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Precipitation and adsorption during fluoride removal from water by calcite in the presence of acetic acid

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ABSTRACT

Defluoridation of groundwater is of major concern in several places around the world, such as North and East Africa, India and China. In this paper, removal of fluoride from model solutions and a Tunisian groundwater sample was performed using calcite particles in the presence of acetic acid in batch experiments. After 1 h decantation, dead-end microfiltration was further used to retain the fluorite (CaF_2) precipitates present in the supernatant. At $5\,mg\,L^{-1}$ fluoride concentration, removal efficiency was found to increase from 17.4% without acid to 30.4% with 0.1 M acetic acid. The increase in fluoride removal with acetic acid was mainly attributed to the renewal of the area available for adsorption on the calcite particles. At the fluoride concentration of $50\,mg\,L^{-1}$, the removal efficiency was equal to 9.5% without acid and 94.3% with the addition of 0.1 M acetic acid. The removal of fluoride was attributed to precipitation as a result of higher supersaturation in the solution. Optimum parameters were selected for the defluoridation of a Tunisian groundwater sample with initial fluoride concentration around $2.7\,mg\,L^{-1}$. The final F^- concentration after treatment with calcite in the presence of 0.1 M acetic acid was found equal to $1.2\,mg\,L^{-1}$, which was below the standard of the World Health Organisation.

Keywords: Acetic acid; Calcite; Defluoridation; Fluoride; Microfiltration; Precipitation; Adsorption

1. Introduction

Groundwater contamination by fluoride may be due to mineral processing industries including coal fired power stations, beryllium extraction plants, brick and iron works and aluminium smelters [1]. High concentrations may also be due to the natural dissolution of fluoride-bearing minerals in rocks and soils. In many regions, such as North and East Africa, India and China where rocks are rich in fluorite (CaF_2) and

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fluorapatite ($Ca_{10}(PO_4)_6F_2$), the concentration of fluoride ions in groundwater may exceed $20\,mg\,L^{-1}$. Groundwater fluoride concentrations as high as $60\,mg\,L^{-1}$ are also reported, for example, in the northern area of the former Republic of Bophuthatswana, South Africa [2]. An excess amount of fluoride ion in drinking water has adverse effects on human health with dental or skeletal fluorosis, which manifests in mild cases by mottling of teeth and in severe cases by softening of bones and neurological damage [3]. The concentration of fluoride ions in drinking water recommended by the World Health Organisation (WHO) varies in a concentration range of $0.8–1.5\,mg\,L^{-1}$ at temperature 12–25˚C [4].

Coagulation precipitation, also called the Nalgonda technique, is one of the popular techniques widely used for defluoridation of water in developing countries (e.g. India, Kenya, Senegal and Tanzania). Lime and alum are the most commonly used coagulants. Addition of lime leads to precipitation of fluoride as an insoluble fluorite. As lime leaves a residue of $8.0\,mg\,L^{-1}$, it is used in conjunction with alum treatment to ensure proper fluoride removal. Coagulation methods are generally found to be effective in defluoridation, but they are unsuccessful in decreasing fluoride to the desired concentration levels. In addition, the method suffers drawbacks such as the formation of toxic soluble aluminium complexes, an increase of pH and total dissolved solids of the treated water, so the process needs a supplementary reaction for eliminating the excess chemicals [3].

Other processes such as adsorption [5,6], ion exchange [7–10], reverse osmosis/nanofiltration [11–13], Donnan Dialysis [14] and electrodialysis [15] have been used for the removal of excess amounts of fluoride from drinking water. However, these methods may be limited by high costs during installation and maintenance, secondary pollution such as the generation of sludge and complicated procedures for local populations [3,16].

The adsorption process is an attractive method for the removal of fluoride in terms of cost, simplicity of design and operation. A very large range of materials has been tested, including calcium-based sorbents, alumina and aluminium-based adsorbents, iron-based sorbents, other metal oxides/hydroxides/oxyhydroxides, natural materials, biosorbents and agricultural and industrial wastes [3]. Among these materials, calcite and limestone have been largely used for the removal of fluoride because they are cheap and abundant, and have good affinity for fluoride anions. Yang et al. [17] used a fixed bed filled with calcite particles to examine the removal of fluoride from contaminated water and concluded that fluoride was removed via precipitation as CaF_2. Fan et al. [18] measured the adsorption capacity of various materials viz. hydroxyapatite, fluorspar, calcite, quartz and quartz activated by ferric ions. The uptake of fluoride (except for hydroxyapatite) was shown to occur by surface adsorption and followed the pseudo-second-order equation. Under stirred conditions, the adsorption of fluoride was controlled by the adsorbent structure and chemical properties. Turner et al. [1] conducted fluoride removal experiments using crushed limestone (99% pure calcite) by batch studies with high fluoride concentration solutions (700 and $2,100\,mg\,L^{-1}$). Using atomic force microscopy, X-ray photoelectron spectroscopy and ζ potential measurements, the authors showed that fluoride was removed by a combination of surface adsorption and precipitation. By passing CO_2 through crushed limestone columns, Reardon and Wang [19] removed fluoride to below $4\,mg\,L^{-1}$. The main mechanism for fluoride removal was reported to be the precipitation of CaF_2 by an increase in Ca^{2+} activity in the limestone column due to dissolution of calcite by CO_2. Turner et al. [20] used calcite and CO_2 addition for a permeable reactive barrier for removing fluoride from contaminated groundwaters. CO_2 gas was bubbled through the influent solution or injected directly into the calcite column. Results showed that approximately 99% of $2,300\,mg\,L^{-1}$ fluoride were removed when CO_2 was injected directly into the barrier. To improve fluoride removal, Nath et al. [21] added acetic acid, citric acid, or oxalic acid to a fixed bed reactor filled with limestone chips. The presence of the acid improved fluoride removal, reached concentrations being less than 0.5 and $1.0\,mg\,L^{-1}$ from initial 5 and $10\,mg\,L^{-1}$ fluoride solutions. The authors suggested that the mechanism of fluoride removal was the increase in Ca^{2+} activity by dissolution of limestone, which precipitated as CaF_2. Precipitation was said to occur simultaneously to adsorption, even if very small quantities of fluorite precipitates were detected. Crushed limestone in presence of acid was also demonstrated to be a suitable technique for the defluoridation of water [22–24].

Mechanisms governing calcite dissolution, CaF_2 precipitation and fluoride adsorption have been investigated by many authors. In the 1980s, Pickering and co-workers [25–27] concluded that fluorite precipitation was the main mechanism of fluoride removal because the mass of fluoride lost from solution was independent of the weight of calcite present. Reardon and Wang [19] employed data from column experiments to conclude that fluoride removal was achieved by dissolution of calcite and subsequent precipitation of CaF_2. Calcite gradually releases calcium ions into the water at a certain pH range. The dissolved calcium ions interact with fluoride in water and formed CaF_2 precipitates. Turner et al. [1] reported that fluoride was removed by a combination of precipitation and surface adsorption. Fluorite precipitation occurred at step edges and kinks, where the dissolved Ca^{2+} concentration was the highest, whereas fluoride adsorption occurred immediately over the entire calcite surface.

Calcite can adsorb fluoride as well as other ions such as fluoride cadmium [28,29], manganese [30], zinc [31] and phosphate [32], with the degree of adsorption being pH-dependent. The removal of fluoride from the aqueous solution was explained as a pseudomorphic replacement involving epitaxial growth of the (1 1 0) plane of fluorite in the (1 0 1) plane of calcite [17]. The fluoride replaced CO_3^{2-} from calcite as shown in reaction 1 and left the Ca^{2+} positions nearly unchanged [33].

$$2F^- + CaCO_{3(s)} \rightleftarrows CaF_{2(s)} + CO_3^{2-} \quad (1)$$

The volume of CaF_2 being smaller than that of $CaCO_3$, the replacement reaction left more porosity. The F^- ion could diffuse into the particle and CO_3^{2-} could diffuse out of the calcite particles, therefore fluoride could exchange with CO_3^{2-} inside calcite [34].

Simonsson [35] also mentioned the increase in porosity of the calcite particles during the defluoridation experiment. The unreacted shrinking core model and the CO_2 formation at the reaction front inside the particles were proposed to explain the physical phenomenon. The model considered a spherical particle whose $CaCO_3$ core shrank as a porous layer of CaF_2 grew around the particle. The fluoride concentration at the unreacted surface approached zero due to diffusion limitations in the porous fluorite layer.

More recently, Fan et al. [18] investigated calcite as a fluoride adsorbent at a low fluoride concentration range from $2.5\ 10^{-5}$ to $6.34 \times 10^{-2}\,mg\,L^{-1}$. Calcite had a poor capacity in fluoride removal, lower than hydroxyapatite and fluorspar. At low fluoride concentrations, the authors concluded that the uptake of fluoride in calcite was surface adsorption and no porosity increase was reported.

In our previous paper, cuttlefish bone particles were used as an adsorbent material for the defluoridation of water [6]. Batch experiments were conducted with synthetic solutions of sodium fluoride and natural groundwaters. The efficiency of cuttlefish bone particles to remove fluoride from water was found to be 80% at pH 7.2, 1 h contact time, $15\,g\,L^{-1}$ of adsorbent dose and $5\,mg\,L^{-1}$ of initial fluoride concentration. Fluoride was mainly removed by adsorption on the cuttlefish bone particles. In the present paper, we investigated the addition of acetic acid for the defluoridation of water using calcite particles as previously reported [24] with the purpose to increase precipitation and therefore fluoride removal. The parameters studied were the concentration of the added acid, contact time, quantity of calcite and initial fluoride concentration between 2.5 and $50\,mg\,L^{-1}$. The aim of this study was to pay a specific attention to the mechanisms which governed fluoride removal, i.e. adsorption and precipitation. Microfiltration was used as a final step to filtrate the supernatants obtained after 1 h decantation. Finally, the Tunisian groundwater sample (Louza 2) with fluoride concentration around $2.6\,mg\,L^{-1}$ [6] was treated by this technique.

2. Materials and methods

2.1. Materials

Sodium fluoride, calcium carbonate and acetic acid were obtained from Sigma Aldrich. Calcite particles were observed using scanning electron microscopy (SEM) and showed a typical cubic shape with most particles in the range of 2–10 μm. All chemical were of analytical grade and used as such.

Fluoride solutions used in the removal experiments and analysis were prepared by diluting a homemade stock NaF solution ($250\,mg\,L^{-1}$) with ultra-pure water obtained from a Millipore Synergy® system (Ultrapure Water System, Millipore).

A tunisian groundwater sample from South of Tunisia (region of Gafsa) was also tested in this study. Some relevant chemical parameters of the groundwater were as follows: pH 7.6; Na^+, Ca^{2+}, Mg^{2+}, F^-, SO_4^{2-} 245, 210, 110, 2.7, 1,030 $mg\,L^{-1}$, respectively, hardness and alkalinity 100°F and $3.1\,meq\,L^{-1}$, respectively [36].

2.2. Equipment

Fluoride concentrations were measured on a SevenMulti™ instrument (Mettler Toledo) using a perfectION™ (Mettler Toledo) ion selective electrode for fluoride. A TISAB II solution (Mettler Toledo) was used to control ionic strength and de-complex the fluoride. The calibration of the ion meter was done with fluoride solutions of 10, 1.0 and $0.1\,mg\,L^{-1}$ concentrations. Standard and samples were added to TISAB II, respectively, 15 mL of standards or samples and 15 mL of TISAB II, before measurements. The pH data were obtained using the same instrument.

X-ray diffraction was performed on a Gemini kappa-geometry diffractometer (Agilent Technologies

UK Ltd) equipped with an Atlas CCD detector and using Cu radiation ($\lambda = 1.5418$ Å). Diffraction images were collected at room temperature and the powder rings were integrated with the Crysalis Pro software.

A SEM combined with energy dispersive X-ray spectroscopy (EDS, HITACHI S800, Scanning Electron Microscopy) was used to record the SEM micrographs and EDS spectra. The samples were coated with Au–Pd before acquisition of SEM pictures and with C before EDS spectra measurements. The energy of the electron beam was set between 10 and 15 keV. The elemental analysis obtained by EDS was expressed in atomic percentage.

The filtration experiments were performed using a Swinnex 47 module (Millipore) with a diameter of 47 mm and a filtration area of 13.8 cm^2. Cellulose nitrate membranes with 0.1 μm pore size (Sartorius) were used. Cellulose nitrate membranes are reported to be resistant to 10% acetic acid.

2.3. Fluoride removal experiments

All experiments were carried batchwise at room temperature (20 ± 2˚C). In most experiments, 15 g L^{-1} calcite was added to 200 mL of fluoride solution and completed with 0.1 M acetic acid. The suspension was then agitated using a magnetic stirrer at 300 rpm for 2 h. At the end of each experiment, the solution was left for decantation during 1 h. The supernatant was then filtered using the 0.1 μm pore size membrane and analysed for residual fluoride content. The pH of the solution was measured, and the residual concentration of fluoride was determined using the fluoride ion electrode connected to the ion meter. The influence of various parameters (contact time, acid concentration, initial fluoride concentration and amount of calcite) was evaluated using the same batch conditions. The groundwater was treated by applying the optimum conditions determined from the experiments performed with the synthetic solutions. The fluoride removal experiments were realised in duplicate. Values given in this paper are the average of values obtained in the two experiments.

The fluoride removal efficiency, R, was calculated using the following relation:

$$R(\%) = \left(1 - \frac{[\mathrm{F}^-]_f}{[\mathrm{F}^-]_i}\right) \times 100 \tag{2}$$

where $[\mathrm{F}^-]_i$ (mg L^{-1}) is the initial concentration of the solution before fluoride removal, and $[\mathrm{F}^-]_f$ (mg L^{-1}) is the final concentration after fluoride removal.

2.4. Microfiltration experiments

A volume of 600 mL of fluoride solution was treated by calcite in the presence of acid followed by 1 h decantation. The supernatant obtained (around 600 mL) was then placed in a pressurised vessel (Millipore) connected to a nitrogen bottle for pressurisation. The pressure was read on the manometer placed on the pressurised vessel. All microfiltration experiments were performed at two bar pressure. The filtrate volume was monitored vs. time using a balance connected to a computer (Fig. 1). Under same the experimental conditions, the microfiltration

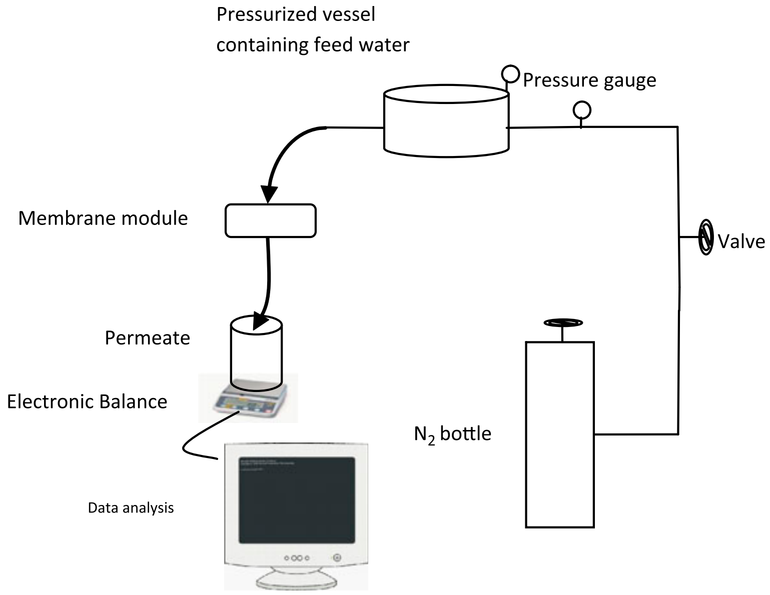

Fig. 1. Dead-end filtration experimental set-up.

experiment was realised in duplicate. In this study, every membrane was used only once.

2.5. X-ray and SEM-EDS

The SEM micrographs and EDS spectra were recorded for two types of samples obtained from the fluoride removal experiments: (1) the powders obtained after 1 h of decantation at the bottom of the flask and (2) the membranes removed from the Swinnex module after microfiltration of the supernatant. The powders and the membranes (recovered by particles retained) were both dried for 2 h at 50˚C in an oven. They were then characterised by X-ray and SEM-EDS. The SEM micrographs and EDS spectra were recorded at least twice for the same samples. The EDS spectra were recorded either on a particle or on the whole picture.

3. Results and discussion

3.1. Influence of contact time

The influence of contact time on fluoride removal by calcite and acetic acid is shown in Fig. 2. At the initial F^- concentration of $5\,mg\,L^{-1}$, the amount of fluoride removed increased rapidly during the first 2 h. The increase was then slowed down, in addition, the equilibrium was not reached after 8 h. After 2 h, *R* was equal to 30.4% and the final fluoride concentration equal to $3.5\,mg\,L^{-1}$. Defluoridation by calcite is usually reported to be a very slow process. For example, Reardon and Wang [19] performed defluoridation experiments in limestone bed during 4 h and Nath and Dutta [24] during 12 h. This may be attributed to the slow penetration of fluoride deeper inside the calcite particles. Faster adsorption was reported with another calcium-based material. During defluoridation using cuttlefish bones, equilibrium was reached after almost 1 h [6]. This result was probably due to the much higher porosity of cuttlefish bones compared to calcite particles, leading to a high surface available for adsorption. In addition, the removal efficiency was higher using cuttlefish bones (around 80%) than calcite particles because of the highest porosity of the cuttlefish bone particles. A similar result was obtained with eggshell powder as an adsorbent for removal of fluoride, the equilibrium was reached in less 2 h with a removal efficiency around 98% [37].

At the initial F^- concentration of $50\,mg\,L^{-1}$, the F^- removal was much faster. After 2 h, the removal efficiency kept almost constant being equal to 94.3% and the final fluoride concentration to $2.8\,mg\,L^{-1}$. At $50\,mg\,L^{-1}$ fluoride initial concentration, supersaturation is higher than at $5\,mg\,L^{-1}$ and precipitation occurs. In the following experiments, the contact time was chosen equal to 2 h as the fast removal step was reached at this time for both concentrations.

3.2. Influence of acid concentration

The influence of acid concentration was investigated between 0 and 0.4 M (Fig. 3). From 0.2 M acetic acid concentration, dissolution of calcite particles was clearly observed, the dissolution being complete at 0.4 M. At the initial $[F^-]$ concentration of $5\,mg\,L^{-1}$, when no acetic acid was added, the fluoride removal efficiency was equal to 17.4% and the final fluoride concentration to $4.1\,mg\,L^{-1}$. With the addition of acetic acid, it increased and reached 30.4% at 0.1 M (final

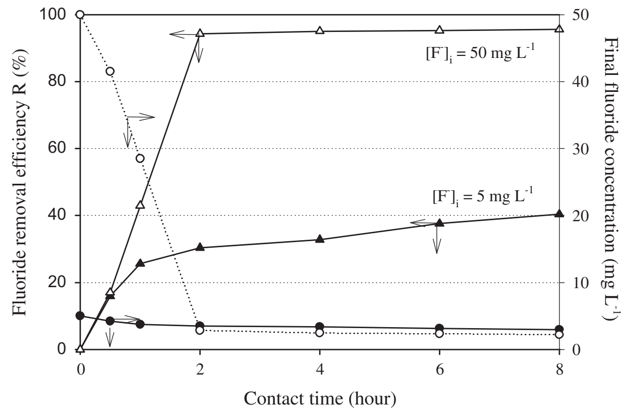

Fig. 2. Fluoride removal efficiency and final fluoride concentration vs. contact time (calcite amount $15\,g\,L^{-1}$, acetic acid concentration 0.1 M).

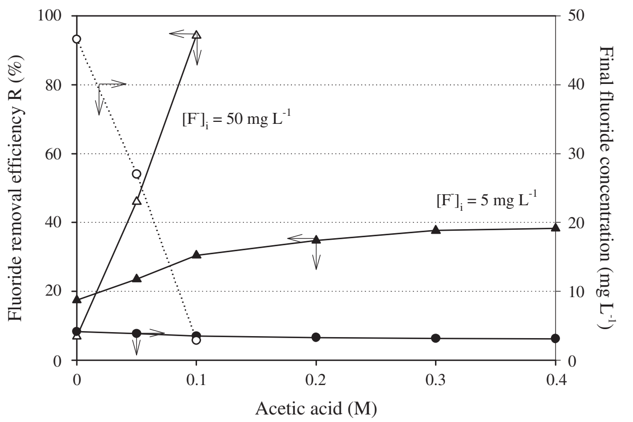

Fig. 3. Fluoride removal efficiency and final fluoride concentration vs. acid concentration (calcite amount $15\,g\,L^{-1}$, contact time 2 h).

fluoride concentration 3.5 mg L^{-1}) and 38.2% at 0.4 M (final fluoride concentration 3.1 mg L^{-1}). This result confirms that acetic acid enhances fluoride removal as previously reported in a crushed limestone reactor [24]. The acid dissolves calcite particles and thus, may increase the porosity and the area available for adsorption [18,34]. In addition, the calcite dissolution by acetic acid may generate zones with high local Ca^{2+} concentration where precipitation may occur. These zones were reported to be step edges and kinks that where dissolved in the Ca^{2+} concentration was the highest [1]. Moreover, a competition exists between adsorption and precipitation, as the dissolution of the calcite particles also results in desorption of fluoride.

At 50 mg L^{-1}, the increase in fluoride removal efficiency with acid was much higher. Without acid, the fluoride removal efficiency was equal to 9.5% (final fluoride concentration 46.6 mg L^{-1}), it increased to 94.3% (final fluoride concentration 2.8 mg L^{-1}) with the addition of 0.1 M acetic acid. By dissolving the calcite particles, acetic acid had the effect to drastically increase supersaturation, and therefore fluoride removal by precipitation.

The pH of the water obtained after defluoridation with calcite in presence of acid was measured for various acetic acid concentrations. The results were the same for the two initial fluoride concentrations 5 and 50 mg L^{-1}. When no acid was added, the pH of the treated water was around 9.5, due to the presence of CO_3^{2-} species. With the addition of acid acetic 0.1 M, the pH of the treated water decreased and was around 6.9 at both initial concentrations. The HCO_3^- species were then largely dominant. In the range of acetic concentration 0.05–0.1 M, the pH of the treated water was in an acceptable range for drinking water.

Fluoride removal is dependent on pH with the amount removed decreasing with increasing pH. When HCO_3^- is predominant, the solubility of calcium carbonate s_1 was calculated from equation:

$$Ps_1 = -\log s_1 = 1/2(pK_{s1} + pH - pK_2) \tag{3}$$

where K_{s1} is the calcium carbonate solubility product, pH is the pH of the solution measured at the end of experiment and K_2 is the constant acidity of (HCO_3^-/CO_3^{2-}). At 25˚C, $K_1 = 10^{-6.35}$; $K_2 = 10^{-10.35}$ and $K_{s1} = [Ca^{2+}][CO_3^{2-}] = 10^{-8.4}$ $(mol\,L^{-1})^2$.

Supersaturation of F^- and Ca^{2+} is the necessary condition for precipitation of CaF_2 [23]. Therefore, F^- removal depends not only on the Ca^{2+} amount but also on the initial F^- concentration making difficult to remove fluoride by precipitation from the solutions with low initial concentrations.

$$CaF_{2(s)} \rightleftarrows Ca^{2+} + 2F^- \tag{4}$$

The fluorite solubility product $K_{s2} = (s_2)^2 = [Ca^{2+}][F^-]^2 = 3.5 \times 10^{-11}$ $(mol\,L^{-1})^2$ at 25˚C.

At pH = 6.9, $s_1 = [Ca^{2+}] = 3.35\ 10^{-3}$ mol L^{-1}. The fluoride concentration which corresponds to the CaF_2 solubility was calculated equal to $[F^-] = K_{s2}\ /\ [Ca^{2+}] = 1.95$ mg L^{-1}. This data is in the range of the final fluoride concentration obtained at 50 mg L^{-1} (2.8 mg L^{-1}). As this initial concentration, supersaturation increased and therefore precipitation.

3.3. Influence of initial concentration of fluoride

Fluoride concentrations between 2.5 and 50 mg L^{-1} were investigated in order to see the effect of the initial concentration of fluoride on its removal by calcite and acetic acid (Fig. 4). From 2.5 to 20 mg L^{-1}, the fluoride removal increased drastically as supersaturation and therefore precipitation increased. At 5 mg L^{-1}, the fluoride removal efficiency was 30.4% which corresponded to a final fluoride concentration of 3.5 mg L^{-1}, and at 50 mg L^{-1}, the fluoride removal was equal to 94.3%, corresponding to a final fluoride concentration of 2.8 mg L^{-1}.

At the initial F^- concentration of 5 mg L^{-1}, the remaining F^- concentration was 3.5 mg L^{-1}. The concentration was then higher than the one obtained at 50 mg L^{-1} (final fluoride concentration 2.8 mg L^{-1}). This suggests that precipitation was increased at 50 mg L^{-1} leading to a lower final fluoride concentration.

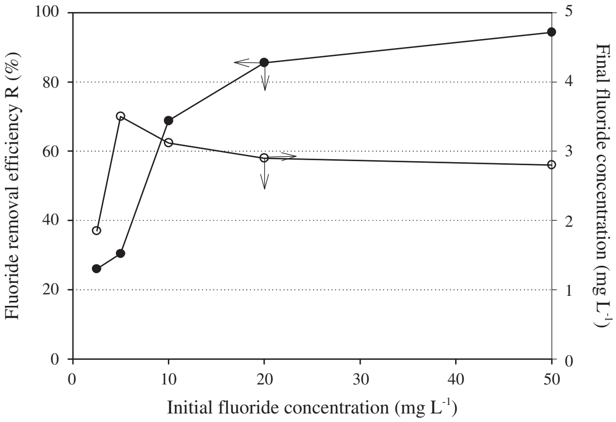

Fig. 4. Fluoride removal and final fluoride concentration vs. the initial fluoride concentration (calcite amount 15 g L^{-1}, acetic acid concentration 0.1 M, contact time 2 h).

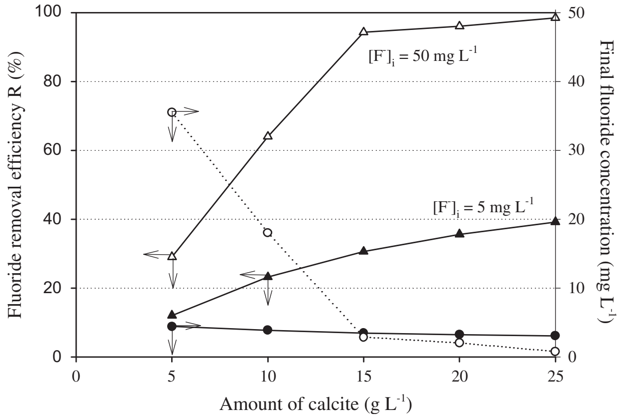

Fig. 5. Fluoride removal and final fluoride concentration vs. the amount of calcite (acetic acid concentration 0.1 M, contact time 2 h).

3.4. Amount of calcite

The effect of the amount of calcite on fluoride removal was investigated for calcite concentrations between 5 and 25 $g\,L^{-1}$ (Fig. 5). The fluoride removal efficiency increased with the amount of calcite for the two initial fluoride concentrations of 5 and 50 $mg\,L^{-1}$. At 5 $mg\,L^{-1}$, this result may be explained by the larger area available for fluoride adsorption at higher amount of calcite particles. Most results on fluoride removal by adsorption reported an increasing removal with the adsorbent amount, for example using cuttlefish bones [6], quick lime [38] and charcoals that contain calcium compounds [39]. Fan et al. [18] showed that the uptake of fluoride in calcite was a surface sorption and that fluoride sorption fitted the Freundlich isotherm. At 50 $mg\,L^{-1}$, the fluoride removal efficiency increased also with the amount of calcite as a higher Ca^{2+} concentration was available for precipitation. In most of our experiments, the amount of calcite was set to 15 $g\,L^{-1}$.

3.5. X-ray diffraction

X-ray diffraction was performed on powders obtained after defluoridation with calcite and acetic acid for the two initial fluoride concentrations, 5 and 50 $mg\,L^{-1}$. Two types of powders were investigated: (1) powders removed from the bottom of the flask after defluoridation followed by 1 h decantation and (2) powders removed from the 0.1 μm pore size membrane surface after filtration of the supernatant. Fluorite was not detected at 5 $mg\,L^{-1}$, which suggested that at this concentration low precipitation has occurred. At 50 $mg\,L^{-1}$, fluorite was not detected in the powder obtained after decantation; the crystalline phase was mainly composed of calcite. On the contrary, CaF_2 was observed in the powder removed from the membrane surface after filtration of the supernatant (Fig. 6). According to the International Centre for Diffraction Data, the characteristic peak found at 2θ of 29.2° is determined as calcite. Minor peak found at 2θ of 28° and 47.2° are determined as fluorite. At 50 $mg\,L^{-1}$, supersaturation was high enough for precipitation to occur. The precipitates

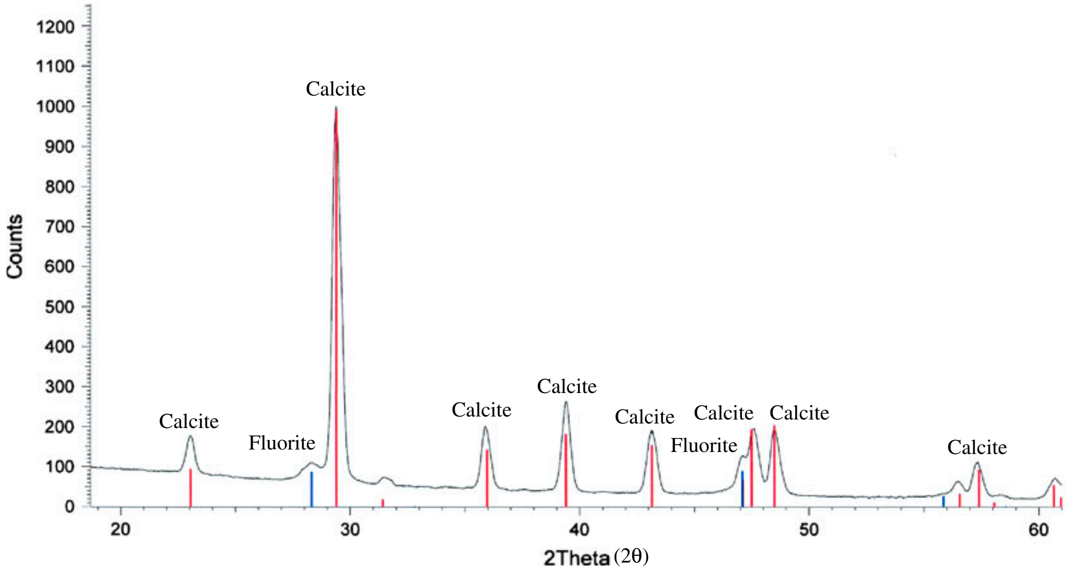

Fig. 6. X-ray diffraction pattern obtained after defluoridation using calcite and acetic acid 0.1 M. Initial fluoride concentration 50 $mg\,L^{-1}$, powder removed from the 0.1 μm pore size membrane after filtration of the supernatant.

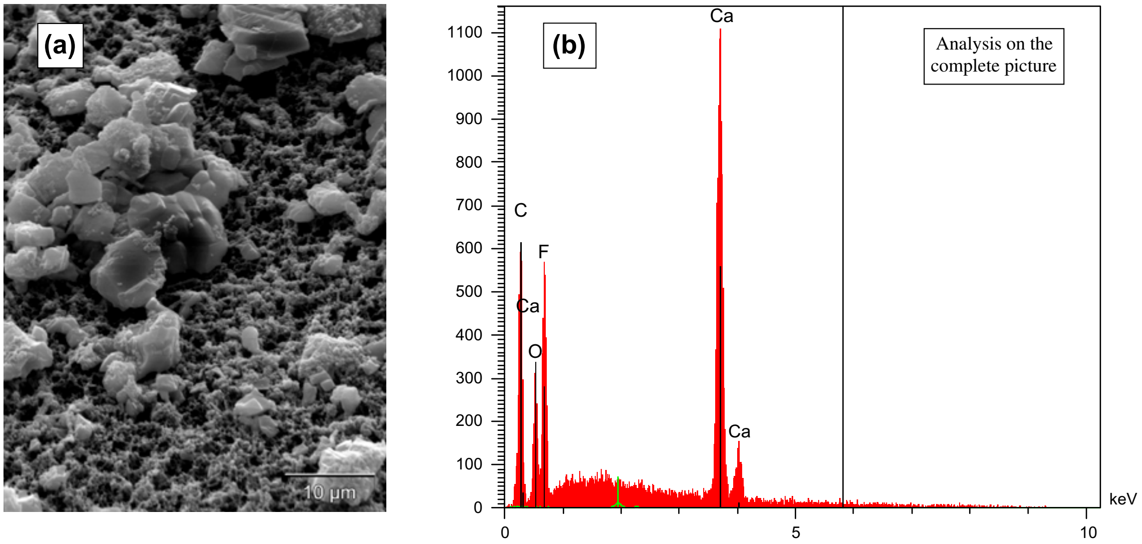

Fig. 7. SEM-EDS characterisation of samples obtained after defluoridation using calcite and 0.1 M acetic acid. Initial fluoride concentration 50 mg L^{-1}, 0.1 μm pore size membrane after filtration of the supernatant.

were so fine that they were still in suspension after 1 h of decantation, and they were retained by the microfiltration membrane.

3.6. SEM-EDS

The suspensions obtained after the defluoridation experiments were characterised by SEM-EDS.

The SEM picture and EDS spectrum are shown in Fig. 7. At 50 mg L^{-1}, the membrane retained particles which presented mainly the characteristic cubic shape of calcite particles (Fig. 7(a)). F atomic percentages were very low with the exception of 50 mg L^{-1} fluoride. At this concentration, the F atomic percentage was high and reached 24% (Fig. 7(b)). Similar high percentages were recorded for several pictures (at least 5). This confirmed that supersaturation was high enough to induce precipitation of CaF_2. The precipitates were, however, so fine that they could not be distinguished clearly on the SEM picture.

3.7. Microfiltration

Microfiltration is a relatively simple and low cost technique. In this study, it is used for filtration of the supernatants obtained after defluoridation and decantation as CaF_2 precipitates were reported to be very fine and they settle very slowly [40]. The filtrates obtained were very clear which confirmed the retention of most particles. In addition, X-ray diffraction measurements, as reported previously, indicated that CaF_2 was detected on the surface of the microfiltration membrane.

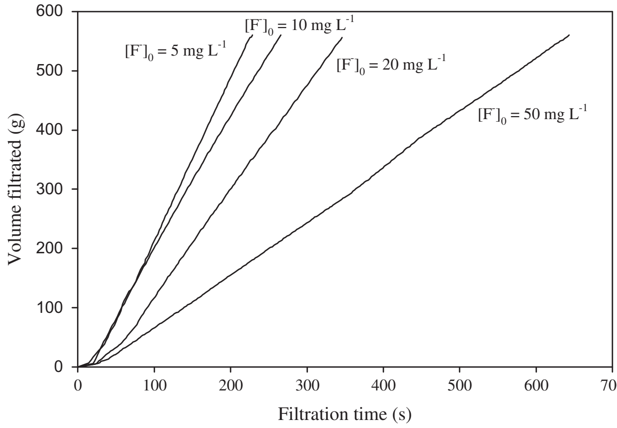

Fig. 8. Filtrated volume versus time for initial fluoride concentration between 5 and 50 mg L^{-1} (calcite amount 15 g L^{-1}, acetic acid concentration 0.1 M, contact time 2 h, transmembrane pressure 2 bar).

The filtrated volume was recorded vs. time (Fig. 8) for initial fluoride concentrations between 5 and 50 mg L^{-1} at the same transmembrane pressure of 2 bar. The volume filtrated increased almost linearly throughout the experiment indicating a constant permeate flux. This result suggested low membrane fouling. In addition, the flux decreased with an increase in fluoride concentration. At 5 mg L^{-1}, the flux was equal to 10.6 cm min^{-1} and at 50 mg L^{-1} to 3.8 cm min^{-1}. The very small CaF_2 precipitates probably accumulated within the membrane structure

Table 1
Initial and final concentrations of fluoride and fluoride removal efficiency, *R*, obtained after defluoridation of a natural water and a model water using calcite and acetic acid (contact time 4 h, adsorbent amount $15\,g\,L^{-1}$, acetic acid concentration 0.1 M)

	Natural groundwater	Model water
$[F^-]_i$ ($mg\,L^{-1}$)	2.7	2.5
$[F^-]_f$ ($mg\,L^{-1}$)	1.24	1.21
R (%)	53.7	51.6
pH_f	7.19	7.23

which caused a reduction of flux without leading to high fouling.

3.8. Defluoridation of a Tunisian groundwater

A naturally fluoridated Tunisian groundwater sample (initial fluoride concentration $2.7\,mg\,L^{-1}$) was treated for defluoridation using calcite particles and acid addition. Table 1 presents the results of defluoridation. The experiments were realised at the following conditions: contact time 4 h, adsorbent amount $15\,g\,L^{-1}$ and acetic acid concentration 0.1 M. The contact time was set to 4 h to increase the fluoride removal. The final fluoride concentration was around $1.2\,mg\,L^{-1}$, which was below the WHO standards of $1.5\,mg\,L^{-1}$. The pH of the treated water was also found in an acceptable range.

The fluoride removal efficiency measured with the groundwater was very close to the one obtained with a model fluoride solution. Indeed, Nath and Dutta [24] previously reported that the dissolved ions (Mg^{+2}, SO_4^{2-}, etc.) present in the groundwater had little effect on the ability of a limestone reactor in the presence of acids to remove fluoride.

In addition, the X-ray measurements did not show any fluorite in: (1) the powder obtained at the bottom of the flask after the defluoridation experiments followed by 1 h decantation and (2) the powder removed from the 0.1 μm pore size membrane surface after filtration of the supernatant. It is then suggested that amount of CaF_2 precipitates was too low to be detected.

4. Conclusion

In this paper, it is shown that addition of acetic acid to calcite particles increased the removal of fluoride in model solutions. X-ray diffraction and SEM-EDS were use to determine the phenomena which governed fluoride removal. At $5\,mg\,L^{-1}$ fluoride concentration, fluoride removal was mainly due to adsorption on calcite particles and no fluorite was detected by X-ray diffraction. The increase in fluoride removal in presence of acid was mainly attributed to the increase in the available area for adsorption on the particles. At $50\,mg\,L^{-1}$, supersaturation was high enough for fluorite precipitation to occur. Fluorite was detected by X-ray diffraction, and SEM-EDS showed the presence of F on top of the microfiltration membrane.

The method is suggested to be suitable for defluoridation of groundwaters, especially for groundwaters with high fluoride concentration such as $50\,mg\,L^{-1}$. The fluoride removal efficiency is then very high (>90%). The pH of the treated groundwater remains in an acceptable range. Moreover, acidification is already used in water treatment. Indeed acidification is a useful pre-treatment technique to prevent scaling to specifically reduce the crystallisation of calcium carbonate.

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