The results obtained after 24 hr contact time, showed that the retention was about 62% of the initial fluoride concentrations. A somewhat higher retention was found with the samples treated with lanthanum that was about 67%. As it was stated before, the experiments were done with two sizes of particles and the same fluoride retention was found in both cases.

When the experiments were made with solutions of pH 7, it was found that after 15 min, 72% of the initial fluoride concentration was removed by the untreated material, and the rest of materials tested, removed only from 22 to 43%. After 8 hr the highest retention was found with the samples treated with sodium (78%) and europium (70%) and finally, for 24 hr of contact time, the maximum retention was 70% by the untreated zeolite and 66% by the material exchanged with sodium ions and the rest removed about 61%. Thus the treated zeolite gave

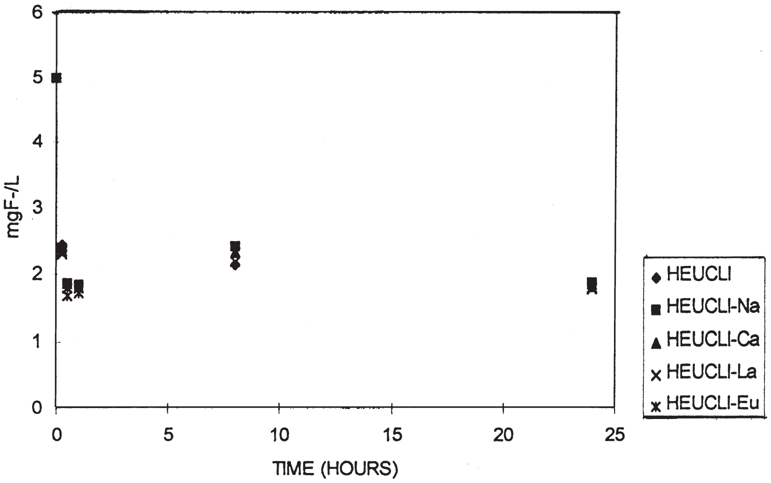

Figure 7. Concentration of F in the solution (mg/L) vs. contact time with HEUCLI, HEUCLI-Na, HEUCLI-Ca, HEUCLI-La or HEUCLI-Eu, at initial pH 5.

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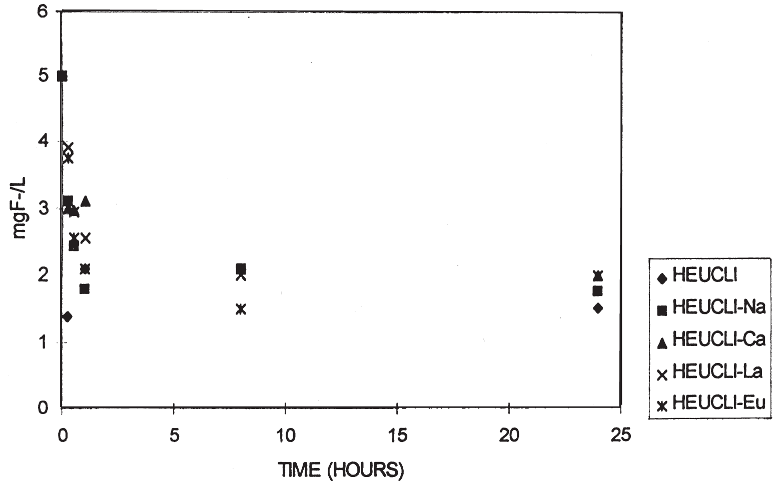

Figure 8. Concentration of F in the solution (mg/L) vs. contact time with HEUCLI, HEUCLI-Na, HEUCLI-Ca, HEUCLI-La or HEUCLI-Eu, at initial pH 7.

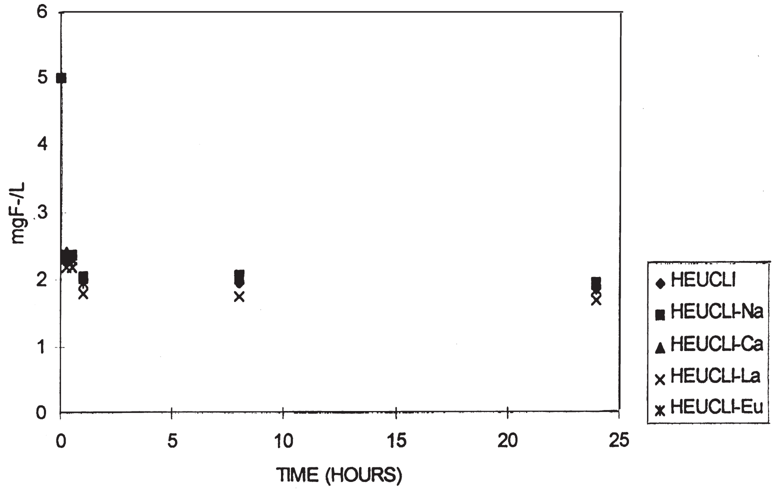

Figure 9. Concentration of F in the solution (mg/L) vs. contact time with HEUCLI, HEUCLI-Na, HEUCLI-Ca, HEUCLI-La or HEUCLI-Eu, at initial pH 9.

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higher removal initially, but the improvement was less pronounced after longer contact times.

When the initial pH of the experiments was 9, after 15 min the retention of the fluoride ions by the materials was about 54% of the initial fluoride concentration in the solution, after 30 min all the samples removed about 66% and after 8 hr the untreated material and the one treated with lanthanum removed about 57%; and the rest of the samples removed about 66% of the initial fluoride concentration. In general, the error bars determined by different sorption experiments, not indicated in the figures, were $<5\%$ of the mean values obtained.

It has been reported in the literature[12] that the lanthanide oxides show high selectivity and adsorption for fluoride ions. In this work, this behavior was not observed probably due to the chemical characteristics of the lanthanide ions in the network of the zeolite or to the low concentration or europium or lanthanum in the zeolite samples.

The water samples from both the wells showed similar results (Fig. 10), the maximum retention of fluoride ions (67%) was observed with the materials

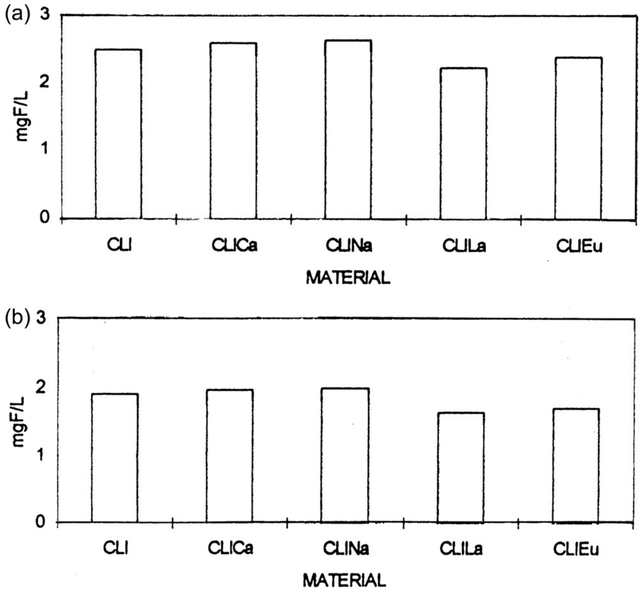

Figure 10. Concentration of F in the water (mg/L) from: (a) the well Tronconal (initial concentration: 6.9 mg F/L; initial pH: 8.43) and (b) the well 14 (initial concentration: 5.9 mg F/L; initial pH:8.51), after being in contact with the zeolitic mineral samples: HEUCLI, HEUCLI-Na, HEUCLI-Ca, HEUCLI-La or HEUCLI-Eu, for 6 hr.

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HEUCLI-La or HEUCLI-Eu and the water samples from well 14 (Fig. 10b). Concerning the water from the Tronconal well, the fluoride retention found was from 48 to 56% for all materials (Fig. 10a). It is important to note that the initial fluoride concentration is higher in the water from the Tronconal well than in the water from well 14.

The fluoride concentration after the treatment was about 2.5 mg/L for the Tronconal well and 2 mg/L for the well 14. These results are similar to those obtained with fluoride solutions at initial pH 9. The physico-chemical characterization of the water from the well in this region, where the Tronconal well and well 14 are located, have been reported.[25] This water contains mainly the following anions: HCO_3^- (99–413 mg/L), SO_4^{2-} (61–402 mg/L), Cl^- (23–205 mg/L), and NO_3^-(0.2–4.6 mg/L). According to the fluoride sorption results, the anion composition of the well-water does not seem to affect the sorption fluoride behavior process over the concentration range tested.

It is important to note that for practical purposes the natural zeolite mineral without any treatment can be used for the separation of fluoride ions from solutions with concentrations of about 5 mg/L.

Table 4 shows the distribution coefficients for the experiments done with zeolite samples (24 mesh), the K_d values are similar for the experiments done with fluoride solutions of pH 5, 7, 9, and for water from well 14. The K_d values obtained for the experiments done with water from the Tronconal well were lower than the other values calculated, and these differences could be due to the physico-chemical properties of the well-water as mentioned above. Also, it was observed that for the materials treated with lanthanum and europium (HEUCLI-La and HEUCLI-Eu) the K_d values were slightly higher than those obtained with the other materials, but this difference is not sufficient to justify the treatment step.

Table 4. Distribution Coefficients After Equilibration with the Zeolitic Mineral and Fluoride Solutions Studied

	K_d				
Material	Solution pH 5.0	Solution pH 7.0	Solution pH 9.0	Tronconal pH 8.4	Well 14 pH 8.5
HEUCLI	159 ± 1	152 ± 3	164 ± 6	91 ± 2	159 ± 8
HEUCLI-Ca	152 ± 1	156 ± 8	166 ± 1	88 ± 1	153 ± 1
HEUCLI-Na	152 ± 12	191 ± 29	169 ± 5	88 ± 1	147 ± 1
HEUCLI-Eu	178 ± 7	156 ± 9	184 ± 7	111 ± 1	183 ± 1
HEUCLI-La	206 ± 10	153 ± 5	183 ± 4	114 ± 2	173 ± 4

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The retention of fluoride ions found in this work with clinoptilolite is much higher than that found with other materials; 24 and 45% for activated carbon,[26] 40 and 50% for natural zeolites treated thermally, with sulfuric acid or aluminum salts.[27] According to the literature, the mechanisms that could take place for the retention of fluoride ions, in the materials studied in this work, are the occlusions which depends on the size of the guest anion as has been explained before; other mechanism could include the retention on the surface of the aluminosilicates where the groups Si—OH and Al—OH of the materials are responsible for the retention of fluoride ions by ion exchange as it has been reported elsewhere.[26] It was observed as well that the particle size had no significant effect on the fluoride retention by the zeolite mineral. Kesraoul-Oukl et al.[28] reported a similar effect and he suggested that an increase in the zeolite surface area would not necessarily affect the ion exchange which takes place within the zeolite cavities rather than in the surface, this suggestion is as well true for occlusion.

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CONCLUSIONS

The zeolite mineral from Sonora, Mexico contains mainly calcium in its structure and its SiO_2/Al_2O_3 ratio is 5.4.

Retention of fluoride was similar for the untreated material and for those treated with sodium, calcium, lanthanum, and europium. According to the literature, the mechanisms proposed to explain the fluoride retention by the zeolitic minerals are occlusion and adsorption.

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