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Fluoride Sorption from Aqueous Solutions and Drinking Water by Magnesium, Cobalt, and Nickel Hydrotalcite-Like Compounds in Batch and Column Systems

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Magnesium, nickel, and cobalt hydrotalcite-like compounds (MgAlHT, NiAlHT, and CoAlHT) were used to remove fluoride ions from aqueous solutions and drinking water in batch and column systems. Mg, Ni, and Co hydrotalcite like compounds with similar $M^{2+}:Al^{3+}$ ratios were synthesized. F^- ions were determined in the remaining solutions using a fluoride ion selective electrode. Kinetic of the fluoride sorption from aqueous solutions by hydrotalcite-like compounds (HT) was best described by the pseudo-second-order model and the equilibrium was reached in less than 200 minutes for all cases (MgAlHT, NiAlHT and CoAlHT); however, this behavior was not observed for fluoride sorption from drinking water by NiAlHT. The sorption isotherms of the fluoride ion by hydrotalcite like compounds could be best fitted to the Langmuir and Freundlich models. NiAlHT showed the highest efficiency for the removal of fluoride ions from aqueous solutions in batch system. The removal of fluoride ions by NiAlHT from aqueous solutions was more efficient than from drinking water in both batch and column systems.

Keywords cobalt; fluoride; hydrotalcite-like compounds; magnesium; nickel; sorption

INTRODUCTION

Fluoride ions are present in natural waters (1) as a contaminant in ground/surface water and it could be from either natural geological sources or industries (2,3).

Fluoride-related health hazards are a major environmental problem in many regions of the world (4). Fluoride is an essential constituent for both humans and animals depending on the total amount ingested or its concentration in drinking water and it is frequently encountered in minerals and other geochemical deposits. Because of erosion and weathering, F can be leached out from these F-bearing phases to contaminate ground and surface

water. Several widely used industrial fluoride compounds, particularly aluminum smelters, are among the common contributors to anthropogenic fluoride pollution (3,5). According to the World Health Organization guidelines (6), the permissible limit of fluoride is 1.5 mg/L, and excessive intake of fluoride causes dental or skeletal fluorosis, which is a chronic disease manifested by mottling of teeth in mild cases, softening of bones, and neurological damage in severe cases (7). Fluorosis typically develops when the F^- concentration of drinking water is greater than 5 to 10 mg/L (1,3). Fluoride, among various other contaminants, has made high-quality drinking water a limited resource, therefore there is a necessity to remove excess fluoride from water (8).

Several methods, such as adsorption, ion exchange, electrolysis, and precipitation, have been adopted for defluoridation (4). Several materials, such as activated alumina, activated carbon, bone charcoal, calcined hydrotalcite like compound and tricalcium phosphate, have been tried for the removal of fluoride.

Layered double hydroxides are anionic clays in which divalent cations within brucite-like layers are replaced by trivalent cations. The resulting positive charge is compensated by hydrated anions located in the interlayer space between two brucite sheets. The general formula for these materials is $[M_{1-x}^{II} M_x^{III} (OH)_2]^{x+} (A_{x/n})^{n-} mH_2O$, where M^{II} is a divalent cation, such as Mg^{2+} , Mn^{2+} , Fe^{2+} , Co^{2+} , Cu^{2+} , Ni^{2+} , Zn^{2+} , or Ca^{2+} ; M^{III} is a trivalent cation, such as Al^{3+} , Cr^{3+} , Mn^{3+} , Fe^{3+} , Co^{3+} , or La^{3+} , and A^{n-} is the anion. Hydrotalcites and hydrotalcite-like compounds belong to this class of materials (9).

The calcined hydrotalcite-like compounds have been demonstrated to reconstruct their original layer structure after adsorption of various anions. These calcined materials have been studied as adsorbents to remove fluoride from aqueous solutions in different experimental conditions (10–12).

Jiménez-Núñez et al. (12) prepared MgAlHT, NiAlHT, and CoAlHT, and these hydrotalcites were calcined and treated with fluoride solutions in a batch system. The

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authors found that the fluoride removal from aqueous solutions by calcined hydrotalcite-like compounds depended on the adsorption properties of the thermal decomposition products and on the regeneration reaction mechanism of the hydrotalcite-like compounds. Because there is an associated energy to calcinate the hydrotalcite-like compounds, it was interesting to evaluate the fluoride sorption behavior in these materials without any thermal treatment. Therefore the purpose of this paper was first to evaluate the fluoride ions removal from aqueous solutions using magnesium, nickel, and cobalt hydrotalcite-like compounds and second to evaluate the removal of fluoride ions from drinking water in batch and column systems using the best adsorbent found in the experimentation. In this work the adsorption kinetics, the isotherms to determine the maximum fluoride capacity of each material, the saturation of columns, and the fluoride sorption mechanisms were also considered.

EXPERIMENTAL METHODS

Materials and Solutions

Magnesium, nickel, and cobalt hydrotalcite-like compounds with aluminum as the trivalent metal were prepared according with the technique reported elsewhere (12). The hydrotalcite-like compounds were milled and sieved, and the diameter of the grains between 0.30 and 0.71 μm was selected for the experiments.

A solution of 5 mg F^-/L and pH 6.5 as well as drinking water containing naturally 6.85 mg F^-/L and pH 6.9 for kinetics and column experiments were used. Solutions from 2 to 50 mg F^-/L were prepared to determine the isotherm. All solutions were prepared using deionized water and the pH of the solutions was 6.5 similar to that found in drinking water.

Elemental Composition

The microanalysis of the hydrotalcite-like compounds was done by EDS (Energy X-ray Dispersive Spectroscopy) using a XL 30 Philips electron microscope with a DX-4 system.

Fluoride Ions Measurements

The concentration of fluoride ions in the solutions was determined using a selective electrode for fluoride ions (Orion 96-09 fluoride combination electrode). TISAB II (Total Ionic Strength Adjustment Buffer) was added to all fluoride standards and samples to control the ionic strength. The calibration curve was obtained using NaF standard solutions (ORION) with a fluoride concentration range from 1 to 5 mg/L.

Kinetics

Batch system was considered to determine the fluoride sorption kinetic by hydrotalcite like compounds.

Centrifuge tubes with mixtures of 50 mg of clays and 5 mL of fluoride solution (5 mg/L) or drinking water were shaken at 200 rpm for different times (from 5 minutes to 24 hours) at room temperature. Later the samples were centrifuged, decanted, and washed. The fluoride ions concentrations in solution were determined as described in fluoride ions measurements section. Each experiment was done in triplicate.

Isotherms

50 mg samples of each HT compound (MgAlHT and CoAlHT) were put in contact with 5 mL of different concentrations of fluoride ions (from 2 to 10 mg F^-/L), for the NiAlHT the concentrations of the solutions were from 15 to 50 mg F^-/L . The mixtures were shaken at 200 rpm, for 600 minute at room temperature. The samples were centrifuged and decanted; fluoride ions were analyzed in the liquid phases as described above.

The hydrotalcite-like compounds, after treatment with fluoride solutions, were labeled as MgAlHT-F, CoAlHT-F, and NiAlHT-F.

Continuous System

Fixed bed experiments were conducted in order to examine the fluoride ions uptake by the NiAlHT compound from aqueous solutions and drinking water. The adsorption process was done in columns of 8 mm internal diameter, the columns were loaded with 0.5 and 1.0 g of hydrotalcite-like compound and the heights of beds were 14 and 28 mm respectively.

The solution was introduced at a constant volumetric flow rate of 2 mL/minute and concentrations were 5 and 6.85 mg F^-/L for aqueous fluoride solutions and drinking water respectively, using a peristaltic pump in up-flow mode, in order to assure complete wetting of the adsorbent. 24 liquid samples of 5 mL were withdrawn and analyzed for fluoride ions as described above. The breakthrough curves were obtained by plotting the eluted fluoride ions concentrations vs. time.

RESULTS AND DISCUSSION

Elemental Composition

The X-ray diffraction, elemental analysis (EDS) and the specific surface areas of the hydrotalcite like compounds were reported elsewhere (12), the same composition was found in the samples used in that work and in the samples used in this work.

The $\text{M}^{\text{II}}/\text{M}^{\text{III}}$ ratios (R) were 1.30, 1.7 and 1.30 for MgAlHT, NiAlHT, and CoAlHT respectively. The $\text{M}^{\text{II}}/\text{M}^{\text{III}}$ ratio is usually in the range $1.5 \leq R \leq 4$, but these limits have been pushed down to $R \approx 1.3$ and up to $R \approx 5$ (13). It has been reported (14) that the number of anions depends on R, as it exactly counter-balances the layer

charge introduced by the trivalent atoms. In the same way, the concentration of water in the formula is directly related to the number of anions, and consequently to R, as water molecules usually fill the interlayer space left unoccupied among the anions. However, the hydration can be strongly reduced by acting on the synthesis conditions or with a subsequent calcination.

Fluoride Solutions

Kinetics

The equilibrium pH values of the solutions after the fluoride sorption by hydrotalcite like compounds were a little higher (between 7.1–8.2, 6.6–7.5, and 6.9–7.3 for MgAlHT, NiAlHT, and CoAlHT, respectively) than the initial pH value of 6.5.

Figure 1 shows the kinetic sorption behavior of fluoride ions by MgAlHT, NiAlHT, and CoAlHT. The sorption rates are fast at the beginning of the processes and remain practically constant thereafter; the equilibriums were reached in less than 200 minutes for all materials. A similar behavior was found by Wang et al. (15). Their results demonstrated that the F-sorption by Mg/Al–CO₃ hydrotalcite-like compounds (HT) is directly proportional to the contact time. The sorption reached a maximum at 15 minutes (optimum time) and they showed that equilibrium was established in this time.

The fluoride adsorption at equilibrium for MgAlHT, NiAlHT, and CoAlHT, were 0.37, 0.45, and 0.31 mg/g, respectively (Table 1), the most efficient adsorbent for fluoride ions was NiAlHT in these experimental conditions, although the sorption capacities for the materials were determined in the Isotherms section. When CoAlHT was used in the sorption process, the presence of cobalt was detected in the remaining solutions; Ulibarri et al. (16) observed that the thermal stability of Co–Al hydrotalcite is much lower than those of Ni–Al or Mg–Al compounds

with the same structure. This instability makes that CoAlHT is not a good candidate for the removal of fluoride ions from water in the experimental conditions of this work.

The data were fitted to kinetic models (models of Lagergren, Elovich, and pseudo-second order) by a non-linear regression analysis by using the software Statistica 6.0.

Lagergren First-Order Model

The model is represented by the equation (17):

$$q_t = q_e(1 - \exp(-Kt)) \quad (1)$$

where:

q_t (mg g⁻¹) is the amount of fluoride ions adsorbed at time t .

q_e (mg g⁻¹) is the amount of fluoride ions adsorbed at equilibrium.

K (h⁻¹) is the Lagergren rate constant.

Table 1 shows the first-order kinetics equations and R , corresponding to fluoride ions sorption on the hydrotalcite-like compounds. Although, the correlation coefficients showed that the experimental data were not well fitted to this model, it showed that the amounts of fluoride ions adsorbed at equilibrium (q_e) is as follows: NiAlHT > MgAlHT > CoAlHT. The Lagergren rate constant K followed the same behavior. These results indicate that the material NiAlHT has the highest affinity for fluoride ions, a similar sorption behavior was found for the corresponding calcined materials (12).

Elovich Model

The Elovich rate equation has been used in the kinetics of chemisorption of gases on solids. However some researchers have applied this model to solid-liquid sorption systems (18). This model is represented by the following equation:

$$q_t = \frac{1}{b} \ln(1 + abt) \quad (2)$$

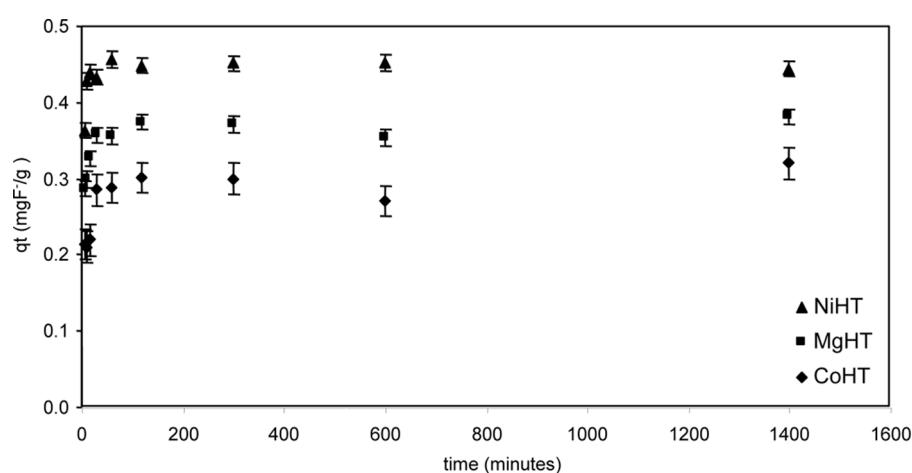


FIG. 1. Fluoride ions sorption from aqueous solution by MgAlHT, NiAlHT and CoAlHT as a function of time.

TABLE 1
Kinetic models applied to the fluoride ions sorption from aqueous solutions by MgAlHT, NiAlHT, and CoAlHT

| Sample | Lagergren | | | Pseudo-second order | | | Elovich | | | | | |
|--------------------|----------------------------|--------------------------------|---------------------------|---------------------|---------------------------------|--------------------------------|--|---|------|------------------------------------|--|----------------------------|
| | $q_t = q_e(1 - \exp(-Kt))$ | q_e (mg g ⁻¹) | K (min ⁻¹) | R | $q_t = Kq_e^2 t / (1 + Kq_e t)$ | q_e (mg g ⁻¹) | K (g mg ⁻¹ h ⁻¹) | $h_o = Kq_e^2$ (mg g ⁻¹ h ⁻¹) | R | $q_t = (1/b) * \ln(1 + a * b * t)$ | a (mg g ⁻¹ h ⁻¹) | b (g mg ⁻¹) |
| HTM _{as} | 0.36 | 0.26 | 0.77 | 0.37 | 0.44 | 0.37 | 0.44 | 0.06 | 0.99 | 5E5 | 62.10 | 0.85 |
| HTNi _{as} | 0.45 | 0.35 | 0.87 | 0.45 | 1.43 | 0.45 | 1.43 | 0.29 | 0.99 | 8E14 | 45.00 | 0.65 |
| HTNi _{dw} | 0.32 | 0.08 | 0.97 | 0.66 | 2.29 | 0.66 | 2.29 | 1.01 | 0.99 | 3.92 | 13.15 | 0.83 |
| HTCo _{as} | 0.29 | 0.15 | 0.66 | 0.31 | 0.24 | 0.31 | 0.24 | 0.02 | 0.99 | 53.19 | 43.90 | 0.65 |

as: aqueous solution.

dw: drinking water.

where

q_t (mg g⁻¹) is the amount of fluoride ions adsorbed at time t

a (mg g⁻¹ h⁻¹) is the sorption constant of the fluoride ions

b (g mg⁻¹) is the desorption constant of the fluoride ions.

Table 1 shows the corresponding equations, the sorption (a), and desorption (b) constants and R obtained by fitting the experimental data to the Elovich model. The adjustment of the experimental data was not good for CoAlHT and NiAlHT, the best adjustment was found for the adsorption of fluoride ions by MgAlHT.

Pseudo-Second Order Model

The linear form of the model can be represented by the following Equation (19):

$$\frac{t}{q_t} = \frac{1}{Kq_e^2} + \frac{t}{q_e} \quad (3)$$

where

K (g mg⁻¹ h⁻¹) constant of pseudo-second order

q_t (mg g⁻¹) is the amount of fluoride ions adsorbed at time t

q_e (mg g⁻¹) is the amount of fluoride ions adsorbed at equilibrium

The experimental data were best fitted to this model; Table 1 shows the pseudo-second order kinetics equations, the pseudo-second order rate constants, K, and R.

The pseudo-second order model is based on the assumption that the rate-limiting step may be chemisorption involving valence forces through sharing or exchange of electrons between adsorbent and adsorbate. Although, the experimental data could be fitted to the first and pseudo-second order kinetics equations, in general the best fit were observed with the pseudo-second order, which is generally applied to heterogeneous materials involving

chemical reactions. The kinetic constants show that the sorption rate is the highest for NiHT and the lowest for HTCo. It was reported as well that the kinetic of fluoride removal from aqueous solution by calcined hydrotalcites followed also the pseudo-second order kinetic model process (12).

Isotherms

Equilibrium studies were carried out in order to determine the optimum conditions for maximum fluoride removal by the hydrotalcite-like compounds. The data obtained were fitted to the Langmuir, Freundlich, and Langmuir-Freundlich models (20–21) in order to describe the fluoride ions sorption behavior by MgAlHT, NiAlHT and CoAlHT (Fig. 2). The data were fitted to isotherm models by a nonlinear regression analysis by using the software Statistica 6.0.

Langmuir Model

The Langmuir model is probably the most widely applied sorption isotherm. This model considers that the sorption energy of each molecule is the same, independently of the surface of the material, the sorption takes place only on some sites and there are no interactions between the molecules (20). It may be represented as follows:

$$q_e = \frac{qbC_e}{1 + bC_e} \quad (4)$$

where

q (mg g⁻¹) is the amount of fluoride ions adsorbed per unit weight of adsorbent in forming a complete monolayer on the surface

q_e (mg g⁻¹) is the amount of fluoride ions adsorbed

C_e (mg L⁻¹) is the concentration of the fluoride ions in the solution at equilibrium

b is a constant related to the energy or net enthalpy of adsorption.

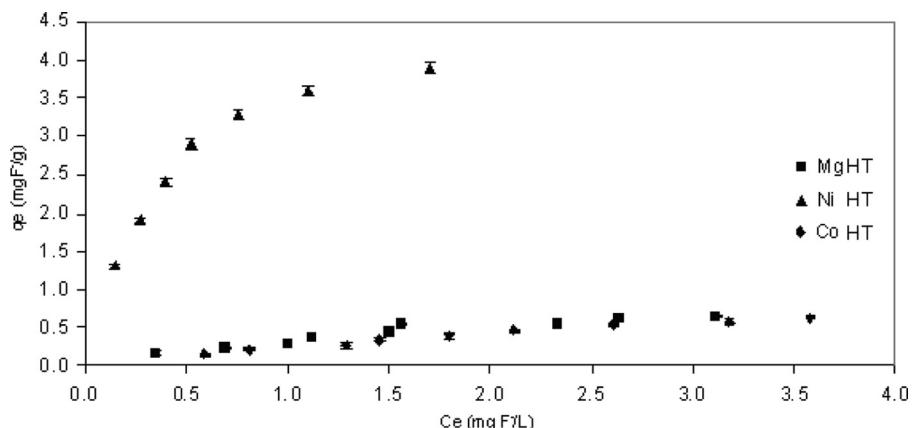


FIG. 2. Fluoride ions sorption isotherms from aqueous solutions by MgAlHT, NiAlHT and CoAlHT.

The experimental data for MgAlHT, NiAlHT and CoAlHT were fitted to this isotherm model and Table 2 shows the equations and the values of q , b , and R for the adsorption of fluoride ions by these materials. The sorption constants, q is the highest for the NiAlHT material (5.35 mg/g), which indicates that this material has the highest sorption capacity for fluoride ions. The q value for MgAlHT is similar to the value reported for MgAlCHT (12), in that previous paper it was reported that the MgAlCHT was regenerated when the calcined material was left in contact with the fluoride solutions. The q values for NiAlHT and CoAlHT were higher than the values reported for the calcined materials NiAlCHT and CoAlCHT, the q value for NiAlHT is more than 4 times higher than the value reported for NiAlCHT and the value for CoAlHT is twice the value reported for CoAlCHT (12).

NiAlHT and CoAlHT were not regenerated when they were calcined and left in contact with fluoride solutions and therefore the sorption of fluoride ions was on the oxides formed after the hydrotalcite-like compounds were thermally treated. In this work the removal mechanism of the fluoride ions from water by the hydrotalcite compounds could be adsorption or ion exchange.

Freundlich Model

This empirical model can be applied to no ideal sorption on heterogeneous surfaces as well as multilayer sorption and can be expressed by the following Equation (20):

$$q_e = K_f C_e^{1/n} \quad (5)$$

where:

q_e (mg g⁻¹) is the amount of fluoride ions per unit weight of calcined of hydrotalcite

C_e (mg L⁻¹) is the equilibrium concentration of fluoride
 n is an empirical constant

K_f is the equilibrium constant indicative of adsorption capacity in solution.

The Freundlich isotherm has been derived by assuming an exponentially decaying sorption site energy distribution. The Freundlich sorption isotherms equations, constants and R obtained are shown in Table 2. The highest $1/n$ value was found for the CoAlHT material, the lowest for the NiAlHT material and all of them are less than unity, and it implies heterogeneous surface structure with minimum interaction between the adsorbed atoms (22). K_f

TABLE 2

Isotherm models applied to the fluoride ions sorption from aqueous solutions by MgAlHT, NiAlHT, and CoAlHT

| Sample | Isotherm models | | | | | | | | | |
|--------|-------------------------------|-------|-------|-----------------------|------|---------------------------------------|---------------------|-------|------|------|
| | Langmuir | | | Freundlich | | | Langmuir-Freundlich | | | |
| | $q_e = q_b C_e / (1 + b C_e)$ | K_f | $1/n$ | $q_e = K_f C_e^{1/n}$ | R | $q_e = K C_e^{1/n} (1 + b C_e^{1/n})$ | K | $1/n$ | b | R |
| MgHT | 1.19 | 0.39 | 0.97 | 0.33 | 0.62 | 0.96 | 0.94 | 1.21 | 0.54 | 0.97 |
| NiHT | 5.35 | 2.52 | 0.98 | 3.57 | 0.37 | 0.98 | 0.01 | 0.59 | 0.30 | 0.95 |
| CoHT | 1.71 | 0.16 | 0.99 | 0.24 | 0.76 | 0.99 | 1.21 | 1.16 | 0.24 | 0.99 |

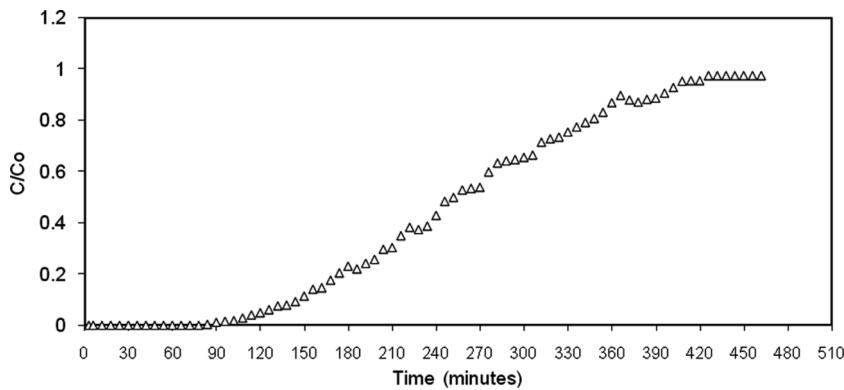


FIG. 3. Breakthrough curve of fluoride ions from aqueous solution by 0.5 g of NiAlHT.

was the highest for the NiAlHT which indicates that the sorption capacity is the highest.

Langmuir-Freundlich Model

This model is a combination of both Langmuir and Freundlich models and it can be expressed by the following Equation (21):

$$q_e = \frac{KC_e^{1/n}}{(1 + bC_e^{1/n})} \quad (6)$$

where

q_e is the amount of fluoride ions per unit weight of material (mg g^{-1}).

C_e is the equilibrium concentration of fluoride ions in solution (mg L^{-1}).

K and b are empirical constants.

In general the correlation coefficients were similar for both Langmuir and Freundlich models (Table 2). Similar results were found for fluoride sorption by hydroxyapatites which were mathematically best described with the Langmuir and the Langmuir-Freundlich adsorption isotherms (23). The experimental results indicate that the main mechanism involved in the adsorption of fluoride ions is chemisorption on heterogeneous materials.

Lv et al. (24) found that the Langmuir-Freundlich model gave a better fit to the experimental isotherm for the sorption of F^- by MgAl-CO_3 layered double hydroxides (LDHs).

According to the kinetic and isotherm results obtained with these three clays, the NiAlHT showed the best properties for fluoride ions removal from aqueous solutions and therefore only this material was used for the fluoride removal from aqueous solution in a column system and for both batch and column systems from drinking water.

Continuous System

Figure 3 shows the breakthrough curve using 0.5 g of NiAlHT and a solution of $5 \text{ mg F}^-/\text{L}$. The adsorption capacity of the column up to the breakpoint was 3.65 mg/g and the capacity obtained in batch system and the Langmuir isotherm was 5.35 mg/g , this behavior is reasonable since the sorption in columns is not at equilibrium. Therefore, the flow rate used in the column experiment may not provide enough time for the fluoride ions to distribute throughout all the adsorbent sorption sites. Thus, the batch processes provide a better interaction between the ions and the adsorbent than column systems (25) and for this reason a significant decrease on

TABLE 3
Characterization of the drinking water

| Parameter | Value |
|--------------------------|------------------------------|
| Total hardness | 196.96 mg/L |
| sulfates | 34.70 mg/L |
| Phosphorus | 0.31 mg/L |
| $\text{N}_2\text{-NO}_3$ | $2.53 \mu\text{g/L}$ |
| Ni | $0.02 \pm 0.01 \text{ mg/L}$ |
| Mg | 7.35 mg/L |
| Al | 0.40 mg/L |
| F^- | $6.85 \pm 0.01 \text{ mg/L}$ |

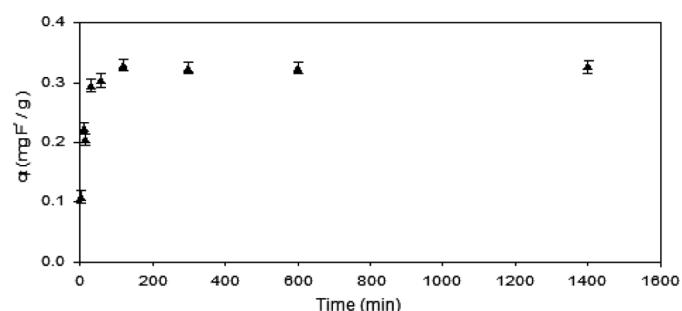


FIG. 4. Fluoride ions sorption from drinking water by NiAlHT as a function of time.

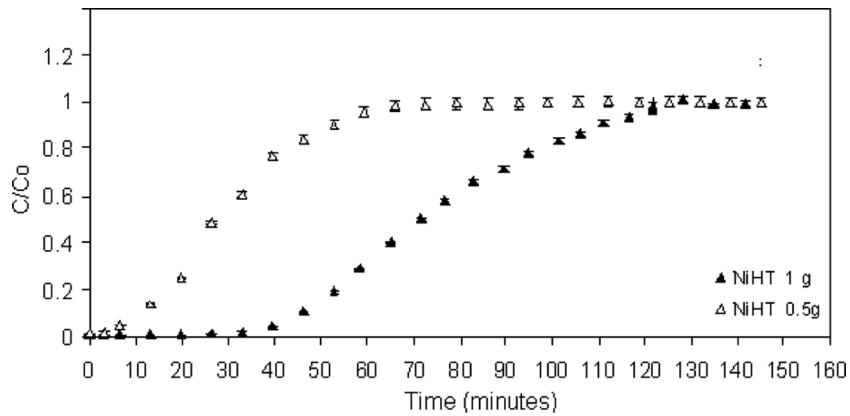


FIG. 5. Breakthrough curve for 0.5 and 1 g of NiAlHT and drinking water containing 6.8 mg F⁻/L.

adsorption capacities in fixed beds is observed. Increasing the residence time in the column could enhance the sorption capacity of the bed and its efficiency.

The saturation percentage of the column was calculated according to Gupta et al. (26) and it was 93.6%.

Drinking Water

Drinking Water Characterization

Table 3 shows the characterization of the drinking water used for the experiments, the concentration of fluoride ions is higher than the limit allowed by the World Health Organization guidelines (6). Some papers have been published on the selectivity of MgAlCHT for some anions (10,27,28) but nothing has been reported on the selectivity or interferences on the sorption of fluoride ions by hydrotalcite-like compounds.

Kinetics

Figure 4 shows the sorption kinetic behavior of fluoride ions using NiAlHT and drinking water containing naturally 6.8 mg F⁻/L. The kinetic sorption rate is fast at the beginning of the processes and then become slower as equilibrium is approached; the equilibrium was reached in less than 200 minutes which was similar to the time required with fluoride solutions. The experimental data were adjusted to the models of Lagergren, Pseudo-second order and Elovich, the best fit was found for the pseudo second-order model (Table 1). The sorption capacity of NiAlHT for fluoride ions in these conditions was only 71% of the capacity obtained with aqueous fluoride solutions. This effect could be due to the composition of the drinking water for example sulfate (Table 3) and carbonate ions could compete for the sorption sites on the materials.

Continuous System

Figure 5 shows the breakthrough curve obtained with 0.5 and 1 g of NiAlHT and drinking water containing

6.8 mg F⁻/L. The adsorption capacities of the columns up to the breakpoints were 0.0511 and 1.11 mg/g for 0.5 and 1 g of NiAlHT respectively, these capacities are lower than the value obtained with fluoride ions solutions (Fig. 3). The column with 1 g of adsorbent showed a capacity 22 times higher than the column with 0.5 g. The profile of breakthrough curves varies with the bed mass or height for NiAlHT, breakthrough curves for 0.5 and 1 g follows the characteristic "S" profile produced in ideal sorption systems which are associated to adsorbates with small ionic radius and simple structure (29). Additionally, a fast increase in the outlet concentration is observed for 0.5 g, whereas for 1 g it can be seen that the "S" profile is more evident. This displacement of the adsorption front with the increase in depth can be explained by mass transfer phenomena that takes place in this process. When the bed depth is reduced, the axial dispersion phenomena predominate in the mass transfer and reduce the diffusion of ions. The solute does not have enough time to diffuse into the whole of the adsorbent mass (30). Consequently an important reduction in time (or volume of treated solution) at the breakthrough point is observed when the bed mass in the column decreases from 1 to 0.5 g.

This increase in the adsorption capacity with that in the bed depth can be due to the increase in the specific surface area of the adsorbent which supplies more active sorption sites. Additionally, the time at breakthrough also increases with the bed mass. For this reason, the breakthrough time is a determining parameter in the process.

The saturation of the columns were 76.47 and 33.33 minutes for 1 and 0.5 gram respectively (Fig. 5), the effluent concentration increases fast for the lowest bed height breakthrough curve (0.5 g) and the curve of the longest bed (1 g) tends to be more gradual, meaning that it is difficult to have the columns completely exhausted.

CONCLUSIONS

The pseudo-second order model describes the fluoride kinetic sorption processes by CoAlHT, MgAlHT, and NiHT. The pseudo-second order kinetic rate constant is the highest for NiAlHT and the lowest for CoAlHT.

The time in which the fluoride sorption equilibrium by NiAlHT is reached varies with the quality of water and the mechanism involved in the sorption of fluoride ions from natural water by NiAlHT is chemisorption on heterogeneous materials.

The sorption fluoride capacity depends on the divalent metal that forms part of the structure of the hydrotalcite-like compounds and follows the order NiAlHT > MgAlHT > CoAlHT, obtained by applying the Langmuir model.

The CO_3^{2-} anions from the interlayer of the three hydrotalcite-like compounds (MgAlHT, NiAlHT, and CoAlHT) can be partially removed under slightly acidic conditions by the incorporation of fluoride.

The height of the bed of the column determines the efficiency of the NiAlHT to remove fluoride ions from water.

The associate components of water (drinking water) influence the NiAlHT sorption capacity for fluoride ions in column systems.

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