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M. L. Jiménez-Núñez[ab]; M. T. Olguín[a]; M. Solache-Ríos[ab]
[a] Depto. de Química. Apdo, Instituto Nacional de Investigaciones Nucleares, D. F., México [b] Instituto Tecnológico de Toluca, Av. Instituto Tecnológico S/N, ExRancho la Virgen, Metepec, México

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M. L. Jiménez-Núñez
Instituto Nacional de Investigaciones Nucleares, Depto. de Química.
Apdo., México, D. F. and Instituto Tecnológico de Toluca, Av. Instituto
Tecnológico S/N, ExRancho la Virgen, Metepec, México

M. T. Olguín
Instituto Nacional de Investigaciones Nucleares, Depto. de Química.
Apdo., México, D. F.

M. Solache-Ríos
Instituto Tecnológico de Toluca, Av. Instituto Tecnológico S/N,
ExRancho la Virgen, Metepec, México

Abstract: Magnesium, nickel and cobalt hydrotalcite-like compounds (MgHT, NiHT, and CoHT), with similar M^{2+}:Al^{3+} ratios were synthesized and characterized by XRD. It was confirmed from XRD that the materials have hydrotalcite-like structure. MgHT, NiHT, and CoHT were calcined and treated with fluoride solutions in a batch system. F^- ions were determined in the remaining solutions using a fluoride ion selective electrode. The kinetics of the fluoride ions sorption on calcined hydrotalcite-like compounds (CHT) was best described by the pseudo-second order model and the equilibrium was reached in less than 300 minutes in all cases (MgCHT, NiCHT, and CoCHT). The sorption isotherms of the fluoride by hydrotalcite like compounds can be explained by the Langmuir-Freundlich model and, the highest fluoride sorption capacity was obtained for NiCHT (1.202 mgF/gCHT). The fluoride removal from aqueous solutions by calcined hydrotalcite-like compounds depends on the adsorption

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Address correspondence to M. Solache-Ríos, Instituto Nacional de Investigaciones Nucleares, Depto. de Química. Apdo., Postal 18-1027, 11801, México, D. F. E-mail: msr@nuclear.inin.mx

properties of the thermal decomposition products and the regeneration reaction mechanism of the hydrotalcite-like compounds.

Keywords: Fluoride, hydrotalcites, sorption

INTRODUCTION

Fluorine occurs in nature and it is an essential constituent for both humans and animals in a low concentration (1). Three different health problems have been associated to excessive exposure of fluoride ions: dental fluorosis, skeletal fluorosis, and non vertebral fractures. The principal source of fluoride ions is drinking water either in endemic areas with naturally fluoridated drinking water or in nonendemic areas where fluoride is added to public drinking water in order to prevent tooth decay (2).

The conventional method used for the removal of fluoride ions 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) (3).

Solid adsorbents have also been studied for fluoride ions removal from aqueous solutions, such as: alumina, iron oxide-rich-soils, trivalent-cation-exchange zeolite F-9, alum-impregnated activated alumina, and manganese-oxide-coated alumina (4–8). However, the efficiency of fluoride ions adsorption depends on the chemical composition and physicochemical characteristics of water. A useful material should have properties such as high capacity, selectivity, and be effective at the pH of drinking water (9).

Hydrotalcite-like compounds have been synthesized and characterized, thermal decomposition and reconstitution reaction mechanism have been studied in detail (10). These compounds have positively charged brucite-like octahedral hydroxide layers, which are neutralized by interlayer anions and water molecules, and are generally formulated as $[M^{2+}_{1\text{-}x}M^{3+}_{x}(OH)_2]A^{n-}_{x/n}$ mH_2O. Magnesium hydrotalcite has been synthesized elsewhere (11), it is stable up to 400°C, it decomposes into an NaCl-type magnesium aluminum oxide above 400°C and into MgO and $MgAl_2O_4$ above 800°C (11). 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. The layered double hydroxides calcined at a certain range of temperature have the memory effect, which means to recover its original layered structure in the presence of appropriate anions (12). Thus, both hydrotalcite and magnesium aluminum oxide could be used to take up anions from aqueous solutions. Magnesium calcined hydrotalcite-like compounds have been used as sorbents for example, Yang et al. (13, 14) used them for the removal of arsenic and selenium from aqueous solution; Díaz-Nava et al. (9) and Liang et al. (1, 15) have shown that magnesium calcined hydrotalcite-like compounds can be used for fluoride removal from aqueous solutions and Lazaridis et al. (16), removed hexavalent chromium from aqueous solutions. These materials have been used as well for the capture of gases such as CO_2 and NO_x (17–19).

Ni-Al hydrotalcite-like compounds have been investigated in catalytic reactions, for example a Ni-Al hydrotalcite prepared in the presence of NO_3^- anion exhibited the greatest catalytic activity for the ethylbenzene oxidation reaction (20). Nickel(II) containing magnesium-aluminum (3:1) hydrotalcite(HT)-type anionic clays have been prepared by co-precipitation and tested for a catalyst for liquid-phase oxidation of alcohols with molecular oxygen (21). Several aromatic and heterocyclic aldehydes are reduced at atmospheric pressure by calcined Ni-Al hydrotalcite and the catalyst has been reused for several cycles with consistent activity and selectivity (22). Co-Mg-Al hydrotalcites like compounds have been investigated in the ozonation of phenol (23). It is important to note that neither Ni nor Co hydrotalcites-like compounds have been investigated for the removal of fluoride ions from water.

The purpose of this paper was to evaluate the fluoride ions removal from aqueous solutions by magnesium, nickel and cobalt calcined hydrotalcite-like compounds, considering both the adsorption kinetics and the isotherms to determine the maximum fluoride capacity of each material. The fluoride sorption mechanisms were also considered in this work.

EXPERIMENTAL METHODS

Materials

Magnesium, nickel, cobalt (M), and aluminum nitrate salts as well as potassium hydroxide and potassium carbonates (Sigma-Aldrich or J. T. Baker) were used for the synthesis of hydrotalcite-like compounds without any further purification.

Hydrotalcites-like compounds (HT) were synthesized considering the techniques reported by López-Salinas et al. (24) and Hesiquio-Garduño et al. (25) as follows: two mixed aqueous solutions, the first one composed of $M(NO_3)_2$ and $Al(NO_3)_3$, and the second of KOH and K_2CO_3 were added to hot deionized water (333 K) maintaining a M^{2+}:Al^{3+} ratio of 2:1. The pH during reaction was around 10 and it was controlled using KOH and K_2CO_3. The precipitates were washed at room temperature until a pH of 7 was reached and then dried at 373 K for 24 hours, these materials were named as NiHT, CoHT, and MgHT. Finally the hydrotalcite-like compounds were calcined at 723 K for 3 hours. The obtained materials were called as NiCHT, CoCHT, and MgCHT.

The calcined hydrotalcite-like compounds were milled and sieved, the diameter of the grains between 0.3 and 0.71 μm was selected.

Characterization Techniques

X-Ray Diffraction

Powder diffractograms of the HT and CHT samples were obtained with a Siemens D500 diffractometer coupled to a copper anode X-ray tube. The conventional diffractograms were used to identify the compounds and to verify crystalline structure.

Elemental Composition

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

Specific Surface Areas

The specific surface areas were determined by standard multipoint techniques of nitrogen adsorption, using a Micromeritics Gemini 2360 instrument. The samples were heated at 373 K for 2 hours before determinations.

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) considering a fluoride concentration range from 1 to 5 mg/L.

Kinetics

Batch system were considered to determine the fluoride sorption kinetic by CHT. Centrifuge tubes with mixtures of 50 mg of calcined clays and 5 mL of fluoride solution (5 mg/L) were shaken at 200 rpm for different times (5, 10, 15, and 30 minutes, 1, 2, 5, and 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 CHT compound were put in contact with 5 mL of different concentrations of fluoride ions (2, 3, 4, 5, 6, 7, 8, 9, 10 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 CHT samples after the treatment with fluoride solutions was named as NiCHT-F, CoCHT-F and MgCHT-F.

RESULTS AND DISCUSSION

Characterization Techniques

X-Ray Diffraction

Figures 1, 2, and 3 show the powder diffraction patterns of the MgHT, NiHT or CoHT (a), MgCHT, NiCHT, or CoCHT (b) and MgCHT-F, NiCHT-F or CoCHT-F (c). The powder diffraction patterns of MgHT, NiHT, or CoHT correspond to the hydrotalcite structure according with the JCPDS card 22-0700 (26, 27). It is important to mention that NiHT and CoHT diffraction patterns are similar to those reported by Obalová et al. (28) and Ulibarri et al. (29) for Ni-Al and Co-Al hydrotalcite-like compounds, respectively.

In the case of MgCHT and NiCHT, the single oxide MgO (cubic structure, JCPDS 45-0946) and NiO (cubic structure, JCPDS 4-0835) are the only crystalline phases identified after thermal treatment at 723 K. Similar results were obtained by Pérez-Ramírez et al. (27) when Mg-Al and Ni-Al hydrotalcite samples were calcined at 823 K during 5 hours. They observed that thermal decomposition of Co-Al hydrotalcite leads to the formation of a solid solution of cobalt spinels [denoted as $Co(Co,Al)_2O_4$]. They commented that due to the similar reflection angles and intensities in XRD, it is not possible to distinguish the components Co_3O_4 (JCPDS 43-1003), $CoAl_2O_4$ (JCPDS 44-0160, and Co_2AlO_4 (JCPDS 38-0814). A similar diffraction pattern was obtained in the present work (Fig. 3b).

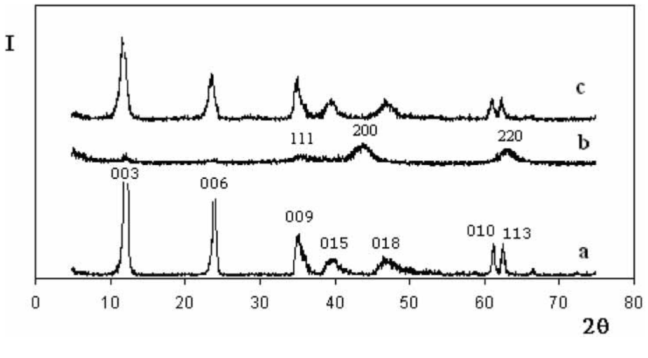

Figure 1. X-ray powder diffraction patterns of (a) MgHT, (b) MgCHT and (c) MgCHT-F.

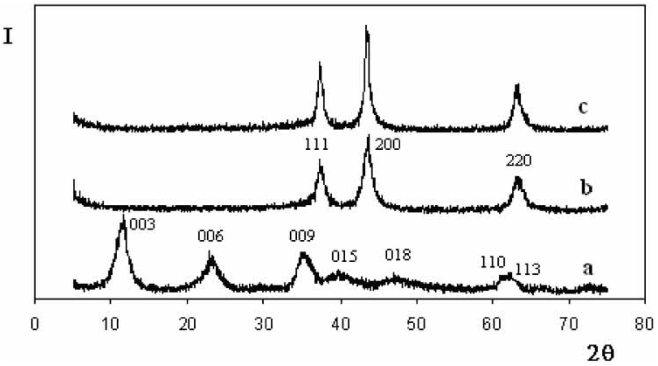

Figure 2. X-ray powder diffraction patterns of (a) NiHT, (b) NiCHT and (c) NiCHT-F.

Obalová et al. (28) found a gradual decrease of thermal stability with increasing Ni^{2+} content in Ni(Mg)/Al hydrotalcites. Perhaps the main difference of MgHT and NiHT with respect to CoHT is their thermal stability; Ulibarri et al. (29) 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, where no collapsing of the layered structure was observed below 523 and 573 K. They suggested that this behavior could be due to the presence of cations such as Co^{2+} that become oxidized during the hydrothermal treatment. Simultaneously, migration of the M(II) and/or M(III) cations from octahedral to tetrahedral sites of the lattice, leading to formation of spinel, may help the collapse of hydrotalcite-like compound structures.

When the MgCHT were in contact with the fluoride ions solutions recovered its original crystalline structure (Fig. 1c) by the memory effect (12). This behavior was not observed for NiCHT and CoCHT samples (Figs. 2c and 3c).

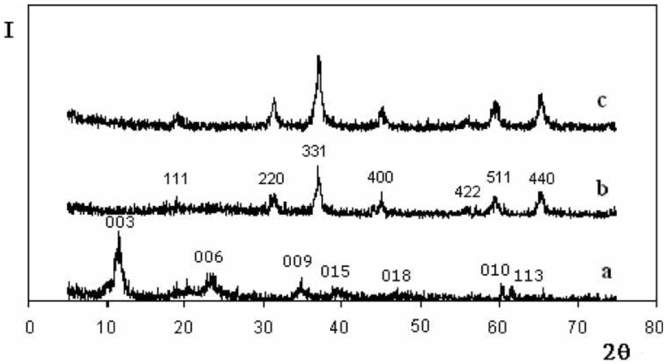

Figure 3. X-ray powder diffraction patterns of (a) CoHT, (b) CoCHT and (c) CoCHT-F.

Table 1. Elemental composition of MgHT, NiHT and CoHT

	Wt.%		
Element	MgHT	NiHT	CoHT
O	53.290 ± 0.004	34.160 ± 0.060	37.660 ± 0.010
Mg	25.060 ± 0.003	—	—
Ni	—	51.790 ± 0.100	—
Co	—	—	45.090 ± 0.010
Al	21.650 ± 0.003	13.970 ± 0.010	16.080 ± 0.010

Elemental Composition (EDS)

The elemental composition of the hydrotalcite-like compounds (Table 1) showed that the content of M^{2+} is as follows $M^{2+}_{NiHT} > M^{2+}_{CoHT} > M^{2+}_{MgHT}$ and the aluminum content in the same samples is $Al_{MgHT} > Al_{CoHT} > Al_{NiHT}$. Therefore the resulting $M^{2+}/(M^{2+} + Al^{3+}$ ratios were 1.3 for MgHT and CoHT and 1.7 for NiHT.

Specific Surface Areas

The specific surface areas (SSA) of each hydrotalcite before and after the thermal treatment are presented in Table 2. The SSA differences for HT and CHT have been explained by Ulibarri et al. (29), these differences have been attributed to changes taking place in the size of the crystallites when samples are calcined around 673 K. In the present work the thermal treatment of the hydrotalcites was at 723 K and notably differences were observed specially for NiHT and NiCHT. Probably, in this last case the SSA plays an important role in the fluoride adsorption processes, as it will be discussed later.

Table 2. Specific surface areas of HT and CHT

Samples	Specific surface area (m^2/g)
MgHT	51.5
NiHT	5.8
CoHT	28.5
MgCHT	55.1
NiCHT	139.6
CoCHT	127.6

Kinetics

The equilibrium pH values of the solutions after the fluoride sorption by HT were a little higher than the initial pH values and were between 7.5–10.5, 7.0–7.6, and 6.9–7.6 for MgCHT, NiCHT, and CoCHT, respectively. It is important to note that the highest equilibrium pH range was for MgCHT, this behavior could be attributed to regeneration the original crystalline structure, which is not the case for the other two materials. This behavior could be useful for NiCHT-F and CoCHT-F because the fluoride water treated with these materials would not require a pH adjustment at the end of the process.

Figure 4 shows the kinetic sorption behavior of fluoride ions by MgCHT, NiCHT and CoCHT. The kinetic curves show that the sorption rate is rapid at the beginning of the processes and then becomes slower as equilibriums are approached, the equilibrium was reached in about 300, 60, and 120 minutes for MgCHT, NiCHT, and CoCHT, respectively.

Thermal treatment of hydrotalcites induces dehydration, dehydroxilation, and loss of compensation ions, forming mixed oxides. These oxides have a small particle size, large specific surface area, and basic properties attributed partially to the presence of Lewis acid-base pair sites, so they are potentially useful as adsorbents (30–32). Fluoride ions could be adsorbed by the NiCHT and CoCHT through Lewis acid-base interaction and for the case of MgCHT by the structure regeneration (the memory effect). The equilibrium time was the longest for this last case.

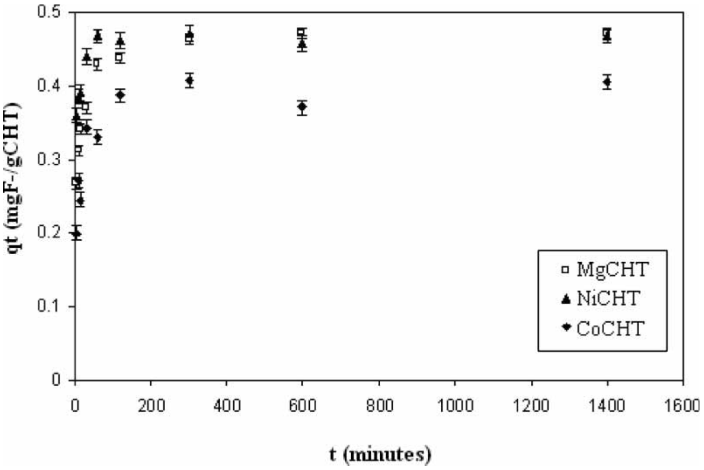

Figure 4. Fluoride ions adsorption from aqueous solution by MgCHT, NiCHT, and CoCHT as a function of time (V = 5 mL, T = 293 K, $[F^-]_o = 5$ mg/L, *w*HT = 50 mg).

The fluoride adsorption at equilibrium for MgCHT and NiCHT were very similar; 0.46 ± 0.01 and 0.45 ± 0.01 mg/g, respectively; and for CoCHT the adsorption was 0.39 ± 0.02 mg/g.

The data were fitted to the following kinetic models by a nonlinear regression analysis by using the software Statistica 6.0:

A. Lagergren First-Order Model

The model is represented by the Eq. (33):

$$q_t = q_e(1 - \exp(-Kt)) \tag{1}$$

where $q_t(\mathrm{mg\,g^{-1}})$ is the amount of fluoride ions adsorbed at time *t*. q_e $(\mathrm{mg\,g^{-1}})$ is the amount of fluoride ions adsorbed at equilibrium. $K(h^{-1})$ is the Lagergren rate constant.

It was found that, this equation did not provide a good description of the current data. Table 3 shows the first order kinetics equations and r^2 corresponding to fluoride ions sorption on the calcined hydrotalcites. Although, the determination 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) were similar for both NiCHT and MgCHT hydrotalcites and it was lower than the values for CoCHT. The Lagergren rate constant K was higher for NiCHT than for the other two materials. These results indicate that the materials MgCHT and NiCHT have more affinity for fluoride ions than the CoCHT. It is important to note that for the case of CoCHT, the fluoride solutions after being in contact with the material showed a dark color, these solutions were analyzed by UV-Vis and showed the presence of cobalt (II) which indicates that the cobalt is desorbed from the CoCHT and it is soluble in the fluoride solutions. This behavior may be explained as discussed in X-Ray diffraction section.

B. 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 (34). This model is represented by the following equation:

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

where $q_t(\mathrm{mg\,g^{-1}})$ is the amount of fluoride ions adsorbed at time t. a $(\mathrm{mg\,g^{-1}})$ is the sorption constant of the fluoride ions. $b(\mathrm{mg\,g^{-1}})$ is the desorption constant of the fluoride ions.

Table 3 shows the corresponding equations, the sorption (a), and desorption (b) constants and r^2 obtained by adjusting to the experimental data to the Elovich model. The sorption constant (a) is the highest for the NiCHT and the lowest for the CoCHT. The desorption constant (b) shows for NiCHT a higher value than for the others two calcined clays which had

Table 3. Lagergren first-order, pseudo- second order and Elovich kinetic models applied to the fluoride ions sorption by MgCHT, NiCHT and CoCHT

	Kinetic models								
	Lagergreen			Pseudo second order			Elovich		
	$q_t = q_e(1\text{-}Exp(\text{-}Kt))$			$q_t = Kq_et/(1 + 2Kq_et)$			$q_t = (1/b)In(1 + abt)$		
Samples	q_e (mg g^{-1})	K (min^{-1})	r^2	q_e (mg g^{-1})	K (mg g^{-1} min^{-1})	r^2	a	b	r^2
MgCHT	0.439	0.131	0.76	0.922	0.117	0.95	15.09	13.28	0.89
NiCHT	0.450	0.262	0.60	0.932	0.295	0.90	3.3E6	22.00	0.73
CoCHT	0.373	0.110	0.77	0.785	0.113	0.89	15.17	12.55	0.80

similar values. This model has proved suitable for highly heterogeneous systems. The best adjustment was found for the adsorption of fluoride ions by MgCHT.

C. Pseudo-Second Order Model

The model can be represented by the following Eq. (35):

$$q_t = Kq_e^2 t/(1 + 2Kq_e t) \tag{3}$$

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 pseudo-second order rate constant, K, equilibrium sorption capacity, q_e, and determination coefficients, r^2, for the fluoride ions were calculated (Table 3) and compared with the adjustments of the models described above.

Table 3 shows the pseudo-second order kinetics equations, the pseudo-second order rate constants, K, and determination coefficients, r^2.

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 the adsorbent and the adsorbate. Although, the experimental points could be fitted to the first and pseudo-second order kinetics equations, in general the best adjustments were observed with the pseudo-second order kinetics equation, which is generally applied to heterogeneous materials involving chemical reactions which is the case of the systems studied. The kinetic constants show that the sorption rate is highest for the calcined NiCHT and it was similar for the other two materials. It was found that the kinetics of fluoride removal from the aqueous solution by calcined MgAl-CO_3 hydrotalcite (1), $Fe_2O_3Al_2O_3 \cdot xH_2O$ and manganese-oxide-coated alumina (MOCA) followed also the pseudo-second order kinetic model process (7, 36).

Sorption Isotherms

The isotherm data obtained in this work were fitted to the Langmuir, Freundlich (37) and Langmuir-Freundlich (38) models in order to describe the fluoride ions sorption behavior in MgCHT, NiCHT, and CoCHT.

A. 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, and independently of the surface of the material, the sorption takes place only on some sites and there are not any interactions between the molecules (37). It may be represented as follows:

$$q_e = \frac{q_0 bC_e}{1 + bC_e} \tag{4}$$

where q_o (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 the constant related to the energy or net enthalpy of adsorption.

The experimental data for MgCHT, NiCHT, and CoCHT were fitted to this isotherm model and Table 4 shows the equations and the values of q_o, b and r^2 for the adsorption of fluoride ions by these materials. The sorption constants, q_o is the highest for the NiCHT material, which indicates that this material has the highest sorption capacity for fluoride ions.

B. 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 Eq. (37):

$$q_e = K_f C_e^{1/n} \tag{5}$$

where: q_e (mg g^{-1}) is the amount of fluoride ions per unit weight of calcined hydrotalcite. C_e (mg L^{-1}) is the equilibrium concentration of calcined hydrotalcite in solution. K_f is the equilibrium constant indicative of adsorption capacity. n is the adsorption equilibrium constant whose reciprocal is indicative of adsorption intensity.

The Freundlich isotherm has been derived by assuming an exponentially decaying sorption site energy distribution. The Freundlich sorption isotherms equations, constants and r^2 obtained are shown in Table 4. $1/n$ values are related to the sorption intensity as noted above and the highest value was found for the MgCHT material and the lowest for the CoCHT material. K_f was the highest for the NiCHT which indicates that the sorption capacity is the highest as well.

In general the determination coefficients were similar for both Langmuir and Freundlich models.

C. Langmuir–Freundlich Model

This model is a combination of both Langmuir and Freundlich models and it can be expressed by the following Eq. (38):

$$q_e = K C_e^{1/n} / (1 + b C_e^{1/n}) \tag{6}$$

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.

Figure 5 shows the adjustments of the experimental data for fluoride ions sorption by the MgCHT, NiCHT and CoCHT and Table 4 shows the Langmuir-Freundlich sorption isotherms equations and the values of K, b, $1/n$, and r^2. In general, the experimental results were best fitted to this last

Table 4. Langmuir, Freundlich and Langmuir-Freundlich isotherm models applied to the fluoride ions sorption by MgCHT, NiCHT and CoCHT

	Isotherm model									
	Langmuir			Freundlich			Langmuir-Freundlich			
	$q_e = q_o bC_e/1 + bC_e$			$q_e = K_f C_e^{1/n}$			$q_e = KC_e^{1/n} / 1 + bC_e^{1/n}$			
Samples	q_o (mg g^{-1})	b (L g^{-1})	r^2	K_f (mg/g) $(mg/L)^{1/nF}$	$1/n$	r^2	K (mg/g) $(mg/L)^{1/nF}$	$1/n$	b (L g^{-1})	r^2
MgCHT	1.185	1.702	0.991	0.740	0.523	0.980	1.650	0.825	0.887	0.993
NiCHT	1.202	4.589	0.965	1.203	0.500	0.983	1.512	3.324	0.565	0.983
CoCHT	0.842	2.262	0.843	0.547	0.372	0.792	2.031	0.405	1.043	0.843

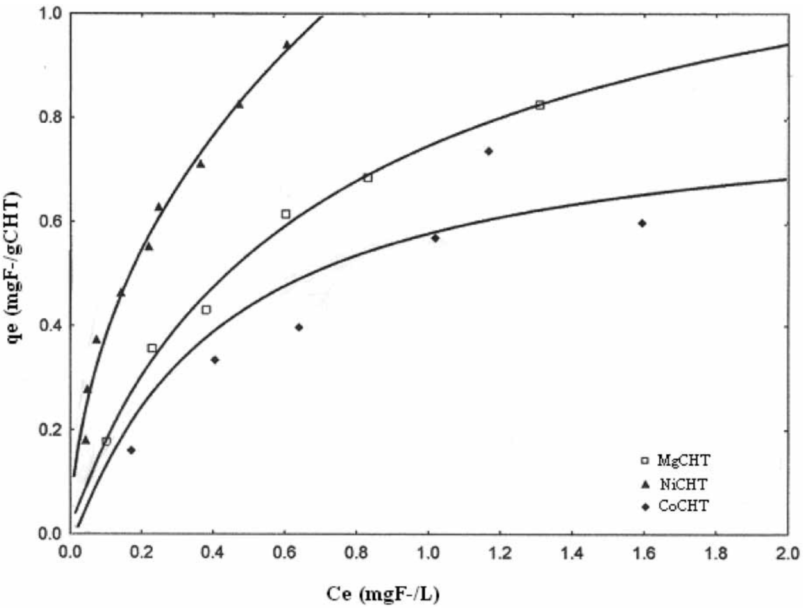

Figure 5. Langmuir-Freundlich isotherm applied to the fluoride ions sorption from aqueous solution by MgCHT, NiCHT, and CoCHT (t = 10 h, V = 5 mL, T = 293 K, $[^{-}F]_o = 1-10$ mg/L, *w*HT = 50 mg).

equation which indicates that the main mechanism involved in the adsorption of fluoride ions is chemisorption by heterogeneous materials. Similar results were found for fluoride sorption by hydroxyapatites which can mathematically were best described with Langmuir and Langmuir-Freundlich adsorption isotherms (39). According to the kinetic and isotherm results obtained with these three clays, the NiCHT showed the best properties for fluoride ions removal from aqueous solutions. The adsorption mechanism was not the regeneration of the original crystalline structure after being in contact with the fluoride ions solution as it was the case of MgCHT.

CONCLUSIONS

The MgCHT is regenerated to its original crystalline structure after being in contact with fluoride ions, but both NiCHT and CoCHT remain as oxide mixtures.

The pseudo second order model describes the kinetics of the fluoride sorption by CHT and the mechanism involved is chemisorption on heterogeneous materials according to the Langmuir–Freundlich isotherm.

NiCHT shows the best characteristics for the fluoride ions sorption from aqueous solutions, considering the sorption capacity, as well the pseudo-second order kinetic parameter K and the pH value after the fluoride sorption process.

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