Clinoptilolite modified by calcium and hydroxyl ions for removal of fluoride from aqueous solution

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Abstract. In Mexico naturally occurring fluoride contamination of groundwater is widespread. Adsorption with local and low-cost materials has been recently studied. In this research, clinoptilolite was modified with hydroxyl, calcium, and hydroxyl followed by calcium to compare their fluoride removal capacity. The sorption of natural and modified materials was investigated for the initial fluoride concentrations from 1.5 mg/L to 15 mg/L, isotherms for these adsorbents were investigated and techniques such as scanning electron microscopy (SEM) and X-ray diffraction (XRD) were used to characterize these adsorbents. It was found that removal fluoride was highest with calcium modified clinoptilolite from 60.2% with 1.5 mg F-/L to 43.0% with 15 mg F-/L. Sorption data for calcium modified clinoptilolite and hydroxyl and calcium modified clinoptilolite was found to fit Freundlich equations with equilibrium constants of 0.12 L/g and 0.021 L/g, respectively. SEM and XRD showed no significant changes of clinoptilolites after and before modification with calcium and sorption of fluoride, suggesting that interaction between adsorbent and adsorbate were only superficial. Modification of clinoptilolite with calcium enhanced its capacity for fluoride removal. This modification process was carried out using an economical and abundant mineral in central Mexico, which gives an additional advantage to the process.

1. Introduction
Fluoride is well known as an agent used to prevent dental cavities, but ingestion of this element in excessive amounts can cause dental and skeletal alterations. Mexican statutes establish that fluoride concentration in drinking water should not exceed 1.5 mg/L [1]. However, groundwater in 17 states, out of 32, of Mexico present naturally occurring fluoride concentrations above 1.5 mg/L. These states are mainly located in central, north-east and south-east regions of the country.

To remove excess fluoride from drinking water many technologies have been developed, including precipitation, coagulation, ion exchange, reverse osmosis, electrodialysis and adsorption [2]. Some of the advantages that adsorption has over other technologies are a low capital cost, and simplicity in design and operation. Numerous adsorbents have been studied for fluoride removal, among these are alumina, activated carbon and local minerals [3-4]. Recently the interest in using local and low-cost adsorbents for removal of water contaminants has grown.

Zeolites are crystalline aluminosilicates, are microporous, with a framework structure that encloses interconnected cavities occupied by metal cations (such as Na⁺ and K⁺) and water molecules. Zeolites can be naturally occurring or synthetic. Clinoptilolite is the most abundant naturally occurring zeolite, it has a structure that consists of silica and alumina tetrahedra. In Mexico, clinoptilolite main deposits
are in Laollaga in Oaxaca (15.12 millions of tons), El Cajón in Sonora (10 millions of tons), Agua Prieta in Sonora (3 millions of tons), and El Chap Ben in San Luis Potosí (2.71 millions of tons) [5].

This research studied the application of two naturally occurred and abundant materials in the country (clinoptilolite and calcium from limestone), suggesting the formation of a geochemical barrier for sorption of fluorite using low-cost materials. The long-term aim of this study is to develop adsorption processes that can be applied to drinking water treatments.

2. Materials and methods
This study was carried out in the Pilot Plant for Wastewater Treatment (PPTAR, acronym in Spanish) of the Autonomous Metropolitan University, Campus Azcapotzalco (UAM-A, acronym in Spanish). The main stages of the methodology were: modification of zeolites, determination of the sorption isotherms and characterization of the modified zeolites.

2.1 Modification zeolites
The zeolite used in this research was a clinoptilolite from the San Francisco Mine, in the San Luis Potosí State, located in north-central Mexico. The clinoptilolite was washed with deionized water and dried at room temperature before modification processes. Three types of clinoptilolite were prepared, hydroxyl modified clinoptilolite (OH-Cli), Ca\(^{2+}\) modified clinoptilolite (Ca-Cli) and hydroxyl and Ca\(^{2+}\) modified clinoptilolite (OH-Ca-Cli).

2.1.1. Hydroxyl modified clinoptilolite (OH-Cli). The zeolite was modified to promote the exchange of hydroxyl ions on the zeolite for fluoride ions in water. A solution of sodium hydroxide (NaOH) 1 M was prepared. Then, 100 mL of this solution was poured into an Erlenmeyer flask, and 10 g of clinoptilolite were added. This mixture was magnetically stirred for 6 h. Next, clinoptilolite was separated from the solution using gravitational filtration (5 µm pore size) followed by vacuum filtration (0.45 µm pore size). The hydroxyl modified zeolite was dried in an oven at 70 °C for 12 h and stored in a clean glass flask [6].

2.1.2. Ca\(^{2+}\) modified clinoptilolite (Ca-Cli). The zeolite was modified to promote removal of fluoride ions from aqueous solution with a superficial interaction between the cation Ca\(^{2+}\) and the anion F\(^-\), inducing the formation of calcium fluoride (CaF\(_2\)). Limestone from Zimapan, in the Hidalgo State in central-eastern Mexico, was used as a calcium source. First, a calcium saturated solution was prepared mixing 20 g of limestone and 110 mL of deionized water. The pH of the solution was adjusted to 5 units, with a sulfuric acid solution (H\(_2\)SO\(_4\)) 20%, to prevent the formation of carbonates and bicarbonates. This solution was magnetically stirred for 12 h. Then, 10 g of clinoptilolite were added to the calcium saturated solution, and the new mixture was magnetically stirred for 12 h. Finally, clinoptilolite was separated from the solution using gravitational filtration (5 µm pore size) followed by vacuum filtration (0.45 µm pore size). The calcium modified zeolite was dried in an oven at 70 °C for 12 h and stored in a clean glass flask.

2.1.3. Hydroxyl and Ca\(^{2+}\) modified clinoptilolite (OH-Ca-Cli). Clinoptilolite was first modified with the hydroxyl method (section 2.1.1), followed by the calcium method (section 2.1.2).

2.2 Sorption isotherms
Sorption isotherms were determined for OH-Cli, Ca-Cli, and OH-Ca-Cli. The fluoride concentrations studied were 1.5 mg/L, 5 mg/L, 5 mg/L, 10 mg/L and 15 mg/L. Experiments were carried out in duplicates and with a blank (unmodified clinoptilolite). Fluoride solutions were prepared from a stock solution of sodium fluoride (NaF) and deionized water.

For each type of clinoptilolite, 100 mL of the fluoride solutions were poured into an Erlenmeyer flask and 1 g of clinoptilolite was added. Then, the flasks were placed on a multi-position magnetic stirrer for 24 h. Clinoptilolite was removed from solution by gravitational and vacuum filtration. Finally, the
fluoride concentration was measured in the filtrate with an Orion 5 Star Thermo Scientific ion selective electrode [7]. Experimental data were fitted to the Langmuir, Freundlich and Redlich-Peterson isotherm linear equations.

2.3 Clinoptilolite characterization
Clinoptilolites that presented the highest fluoride removal were characterized with scanning electron microscopy (SEM) and X-ray diffraction (XRD). SEM analyses were carried out with a microscopy model SUPRA 55 PV and brand Carl Zeiss Mexico at 3.00 kV without graphite coating, images were obtained using secondary electrons and 10.00 kx magnification. XRD was conducted with a Philips X’PERT PRO diffractometer with CuKα radiation from 4 (θ) to 80 (θ), scanning time of 0.4 s, and results were analysed with the software X´PERT HighScore Plus® version 2.2a.

3. Results

3.1 Sorption of fluoride with unmodified and modified clinoptilolite
Fluoride removal at initial concentrations from 1.5 mg F/L to 15 mg F/L was the highest with Ca-Cli at 1.5 mg F/L (60.2%), followed by OH-Cli at 1.5 mg F/L (49.0%); Cli at 5 mg F/L (31.9%) and 10 mg F/L (29.4%); and OH-Ca-Cli at 15 mg F/L (32.3%). Adsorption with Ca-Cli diminished with increments of the initial fluoride concentration, from 60.2% at 1.5 mg F/L to 43.0% at 15 mg F/L (figure 1). This behaviour is typical of adsorption processes, for instance, fluoride adsorption with aluminium oxide (Al2O3) nanoparticles decreased from ~45% at 10 mg F/L to ~10% at 50 mg F/L [8]. Since adsorption experiments are carried out at different conditions (adsorbent doses, initial fluoride concentration, temperature, pH) is difficult to compare performance of different materials. However, clinoptilolite and modified clinoptilolite presented similar removal percentages of those reported on the literature. For instance, at an initial concentration of 10 mg F/L Al2O3 nanoparticles (0.5 g/L) achieved 45% F removal and tamarind fruit covers (0.8 g/L) ~ 70% F removal [8, 9]. However, the use of aluminium based materials in drinking water treatment has been a cause of concern due to the link between this metal and Alzheimer's disease [10], and economic viability of natural adsorbents generally depends on availability, and preparation and transport cost. Although, in this study concentration of fluoride, for initial F concentrations higher than 1.5 mg/L, after adsorption was higher than the Mexican drinking water statute (1.5 mg/L), it is necessary to investigate the effect of adsorbent dose and pH on the removal capacity of this material. Factors such as widespread availability, cost and simplicity of the modification process could make adsorption with clinoptilolite a viable option.

3.2 Sorption isotherms
3.2.1 Unmodified clinoptilolite (Cli). Figure 2 presents the equilibrium concentration of fluoride in the solid (q) and aqueous (Ce) phases. Sorption data were fitted to isotherms, founding correlations factors of 0.852 for Langmuir, 0.342 for Freundlich and 0.888 for Redlich-Peterson. Sorption data differ from

![Figure 1. Fluoride removal for clinoptilolite (Cli), hydroxyl modified clinoptilolite (OH-Cli), calcium modified clinoptilolite (Ca-Cli) and hydroxyl and calcium modified clinoptilolite (OH-Ca-Cli) vs Initial fluoride concentration (mg/L) graph.](image)
those reported in the literature elsewhere, isotherms for clinoptilolite normally are linear, C or S-shaped [11].

Removal mechanisms for fluoride removal for clinoptilolite are not well understood. However it has been proposed that the structural defects of clinoptilolite with Al-OH sites may provide room for anion exchange [12].

3.2.2 Hydroxyl modified clinoptilolite (OH-Cl). Isotherm obtained for this material presents a convex form (figure 3), this shape relates to strong interaction among adsorbate molecules and weak interaction between adsorbate molecules and the adsorbent surface [13]. Then, it can be assumed that there was a strong interaction among hydroxyl and fluoride ions, caused by their similar ionic radius, resulting in competition for the sorption sites, mainly located on the structural defects of clinoptilolite.

Correlation factor for Langmuir isotherm was 0.1588, for Freundlich was 0.8022 and for Redlich-Peterson was 0.3168.

3.2.3 Calcium modified clinoptilolite (Ca-Cl). Sorption data were found to fit Freundlich isotherm (correlation factor 0.998), with an equilibrium constant (K_f) of 0.12 (L/g) and heterogeneous factor (1/n) of 0.73. Correlation factor for Langmuir isotherm was 0.8462 and for Redlich-Peterson was 0.8279. Ramirez et al. [14] found that fluoride sorption with limestone fit Freundlich isotherm. Also, Labastida et al. [15] observed that for fluoride concentrations above 10 mg/L removal can occur by formation of CaF_2, demonstrating limestone capacity to remove fluoride ions. The following reactions are proposed for fluoride removal [16]:

\[
\text{clinoptilolite} - MeOH_2^+ + OH^- \leftrightarrow \text{clinoptilolite} - MeOH + H_2O \quad (1)
\]

\[
\text{clinoptilolite} - MeOH_2^+ + F^- \leftrightarrow \text{clinoptilolite} - MeF + H_2O \quad (2)
\]

\[
\text{clinoptilolite} - MeOH + F^- \leftrightarrow \text{clinoptilolite} - MeF + OH^- \quad (3)
\]
3.2.4 Hydroxyl and calcium modified clinoptilolite (OH-Ca-Cli). Sorption data were found to fit Freundlich isotherm (correlation factor 0.9915), with an equilibrium constant ($K_F$) of 0.021 (L/g) and heterogeneous factor ($1/n$) of 1.31. Since the equilibrium constant is smaller than the obtained for Ca-Cli and the heterogeneous factor is higher, it can be assumed that OH-Ca-Cli had a negative effect on both capacity and intensity of sorption. Correlation factor for Langmuir isotherm was 0.750 and for Redlich-Peterson was 0.877.

3.3 Clinoptilolite characterization

3.3.1 Scanning electron microscopy (SEM). Figure 5 show SEM of Cli, Ca-Cli and Ca-Cli after fluoride sorption. Clinoptilolite presents crystals of different geometries with an approximate size of 1 µm; clinoptilolite does not present apparent changes in morphology before and after fluoride removal.

3.3.2 X-Ray diffraction (XDR). The structure of clinoptilolite reported in the literature is (Na,K Ca$_{0.5}$ Sr$_{0.5}$ Ba$_{0.5}$, Mg$_{0.5}$)$_6$[Al$_{6}$Si$_{30}$O$_{72}$]·20H$_2$O [17]. The XDR clinoptilolite pattern presented in figure 7 is consistent with those reported elsewhere from San Francisco mine clinoptilolite, the material used in this study (2$\theta$ = 10 [020], 11.4 [200], 13 [-201], 17 [-311], 17.6 [111], 19.3 [-131], 22.5 [330], 31 [151] [18]).

XDR of Ca-Cli does not present any shift at 20 from the Cli pattern (figure 7), indicating that the chemical structure of Cli was not altered due to the modification with calcium. However the shift in intensity suggests superficial changes.
XRD of Cli and Ca-Cli does not present any shift at 2θ after sorption of fluoride ions (figure 8), suggesting that interaction of these materials with fluoride ions occurred only superficially.

4. Conclusions
This study demonstrated that zeolite could be successfully used to remove anions from aqueous solutions. Modification of clinoptilolite with calcium enhanced its capacity for fluoride removal. XDR results suggest that interactions between adsorbent and adsorbate are only superficial. The modification method was carried out using an economical and abundant mineral in central Mexico (limestone), giving an additional advantage to the process.

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