



Sorption behavior of fluoride ions from aqueous solutions by hydroxyapatite

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ABSTRACT

The effects of pH, contact time, fluoride-ion concentration, and the dose of sorbent on the sorption of fluoride ions by hydroxyapatite were studied. Equilibrium was reached in 16 h of contact time and the maximum sorption of fluoride ions was in the pH_{eq} range between 5 and 7.3. The highest efficiency in the sorption system was determined by using 0.01 g of hydroxyapatite and 25 mL of solution. The pseudo-second order model described the kinetic sorption processes, and the Freundlich model, the sorption isotherm process. These results indicated that the mechanism was chemisorption on a heterogeneous material. Fluoride ions were partially desorbed using an alkaline solution.

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1. Introduction

Fluoride is an essential constituent for both human and animals; however, the total amount ingested or its concentration in drinking water must be within certain limits [1]. For example, according to The World Health Organization (WHO) standards the permissible limit of fluoride is 1.5 mg L^{-1} . Fluoride-related health hazards are a major environmental problem in many regions of the world. When the fluoride concentration is higher than the permissible limit, it causes dental and skeletal fluorosis, bone diseases, mottling of teeth and lesions of the thyroid, liver and other organs [2]. The contamination of ground/surface water could come either from natural geological sources or from industries that use fluoride-containing compounds as raw materials [3].

The conventional method used for the removal of fluoride ions is by precipitation with calcium compounds. However, due to the relatively high solubility product, they do not remove fluoride ions to the level required by the WHO [4]. Several methods, such as sorption, ion exchange, electrolysis and precipitation, have been adopted for defluoridation [3]. Materials such as calcium phosphate, bone charcoal, apatite, activated alumina, activated carbon have been experimented for the removal of fluoride. Recently, hydrotalcite-like compounds and their calcined materials have been used for the same purpose [3,5–7]. Hydroxyapatite was studied as a fluoride sorbent either at fixed conditions [8] or by considering the effect of some important parameters such as contact time [9–12], sorbent dose [9–11], particle size [10], solution pH [9–11,13], the presence of other anions [9] and fluoride concentration [9–11,13,14]. Sundaram et al. [15] considered contact time, pH,

the effect of other anions, and the concentration of fluoride ions in the fluoride sorption with a nano-hydroxyapatite/chitin composite. The purpose of the present paper was to carry out a systematic study of parameters such as pH, contact time, fluoride-ion concentration and sorbent dose in order to elucidate the sorption behavior of fluoride ions by hydroxyapatite as well as the desorption of fluoride ions from this material by different solutions.

2. Materials and methods

2.1. Sorbent and solutions

Hydroxyapatite was prepared according to the technique reported elsewhere [8]. This hydroxyapatite was milled and sieved; the diameter of the grains between 20 and 30 mesh was selected for the experiments.

For the present study, a batch system was used with 25 mL of a sodium fluoride solution ($5 \text{ mg F}^{-1} \text{ L}^{-1}$) and 0.075 g of hydroxyapatite (HAP) except in the experiments where sorbent dose was varied. Each experiment was carried out in duplicate.

2.2. X-ray diffraction (XRD)

Powder diffractogram of the hydroxyapatite was obtained with a Siemens D500 diffractometer coupled to a copper-anode X-ray tube. The conventional diffractograms were used to identify the compound and to verify its crystalline structure.

2.3. Fluoride ion measurements

The concentration of fluoride ions in the solutions was determined with a selective electrode for fluoride ions (ISEC301F Combined Fluoride Electrode). TISAB II (total ionic strength adjust-

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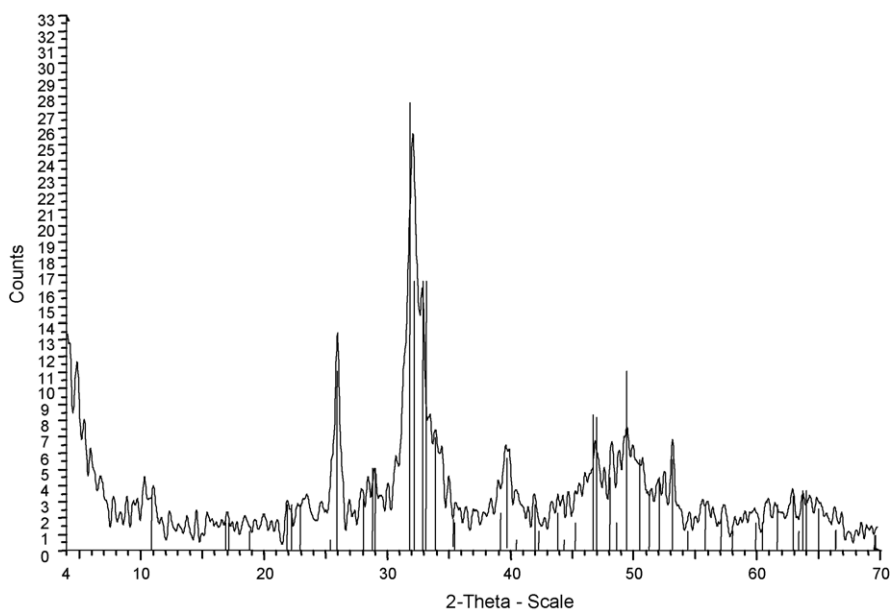


Fig. 1. X-ray diffractogram of the hydroxyapatite compared with the JCPDS 00-009-0432.

ment buffer) and a 0.1 M NaCl solution were added to all fluoride standards and samples to control the pH and ionic strength, respectively. The calibration line was obtained by using NaF solutions with a fluoride concentration range from 0.5 to 5 mg L⁻¹. The corresponding equation was: $mV = -\log[F^-] \times 55(\pm 2) + 30(\pm 8)$; $R^2 = 0.999$.

Sorbed quantities of fluoride ions (q) were calculated as following:

$$q = \frac{m(F^-)_I - m(F^-)_F}{m_{HAP}} \quad (1)$$

where $m(F^-)_I$ and $m(F^-)_F$ were the initial and the final masses (mg) of fluoride ions measured in solution, respectively, and m_{HAP} was the mass (g) of HAP.

2.4. Sorption kinetics

Centrifuge tubes with mixtures of HAP and the fluoride solution were shaken from 7 min to 23 h at room temperature. Subsequently, the suspensions were centrifuged, the liquid phases were decanted and the fluoride concentrations were determined as described in Section 2.3.

2.5. Effect of sorbent dosage

The experiments were performed by using different amounts of HAP (from 0.01 to 0.1 g) and 25 mL of the fluoride solution. The mixtures were shaken (24 h) until equilibrium was reached.

2.6. Effect of pH

To examine the effect of pH on the fluoride ion uptake by HAP, initial pH values were adjusted to 2.6, 4.6, 7.1, 8.9 and 11.5 by adding 0.1 M HCl or NaOH. These values were periodically measured and readjusted until they were constant (72 h). All pH measurements were performed with a pH STAT Controller MeterLab PHM 290.

2.7. Effect of fluoride concentration

Equal masses of HAP were put into contact with solutions of different concentrations of fluoride-ion solutions (from 2 to

20 mg L⁻¹). The mixtures were shaken for 24 h at room temperature.

2.8. Desorption experiments

A sample of HAP was shaken with a 20 mg F⁻ L⁻¹ solution for 24 h, using the same solid/liquid ratio as in the sorption experiments and the highest fluoride concentration investigated in Section 2.7. The liquid was discarded and the solid dried at 60 °C. Portions of 0.075 g of this solid were put into contact for 48 h with 25 mL of (A) a hydrochloric acid solution of pH=3 ($[Cl^-] = 35 \text{ mg L}^{-1}$); (B) a 0.1 M sodium chloride solution of pH ca. 6 ($[Cl^-] = 3550 \text{ mg L}^{-1}$) and (C) a sodium hydroxide solution of pH=10.4. After shaking, the samples were centrifuged and decanted and the fluoride ions were analyzed in the liquid phases as described in Section 2.3.

3. Results and discussion

3.1. Sorbent characterization

The X-ray powder diffraction pattern of the HAP is shown in Fig. 1. This diffractogram was identical to the pattern JCPDS 00-009-0432 – hydroxyapatite – $Ca_5(PO_4)_3(OH)$. The synthesized compound was crystalline and its structure did not change after fluoride sorption.

3.2. Sorption kinetics

Fig. 2 shows the kinetic sorption behavior of fluoride ions by HAP. The sorption rate was fast at the beginning of the process, and then it decreased until equilibrium was reached in about 16 h. Equilibrium times lower than 100 min have been reported for this system [9–11], but it is clear in some cases that the equilibrium was not completely reached. Fan et al. [12] found that equilibrium was not reached in a shaking time of 150 min because the sorption was still increasing. This different behavior could be attributed to experimental conditions such as more vigorous mixing or lower initial concentrations.

The fluoride sorption at equilibrium by HAP was $1.534 \pm 0.001 \text{ mg F}^- \text{ g}^{-1} \text{ HAP}$ ($pH_{eq} = 7.25 \pm 0.01$), which was about

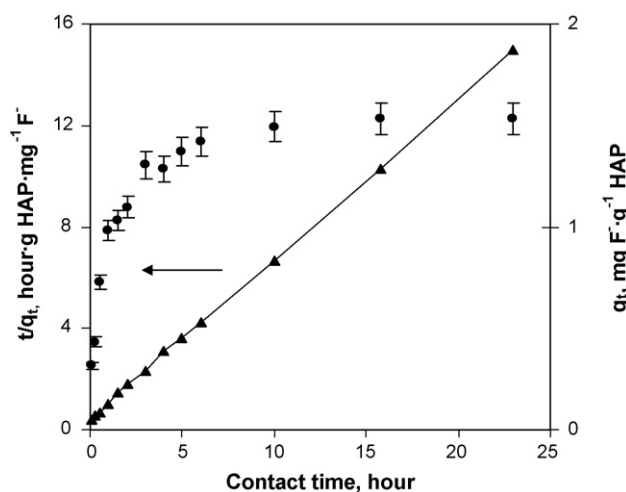


Fig. 2. Fluoride ions sorption from aqueous solution by hydroxyapatite as a function of time (circles). Kinetic pseudo-second order model applied to the fluoride ions sorption from aqueous solutions by hydroxyapatite as a function of time (triangles).

5 times higher than the values reported for the hydroxalite-like compounds of Al–Mg, Al–Co and Al–Ni [7].

The data were fitted to kinetic models (Lagergren, Elovich and pseudo-second order models) by linear regression analysis.

3.2.1. Lagergren first-order model [16]

This model is represented by the following equation:

$$q_t = q_e(1 - e^{-Kt}) \quad (2)$$

where q_t (mg g^{-1}) is the amount of fluoride ions sorbed by HAP at time t (h); q_e (mg g^{-1}) is the amount of fluoride ions sorbed by HAP at equilibrium and K_t (h^{-1}) is the Lagergren rate constant.

The linear form of Eq. (1) can be represented as:

$$\ln\left(1 - \frac{q_t}{q_e}\right) = -Kt \quad (3)$$

The correlation coefficient (Table 1) showed that the experimental data were not well fitted to this model; the calculated Lagergren rate constant is given in Table 1.

3.2.2. 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 [17]. This model is represented in its linear form by the following equation:

$$q_t = \frac{1}{b} \ln(ab) + \frac{1}{b} \ln t \quad (4)$$

where q_t (mg g^{-1}) is the amount of fluoride ions sorbed by HAP at time t (h); a ($\text{mg g}^{-1} \text{h}^{-1}$) is the sorption constant of the fluoride ions and b (g mg^{-1}) is the desorption constant of the fluoride ions.

The equation and the values of the corresponding parameters are included in Table 1. However, the correlation coefficient showed that the experimental data were not well fitted to the model.

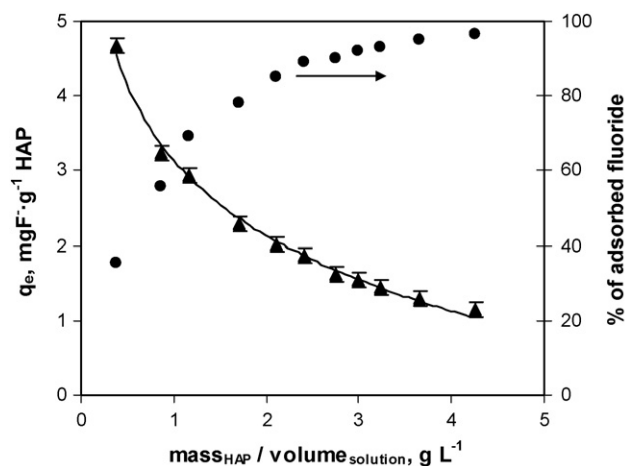


Fig. 3. Effect of the sorbent dosage on the fluoride ions sorption from aqueous solutions by hydroxyapatite. Circles: percentage of adsorbed F^- . Triangles: amount of fluoride ions sorbed at equilibrium ($\text{mg F}^- \text{g}^{-1}$ HAP). The equation of the line is the following: $q_e = -3.3(\pm 0.2) \times (\ln X) - 2.2(\pm 0.2)$; $R^2 = 0.996$.

3.2.3. Pseudo-second order model [18]

The linear form of the model can be represented by the following equation:

$$\frac{t}{q_t} = \frac{1}{Kq_e^2} + \frac{t}{q_e} \quad (5)$$

where K ($\text{g mg}^{-1} \text{h}^{-1}$) is the constant of pseudo-second order; q_t (mg g^{-1}) is the amount of fluoride ions sorbed by HAP at time t (h) and q_e (mg g^{-1}) is the amount of fluoride ions sorbed by HAP at equilibrium.

The experimental data were well fitted to this model; Fig. 2 shows the linear fitting of the experimental results whose equation and corresponding parameters are included in Table 1. The calculated q_e value, as a parameter of the pseudo-second order model, was $1.56 \text{ mg F}^- \text{g}^{-1}$ HAP, which was quite similar to the experimental one ($1.53 \text{ mg F}^- \text{g}^{-1}$ HAP).

The pseudo-second order model is based on the assumption that the rate-limiting step may be the process of chemisorption involving valence forces through sharing or exchange of electrons between sorbent and sorbate. Although the experimental data could be fitted to other equations, the best fit was obtained with the pseudo-second order, which is generally applied to heterogeneous materials involving chemical reactions.

3.3. Effect of the sorbent dosage

The sorption capacities of HAP for fluoride ions decreased with the increase of the sorbent dosage from 0.01 to 0.1 g of HAP. Fig. 3 shows the fluoride ions sorption capacities versus sorbent dosage ($\text{mass}_{\text{HAP}}/\text{volume}_{\text{solution}}$) at $\text{pH}_{\text{eq}} = 7.5 \pm 0.1$. The maximum sorption capacity was found by using 0.01 g of hydroxyapatite ($4.7 \text{ mg F}^- \text{g}^{-1}$ HAP). Similar behavior was reported elsewhere, but a lower sorption capacity was found [11], which was probably due to shaking times shorter than the time required to reach sorption

Table 1
Kinetics models applied to experimental data.

Models	Equations	Parameters
Lagergren first-order ^a	$\ln(1 - q_t/q_e) = -0.48(\pm 0.03)$; $R^2 = 0.94$	$K_t = 0.48 \text{ h}^{-1}$
Elovich	$q_t = 0.25(\pm 0.03) \times \ln t + 0.90(\pm 0.06)$; $R^2 = 0.96$	$a = 7.14 \text{ mg g}^{-1} \text{h}^{-1}$ $b = 3.54 \text{ mg g}^{-1} \text{h}^{-1}$
Pseudo-second order	$t/q_t = 0.631(\pm 0.009) \times t + 0.44(\pm 0.08)$; $R^2 = 0.9996$	$K = 0.91 \text{ g mg}^{-1} \text{h}^{-1}$ $q_e = 1.56 \text{ mg g}^{-1}$

^a $q_e (t \geq 16 \text{ h}) = 1.534 \pm 0.001 \text{ mg g}^{-1}$.

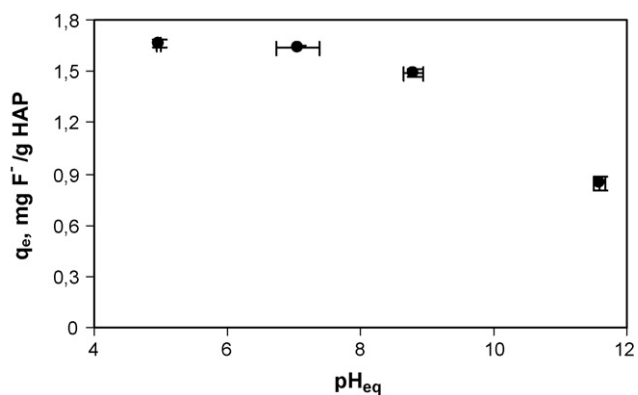


Fig. 4. Effect of pH on the fluoride ions sorption from aqueous solutions by hydroxyapatite.

equilibrium or due to other properties of the materials such as lower specific surface areas, higher crystallinity or different composition. The sorption was not proportional to the sorbent dosage. The equation of the best fitting of experimental data of q_e is given in the caption of Fig. 3, in which the percentages of adsorbed fluoride anions are also indicated. The efficiency of fluoride removal increased with the increase of the sorbent dose because of the presence of a greater number of active sites [9,10]. The maximum fluoride removal of $96 \pm 1\%$ was obtained using 0.1 g of HAP.

3.4. Effect of pH

Solution pH is an important parameter that controls sorption process, because of the ionization of surface functional groups and the alteration of the solution composition. Fig. 4 shows the variation of fluoride ion sorption by HAP at various pH_{eq} values. According to this figure, the pH_{eq} interval for maximum sorption ($1.65 \pm 0.02 \text{ mg F}^- \text{ g}^{-1} \text{ HAP}$) was between 5 (pH_{initial} = 4.7) and 7.3 (pH_{initial} = 7.1) with a shaking time of 72 h. This value is quite similar to the value given above for shaking times between 16 and 23 h ($1.534 \pm 0.001 \text{ mg F}^- \text{ g}^{-1} \text{ HAP}$; pH_{initial} ca. 6 and pH_{eq} = 7.25 ± 0.01).

Gao et al. [10,11] and Sundaram et al. [9] reported that the maximum fluoride removal by hydroxyapatite was reached at pH_{initial} = 2 and showed a gradual decreasing trend with the increase of pH_{initial}, but pH_{eq} was not measured. They reported, moreover, that the point of zero charge value of HAP samples varied from 4.35 to 7.8, attributing the higher fluoride removal in the acid medium to the attraction forces between positively charged sorbent surface and the negatively charged fluoride ions and to the repulsion between the negatively charged surface and negatively charged fluoride in the alkaline medium. However, in the present study it was found that the maximum retention of fluoride ions is at pH_{eq} values higher than 5 and this is due to the variation of pH during the sorption process, which could be attributed to the fluoride sorption, as discussed below. It was observed that pH increases during the contact time, most notably for acid pH_{initial}. For the experiments at pH_{initial} = 4.6 it changed to 8.3 after 24 h, and after 48 h the pH was 5.2; later it was constant at 4.6. When pH_{initial} was 2.6, it changed to 6.8 after 24 h and after being adjusted again, the sorbent was dissolved in a great proportion, pH_{final} being 2.8. For experiments with pH_{initial} = 7.1 the variation of pH was less notable: it was 8.3 after 24 h and was kept at 7.1 between 48 and 72 h. For pH_{initial} 8.9 and 11.5, no changes were observed during contact time.

According to the species-distribution diagram [19], hydroxyapatite forms soluble species (Ca^{2+} and $\text{CaH}_2\text{PO}_4^+$) in acid aqueous solutions (pH < 4) whereas at pH > 4 only the insoluble $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ are present. Sorbent dissolution

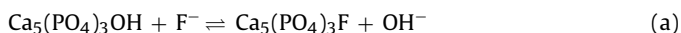
Table 2

Sorption models applied to experimental data.

Models	Equation	Parameters
Langmuir	$q_e = \frac{3.5 \times 1.6 \times C_e}{1 + 1.6 \times C_e}$; $R^2 = 0.94$	$q = 3.5 \text{ mg g}^{-1} b = 1.6 \text{ L mg}^{-1}$
Freundlich	$q_e = 1.9 \times C_e^{1/3.5}$; $R^2 = 0.994$	$K_f = 1.9 \text{ L g}^{-1}$ $n = 3.5$

would be the reason for the high pH increase for pH_{initial} = 2.6 whereas for the $4.6 < \text{pH}_{\text{initial}} < 7.1$, the increase could be attributed to fluoride sorption. For pH_{initial} 8.9 and 11.5, sorption decreased and this behavior could be attributed to the presence of OH⁻ ions that may compete with F⁻ ions for the sorption sites in the sorbent material.

Since the stability constant of the fluoroapatite ($\log K = 54.6$) is higher than that of the hydroxyapatite ($\log K = 40.4$) [19], the chemical sorption of fluoride may be explained by the following reaction:



Moreover, according to the species-distribution diagram, fluoroapatite is formed between pH 5 and 10 whereas hydroxyapatite is the predominant species at pH > 7.

3.5. Sorption isotherm models

Equilibrium studies were carried out in order to determine the optimum conditions for the maximum fluoride removal by the HAP. The data obtained were fitted to the Langmuir and Freundlich models [20,21] in order to describe the fluoride ions sorption behavior by hydroxyapatite. The data were fitted to isotherm models by a nonlinear regression analysis by using the software Statistica 6.0.

3.5.1. 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:

$$q_e = \frac{qbC_e}{1 + bC_e} \quad (6)$$

where q (mg g^{-1}) is the amount of fluoride ions sorbed per unit weight of HAP in forming a complete monolayer on the surface; q_e (mg g^{-1}) is the total amount of fluoride ions sorbed per unit weight of HAP at equilibrium; C_e (mg L^{-1}) is the concentration of the fluoride ions in the solution at equilibrium and b is a constant related to the energy or net enthalpy of sorption.

The experimental data after the sorption of fluoride ions by hydroxyapatite were fitted to this isotherm model, the results being shown in Table 2.

Sorption capacity gives the amount of sorbate for complete monolayer coverage, representing the maximum sorption capacity of the sorbent. Many studies have been published on this subject and it is difficult to compare the present results with those of the literature because the experimental conditions are different. For example, the sorption capacities for fluoride ions have been reported higher than those obtained in this study for hydroxyapatite [12] and for the nano-hydroxyapatite/chitin composite [15] and lower for fluor spar, activated quartz, calcite and quartz [12], magnesium, nickel, and cobalt calcined hydroxalite-like compounds [6], and nano-hydroxyapatite [9].

In order to determine the feasibility of the process, the essential characteristics of the Langmuir isotherm can be expressed in terms

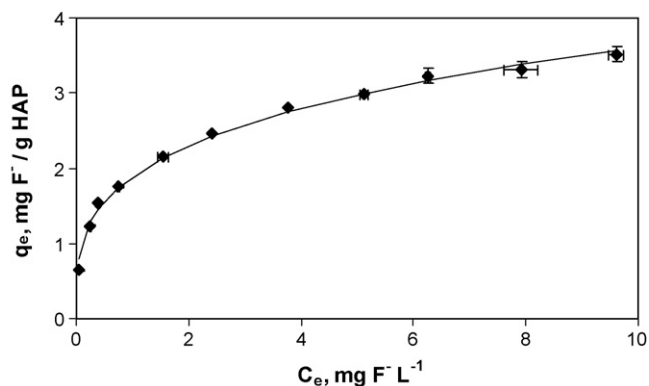


Fig. 5. Freundlich isotherm model applied to the fluoride ions sorption from aqueous solutions by hydroxyapatite.

of a dimensionless constant or separation factor, R_L [9]:

$$R_L = \frac{1}{1 + bC_0} \quad (7)$$

where b is the Langmuir isotherm constant (see Table 2) and C_0 is the initial concentration of fluoride (mg L^{-1}). The values of R_L calculated according to Eq. (7) were between 0.24 and 0.03 for C_0 from 2 to 20 mg L^{-1} . These R_L values lying between 0 and 1 indicated favorable conditions for sorption.

3.5.2. Freundlich model

This empirical model can be applied to a non-ideal sorption on heterogeneous surfaces as well as to a multilayer sorption and can be expressed by the following equation [5]:

$$q_e = K_f C_e^{1/n} \quad (8)$$

where q_e (mg g^{-1}) is the total amount of fluoride ions sorbed per unit weight of HAP at equilibrium; C_e (mg L^{-1}) is the concentration of the fluoride ions in the solution at equilibrium; K_f is the equilibrium constant indicative of sorption capacity and n is an empirical constant.

The Freundlich model has been derived by assuming an exponentially decaying sorption site energy distribution. Fig. 5 shows the experimental data fitted to this model, the equation and corresponding parameters being shown in Table 2. The value of $1/n$ (0.28) lying between 0.1 and 1.0 and that of n (3.5) lying in the range 1–10 both confirmed the favorable conditions of sorption [9]; they implied, as well, a heterogeneous surface structure with a minimum interaction between the sorbed atoms [22]. The experimental data were very well fitted to this model ($R^2 = 0.994$), indicating that the sorbent surface is heterogeneous. This is in good agreement with the results given above referring to the pseudo-second order kinetics.

3.6. Desorption

The percentages of fluoride desorption from HAP were the following: 2% for both hydrochloric acid solution of pH 3 and 0.1 M sodium chloride of pH ca. 6 and 25% for the sodium hydroxide of pH 10.4. The pH_{eq} were: 6, 7.7 and 10, respectively. For the first two cases initial pH increased and independently of the chloride ion concentrations no desorption was virtually observed. These results agreed with the results [15] on the effects of other anions in the sorption capacity of hydroxyapatite/chitin for fluoride ions since it was found that sulfate, nitrate and chloride ions did not interfere with the fluoride sorption. Desorption was evident even if not complete with the alkaline solution, and in this case the pH decreased. This behavior suggested that fluoride ions may be

replaced by hydroxyl anions; this is supported by the results found on the effect of pH as discussed above. However, the details on desorption process need to be further investigated.

4. Conclusions

The pseudo-second order model described the fluoride kinetic sorption processes by hydroxyapatite. Therefore, the rate-limiting step may be chemisorption involving valence forces through sharing or exchange of electrons between sorbent and sorbate.

The effect on the sorbent dosage ($\text{mass}_{\text{HAP}}/\text{volume}_{\text{solution}}$) in the sorption system was significant. The higher efficiency was found by using 0.01 g of HAP and 25 mL of solution ($4.7 \text{ mg F}^{-1} \text{ g}^{-1} \text{ HAP}$); whereas with 0.1 g of HAP and 25 mL of solution $96 \pm 1\%$ of fluoride was removed. The maximum sorption of fluoride ions was in the pH range between 5 and 7.3, when the insoluble $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ exchanged OH^{-} for F^{-} .

The Freundlich model described the sorption isotherm process. This fact indicated that the sorbent is heterogeneous and that the sorption reaction followed the pseudo-second order kinetics.

An alkaline solution of pH = 10 could partially remove fluoride ions from hydroxyapatite.

According to these results hydroxyapatite is a potential material that could be used for the treatment of water contaminated with fluoride ions.

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References

- [1] L. Lv, J. He, M. Wey, X. Duan, Kinetic studies on fluoride removal by calcined layered double hydroxides, *Ind. Eng. Chem. Res.* 45 (2006) 8623–8628.
- [2] K. Othmer, *Encyclopedia of Chemical Technology*, vol. 10, 3rd ed., Wiley-Interscience, New York, 1980.
- [3] D.P. Das, J. Das, K. Parida, Physicochemical characterization and sorption behavior of calcined Zn/Al hydrotalcite-like compound (HTLc) towards removal of fluoride from aqueous solution, *J. Colloid Interface Sci.* 261 (2003) 213–220.
- [4] W.W. Choi, K.Y. Chen, The removal of fluoride from waters by sorption, *J. AWWA* 71 (1979) 562–570.
- [5] L. Liang, J. He, M. Wei, D.G. Evans, Z. Zhou, Treatment of high fluoride concentration water by MgAl–CO₃ layered double hydroxides: kinetic and equilibrium studies, *Water Res.* 41 (2007) 1534–1542.
- [6] M.L. Jiménez-Núñez, M.T. Olguín, M. Solache-Ríos, Fluoride removal from aqueous solutions by magnesium, nickel and cobalt calcined hydrotalcite-like compounds, *Sep. Sci. Technol.* 42 (2007) 3623–3639.
- [7] M.L. Jiménez-Núñez, M. Solache-Ríos, M.T. Olguín, Fluoride sorption from aqueous solutions and drinking water by magnesium, cobalt and nickel hydrotalcite-like compounds in batch and column systems, *Sep. Sci. Technol.* 45 (2010) 786–793.
- [8] G.L. He, S.R. Cao, Assessment of fluoride removal from drinking water by calcium phosphate systems, *Fluoride* 29 (1996) 212–216.
- [9] C.S. Sundaram, N. Viswanathan, S. Meenakshi, Defluoridation chemistry of synthetic hydroxyapatite at nano scale: equilibrium and kinetic studies, *J. Hazard. Mater.* 155 (2008) 206–215.
- [10] S. Gao, R. Sun, Z. Wei, H. Zhao, H. Li, F. Hu, Size-dependent defluoridation properties of synthetic hydroxyapatite, *J. Fluorine Chem.* 130 (2009) 550–556.
- [11] S. Gao, J. Cui, Z. Wei, Study on the fluoride sorption of various apatite materials in aqueous solution, *J. Fluorine Chem.* 130 (2009) 1035–1041.
- [12] X. Fan, D.J. Parker, M.D. Smith, Adsorption kinetics of fluoride on low cost materials, *Water Res.* 37 (2003) 4929–4937.
- [13] V.E. Badillo-Almaraz, J.A. Flores, H. Arriola, F.A. López, L. Ruiz Ramírez, Elimination of fluoride ions in water for human consumption using hydroxyapatite as a sorbent, *J. Radioanal. Nucl. Chem.* 271 (2007) 741–744.
- [14] L.E.L. Hammari, A. Laghzizil, P. Barboux, K. Lahlil, A. Saoiabi, Retention of fluoride ions from aqueous solution using porous hydroxyapatite: structure and conduction properties, *J. Hazard. Mater.* 114 (2004) 41–44.
- [15] C.S. Sundaram, N. Viswanathan, S. Meenakshi, Fluoride sorption by nano-hydroxyapatite/chitin composite, *J. Hazard. Mater.* 172 (2009) 147–151.
- [16] T. Mathialagan, T. Viraraghavan, Adsorption of cadmium from aqueous solutions by vermiculite, *Sep. Sci. Technol.* 38 (2003) 57–76.
- [17] R. Cortés-Martínez, V. Martínez-Miranda, M. Solache-Ríos, I. García-Sosa, Evaluation of natural and surfactant-modified zeolites in the removal of cadmium from aqueous solutions, *Sep. Sci. Technol.* 39 (2004) 2711–2730.

- [18] Y.S. Ho, J.C.Y. Ng, G. McKay, Removal of lead (II) from effluents by sorption on peat using second-order kinetics, *Sep. Sci. Technol.* 36 (2001) 241–261.
- [19] I. Puigdomenech, Program MEDUSA (Make Equilibrium Diagrams Using Sophisticated Algorithms), 1999, <http://www.kemi.kth.se/medusa/>.
- [20] G. Bitton, *Formula Handbook for Environmental Engineers and Scientist*, John Wiley & Sons, New York, NY, 1998.
- [21] Y.S. Ho, G. McKay, Application of kinetics models to the sorption of copper (II) on to peat, *Adsorpt. Sci. Technol.* 20 (2002) 797–815.
- [22] M.M. Abou-Mesalam, Applications of inorganic ion exchangers. II. Adsorption of some heavy metals ions from their aqueous waste solution using synthetic iron (III) titanate, *Adsorption* 10 (2004) 87–92.