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Defluoridation by calcined layered double hydroxides synthesized from seawater

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Abstract

This work used calcined layered double hydroxides synthesized from seawater (LDH_{sw}) in order to take advantage of its adsorption properties, especially in trapping fluoride anions as we aim to remove them from polluted water. In order to determine the experimental conditions suitable for removing the fluoride anions the influences of many parameters on the adsorption process were examined such as calcination temperature, time of contact, pH of aqueous solution, the dosage of adsorbent, charge density as well as the competition between the sulphate, nitrate and chloride anions. The results show that the adsorption of the fluoride by calcined LDH_{sw} was very fast, the removal of the fluoride was almost complete. For one hour of contact time and a pH between 6 and 7 at room temperature, the removal rate was 99.2 %. For the co-existing anions, it seems that the nitrate anions do not have a significant impact on the defluoridation. However, the defluoridation rate constant decreases in presence of the chloride and the sulphate anions.

Keywords: Layered double hydroxide; Adsorption; Defluoridation; Seawater.

1. Introduction

Layered double hydroxides (LDHs), also known as anionic clays, have attracted considerable attention in recent decade for their application as precursors to heterogeneous catalysts [1,2], electrode surface modifiers [3] and adsorbents [4-6]. Their general formula can be expressed as

$$[M^{2+}_{1-x}M^{3+}_{x}(OH)_2][A^{n-}]_{x/n}.yH_2O$$

where M^{2+} and M^{3+} represent di- and tri-valent metal cations, A^{n-} is the intercalated anion and x normally ranges from 0.17 to 0.33 [7]. The high charge density of the sheets from the isomorphic substitution of M^{2+} by M^{3+} and the exchangeability of interlayer anions make LDHs excellent and cheap adsorbents for removing anion pollutants from aqueous environments [8-10].

Fluoride has been known for centuries as a toxic element. The main source of fluoride in aqueous solution is represented by fluoride-rich rocks through which the water has percolated. Fluoride may also be derived from mining or industrial activity in some areas. The acceptable standard limit of fluoride concentration ranges between 0.5–1.5 mg/L for drinking water [11]. High level of fluoride in aqueous solution is a world-wide problem. Many people from North Africa have been suffering from fluoride poisoning [12].

The conventional method of removal of fluoride includes ion-exchange [13], reverse osmosis [14-16] and adsorption [17-20]. The ion-exchange and reverse osmosis are relatively expensive. Therefore, still adsorption is the viable method for the removal of fluoride. A large number of adsorbents have been studied for the removal of fluoride ions, including activated alumina, calcite, and layered double hydroxides [21, 22]. Due to high exchange capacity and an ability to recover their original layered structure in the presence of appropriate anions the LDH are known as the best conventional adsorbents.

In this paper, we are interested in studying the fluoride removal in aqueous solution by sorption on calcined LDH and LDH prepared from seawater [23]. For this work the influence of parameters on the adsorption is studied to determine the optimal experimental conditions for the fluoride removal. The parameters studied are the calcination temperature, the contact time, the pH of aqueous solution, the ratio adsorbent/adsorbate, and charge density.

2. Materials and methods

2.1. Synthesis of anionic clays from seawater

The synthesis of Mg/Al–CO_3 LDHs (with a molar ratio R = Mg/Al = 1, 2 and 3) was conducted using a constant-pH co-precipitation method. The solutions containing of trivalent metal $Al_2(SO_4)_3$,18 H_2O was added very slowly at a constant rate in a reactor initially composed of sea water containing the divalent metal Mg^{2+} (1294 mg/L). The pH of mixture was maintained at a value of 10 by the simultaneous addition of a ($NaOH+Na_2CO_3$) basic solution. After curing for 24 hours, the precipitate was recovered by filtration. The collected precipitate was washed three times with distilled water and dried at 60°C in oven.

2.2. Adsoption experiments

The quantities of LDH synthesized from seawater (denoted as LDH_{sw}), calcined at different temperatures are dispersed in 20 mL of fluoride solutions of varying concentrations. The suspensions were placed in beakers of polymer, under stirring in open air and at room temperature. The pH of the suspension is adjusted to the desired value by adding sodium hydroxide or nitric acid. The solids obtained after filtrations were characterized by X-ray diffraction using a Siemens D501 diffractometer. The precipitate containing residual fluorine was analyzed later by the potentiometric method with a specific electrode and a reference electrode, after the addition of a complexing buffer: TISAB II (Total Ionic Strength Adjustment Buffer) [24].

3. Results and discussion

3.1. Influence of calcination temperature

The adsorption capacity of LDH_{sw} with a Mg/Al molar ratio of 3 as a function of the calcination temperature (Fig. 1) was investigated.

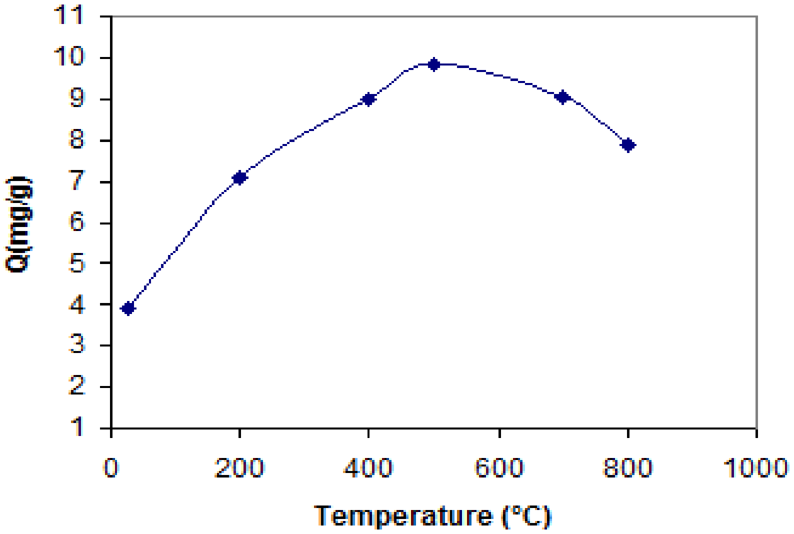

Figure 1: The fluoride-adsorption capacity versus the calcination temperature.

We notice that the LDH_{sw} calcined at 500°C exhibits the highest retention capacity of fluoride. At this temperature, the diffraction lines corresponding to the lamellar phase disappear. The lamellar structure is completely destroyed, and only reflections corresponding to an oxide such as MgO and to the calcium carbonate ($CaCO_3$) phase are observed (Fig. 2). Aluminum oxide is not detected [25]. This destruction causes drastic morphological changes. The particle size decreases and the surface area increases. For temperatures above 500°C, the surface area decreases as the mixed oxides appear and their crystallinity increases [26,27].

The diffractogram of the phase obtained after adsorption of fluoride on the LDH_{sw} calcined at 500°C (Figure (3b)) shows that the regeneration LDH_{sw} phase is possible. During the rehydration process, the calcined compound releases hydroxide ions. This results in an increase in pH of the solution. Such effects have been reported by other authors on the sorption of fluoride and other anions [27,28].

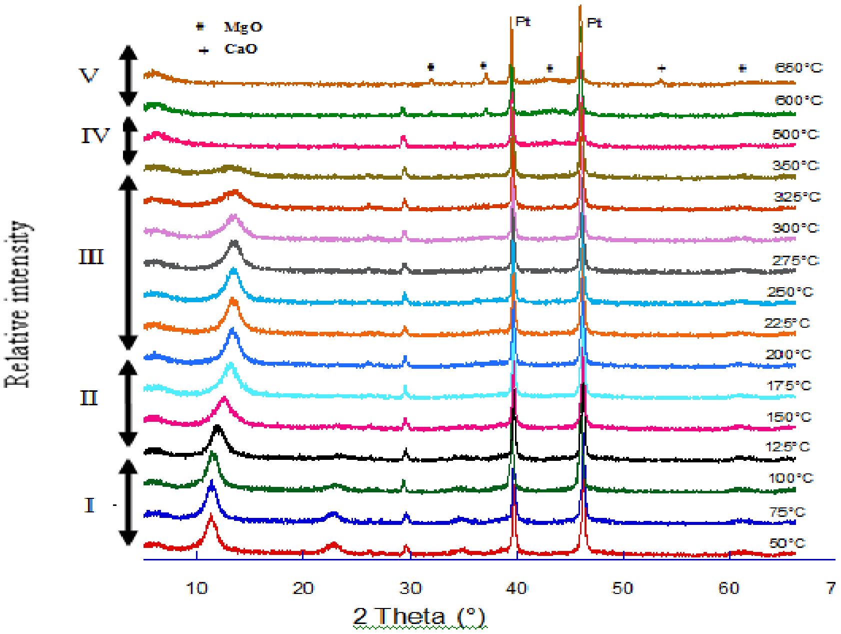

Figure 2: XRD patterns of the LDH_{SW} phases obtained after different calcinations temperature with a Mg/Al molar ratio of 3.

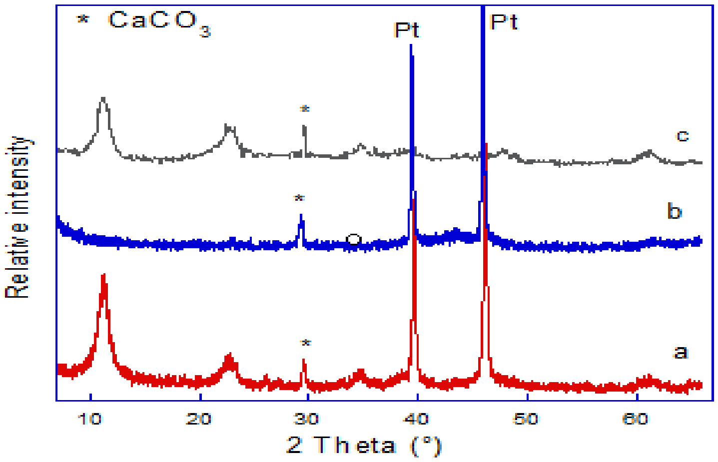

Figure 3: XRD patterns of (a) LDH_{SW}, (b) LDH_{SW} calcined at 500°C, (c) LDH_{SW} calcined after uptake of fluoride.

We can also notice in Figure 1 that the materials have higher retention capacity after calcination, suggesting that in addition to adsorption process on the external surface, there is also a process of intercalation of anions, during the reconstruction of the interlamellar domain, according to the following mechanism:

$$[Mg_{1-x}Al_x(OH)_2](CO_3)_{x/2} \rightarrow Mg_{1-x}Al_xO_{1+x/2} + (x/2)CO_2 + H_2O$$

$$Mg_{1-x}Al_xO_{1+x/2} + (x)F^- + (1 + (x/2))H_2O \rightarrow [Mg_{1-x}Al_x(OH)_2](F)_x + xOH^-$$

This is in agreement with several previous observations for the sorption of fluoride [19].

3.2. Kinetic study

The kinetic study was conducted at neutral pH. 20 mg of LDH_{sw} and LDH_{sw} calcined at 500°C were dispersed in 20 mL of fluoride solution of 10 mg/L as initial concentration.

This study shows also that the retention capacity of LDH_{sw} is faster after calcinations (Fig. 4). This is probably due to the fact that intercalation and fluoride adsorption happen simultaneously during the reconstruction of the layers. In fact, for calcined LDH_{sw} about 93% of fluoride is adsorbed after 10 min and equilibrium is reached after 30 min. Similar contact times were obtained by Liang Lv et al. during the adsorption of fluorine with [Mg-Al-CO_3] LDH under a stream of N_2 in order to avoid, or at least minimize, the contamination by atmosphere CO_2 [27]. Subsequently, a contact time of one hour has been adopted to ensure that equilibrium state is reached.

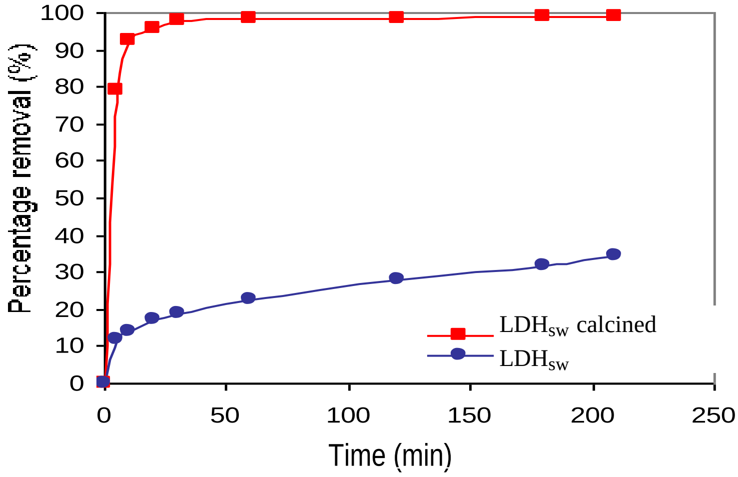

Figure 4 : Effect of time on the adsorption of fluoride on LDH_{sw} and LDH_{sw} calcined at 500°C. ($[F^-]$=10mg/L, $m_{adsorbant}$=20 mg,V=20mL, pH between 6 et 7)

3.3. Effect of pH

The influence of pH on the retention phenomenon was examined using 20 mg of the product calcined at 500 °C, dispersed in 20 mL of fluoride of 10 mg/L as initial concentration (Fig. 5). The maximum retention of fluoride occurs at pH values ranging from 6 to 7; pH close to that of natural waters. For pH values below 6, the materials used have a low retention capacity of fluoride, a similar result was observed by Liang Lv et al. concerning the adsorption of fluoride on [Mg-Al-CO_3] under nitrogen [27]. This could be explained by the fact that lower pH values favor a partial dissolution of the matrix by acid hydrolysis of LDH. For values higher than 7, there is a decrease in retention of fluoride, this reduction was also highlighted by other authors «Dipti Prakasini Das et al.», « Liang Lv et al. » for fluorine [22,27], and it is commonly interpreted by the contamination of the LDH matrix by OH^- ions and carbonate. These ions compete with fluoride to be adsorbed by LDH. In our case of study, we can explain it by the retention decrease of $CaCO_3$ solubility.

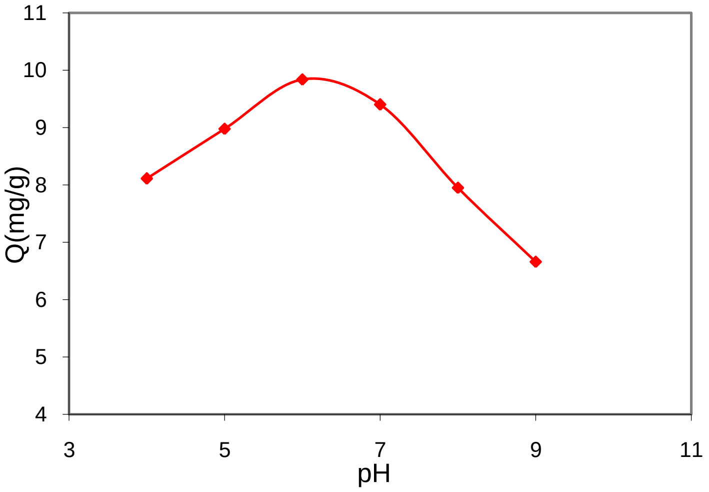

Figure 5 : The percentage removal of fluoride on the LDH_{sw} calcined at 500°C as a function of the pH ($[F^-]$=10mg/L, $m_{adsorbant}$=20 mg,V=20mL).

3.4. Effect of Mg/Al ratio

We follow the same approach used in studying the contact time effect, but with various metal ratios Mg/Al (R = 1, 2, 3). These essays showed the increase of fluoride adsorption capacity when the Mg/Al ratio decreases, i.e. when the charge density increases (Fig. 6).

The LDH_{sw} calcined at 500°C precursor exhibits the best fluorine retention capacity that reaches 99.2% for R= 1 and 98.43 for R = 2.

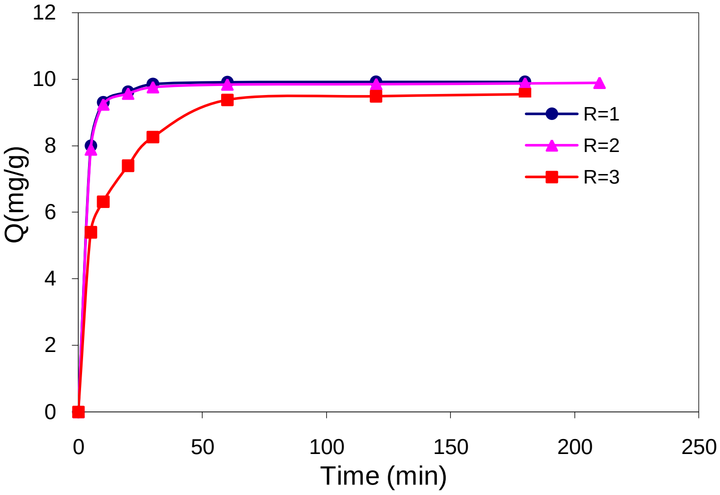

Figure 6: Relationship between the adsorption loading of fluoride and the time, for 20 mg of the LDH_{sw} calcined at 500°C with various Mg/Al molar ratios (R = 1, 2, 3).

3.5. Effect of adsorbent dose

A series of assays have been investigated. For all these runs, initial fluoride ion concentration was fixed at 10 mg/L. The variable amount of adsorbent dose was added (10, 20, 40, 60 and 80) to 20mL of fluoride solution (Fig. 7).

We conclude that the adsorption capacity decreases with increasing the adsorbent dose. Anterior studies supposed that this is due to the aggregation of big amounts of solid that reduces the contact area [29].
Then we use a solid/liquid ratio suitable in optimal conditions to trap the maximum amount of fluoride.

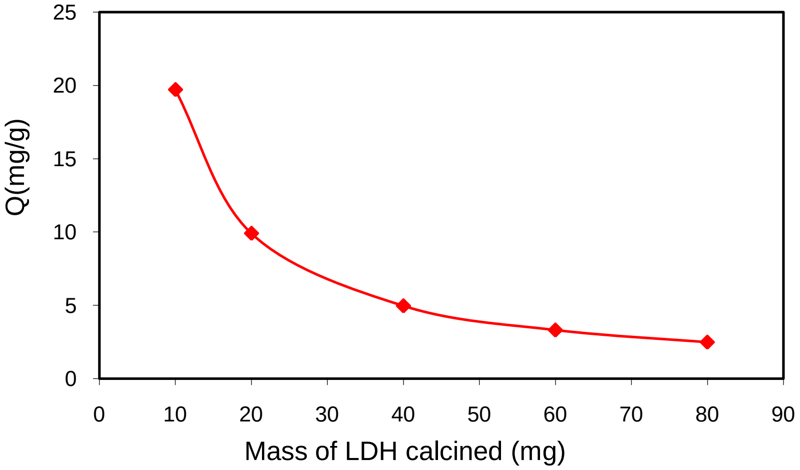

Figure 7: The amount of fluoride retained versus the mass of LDH_{sw} calcined at 500 °C, ($[F^-]$=10mg/L l, V=20mL, pH between 6 and 7).

3.6. Effect of initial concentration of fluoride.

For a mass of 10 mg of adsorbent, we used different initial concentrations of fluoride ranging from 10 to 100 mg/L.

Figure 8 shows the effect of the initial fluoride concentration on the process of fluoride retention on LDH_{sw} calcined at 500°C. There was a decrease in the percentage retention along with the increase of initial fluoride concentration.

For solutions of 40 mg/L and 30 mg/L as initial concentrations, the residual fluoride concentrations obtained are 1.3 mg/L and 0.66 mg/L respectively. So, removing the fluoride from LDH_{sw} leads to a residual fluoride concentration lower than the standards required for drinking water quality (which is about 1.5 mg/L)

These experimental results can be described by Langmuir (Eq. (1)) and Freundlich(Eq. (2)) equations:

$$Q = KQ_mC_e / (1+ K\,Q_m) \quad (1)$$

$$Q = k_f\, C_e^{1/nf} \quad (2)$$

with

Q : is the amount of fluoride adsorbed per unit weight of calcined LDH_{sw} (mg/g)
Q_m : is the maximal amount of fluoride adsorbed per unit weight of calcined LDH_{sw} (mg/g)
C_e : is the fluoride concentration at equilibrium (mg/L)
K : is the Langmuir constant associated to the adsorbate/adsorbent affinity (L/mg).
K_f : is the Freundlich constant associated to the adsorption capacity L/g).
n_f : is the Freundlich constant associated to the adsorbate/adsorbent affinity.

The adsorption isotherm of fluoride by calcined LDH_{sw} is represented in Figure 9. According to Giles classification, it is an L_shaped isotherm. So it can be modeled by the Langmuir equation (Table 1). The choice of this model is justified by the high values of correlation factors. The weak slope of the curve reveals a strong adsorbate/adsorbent affinity (L= 0.74 L/mg), caused by the adsorption of the pollutant by chemisorptions mechanism.

The modeling results are listed in Table 1.

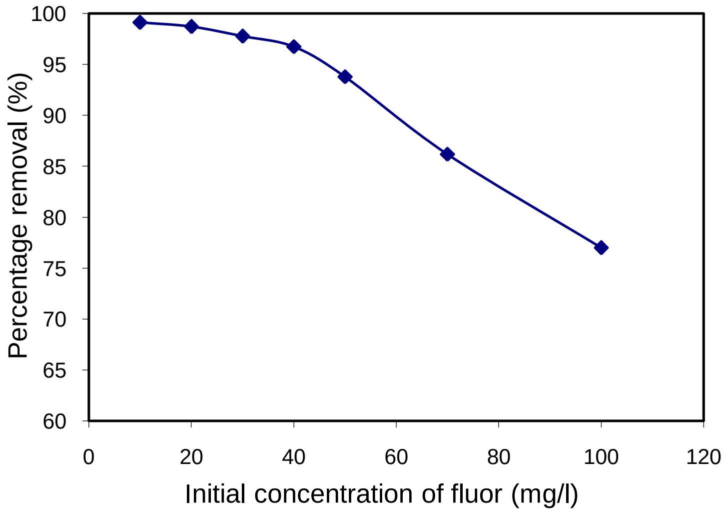

Figure 8: The percentage removal of fluoride on the LDH_{sw} calcined at 500°C as a function of initial concentration ($m_{adsorbant}$=10 mg,V=20 mL, pH between 6 and 7)

Table 1: Langmuir and Freundlich constants

Langmuir			Freundlich		
Q_m (mg/g)	L (L/mg)	r^2	K_f (mg/g)	n_f	r
79,37	0,74	0,991	29,75	2,77	0,966

The Q_m value obtained in this study is the highest among those obtained with other adsorbents such as activated alumina (16.34mg/g) [21], fly ash (20 mg/g) [30], lignite (7.09 mg/g) and the bitumen coal (7.44 mg/g) [31].

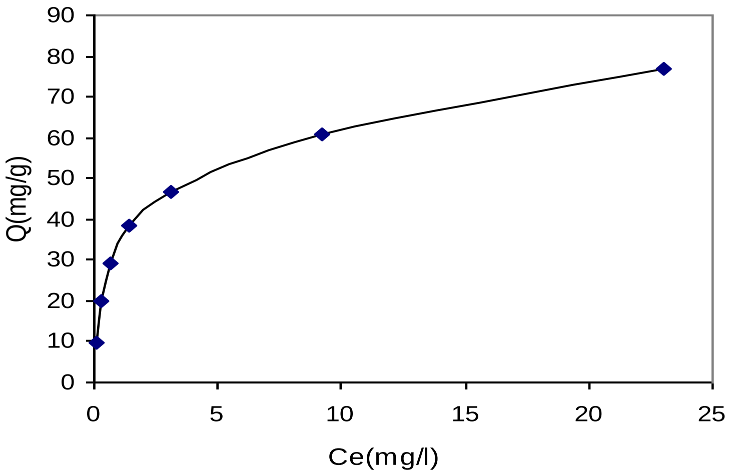

Figure 9: Adsorption isotherms for fluoride sorption by LDH_{sw} calcined.

3.7. Effect of counter-ion

Natural waters have a more complex composition than the solution studied here. So we proceed to the defluoridation of a solution containing other ions such as sulfates, chlorides and nitrates.

Figure 10 shows the effect of counter-ions on the defluoridation for an initial fluoride concentration of 10 mg/Land 50 mg/L of counter-ions. 10 mg of calcined LDH_{sw} were used at constant volume (V=20mL), pH values between 6 and 7, at open air and at room temperature.

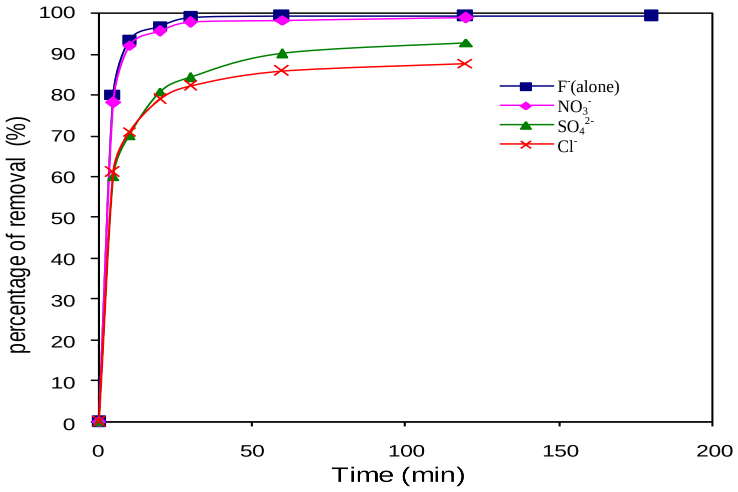

Figure 10: Effect of counter-ions on the defluoridation

We notice that nitrate ions have no significant effect on defluoridation. This is probably due to the weak interaction of NO_3^- with LDH_{sw}. However, the defluoridation rate in the presence of chloride and sulfate ions decreases.

The effect of these ions on the defluoridation may be due to their affinity towards the LDH_{sw}. Indeed LDH exhibits selectivity for interlayer anions in the following order [32]:

$$CO_3^{2-} >> SO_4^{2-} > Cl^- > NO_3^-$$

This selectivity is related to the anion size as well as the charge density. In fact, the affinity for divalent anions is higher than for the monovalent ones. Instead, we notice that chlorides have higher effect on defluoridation than sulfates. Indeed, due to his low molar weight, the molar concentration of chloride is higher than that of the other anions.

We can conclude that the adsorption capacity of fluoride decreases with co-existing anions that compete with fluoride in this order: $Cl^- > SO_4^{2-} > NO_3^-$.

Conclusion

In this study we aim to synthesize layered double hydroxides from seawater (LDH_{sw}) and to take advantage of their adsorption properties in trapping the fluoride and then, their eventual removal from polluted water. The X-rays results show that the resulting material is a hydrotalcite-like compound with the appearance of a secondary phase of $CaCO_3$.

Through this study, it was proven that the LDH_{sw} were efficient in fluoride removal. Furthermore, the calcined LDH_{sw} was found to have better fluoride retention capacity than the uncalcined LDH_{sw}. Indeed, while the fluoride removal rate reaches 99% with calcined clay, it does not exceed 24% with the uncalcined clay during 1 hour of time contact, at pH value between 6 and 7, at open air and at room temperature. The kinetics study reveals that the adsorption is very fast. This might be due to the intercalation of fluoride during the regeneration of the clay. The L-shaped adsorption isotherm found in this study points to a high adsorbate/adsorbent affinity. The shape of the adsorption curve is characteristic of a chemisorption process then modeled by the Langmuir equation. The influence of co-existing anions was studied and it indicates that the nitrates have no significant effect on the defluoridation while the co-existence of chloride and sulfate ions decreases the defluoridation rate.

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