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Defluoridation Performance Comparison of Nano-hydrotalcite/Hydroxyapatite Composite with Calcined Hydrotalcite and Hydroxyapatite

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Abstract Fluoride retention from water is nowadays a serious health problem. This study reports the potential of a newly developed nano-hydrotalcite/hydroxyapatite (n-HT/HAp) composite, and its constituent materials, hydrotalcite (HT) and hydroxyapatite (HAp), in fluoride removal. Calcined hydrotalcites (cHT) showed a remarkable fluoride removal ability from water through memory effect mechanism. HAp, the mineral compound of bones, adsorbs fluoride as well but through ion exchange mechanism. Fluoride substitutes hydroxyls to produce fluorapatite. Among the tested calcined hydrotalcites, cHT Mg-Al (4:1) sample, composed of magnesium divalent cation to aluminum ratio of 4, was identified as the best-performing hydrotalcite. The differences among cHT samples in fluoride removal capacities are attributed to hydrotalcite composition as well as to particle size. The performance of these materials is compared with that of n-HT/HAp composite whose main features are basic acidic material and not yet tested in fluoride retention. Interestingly, n-HT/HAp also performs best, 98 %, slightly higher than the best cHT Mg-Al (4:1) sample with 97 % fluoride removal efficiency from such a high initial fluoride solution of 20 mg/L at 10 g/L dose, yielding the final residual fluoride concentrations of 0.36 and 0.6 mg/L, respectively; both meet the WHO standard for drinking water. Besides, the uncalcined hydrotalcite constituent added virtue to the advantage of using n-HT/HAp in fluoride removal as the efficiency was compensated by the nanometric size of the hydrotalcite particle.

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1 Introduction

Fluoride affects human health, either positively or negatively. Fluoride at a relative low level seems to be beneficial in human body for the calcification of dental enamel and maintenance of healthy bones. Furthermore, often, fluoride is added to drinking water up to approximately 1.0 mg/L to prevent dental decay. However, excessive fluoride intake can result in dental and skeletal fluorosis and lesion of the endocrine glands, thyroid, liver, and other organs (Chinoy et al. 1991; Abe et al. 2004; Hichour et al. 2000). According to WHO guidelines, the acceptable fluoride concentration in drinking water must be in the range 0.5 to 1.5 mg/L (The World

Health Organization 1996). Despite its frequent high fluoride content, groundwater is widely distributed and more than 260 million people all over the world consume drinking water with a fluoride concentration higher than 1.0 mg/L. The majority of these people live in tropical regions, 14 countries in Africa, eight in Asia, and six in the Americas (The World Health Organization 1984; UNICEF's Position on Water Fluoridation 2014), and many of them are confronted with problems due to endemic fluorosis, either dental or skeletal. For instance in the Rift Valley (Ethiopia) as well as in the north of Mexico, the fluoride content may reach as much as 36 mg/L (Kloos and Tekle Haimanot 1999; Tekle-Haimanot et al. 1995) and 8 mg/L (Díaz-Barriga et al. 1997; Galicia Chacón et al. 2011), respectively. Thus, the problem is severe and needs immediate solution. At present, a series of technologies exists to alleviate or at least to minimize the effect of fluoride problem. Since more than 100 years (Mullen 2005), a large number of materials and methods have been proposed. The methods may be classified as chemical precipitation, ion exchange, adsorption, and membrane-based mechanisms. However, most of them present disadvantages which may be summarized as follows: Chemical precipitation requires large dosage of chemicals, appropriate safety precautions in handling and disposal besides its low treatment efficiency. In the case of ion exchange, the presence of other anions such as sulfate, phosphate, and bicarbonate results in ionic competition, it is relatively costly, and treated water sometimes has a low pH and high levels of chloride. Finally, membrane-based mechanisms require skilled manpower, it is pricy, and it may not be suitable for water with high salinity and high total dissolved solids (TDS). Instead, adsorption processes are attractive due to their effectiveness, convenience, easy availability, ease of operation, and economical as well as environmental low impact (Jagtap et al. 2012).

In this regard, several adsorbents have been reported in the literature, out of which hydroxyapatite (HAp) is of great importance because of the similarity in chemical composition with the human bone and the potential for fluoride retention. Many researchers studied on HAp-based adsorbents and indicated their potential for fluoride removal (Hammari et al. 2004; Badillo-Almaraz et al. 2007; Jiménez-Reyes and Solache-Ríos 2010; Mourabet et al. 2012). Although HAp has shown an excellent potential towards the retention of fluoride from water, current research is applied in an attempt to further

enhance its fluoride-removal capacity through the production of nanostructured HAp materials, which in recent years have gained much attention due to their unique properties. In this context, also a significant number of nano-hydroxyapatite (n-HAp) adsorbents have been synthesized and studied (Sundaram et al. 2008a; Gao et al. 2009; Poinern et al. 2011; Sternitzke et al. 2012; Zhang et al. 2012). In fact, this nanostructured HAp showed a much higher defluoridation capacity. However, the potential application of these materials in the field is not easily achievable, due to the cost associated with their production and significant pressure drops during filtration owing to the small particle size. To overcome such permeability problems and at the same time utilize the advantages of n-HAp, it is essential to prepare adsorbents based on n-HAp in a usable form by combining them with other high-surface materials (Sundaram et al. 2009; Feng et al. 2012; Pandi and Viswanathan 2014), on which surface the HAp nanoparticles are supported. By having the HAp nanoparticles not free but supported on the external surface of a material with a large particle size, we can avoid pressure drops associated with the nanosize of n-HAp, as well as prevent the potential toxicity typical of nanoparticles and possible sintering (and loss of efficiency) during defluoridation treatments.

In our previous work, we developed the stilbite/hydroxyapatite composite n-HAST for fluoride removal by growing of n-HAp on the surface of natural stilbite zeolite from Ethiopia (Gómez-Hortigüela et al. 2014). The aim of the present study is another option based on the use of HAp as a support material to grow the hydrotalcite nanoparticles (n-HT) on hydroxyapatite (HAp) surface to develop the nano-hydrotalcite/hydroxyapatite composite n-HT/HAp. Detailed defluoridation experimental results including the comparison performance of calcined hydrotalcite (cHT) and HAp are presented.

Hydrotalcites, also known as layered double hydroxides (LDH), are anionic clays with positively charged octahedral hydroxide layers, which are neutralized by interlayer anions and water molecules and which are generally formulated as $[M^{2+}_{1-x}M^{3+}_x(OH)_2](A^{m-})_{x/m}\cdot nH_2O$, where M^{2+} and M^{3+} are di- and tri-valent cations, respectively, A^{m-} is an anion whose charge is $m-$. Magnesium-aluminum hydrotalcite is stable up to 400 °C. It decomposes into a NaCl-type magnesium-aluminum mixed oxide above 400 °C and into MgO and $MgAl_2O_4$ above 800 °C (Sato et al. 1988). It is noteworthy that the NaCl-type magnesium-aluminum mixed

oxide is able to rehydrate and to combine with environmental anions to resume the original hydrotalcite structure. Liang et al. (Liang et al. 2006a, b) among others have already shown that magnesium cHT-like compounds can be used for fluoride removal from aqueous solutions. Hydrotalcites show great performance in fluoride removal when they are previously thermally calcined. The mechanism is known as memory effect (Erickson et al. 2004). The thermal calcination of the hydrotalcites has to be between 300 and 800 °C. In this interval of temperatures, the interlayer water and compensation anions are removed and the resulting compound turns out to be a mixed metal oxide (Wang et al. 2007). The exceptional property of cHT is that when they are exposed to water and a source of anions, the hydrotalcite structure is recovered incorporating anions and water. To maximize the memory effect, the maximum number of anions must be removed during thermal activation. It is therefore important to choose anions that can be easily removed at elevated temperatures forming stable non-toxic decomposition products. Carbonate is an ideal anion for this purpose. As a carbonate containing hydrotalcite decomposes, it releases carbon dioxide and water vapor which are both stable and non-toxic (in low concentration).

Hydroxyapatite (HAp), $Ca_{10}(PO_4)_6(OH)_2$, is a double salt of tri-calcium phosphate and calcium hydroxide, and it is the principal inorganic constituent of the human bones and teeth. Over the past three decades, several aspects of the uptake of fluoride ions by synthetic hydroxyapatite and tooth enamel have been studied (Jiménez-Reyes and Solache-Ríos 2010; McCann 1953; Leach 1959). The surface and composition of hydroxyapatite have a remarkable capacity for retaining fluoride ions from an aqueous solution. This process is governed by solution factors such as fluoride concentration, its pH, the exposure time, the temperature and by the apatite composition and surface, which depend mostly on the Ca/P molar ratio.

Hydrotalcite/hydroxyapatite, n-HT/HAp, composite is an acid-basic solid whose features are due to the interaction of hydroxyapatite and hydrotalcite (Rivera et al. 2009a). The association of hydrotalcite and hydroxyapatite in a single material should present a rather unique fluoride retention behavior. It has to be emphasized that this composite has been recently reported and that it has not been tested in F^- retention (Rivera et al. 2009a, b). In this manuscript, we study the effect of the type and amount of divalent cations (nickel and

magnesium) of hydrotalcites in their defluoridation capacity via the memory effect. Furthermore, we compare them with a newly developed n-HT/HAp composite and with pure hydroxyapatite. A correlation between adsorbent features and F^- retention is established.

2 Materials and Methods

2.1 Adsorbents Preparation

The adsorbents (hydrotalcites, hydroxyapatite, and composite) were synthesized in the Universidad de Puebla, Mexico (Rivera et al. 2009a, b; Fetter et al. 1997). The synthesis processes are described as follows:

Hydrotalcite Samples The Mg/Al and Ni/Mg-hydrotalcite samples were synthesized from water solutions, 2.5 M of $Mg(NO_3)_2 \cdot 9H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, and $Al(NO_3)_3 \cdot 9H_2O$ (Aldrich 99, 99, and 98 %, respectively). A second aqueous solution, 1.86 M, was prepared with NaOH (Aldrich 98 %). The precipitation was carried out adjusting the flow of each solution to maintain a pH constant at 9. The solution amounts were adjusted to correspond to Mg/Al of 3:1 and 4:1 or Ni/Al molar ratios of 2:1 and 3:1. The resulting gels were treated in a microwave autoclave (MIC-I, Sistemas y Equipos de Vidrio S.A. de C.V.) for 10 min operating at 2.45 GHz. The microwave irradiation power was 200 W and the temperature was fixed at 80 °C. The solids were recovered by decantation and washed several times with distilled water until the residual solution reached a pH value of 8. The solids were, then, dried in an oven at 70 °C for 24 h. Part of these samples were calcined in air at 500 °C for 8 h to be used in the fluoride removal experiments.

Hydroxyapatite Sample This sample was prepared from a 0.8 M (Baker, 99 %) H_3PO_4 solution dropped in a 2 M (Baker, 98 %) $Ca(OH)_2$ solution adjusting the flow in such a way that the pH was maintained constant and equal to 11.5. The amount of reactants was adjusted to have a molar ratio Ca/P of 1.67. The mixture was treated in a microwave autoclave at the same conditions as described above. The sample was washed with distilled water until the waste water reached a pH 10. The solids were recovered by decantation and dried in an oven at 70 °C for 24 h.

Nano-hydrotalcite/Hydroxyapatite Composite The same solutions used to synthesize a Mg/Al 3:1 hydrotalcite sample were used to synthesize a composite by dropping those solutions over a slurry of a previously precipitated and irradiated hydroxyapatite. The nominal weight ratio hydrotalcite/hydroxyapatite was 1. The resulting mixture was submitted to microwave irradiation for 10 min as previously. The solids were washed up to pH 10, recovered by decantation, and dried at 70 °C.

2.2 Characterization Method

Powder X-ray diffraction (XRD) patterns were collected with a X'Pert Pro PANalytical equipment.

2.3 Fluoride Solution Preparations

A 0.1 mol L^{-1} sodium fluoride stock solution was prepared by dissolving 2.0995 g of anhydrous sodium fluoride (99.0 % NaF, SIGMA-ALDRICH, Germany) in 0.5-L round-bottom flask with deionized water from which the samples 5 and 20 mg/L for batch adsorption studies were prepared by appropriate dilution. The total ionic strength adjusting buffer (TISAB II) was prepared by dissolving 58.5 g of sodium chloride, 57 mL of glacial acetic acid, 7 g of tri-sodium citrate, and 2 g cyclohexanediamine tetraacetic acid (CDTA) in 0.5-L round-bottom flask. The pH was adjusted to 5.0–5.5 with a solution of 5 M NaOH, which was then diluted to 1 L in round-bottom flask with deionized water.

2.4 Batch Adsorption Studies

The adsorption was studied using an adsorbent dose of either 5 or 10 g/L and two initial fluoride solutions, 5 and 20 mg/L, that were chosen based on the most reported values, 1.5 up to 11.6 mg/L, from drinking water samples in the Rift Valley (Ethiopia) (Reimann et al. 2003). The desired weight of the adsorbent was added to the desired fluoride solution in a plastic bottle. After thoroughly stirring in a magnetic stirrer for 20 h at room temperature, the samples were filtered. After filtration, a total ionic strength adjusting buffer (TISABII) was added to the filtrate in 1:1 ratio in order to maintain ionic strength and the pH, and eliminate the interference effect of complexing ions. Finally, the equilibrium fluoride concentration was determined using A pH/ISE meter (CRISON GLP 2^2, China) equipped with a

combination fluoride-selective electrode (CRISON Code 96 55). The pH was measured with a pH/ion meter (CRISON GLP 2^2) using an unfilled pH glass electrode. The residual fluoride concentration was measured according to the procedure described in the instrument manual. The electrode was calibrated prior to each experiment over a concentration range of interest. All experiments were performed in duplicate and mean values are reported. All measurements were made at room temperature (23 ± 2 °C). The retention percentage and defluoridation capacity were calculated as follows:

$$\text{Retention percentage}(\%) = \frac{[F^-]_i - [F^-]_f}{[F^-]_i} \times 100$$

$$\text{Defluoridation capacity}(DC) = \frac{[F^-]_i - [F^-]_f}{\text{Adsorbent Dose}}$$

where $[F^-]_i$ = initial fluoride concentration and $[F^-]_f$ = final fluoride concentration.

3 Results and Discussion

The fluoride retention of various hydrotalcite samples was analyzed. The main difference among the studied samples is the type of divalent metal and the ratio between the divalent and trivalent metal in each hydrotalcite; those parameters determine the amount of retained fluoride. Samples with nickel and magnesium as divalent cations, and at ratios of Ni-Al (2:1), Ni-Al (3:1), Mg-Al (3:1), and Mg-Al (4:1), were tested for fluoride removal using the memory effect mechanism. In all cases, the samples were calcined at 500 °C for 8 h prior to the adsorption tests. Figure 1 displays the fluoride retention (%) and defluoridation capacity (DC) of the cHT samples with different composition. Figure 1a corresponds to an initial fluoride concentration of 20 mg/L and Fig. 1b to 5 mg/L, both at an adsorbent dose of 10 g/L. If the initial fluoride concentration is 20 mg/L, the performance of the cHT samples Ni-Al (2:1), Ni-Al (3:1), Mg-Al (3:1), and Mg-Al (4:1) reaches 58, 82, 95, and 97 % of fluoride retention, respectively. Thus, the fluoride retention in hydrotalcites is clearly determined by the type of divalent metal cation as well as by the divalent to trivalent metal ratio. Samples Ni-Al (3:1) and Mg-Al (3:1) only differ in their divalent metal but the fluoride retention increases 13 %. cHT having the same divalent cation but in a higher amount show an increase of 24 % in the case of Ni:Al cHT, and of only
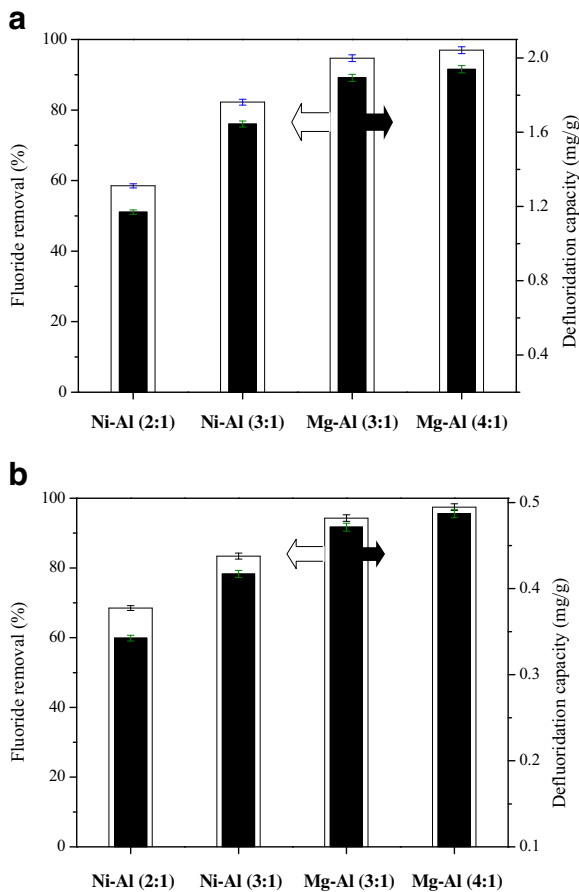
Fig. 1 Fluoride removal percentage retention (%) and defluoridation capacities (DC) of calcined hydrotalcites (cHT) with different composition at an initial fluoride concentration of **a** 20 mg/L and **b** 5 mg/L at an adsorbent dose of 10 g/L

2 % in the Mg:Al system. Such a different behavior in the two systems still remains unclear.

Nevertheless, Mg-Al cHT samples were better than Ni-Al cHT samples due to the higher atomic weight of Ni compared to Mg, as already shown in previous works (Jiménez-Núñez et al. 2007). The advantage of the smaller atomic weight is that atoms are fully dispersed in the hydrotalcite structure. The hydrotalcite which has the best fluoride retention percentage among the four tested samples is Mg-Al (4:1). Comparison of this sample to Mg-Al (3:1) sample having the same divalent cation but in a lower amount shows a slight increase in fluoride removal possibly due to the increase in the surface positive charge caused by the excess amount of Mg than in Mg-Al (3:1), which is neutralized through adsorption of anions; thus it is not surprising that it retains more fluoride. Still, Jiménez-Núñez et al. found

that the Ni-Al cHT presented a higher fluoride sorption than the corresponding Mg-Al sample; the obtained capacity was 1.202 mg/g of Ni-Al cHT (Jiménez-Núñez et al. 2007). Such result has to be attributed to a different adsorption mechanism in the case of Ni-Al cHT. Indeed, their X-ray diffraction patterns show that Ni-Al cHT after calcination and being put in contact with the fluoride solution do not present a memory effect, whereas in our case, the XRD patterns of Mg:Al (3:1) cHT sample prove the loss of the typical hydrotalcite structure upon calcination (Fig. 2 dotted line) and the recovery of the hexagonal structure after fluoride removal test (Fig. 2 solid line). Thus the use of Mg instead of Ni provides a better sorbent for fluoride via the memory effect mechanism. Mg:Al (4:1) cHT shows the best defluoridation capacities for 20 mg of F/L (1.94 mg/g), but for the same sample, the defluoridation capacity is reduced around 75 % for 5 mg of F/L (0.49 mg/g), Fig. 1.

In order to justify this effect, the exchange of anions may be described through the following equilibrium: $F^-_{(S)} + A^-_{(HT)} \longleftrightarrow F^-_{(HT)} + A^-_{(S)}$, where (S) means "in solution" and (HT) means "retained into the hydrotalcite", F^- the fluoride anion, and A^- the compensation anion originally in the hydrotalcite. The corresponding equilibrium constant is $K = [A^-_{(S)}] / [F^-_{(S)}]$ which turns out to be for an initial fluoride concentration of 20 mg/L, $K = [A^-_{(S)20}] / (20 - [A^-_{(S)20}])$, and for an initial fluoride concentration of 5 mg/L, it turns out to be $K = [A^-_{(S)5}] / (5 - [A^-_{(S)5}])$.
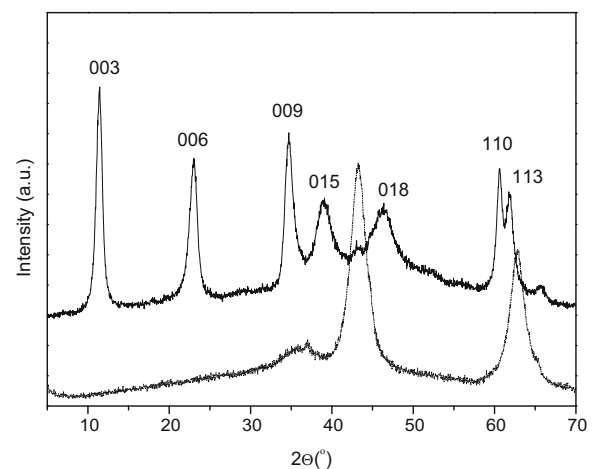

Fig. 2 X-ray diffraction patterns of the cHT Mg:Al (3:1) samples after calcination at 500 °C for 8 h (*dotted line*) and after F removal (*solid line*)

Hence, $[A^-_{(S)20}]/(20-[A^-_{(S)20}])=[A^-_{(S)5}]/(5-[A^-_{(S)5}])$. As $[A^-_{(S)20}]$ and $[A^-_{(S)5}]$ are very small if compared to 20 or 5 mg/L, the previous equation is $([A^-_{(S)20}]/20)=([A^-_{(S)5}]/5)$ which means that $[A^-_{(S)20}]/[A^-_{(S)5}]=4$ in agreement with the experimental observations.

The best cHT sample (MgAl 4:1) was further compared to a pure hydroxyapatite (HAp) and the newly developed composite in which small crystals of n-HT are grown on HAp (n-HT/HAp) (Rivera et al. 2009b; Fetter et al. 1997). In all cases, the fluoride retention percentage increases with the increasing adsorbent dose as observed in Fig. 3 for the initial concentration of 20 and 5 mg of F/L, respectively. The n-HT/HAp composite shows the best defluoridation capacity for $[F]_0 = 20$ mg/L at an adsorbent dose of 5 g/L (3.65 mg/

g), if compared with HAp (3.37 mg/g) or cHT Mg-Al (4:1) (3.54 mg/g) or even with the maximum adsorption capacity of the "excellent ceramic" adsorbent reported by Chen et al. (2010) which for an initial fluoride concentration of 10 mg/L obtain an exchange capacity of 2.16 mg/g (McCann 1953). For an adsorbent dose of 10 g/L in the same initial fluoride concentration, the defluoridation capacities reached 1.94, 1.79, and 1.96 mg/g for cHT Mg-Al (4:1), HAp, and n-HT/HAp samples, respectively. Again, the n-HT/HAp is the best adsorbent. The final residual fluoride concentration was found to be 0.36 mg/L in the case of n-HT/HAp composite as compared with the slightly higher value, 0.6 mg/L, of cHT Mg-Al (4:1) from such a high initial fluoride concentration of 20 mg/L at an adsorbent dose of 10 g/L; in both cases, the WHO standard for drinking water was met very well.

The composite n-HT/HAp presents a synergetic effect between hydrotalcite and hydroxyapatite that can be explained through two mechanisms, a mechanism determined by pH values and another mechanism due to the very small particle size of hydrotalcite particles which favors diffusion. n-HT/HAp is an acidic and basic material as hydroxyapatite is acidic and hydrotalcite is basic. Fluoride adsorption is low at very low and very high pH values, and the best value is between 4 and 8. It seems then that hydrotalcite diminishes locally hydroxyapatite acidity and vice versa hydroxyapatite reduces hydrotalcite basicity; in such conditions F^- retention must be favored in special sites of both hydrotalcite and hydroxyapatite.

The second factor which improves retention is the small particle size obtained for the hydrotalcite supported on hydroxyapatite. Figure 4 describes the X-ray diffraction patterns of n-HT/HAp composite before and after F removal, and HAp for comparison purposes. The profile of the composite is similar to the one of the hydroxyapatite, and the presence of hydrotalcite is envisaged as peaks of low intensity, found at 12° to 13° and 22° (2θ) whose broadness has to be attributed to very small particle sizes.

Therefore, the hydrotalcite crystallites covering the large particles of hydroxyapatite must be nanometrical. Diffusion of fluoride ions to the center of the hydrotalcite particles is then easier and faster. Such scenario is based also on the fact that the sample n-HT/HAp was not calcined previously; therefore, hydrotalcite on the hydroxyapatite support does not retain fluoride through a memory effect; the exchange is a simple ionic exchange. In previous works, using composites
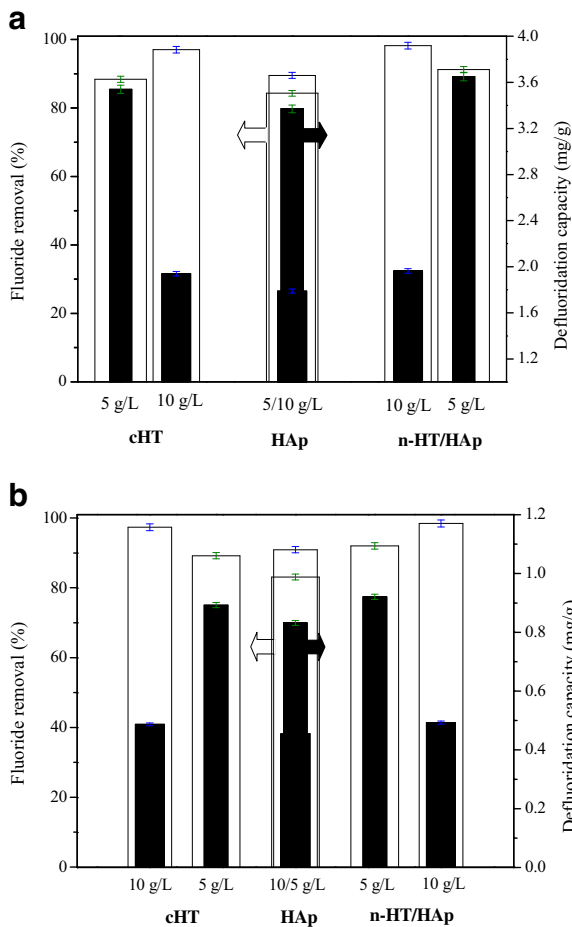

Fig. 3 Fluoride retention percentage of the n-HT/HA composite, and HAp samples compared to cHT Mg-Al (4:1) sample as a function of adsorbent dose with an initial fluoride concentration of **a** 20 mg/L and **b** 5 mg/L
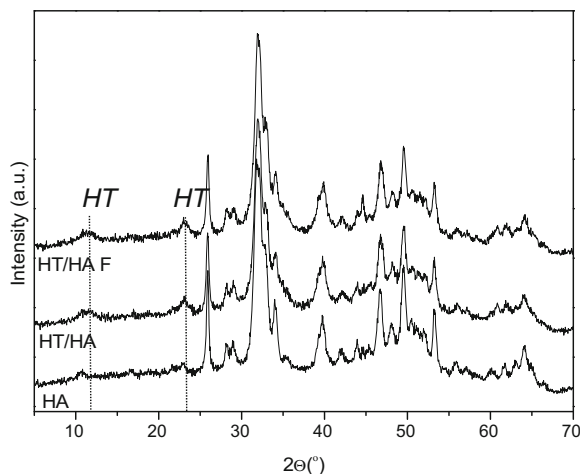
Fig. 4 Comparison of the X-ray diffraction patterns of the pure hydroxyapatite (HAp), composite n-HT/HAp before and after F removal experiment

constituted by nano-hydroxyapatite and chitosan (Sundaram et al. 2008b) or zeolites (Gómez-Hortigüela et al. 2014), or hydrotalcite and chitosan (Viswanathan and Meenakshi 2010), the exceptional fluoride adsorption of these materials is attributed to the small size of hydroxyapatite or hydrotalcite particles and the proposed mechanism is both ion exchange and adsorption.

As stated by Loganathan et al. (2013), there are five mechanisms of retention of F: (1) Van der Waals forces, (2) ion exchange, (3) hydrogen bonding, (4) ligand exchange, and (5) chemical modification of the adsorbent surface. Each mechanism implies different retention strengths, weak for the first two but strong for the third and fourth. The fifth is governed by specific and non-specific adsorption. Hydrotalcites are known to be anionic exchangers; therefore, the strength of the retention is weak and the mechanism is clear (de Roy et al. 2006; Miyata 1983). Instead, in hydroxyapatite, F^- ions are strongly retained through a mechanism of chemical modification (Bengtsson et al. 2009; Christoffersen et al. 1995). Indeed, fluoride ions substitute hydroxyl ions in the apatite structure.

4 Conclusion

The proposed mechanism for fluoride retention by the calcined hydrotalcites is through memory effect as we used a calcined hydrotalcite which primarily contains carbonate ions. Mg gives better performance than Ni and the higher concentrations shows up to 3.53 mg/g

defluoridation capacity. The hydrotalcite/hydroxyapatite composite has a better fluoride retention capacity than hydrotalcite or hydroxyapatite; it retains as much as 98 % in 5 or 20 mg F/L solutions (3.65 mg/g defluoridation capacity). The high fluoride retention of the hydrotalcite/hydroxyapatite composite is attributed mainly to the small particle size of the supported hydrotalcite. Still, the acidic and basic properties of this material guarantee the modulation of pH. For the hydroxyapatite, the mechanism must be the chemical modification of the adsorbate surface to form a layer of fluorapatite.

References

Abe, I., Iwasaki, S., Tokimoto, T., Kawasaki, N., Nakamura, T., & Tanada, S. (2004). *Journal of Colloid and Interface Science, 275*, 35–39.

Badillo-Almaraz, V. E., Flores, J. A., Arriola, H., López, F. A., & Ruiz-Ramírez, L. (2007). *Journal of Radioanalytical and Nuclear Chemistry, 271*, 741–744.

Bengtsson, Å., Shchukarev, A., Persson, P., & Sjöberg, S. (2009). *Langmuir, 25*, 2355–2362.

Chen, N., Zhang, Z., Feng, C., Li, M., Zhu, D., Chen, R., & Sugiura, N. (2010). *Journal of Hazardous Materials, 183*, 460–465.

Chinoy, N. J., Rao, M. V., Narayana, M. V., & Neelakanta, E. (1991). *Reproductive Toxicology, 5*, 505–512.

Christoffersen, J., Christoffersen, M. R., Arends, J., & Leonardsen, E. S. (1995). *Caries Research, 29*, 223–230.

de Roy, A., Forano, C., & Besse, J. P. (2006). Layered double hydroxides: synthesis and post-synthesis modification. In V. Rives (Ed.), *Layered double hydroxides: present and future*. New York: Nova Science Publishers Inc.

Díaz-Barriga, F., Navarro-Quezada, A., Grijalva, M. I., Grimaldo, M., Loyola-Rodríguez, J. P., & Deogracias-Ortiz, M. (1997). *Fluoride, 30*, 233–239.

Erickson, K. L., Bostrom, T. E., & Frost, R. L. (2004). *Materials Letters, 59*, 226–229.

Feng, L., Xu, W., Liu, T., & Liu, J. (2012). *Journal of Hazardous Materials, 221–222*, 228–235.

Fetter, G., Hernández, F., Maubert, M., Lara, V. H., & Bosch, P. (1997). *Journal of Porous Materials, 4*, 27–30.

Galicia Chacón, L., Molina Frechero, N., Oropeza, A., Gaona, E., & Juárez López, L. (2011). *Revista Internacional de Contaminacion Ambiental, 27*, 283–289.

Gao, S., Sun, R., Wei, Z. G., Zhao, H. Y., Li, H. X., & Hu, F. (2009). *Journal of Fluorine Chemistry, 130*, 550–556.

Gómez-Hortigüela, L., Pérez-Pariente, J., Chebude, Y., & Díaz, I. (2014). *RSC Advances, 4*, 7998–8003.

Hammari, L. E. L., Laghzizil, A., Barboux, P., Lahlil, K., & Saoiabi, A. (2004). *Journal of Hazardous Materials, B114*, 41–44.

Hichour, M., Persin, F., Sandeaux, J., & Gavach, C. (2000). *Separation and Purification Technology, 18*, 1–11.

Jagtap, S., Yenkie, M. K., Labhsetwar, N., & Rayalu, S. (2012). *Chemical Reviews, 112*, 2454–2466.

Jiménez-Núñez, M. L., Olguín, M. T., & Solache-Ríos, M. (2007). *Separation Science and Technology, 42*, 3623–3639.

Jiménez-Reyes, M., & Solache-Ríos, M. (2010). *Journal of Hazardous Materials, 180*, 297–302.

Kloos, H., & Tekle Haimanot, R. (1999). Distribution of fluoride and fluorosis in Ethiopia and prospects for control. *Tropical Medicine and International Health, 4*, 355–364.

Leach, S. A. (1959). *British Dental Journal, 106*, 133–142.

Liang, L., Jing, H., Min, W., & Xue, D. (2006a). *Industrial and Engineering Chemistry Research, 45*, 8623–8628.

Liang, L., Jing, H., Min, W., Evans, D. G., & Xue, D. (2006b). *Journal of Hazardous Materials, B133*, 119–128.

Longanathan, P., Vigneswaran, S., Kandasamy, J., & Naidu, R. (2013). *Journal of Hazardous Materials, 248–249*, 1–19.

McCann, H. G. (1953). *Journal of Biological Chemistry, 201*, 247–246.

Miyata, S. (1983). *Clay Minerals, 31*, 305–311.

M. Mourabet, A. El Rhilassi, H. El Boujaady, M. Bennani-Ziatni, R. El Hamri, A. Taitai, J. Saudi Chem. Society (2012). doi: 10.1016/j.jscs.2012.03.003.

Mullen, J. (2005). *British Dental Journal, 199*, 1–4.

Pandi, K., & Viswanathan, N. (2014). *Carbohydrate Polymers, 112*, 662–667.

Poinern, G. E. J., Ghosh, M. K., Ng, Y.-J., Issa, T. B., Anand, S., & Singh, P. (2011). *Journal of Hazardous Materials, 185*, 29–37.

Reimann, C., Bjorvatn, K., Frengstad, B., Melaku, Z., Tekle-Haimanot, R., & Siewers, U. (2003). *Science of the Total Environment, 311*, 65–80.

Rivera, J. A., Fetter, G., Baños, L., Guzman, J., & Bosch, P. (2009a). *Journal of Porous Materials, 16*, 401–408.

Rivera, J. A., Fetter, G., & Bosch, P. (2009b). *Journal of Porous Materials, 16*, 409–418.

Sato, T., Fujita, H., Endo, T., & Shimada, M. (1988). *Solid, 5*, 219–228.

Sternitzke, V., Kaegi, R., Jean-Nicolas, A., Lewin, E., Hering, J. G., & Johnson, C. A. (2012). *Science and Technology, 46*, 802–809.

Sundaram, S. C., Viswanathan, N., & Meenakshi, S. (2008a). *Journal of Hazardous Materials, 155*, 206–215.

Sundaram, C. S., Viswanathan, N., & Meenakshi, S. (2008b). *Bioresource Technology, 99*, 8226–8230.

Sundaram, C. S., Viswanathan, N., & Meenakshi, S. (2009). *Journal of Hazardous Materials, 172*, 147–151.

Tekle-Haimanot, R., Fekadu, A., Bushera, B., Mekonnen, Y. (1995). Fluoride levels in water and endemic fluorosis in Ethiopian Rift valley. 1st International Workshop on Fluorosis Prevention and Defluoridation of Water. Int. Soc. Fluoride Res. eds E. Dahi & H. Bregnhoj. Ngurdoto, Tanzania, October (1995) 18–22.

The World Health Organization. (1984). *Guidelines for drinking water quality, WHO, volume 1, recommendations*. Geneva, Switzerland.

The World Health Organization. (1996). *Guidelines for drinking water quality, WHO, volume 2, health criteria and other information, second edition*. Geneva, Switzerland.

UNICEF's Position on Water Fluoridation: http://www.nofluoride.com/Unicef_fluor.cfm; consulted on march 31, (2014).

Viswanathan, N., & Meenakshi, S. (2010). *Applied Clay Science, 48*, 607–611.

Wang, H., Chen, J., Cai, Y., Ji, J., Liu, L., & Teng, H. H. (2007). *Applied Clay Science, 35*, 59–66.

Zhang, D., Luo, H., Zheng, L., Wang, K., Li, H., Wang, Y., & Feng, H. (2012). *Journal of Hazardous Materials, 241–242*, 418–426.