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Sorption of Fluoride Ions from Aqueous Solutions and Well Drinking Water by Thermally Treated Hydrotalcite

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ABSTRACT

Fluoride is a naturally occurring element in many water supplies, and it may cause fluorosis. The hydrotalcite was synthesized and characterized before and after the retention of fluoride ions by x-ray diffraction, electron microscopy, and IR. The thermally treated hydrotalcite was evaluated for the sorption of fluoride ions from aqueous solutions at pH 5, 7, and 9 and well water. It was found that the retention of fluoride ions by the material was 80% or higher. The Kd values show that the best conditions for the sorption of F^- ions from the solutions is at pH 5, and they show as well that the physicochemical properties affect the uptake process.

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Key Words: Hydrotalcite; Retention; Fluoride ions.

1. INTRODUCTION

Fluorine is a naturally occurring element in many water supplies around the world.[1] Fluoride ions are found in ground waters as a result of dissolution from geologic formations. Surface waters generally contain much smaller concentrations of fluoride.[2]

An excess amount of fluoride ions in drinking water has been known to cause adverse effects on human health.[3] The conventional method used for the removal of fluoride ion is by precipitation using calcium compounds. However, due to the relatively high solubility product, it does not remove fluoride ions to a level required by The World Health Organization (1.5 mg F/L).[4]

Solid adsorbents and modified ion exchange resins have also been studied for fluoride removal.[5,6] However, the efficiency of fluoride ion adsorption depends on the chemical composition of water and pH. A useful material should have properties such as high capacity and selectivity and be effective at the pH of the drinking water.

Hydrotalcite-like compounds have been synthesized and characterized, thermal decomposition and reconstitution reaction mechanism have been studied in detail. These compounds have positively charged brucite-like octahedral hydroxide layers, which are neutralized by interlayer anions and water molecules, and are generally formulated as $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]A^{n-}_{x/n}mH_2O$. Magnesium hydrotalcite has been synthesized elsewhere[7]; it is stable up to 400°C, and it decomposes into an NaCl-type magnesium aluminum oxide above 400°C and into MgO and $MgAl_2O_4$ above 800°C.[8] It is noteworthy that the NaCl-type magnesium aluminum oxide is able to rehydrate and to combine with the anions to resume the original hydrotalcite structure. Thus, both hydrotalcite and NaCl-type magnesium aluminum oxide could be used to take up anions from aqueous solutions.[9]

In this work we describe the properties of a thermally treated hydrotalcite for removal of fluoride ions from aqueous solutions at different pH values. The results of fluoride ions removal from well drinking water samples are also reported.

2. EXPERIMENTAL METHODS

2.1. Materials

A. Synthesis

Hydrotalcite was prepared as it has been reported previously by Sato et al.[7]: 1 L of a mixed aqueous solution of $MgCl_2$ and $AlCl_3$ was added continuously to 1 L of NaOH and Na_2CO_3 $[Na^+/(2Mg^{2+} + 3Al^{3+}) = 1.1$; $(CO_3^{2-}/Al^{3+}) = 2$ at 333 K] aqueous solution. The mixture was stirred during reaction. The precipitate was washed at 291 K until chloride ions were not detected in the aqueous phases with silver nitrate solution and dried at 353 K for 48 hours. Finally, the HT samples prepared and dried as previously described were calcined at 773 K for 5 hours.

B. Chemical HT Composition

Na, Mg, and Al were determined by atomic absorption spectroscopy; CO_3^{2-} was determined by titration. These analyses were performed in the analytical chemical laboratory of the ININ.

2.2. Characterization Techniques

The hydrotalcite was characterized before and after the sorption of fluoride ions by x-ray diffraction, IR, thermogravimetric analysis, and electron microscopy.

A. IR Spectrometry

IR spectra of KBr pellets in the range 4000–400 cm^{-1} were recorded on a FTIR Nicolet Magna IR™ 550 spectrometer.

B. X-Ray Diffraction

Powder diffractograms of the 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.

C. 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 with a DX-4 sonde.

2.3. Sampling

Samples were collected from two wells of Hermosillo City, Mexico. They were chosen by taking into consideration the fluoride ions concentrations. The pH and fluoride concentrations were determined about 2 hours after sampling and the temperature was taken during sampling. The water samples were collected in plastic bottles which were treated previously with "extran" and nitric acid at 70°C and rinsed several times with distilled water.

2.4. F^- 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 of the ionic strength in the samples. This buffer contains a chelate that forms complexes with other ions such as iron and aluminum that could interfere in the determinations.

A calibration curve was obtained using NaF standard solutions with different F^- concentrations from 0.1 to 10 mg/L. The results were plotted as fluoride concentration (mg/L) versus potential (mV).

Fluoride was determined as well by the "Departamento de Análisis Químicos" from the Instituto Nacional de Investigaciones Nucleares. It was done by a pyro-chemical method, and then the determination of fluoride was done using an SPADNS reactive from HACH for the colorimetric determination.

2.5. Sorption of Fluoride Ions

Calcined hydrotalcite samples of 150 mg were left in contact with 15 mL of fluoride solutions containing 5 mg F/L and shaken for 0.25, 0.50, 1, 8, 12, and 24 hours or with 15 mL of water from two wells of Hermosillo, Sonora Mexico (containing 6.86 and 5.9 mg F/L) for 6 hours; then the phases were separated by centrifugation. For the case of fluoride ion solutions, the experiments were done at initial pH values 5, 7, and 9, and for natural well water the pH was not adjusted, two equilibration experiments were done for each chosen condition.

Fluoride ions were measured in the aqueous phases, and the solid phases were characterized by x-ray diffraction, IR, and electron microscopy.

The distribution coefficients after equilibration were calculated as reported elsewhere,[10,11] using the following equation:

$$\mathrm{Kd} = \frac{[\mathrm{F}^- \ \mathrm{mmol}]_{\mathrm{HT}}}{[\mathrm{F}^- \ \mathrm{mmol}]_{\mathrm{S}}} \cdot \frac{\mathrm{volume}(100\,\mathrm{mL})_{\mathrm{S}}}{\mathrm{mass(g)}_{\mathrm{HT}}}$$

where HT corresponds to the hydrotalcite and s to the solution.

3. RESULTS AND DISCUSSION

3.1. Chemical HT Composition

Table 1 shows the chemical composition of the hydrotalcite prepared in the laboratory, and it corresponds to the composition of a magnesium hydrotalcite.

3.2. Characterization Techniques

A. X-Ray Diffraction

The x-ray diffractogram of the prepared hydrotalcite is shown in Fig. 1a. This diffractogram is very similar to that reported for a hydrotalcite (Joint Committee of Power Diffraction Standards (JCPDS) 22-0700 card). It is

Table 1. Chemical composition of the hydrotalcite.

Element	Weight %
Mg	15.1 ± 0.07
Al	14.2 ± 0.2
CO_3^{2-}	9.9 ± 0.3

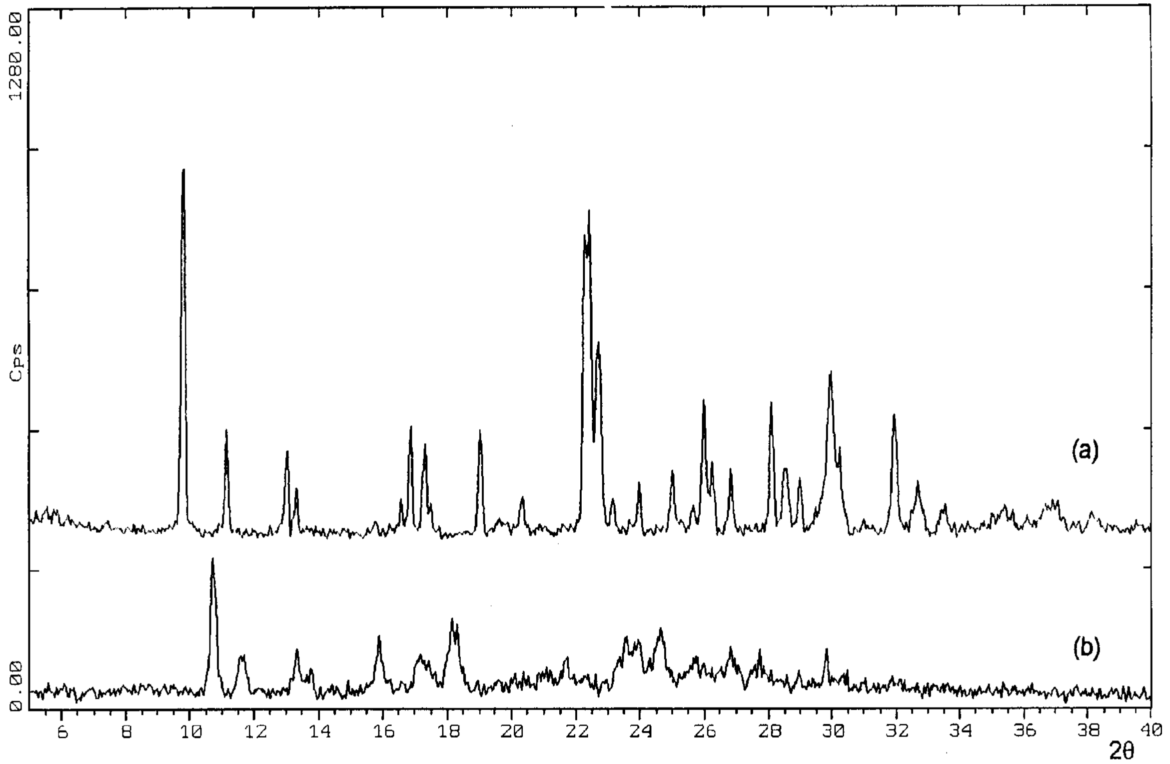

Figure 1. X-ray diffraction patterns of the (a) hydrotalcite, (b) thermally treated hydrotalcite, (c) thermal treated hydrotalcite in contact with water from well Tronconal, (d) thermally treated hydrotalcite in contact with water from well 14.

observed as well that some reflections of the 2θ angles between 17 and 22° do not correspond to a hydrotalcite. Those reflections could be due to the bayerite (JCPDS 15-0136 card), which indicates that the hydrotalcite had some impurities of this material.

Fig. 1b shows the diffractogram of the calcined hydrotalcite at 500°C, which was used for the retention of fluoride ions. In this figure, the original structure disappears completely, and there is only a mixture of aluminum and magnesium oxides, whose crystallinity is of NaCl type. If the calcination temperature is higher than 500°C a different mixture of magnesium and aluminum oxides is formed, and the structure of the hydrotalcite with an aqueous solution is not regenerated as reported elsewhere.[7,12]

When the hydrotalcite was put in contact with the fluoride solutions, the original hydrotalcite structure was regenerated, independent of the pH of the solutions. The intensities of the reflections found between the angles (2θ) 18 and 21° decreased. Similar results were obtained with the water from the wells Tronconal and 14 (Fig. 1c and 1d). The regeneration of the HT is due to the capacity of calcined hydrotalcite to incorporate anions in its structure by the memory effect.[7]

B. IR Spectroscopy

Fig. 2 shows the IR spectra of the (a) hydrotalcite and (b) calcined hydrotalcite at 500°C for 5 hours. Cavani et al.[13] have indicated a band between 3500 and 3600 cm^{-1} for brucite which corresponds to the stretching vibration of the OH^- groups, and for the synthesized hydrotalcite it was found at 3447 cm^{-1}, Fig. 2a. This vibration mode corresponds as well to the band localized at 1630 cm^{-1} which is due to the water molecules. The free carbonate ions show three vibration frequencies between 670 and 690, 850 and 880, 1350 and 1380 cm^{-1}, and the carbonate ions located in the hydrotalcite structure show a shoulder or double band at 1400 cm^{-1}. In the hydrotalcite obtained in the laboratory (Fig. 2a), the free carbonate ions show a band at 1370 cm^{-1} and it disappears in the calcined sample, as well as the shoulder at 1400 cm^{-1} and the bands at 676, 796, 875, 1415 cm^{-1}, which correspond to the carbonate ions of the hydrotalcite structure (Fig. 2b). The vibrations between 600 and 400 cm^{-1} could be due to the bending vibrations of Mg–O and Al–O in the hydrotalcite (Fig. 2a), which were modified when the material was calcined (Fig. 2b).

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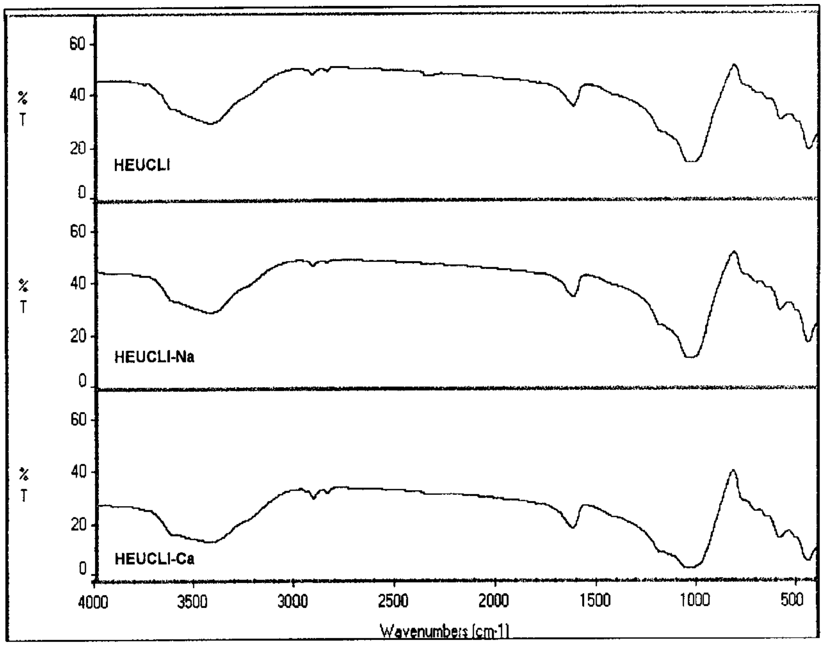


Figure 2. IR spectra of the (a) hydrotalcite and (b) thermally treated hydrotalcite at 500°C for 5 hours.

C. Electron Microscopy

The elemental composition found by EDAX for the clay is similar to that found by chemical analysis. However the quantitative analysis was different; this could be due to the characteristics of the EDAX analysis which is performed in small grains and therefore it is not representative of the elemental composition of the whole sample. The elements found in the samples were aluminum, magnesium, oxygen, and carbon (Fig. 3).

3.3. Fluoride Content in the Well Water

The pH values and the fluoride ions concentrations determined during sampling were pH 8.43 with 6.9 ± 0.1 mg F/L and pH 8.51 with 5.9 ± 0.2. mg F/L for the wells Tronconal and 14, respectively. Twelve days after sampling the fluoride ions were determined again by both

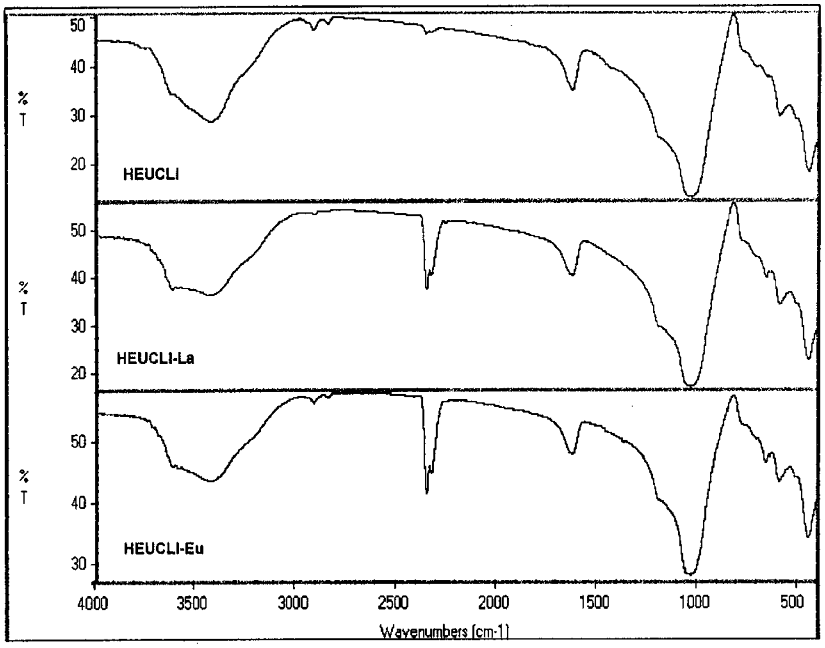


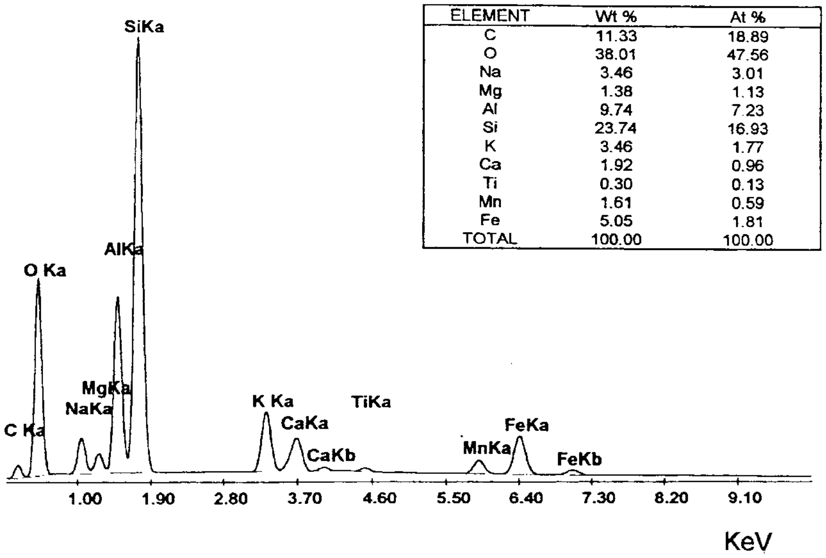
Figure 3. Hydrotalcite elemental microanalysis.

colorimetric and potentiometric techniques, and the results were similar to those determined during sampling. Therefore the changes of temperature, transport, and storage did not affect the fluoride composition of the samples.

3.4. Fluoride Ions Retention

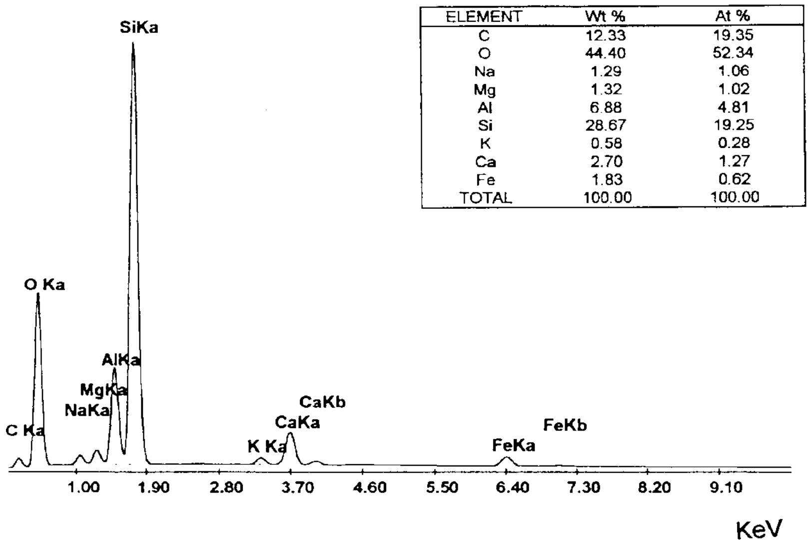
The final concentrations of fluoride ions in the solutions (initial pH 5, 7, and 9) after the contact with the thermally treated hydrotalcite are shown in Fig. 4. These fluoride concentrations were determined using a calibration curve obtained with fluoride concentrations from 0.1 to 10 mg of fluoride per liter versus potential (mV) with a correlation factor of 0.9999. Therefore, it was possible to measure the fluoride levels in the working range. (Figs. 5–10).

The final pH of the solutions after the sorption process was about 10 for the three cases, and it was independent of the initial pH of the solutions. According to Hermosin et al.,[14] this behavior may be due to protons



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. mg/L of F in the solution versus contact time with the thermally treated HT, at initial pH 5, pH 7, and pH 9.



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.

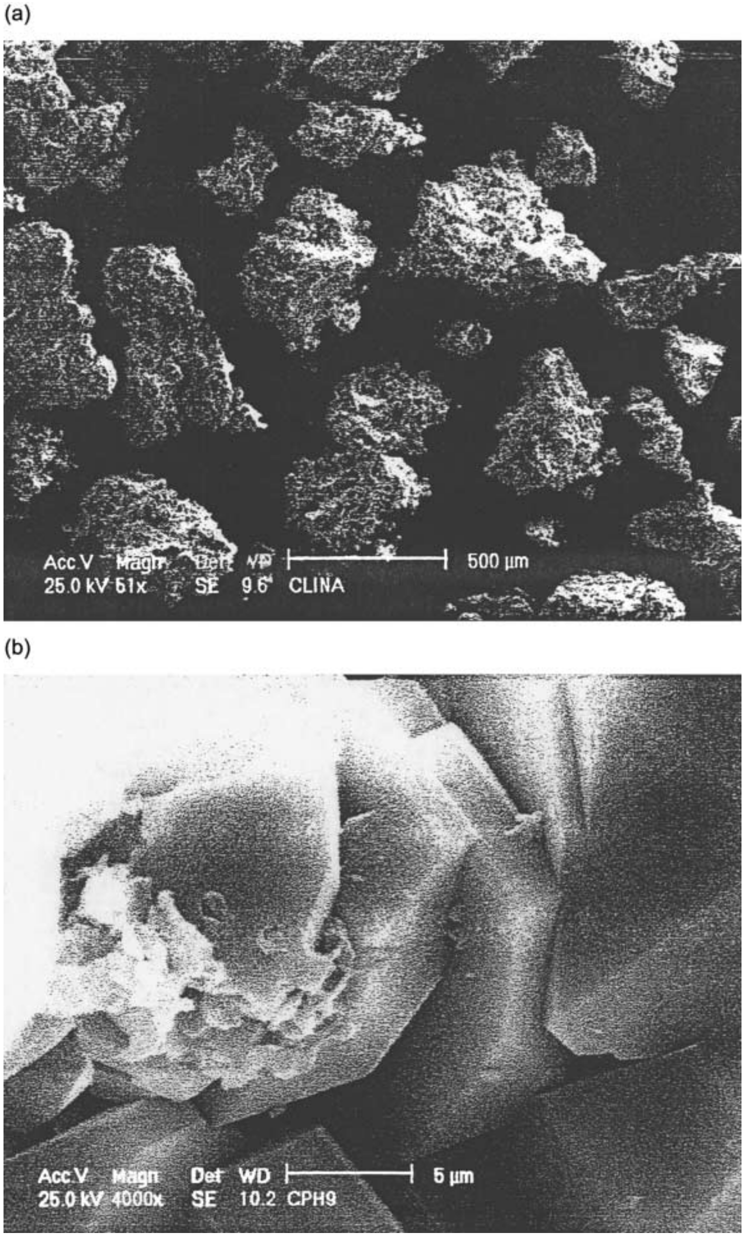

(a)
Acc.V Magn Det WD
25.0 kV 51x SE 9.6 CLINA
500 µm
(b)
Acc.V Magn Det WD
25.0 kV 4000x SE 10.2 CPH9
5 µm

Figure 6.

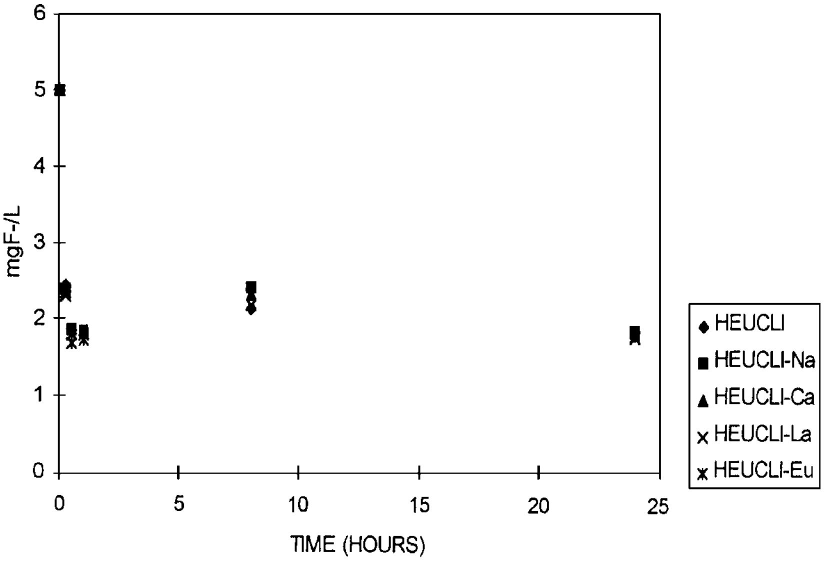


Figure 7.

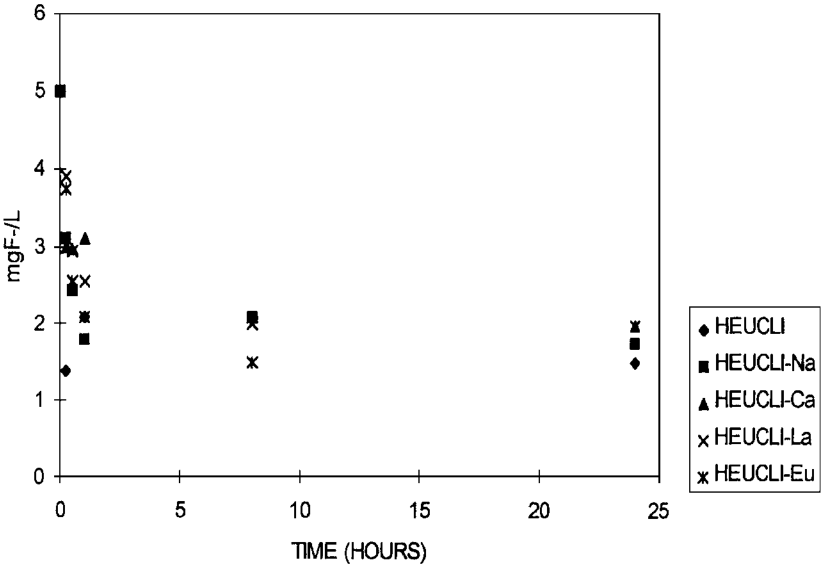


Figure 8.

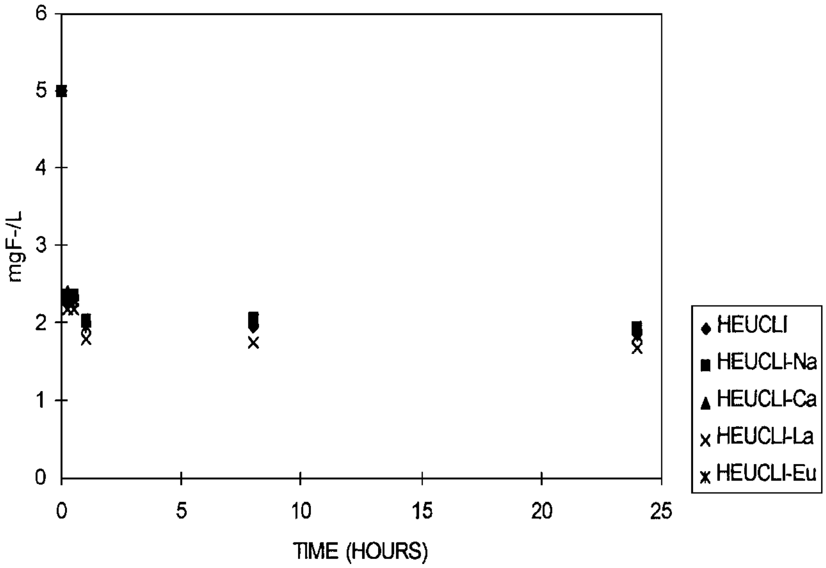


Figure 9.

consumption and the formation of OH^- for the reconstruction of the laminar structure of the hydrotalcite.

For the retention experiments at initial pH 5, it was observed after 15 minutes contact time that 80% of the fluoride ions from the solution were retained by the material. From 1 hour to 24 hours contact time, the retention was 97% of the initial fluoride concentrations.

When the experiments were done with solutions of pH 7, it was found that from 15 minutes to 24 hours the retention was about 90%.

When the initial pH of the experiments was 9, after 15 minutes contact time, the retention of fluoride ions was about 80% of the initial fluoride concentration in the solution, after 30 minutes and 1 hour it was 90%, after 8 hours it was 97%, and finally after 24 hours contact time the retention was 92%.

The concentration of fluoride ions in the water from the two wells, Tronconal and 14, from Hermosillo, Sonora, were 6.9 and 5.9 mg F/L and their pH values were 8.4 and 8.5, respectively. The retention and pH values found after being in contact with the well water and the clay for 6 hours were 80% and around 10, respectively, for both cases. These results were lower than the retention found for fluoride solution samples at similar pH. This means that

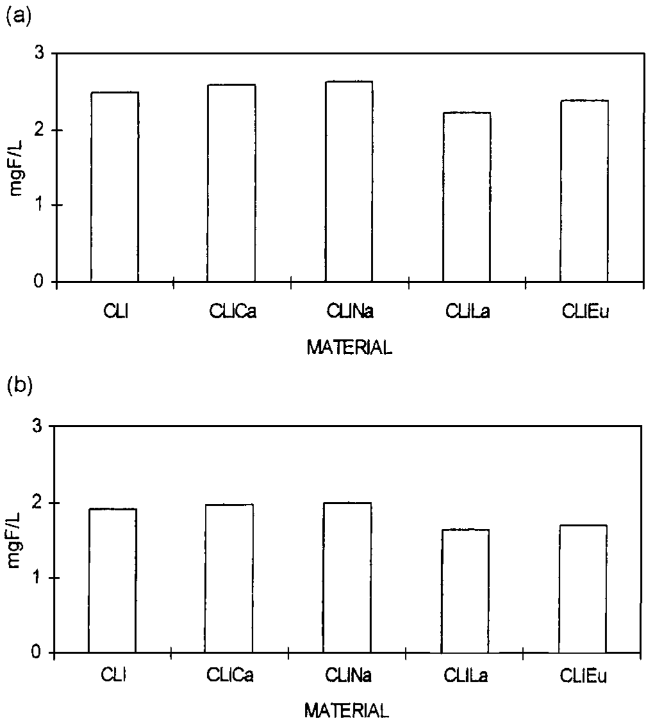


Figure 10.

other anions from the well water could affect the F^- sorption by the thermally treated hydrotalcite.

The retention of fluoride ions by the thermally treated hydrotalcite found in this work is similar to those found with activated alumina (95%)[15] and ionic exchange resins (95 and 98%). The advantage of thermally treated hydrotalcite is that after 1 hour contact time at initial pH 5 and 7 the retention was 90% or higher. After 8 hours contact time the retention was about 90% or higher for the solutions with different initial pH values. The time required with activated alumina is about 12 hours, and the pH of the solutions should be between 5 and 5.5[4] and for the ion exchange resins the contact time required is 16 hours and the pH values between 3.2 and 5.7.[6] The pH required for the treatment of water with these materials is too low to be used in potable water.

According to Hermosin et al.[14] the calcined hydrotalcite can retain anions from aqueous solutions to regenerate its laminar structure, and the reaction suggested for fluoride is the following:

$$Mg_3AlO_4(OH) + 4H_2O + F^- \rightarrow [Mg_3Al(OH)_8]F^- + OH^-$$

According to this reaction and with the amounts (150 mg of thermally treated hydrotalcite and 15 ml of fluoride solution) used in this work for the fluoride retention processes, the maximum miliequivalents of F^- that could have been retained by the material were 0.825 meq F^-/150 mg. In this work, the initial fluoride concentration in solution was 5 mg/L and for this concentration, 0.0035 meq F^-/150 mg of hydrotalcite were retained. It was observed as well, that the pH was 10 at the end of the process, which corresponds to 0.00015 meq OH^-/15 mL of solution. If the uptake process was by an ideal ion exchange, then both the miliequivalents of OH^- and F^- would be equal. The results obtained in this work can be explained as follows:

(a) The difference between the miliequivalents of OH^- and the F^- found at the end of the uptake process could be due to the neutralization of OH^- ions by the H^+ produced when the carbonate formation takes place in solution at basic pH, as shown below[16]:

$$CO_2(\text{atmosphere}) + H_2O \leftrightarrow HCO_3^- + H^+$$

$$HCO_3^- \leftrightarrow CO_3^{2-} + H^+$$

(b) Other F^- uptake mechanisms could be involved in the process.

Table 2 shows the distribution coefficients after equilibration. The highest Kd value found was at pH 5 and it decreased at pH 7 and 9, this effect could be due to the presence of hydroxo and carbonate ions in the solutions. The lowest Kd value was found for well water, probably due to the competition of F^- ions with other anions such as 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) from the well water of Hermosillo, Sonora Mexico[17] when the thermally treated hydrotalcite was regenerated.

Table 2. Effect of pH and physicochemical water characteristics on Kd measurements for F^- on thermally treated hydrotalcite.

	Kd				
Material	Solution pH 5.0	Solution pH 7.0	Solution pH 9.0	Tronconal pH 8.4	Well 14 pH 8.5
HT	3501 ± 713	1047 ± 61	1155 ± 69	437 ± 6	414 ± 19

The selectivity of each anion plays an important role in the fluoride sorption process.[18]

4. CONCLUSIONS

The hydrotalcite is efficient for the removal of fluoride ions (80–97%) from aqueous solutions in relatively short time (1 hour).

The characteristics of the well water from Hermosillo City affected the fluoride retention by the thermally treated hydrotalcite; however, this material shows good qualities for the removal of F^- ions from the water with concentrations about 5 mg F/L. According to the literature, the mechanism proposed to explain the fluoride retention by the calcined hydrotalcite is the regeneration of its laminar structure. It would be interesting to study the influence of each physicochemical property of natural waters on the retention of fluoride ions by hydrotalcite.

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