Journal of Fluorine Chemistry 132 (2011) 57–62

Contents lists available at ScienceDirect

Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor

Removal of fluoride ions using cuttlefish bones

A. Ben Nasr [a], K. Walha [a,*], C. Charcosset [b], R. Ben Amar [a]

[a] Laboratoire des Sciences des Matériaux et Environnement, Faculté des Sciences de Sfax, University of Sfax, Tunisia
[b] Laboratoire d'Automatique et de Génie des Procédés, Université de Lyon 1, Villeurbanne, France

ARTICLE INFO

Article history:
Received 22 July 2010
Received in revised form 10 November 2010
Accepted 10 November 2010
Available online 18 November 2010

Keywords:
Brackish water
Defluoridation
Sorption
Desorption
Cuttlefish bone

ABSTRACT

Because of the high toxicity of fluoride to mankind, there is an urgent need to treat fluoride-contaminated drinking water to make it safe for human consumption. This work investigated the possibility of eliminating, by sorption, the excess of fluoride in overloaded water according to World Health Organization WHO recommendations. We tested the cuttlefish bone as an adsorbent material (available in Tunisia) for the defluoridation of water. Initially, we determined the optimal conditions of use (contact time, pH effect, adsorbent dose, initial fluoride concentration) of the cuttlefish bone on synthetic solutions of sodium fluoride. The second step was to verify the effectiveness of the sorption process on the cuttlefish bone by testing it on natural waters loaded with fluoride. The results obtained showed that sorption on the cuttlefish bone could be an effective method for the removal of fluoride. The efficacy of cuttlefish bone to remove fluoride from water was found to be 80% at pH 7.2, 1 h contact time, 15 g L^{-1} adsorbent dose and 5 mg L^{-1} initial fluoride concentration. Despite the different anions (Cl^- and SO_4^{2-}) generally present in natural waters, a fluoride concentration in agreement with the norm (<1.5 mg L^{-1}) could be reached whatever the water treated. The regeneration of the cuttlefish bone was performed with a NaOH solution (10 g of cuttlefish bone/1000 mL NaOH 3 M). After 1 h of agitation, 95% of fluorides were desorbed. Following regeneration, the adsorbent can be used for further removal of fluoride.

1. Introduction

Many countries, producers of phosphates such as Tunisia, Morocco, Algeria and Senegal, are confronted with an excess of fluoride in drinking water and are concerned with reducing its impact on the consumer's health. In the south of Tunisia, especially in the regions of Gafsa, Metlaoui and Redayef, fluoride contents in drinking water (Table 1) are significantly higher than the drinkability standards set by the various legislations, in particular by the World Health Organization WHO. The maximum permissible level of fluoride in drinking water as regulated by the WHO is 1.5 mg L^{-1} [1].

The continuous consumption of water containing fluoride ions can be either beneficial or harmful. When fluoride is present in drinking water at optimal levels (0.7–1.2 mg L^{-1}), it has been shown to promote oral health by preventing tooth decay. Waters with fluoride concentrations higher than 2 mg L^{-1} and 4 mg L^{-1} promote dental fluorosis (hypercalcification of tooth enamel due to excessive adsorption of fluoride ions) and bone fluorosis, respectively [2–4].

The current methods which are used to reduce the concentration of fluoride ions from water can be divided into two categories: precipitation and sorption [5]. Precipitation of fluoride with calcium and aluminum salts is used to remove fluoride from industrial wastewater [6]. Sorption is another technique, in which fluoride is sorbed onto a membrane or a fixed bed packed with resin or other mineral particles. Many others techniques have been reported, such as reverse osmosis, electrodialysis, Donnan dialysis, nanofiltration, ion exchange, limestone reactor and activated aluminum column [3,7–18]. Recent attention of scientists has been devoted to the study of low cost, but effective materials. A large number of materials have been tested, such as activated alumina, calcite, clay, zeolite, charcoal, fly ash, bleaching earth and red mud [19–32]. However, the lowest limit for fluoride reduction by most of the adsorbents is higher than 2 mg L^{-1}, therefore, they are not suitable for the drinking water treatment purpose, especially as some of them can only work at an extreme pH value, such as activated coal which is only effective for fluoride removal at pH less than 3.0 [33].

This work investigates the possibility of eliminating, by sorption, the excess of fluoride in overloaded water using cuttlefish bone, available in Tunisia, as an adsorbent material. With respect to the first objective of this study, the sorption experiments of water soluble F^- ions from synthetic solutions or natural waters were carried out using cuttlefish bone. The first step was to

---

[*] Corresponding author. Tel.: +216 74 276 400; fax: +216 74 274 437.
E-mail address: walhakhaled@yahoo.fr (K. Walha).

0022-1139/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jfluchem.2010.11.006

Table 1
Fluoride concentration of drinking waters from Gafsa regions (South of Tunisia).

	Metlaoui Louza 1	Metlaoui Louza 2	Redayef Tabeddil	Om Elarayes	Gafsa SM4	Foum El Maaza
C_F (mg L^{-1})	3.25	3.39	2.73	2.35	2.61	2.20

Table 2
Physico-chemical analysis of two natural waters collected from the regions Gafsa (South of Tunisia).

	Louza 2	Gafsa SM4
pH	7.59	7.35
TAC (°F)[a]	15.4	15
TH (°F)	99	152
Ca^{2+} (mg L^{-1})	210	467
Mg^{2+} (mg L^{-1})	113	86
Cl^- (mg L^{-1})	312	143
SO_4^{2-} (mg L^{-1})	1032	1390
F^- (mg L^{-1})	3.39	2.61

[a] 1 °F (French degree) = 4 mg L^{-1} of Ca^{2+} = 2.43 mg L^{-1} of Mg^{2+} = 12.2 mg L^{-1} of HCO_3^-.

determine the optimal conditions for the use of cuttlefish bone on synthetic sodium fluoride NaF solutions. A second step was to verify the effectiveness of the sorption process on the cuttlefish bone through tests on natural waters loaded with fluoride. With respect to the second objective, the study of desorption of fluorides from cuttlefish bone was carried out using a NaOH solution.

2. Experimental

2.1. Synthetic fluoride solution and natural waters

A stock solution of 250 mg L^{-1} fluoride was prepared by dissolving 552.5 mg of sodium fluoride (Merck, Germany) in 1.0 L of distilled water and all synthetic solutions for the removal experiment and the analysis were prepared by an appropriate dilution from the freshly prepared stock solution. Two Tunisian underground waters were considered in the study: Louza 2 and Gafsa SM4. The salt compositions of these waters are given in Table 2. The two waters have particularly high levels of fluorides, which represent a permanent risk for the population which relies on underground water (wells) for the daily consumption. The concentration of about 3 mg L^{-1} of fluoride was higher than the acceptable value.

2.2. Characterization of the cuttlefish bone

Before use, cuttlefish bone was rinsed with deionized water, boiled for 10 min to desorb any impurities, dried at 103–105 °C for 24 h and allowed to cool in a dessicator. Turner et al. [25] showed that the performance of defluoridation of water was very good (≈90–96%) for small particles (150–300 μm) of calcite: the thermodynamically stable variety of calcium carbonate at room temperature. In our study, cuttlefish bone was crushed and sieved. The sorption properties of 150–200 μm-particles were studied. The X-ray diffraction pattern of the cuttlefish bone was recorded by a D8 Bruker X-ray diffractometer (Germany). The XRD data were matched with standard JCPDS data files. Elemental analysis was conducted by a Philips PW 104 wavelength dispersive sequential XRF (X-ray fluorescence) analyzer, with less than ±2% error. The spectroscopic studies were performed by using a scanning electron microscopy (SEM, Hiatchi S2500). The Brunauer–Emett–Teller (BET) surface area was determined by the low temperature N_2 adsorption method. The pH of the zero point charge (pH_{zpc}) was determined by placing 1 g of cuttlefish bone into 250 mL glass stopper bottle containing 100 mL of 0.01 M NaCl solutions. The initial pH of these solutions was adjusted to 5.5, 6.5, 7.5, 8.5, 9.5, 10.5 and 11.5 by either adding 0.1 M NaOH or 0.1 M HCl. The bottles were then placed in the incubator shaker at 30 °C for 48 h, and the final pH of supernatant measured. The ΔpH (=$pH_{(final)} - pH_{(initial)}$) was plotted against the initial pH, the pH at which ΔpH was zero was taken as a pH_{zpc}.

2.3. Ionic analysis methods

Calcium and magnesium concentrations were successively obtained by complexometric determination with EDTA on the same water sample. The determination of OH^-, CO_3^{2-} and HCO_3^- concentrations of the sample were carried out by the neutralization of a given volume of water by hydrochloric acid 2×10^{-2} M in the presence of phenolphthalein and helianthin. Chlorides and sulfates were analyzed by ion chromatography in an AS11 4 mm column (DIONEX). However, this analytical method was not accurate for fluorides owing to the high amount of chloride ions. Fluoride concentrations were therefore determined with an ion-specific fluoride electrode TACUSSEL according to a standardized method (AFNOR T90-0004) [34].

2.4. Batch tests

Sorption was carried out in batch tests. Crushed cuttlefish bone was added to synthetic sodium fluoride solution or to underground waters (Louza 2 and Gafsa SM4). All experiments were conducted at room temperature (25 ± 2 °C). Batch sorption was conducted to investigate the effect of controlling parameters like contact time, pH, dose of adsorbent and initial fluoride concentration on the sorption capacity of the cuttlefish bone. In addition, we tested the effect of certain ions (Ca^{2+}, Cl^- and SO_4^{2-}) on the defluoridation process. Two underground waters naturally fluoridated, from the Gafsa region, were treated at the optimum conditions determined from synthetic solutions tests. The sample solution containing fluoride ion (5 mg L^{-1}) was taken in a 300 mL Erlenmeyer flask. The quantity of crushed cuttlefish bone was added. Then the pH was adjusted to a definite value and the solution was stirred at 300 rpm at various times. At the end of each experiment, the sample was filtered using a Whatmann (45 μm) filter paper and analyzed for residual fluoride content.

The amount of the removed fluoride was calculated by subtracting the fluoride remaining in the solution initially taken. In all cases mass balance was confirmed. The removed fluoride R was calculated using the following equation:

$$R\,(\%) = \frac{1 - C_0}{C_f} \times 100$$

where C_0 (mol L^{-1}) is the initial concentration of the solution before sorption and C_f (mol L^{-1}) is the final concentration after the sorption of the fluoride ion.

To determine the equilibrium sorption time, experiments were conducted by varying contact time of 30, 60, 90, 120, 150 and 180 min to a solution containing initial concentration of 5 mg L^{-1} and 15 g L^{-1} of cuttlefish bone. The pH of the solutions was adjusted at 7.2 ± 0.1. Samples were agitated, filtrated and the residual concentration determined.

The effect of pH on fluoride removal was found by adjusting the pH of synthetic solution of 5.0 mg L^{-1} to initial pH value of 10.5, 9.5, 8.5, 7.5, 6.5, 5.5, 4.5 using 0.5 M HCl or 0.5 M NaOH; a fixed quantity (15 g/1000 mL) of cuttlefish bone was added and mixed for the equilibrium sorption time and analyzed for residual fluoride content.

To study the effect of an increase in the amount of cuttlefish on fluoride removal, experiments were conducted by varying amounts of 5, 10, 15, 20, and 25 g L^{-1} to a solution containing initial concentration of 5 mg L^{-1}. The samples were agitated up to equilibrium and the fluoride residual concentrations were determined.

The effect of certain ions (Ca^{2+}, Cl^-, and SO_4^{2-}) on the defluoridation process was found by spiking synthetic fluoride solution ($C_F = 5$ mg L^{-1}) with different concentration of Ca^{2+}, Cl^- and SO_4^{2-}.

2.5. Desorption study

Desorption of fluorides from cuttlefish bone was carried out with a NaOH solution. The same solution was used several times to realize the cuttlefish bone regeneration. The method used for desorption consisted of brewing the cuttlefish bone in the basic solution (10 g of cuttlefish bone/1000 mL of NaOH 3 M) for 1 h at a stirring speed of 300 rpm. The concentration of fluorides was then measured in this solution following filtration. The cuttlefish bone was removed and rinsed with distilled water and then reused for a new adsorption.

2.6. Data accuracy

Each removal experiment was conducted twice to obtain reproducible results with an error of less than 3%. The original fluoride solution (control) was used in all analysis, which considerably reduced the absolute error associated with the fluoride error analyzer to <2%.

3. Results and discussion

3.1. Characterization of the cuttlefish bone

The X-ray diffraction (XRD) pattern shows that the cuttlefish bone has well crystallized form (Fig. 1) with a weak peak at 3.40 Å which is characteristic of aragonite variety [35]. Elemental analysis showed that the cuttlefish bone was 96% pure calcium carbonate $CaCO_3$ with trace quantities of Na (1.28% as Na_2O), P (0.53% as P_2O_5) and other elements at concentration <50 mg L^{-1}. Cuttlefish bone had a very porous structure as shown in Fig. 2. The specific surface area of the crushed cuttlefish bone was found to be 0.070 ± 0.002 $m^2\ g^{-1}$. According to the definition given earlier, the experimental pH_{zpc} of the cuttlefish bone is 9.8 (Fig. 3), which agrees closely with the experimental value of calcite determined by Somasundaran and Agar [36].

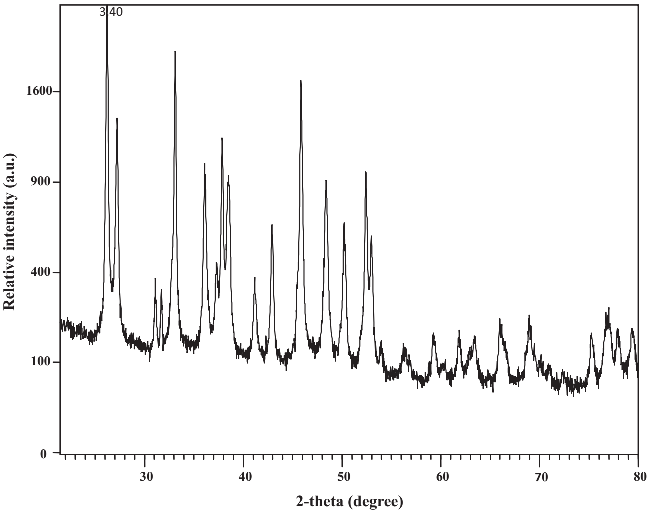

Fig. 1. XRD pattern of cuttlefish bone.

3.2. Effect of contact time

Fig. 4 shows fluoride removal at different contact times using cuttlefish bone as an adsorbent. With increasing contact time, fluoride removal increased rather rapidly, but then gradually approached a more or less constant value denoting attainment of equilibrium. The sorption reaction may be considered to be occurring in three distinct phases. First, the initial rapid phase in which the rate of fluoride removal was very rapid in less than 30 min. This may be the result of the instantaneous sorption reaction in which fluoride ions sorbed quickly onto the surface of the cuttlefish bone due to a specific chemical interaction (or affinity) and to diffusion and other driving forces. In the second phase, the sorption rate decreased due to less sorption as a result of the migration of fluoride ions from the film/boundary layer to the interior pore/capillary surfaces. In the last phase, i.e., after 60 min, fluoride removal rate leveled off significantly, denoting attainment of equilibrium and the non-availability of sorption sites. Our results are in agreement with those of Fan et al. [6] who showed

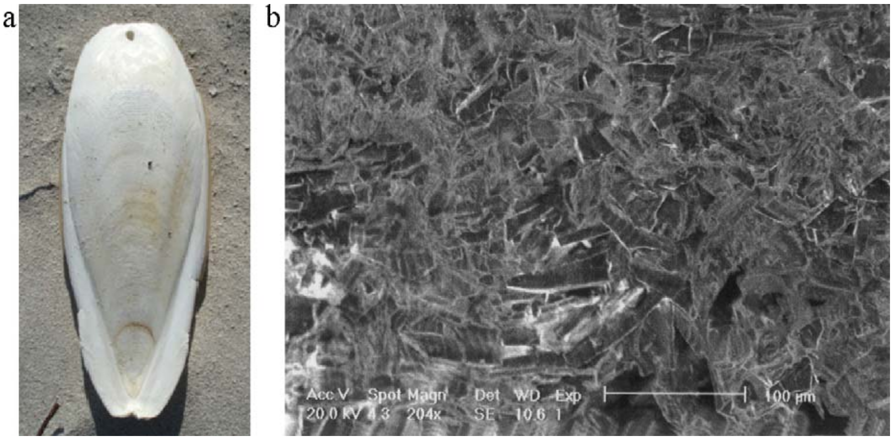

Fig. 2. Cuttlefish bone: (a) internal cuttlefish shell and (b) scanning electron microscopy SEM micrograph of the cuttlefish bone.

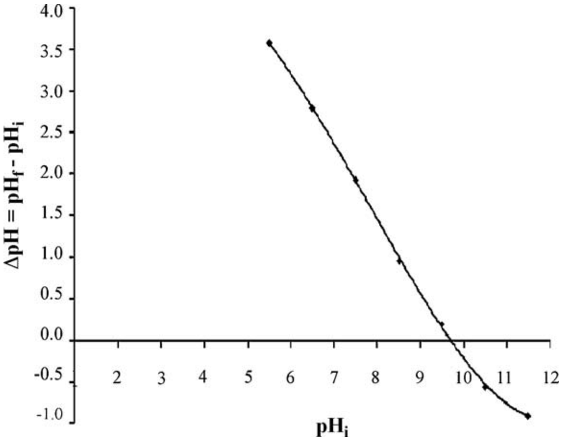

Fig. 3. Zeta potential of cuttlefish bone.

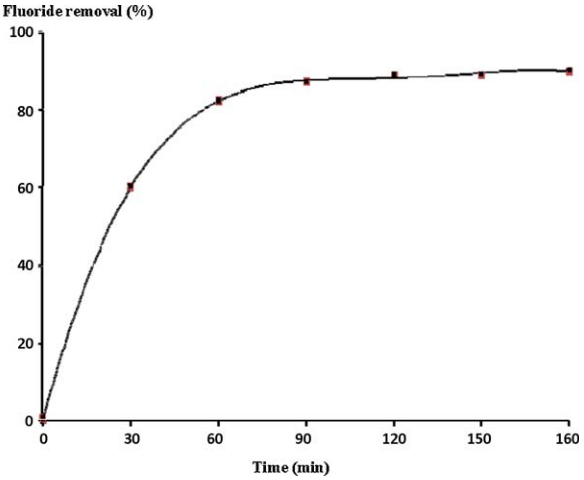

Fig. 4. Fluoride removal as a function of equilibrium time (adsorbent dose 15 g L^{-1}, fluoride concentration 5 mg L^{-1} and pH 7.2).

that sorption times designed for reaching the equilibrium was 60 min in the experiment conditions (initial fluoride concentration of 3 mg L^{-1}, pH of 6 and 15 g L^{-1} of calcite with 212–250 μm-particles). As there was no significant increase in the fluoride removal rate after 60 min, an equilibrium time of 60 min was chosen and this was used in all subsequent experiments.

3.3. *Effect of pH*

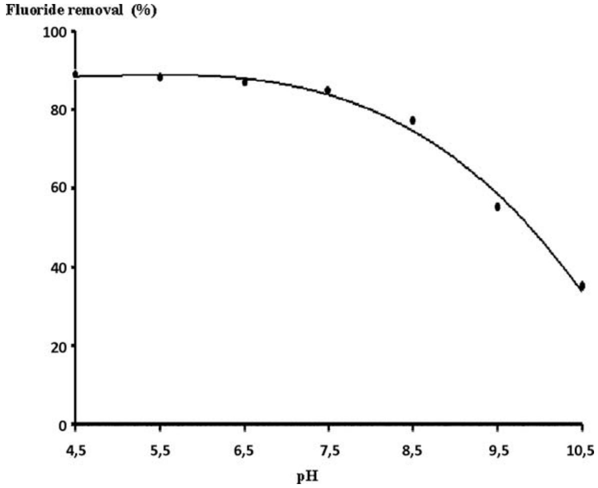

Fig. 5. Fluoride removal as function of pH (adsorbent dose 15 g L^{-1}, fluoride concentration 5 mg L^{-1} and equilibrium time (1 h).

Fig. 5 shows the effect of pH on the removal of fluoride by sorption on the cuttlefish bone. As the pH of the fluoride solution increased from 4.5 to 10.5, fluoride removal was more or less constant around 85–82% for a pH between 4.5 and 7.5. But, it drastically dropped to 35% at pH 10.5. The mechanism of fluoride removal can be better understood by examining the cuttlefish bone surface composition. Cuttlefish bone, when dissolved in water, will produce the following species, HCO_3^-, CO_3^{2-}, Ca^{2+}, $CaHCO_3^+$ and $CaOH^+$. When the solution is more basic than the point at zero charge ($pH > pH_{zpc}$), negative species will predominate and the surface will be negatively charged. Similarly, when the solution is more acidic than the point at zero charge ($pH < pH_{zpc}$), positive species will predominate and the surface will be positively charged. A number of authors [37–41] showed that Ca^{2+} and CO_3^{2-} were the potential determining ions in a pure calcite solution. Decreasing pH effectively provides more Ca^{2+} in a solution from the dissolution of cuttlefish bone and increases the number of positive sites, leading to an increase in the amount of fluoride removed from the solution. Lower fluoride removal at higher pH values may be due to surface reactions of the type ion-exchange leading to a change in the electrokinetic properties of the surface of cuttlefish bone, increasing the negative charges at the surface of the adsorbent which reduced the sorption of fluoride ions. Fan et al. [6] showed that the uptake of fluoride in calcite was a surface sorption and that fluoride sorption fitted Freundlich isotherm. Yang and Dluhy [19] and Turner et al. [25] showed that the best performance of defluoridation of water using calcite was obtained at neutral pH. For the following adsorption tests, we adjusted the solution pH to 7.2 ± 0.1.

3.4. *Effect of cuttlefish amount on fluoride removal*

The fluoride removal increases with the amount of cuttlefish bone used (Fig. 6). According to the figure, when the adsorbent amount increased from 5 to 15 g L^{-1}, the fluoride removal increased from 40% to 85%, respectively. This rise was due to the larger surface available to sorption which promoted the sorption of fluoride. For cuttlefish bone amount more than 15 g L^{-1} no significant increase in fluoride removal was observed (R = 89%

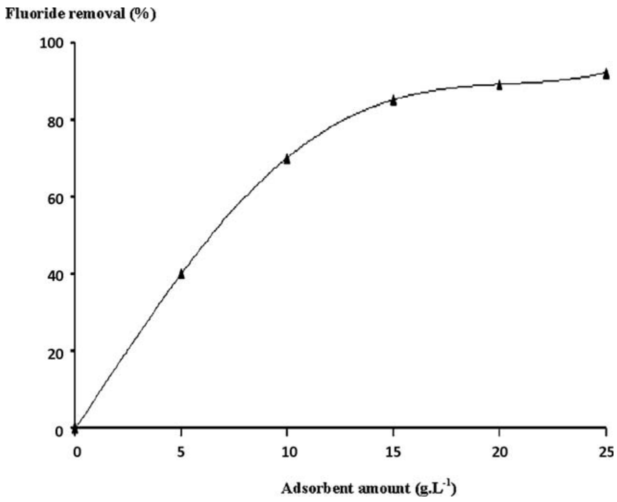

Fig. 6. Fluoride removal as function of adsorbent amount (fluoride concentration 5 mg L^{-1}, pH 7.2 and equilibrium time 1 h).

Table 3
Results of defluoridation solutions with different concentrations of fluoride (adsorbent amount 15 g L^{-1}, pH 7.2, and equilibrium time 1 h).

C_{initial} (mg L^{-1})	2.5	5.0	7.5	10
C_{residual} (mg L^{-1})	0.50	1.05	1.53	2.20
R (%)	80.0	79.0	79.6	78.0

at an amount of cuttlefish bone 25 g L^{-1}). Turner et al. [25] showed that fluoride removal was more important (96%) with a fluoride concentration of 3 mg L^{-1} at pH 7 using calcite as adsorbent at a dose of 33.3 g L^{-1}: greater than the cuttlefish bone dose we used. We have thus chosen for the following tests a constant amount of cuttlefish bone (15 g L^{-1}).

3.5. Effect of initial fluoride concentration

To demonstrate the effectiveness of the cuttlefish bone, we varied the initial content of fluoride. The results are summarized in Table 3. Fluoride removal was not affected by the initial F^{-} concentration over the whole range from 2.5 to 10 mg L^{-1}, which could be considered to be an important advantage over the conventional method. Similar results were obtained by Huang et al. [42]. It should be noted that the residual fluoride after treatment with cuttlefish bone was consistent with drinking water standards for an initial concentration of fluoride in the range of 7.5 mg L^{-1}.

3.6. Effect of mineralization

3.6.1. Effect of chloride, sulfate and calcium on fluoride removal

Drinking water contains many different ions, which may influence the sorption of fluoride by cuttlefish bone. Therefore, the effect of chloride, sulfate and calcium on the adsorption of fluoride on cuttlefish bone was examined. Sorption experiments have been made with some salts (NaCl, $CaCl_2$ and Na_2SO_4). The initial concentration of fluoride was fixed at 5 mg L^{-1} while the initial concentration of ions (Cl^{-}, SO_4^{2-} and Ca^{2+}) varied from 100 to 400 mg L^{-1}. We found that chlorides had no effect on the sorption of fluoride on cuttlefish bone. Similar results were obtained by Yang and Dluhy [19] for the sorption of fluoride on a fixed bed packed with granular calcite. The presence of SO_4^{2-} reduced the adsorption of fluoride on cuttlefish bone. The decreased sorption of fluoride in the presence of sulfate may be because of the lower affinity for sorption. The results are in agreement with those of Sujana et al. for the removal of fluoride with alum sludge [43]. The presence of calcium promotes defluoridation (increased efficiency) of water as shown in Fig. 7.

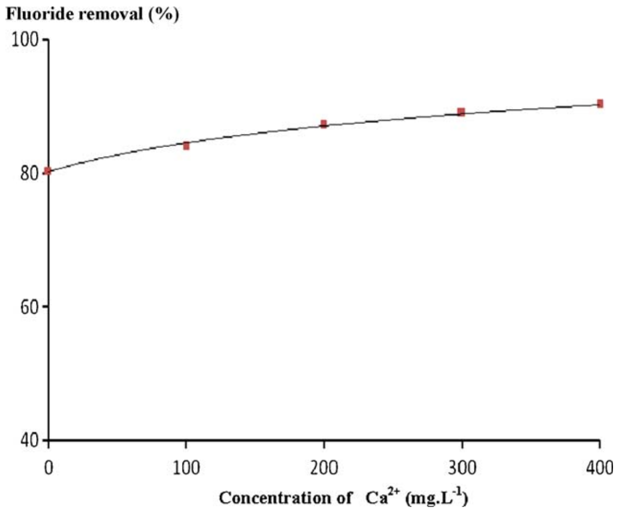

Fig. 7. Fluoride removal as function of calcium concentration (adsorbent amount 15 g L^{-1}, fluoride concentration 5 mg L^{-1}, pH 7.2 and equilibrium time 1 h).

Table 4
Fluoride residual concentration and fluoride removal R obtained at the end of adsorption test of natural waters using cuttlefish bone (adsorbent amount 15 g L^{-1}, pH 7.2, and equilibrium time 1 h).

	Louza 2	Gafsa SM4
C_{initial} (mg L^{-1})	3.39	2.61
C_{residual} (mg L^{-1})	1.09	0.87
R (%)	67.8	66.7

3.6.2. Defluoridation of natural waters

This step was performed on two underground waters (Louza 2 and Gafsa SM4) naturally fluoridated. In Table 4, we present the results of the defluoridation of the two waters. The values were obtained at optimum conditions (pH 7.2, contact time 60 min, adsorbent amount 15 g L^{-1}). The sorption of fluoride on the cuttlefish bone was effective. Indeed, the residual fluoride was below the WHO standards. Except for fluoride, the other physico-chemical parameters of the treated water were not modified. Analysis of the precipitate obtained showed that it was mainly composed of calcium carbonate and a small amount of CaF_2. For CaF_2 precipitation, supersaturation of F^{-} and Ca^{2+} was the major premise. Indeed, with Louza 2 water, $C_F = 3.39\ \text{mg L}^{-1} = 1.79 \times 10^{-4}$ M; $C_{Ca}{}^{2+} = 210\ \text{mg L}^{-1} = 5.25 \times 10^{-3}$ M. The ionic product $Q = C_{Ca} \times (C_F)^2 = 5.25 \times 10^{-3}\ \ (1.79 \times 10^{-4})^2 = 16.9 \times 10^{-11}$ was higher than solubility product K_s of CaF_2 ($K_s = 3.5 \times 10^{-11}$). Turner et al. [25] and Nath and Dutta [44] confirmed that besides sorption, precipitation of CaF_2 could also occur.

3.7. Desorption of fluoride and regeneration of the cuttlefish bone

To make a cost-effective process, the adsorbent should be regenerated so that reuse is possible for further fluoride sorption. We found that, after 1 h of agitation at 300 rpm, more than 95% of fluorides were desorbed. The cuttlefish bone was removed and rinsed with distilled water. Regenerated cuttlefish bone was placed again in contact with natural water containing fluoride. A new sorption of fluoride was noted. This result led us subsequently to examine the effect of the number of sorption–desorption fluoride cycles in relation to the regeneration efficiency. A histogram (Fig. 8) of the results demonstrated that fluorides quantities sorbed and desorbed for the same cycle were practically equal for the five cycles carried out. The performance of the regenerated cuttlefish bone was found to be slightly inferior to that of the fresh one. A decrease of 2–3% in efficiency was showed after each cycle of sorption–desorption.

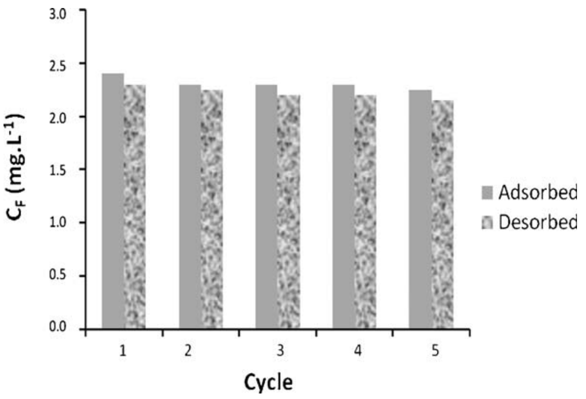

Fig. 8. Quantity of fluorides adsorbed and desorbed during 5 cycles of adsorption–desorption.

4. Conclusion

From the present investigation, it was clear that cuttlefish bone was effective towards fluoride removal from naturally fluoridated water. The material is non-toxic, which makes it easily acceptable to common people. The following conclusions may be drawn:

(1) Elemental analysis showed that cuttlefish bone was 96% pure calcium carbonate. X-ray diffraction pattern and SEM studies reveal that cuttlefish bone is well crystallized and uniform.
(2) Fluoride removal was found to be very rapid during the initial period (less than 30 min) and reached 80% at 60 min.
(3) The degree of removal is dependent on cuttlefish bone surface area. The optimum pH was found to be 7, which is suitable for the drinkable purpose. At this pH, the removal of fluoride was around 80%.
(4) Adsorbent dose of $15\ \mathrm{g\ L^{-1}}$ is sufficient for the removal of fluoride from water at the initial fluoride concentration up to $7.5\ \mathrm{mg\ L^{-1}}$.
(5) Chloride had no significant effect on the defluoridation of treated water from the cuttlefish bone while sulfate reduced the sorption of fluoride on cuttlefish bone. Calcium promoted the defluoridation of water.
(6) Despite the different anions (Cl^- and SO_4^{2-}) generally present in natural waters, a fluoride concentration in agreement with the norm ($<1.5\ \mathrm{mg\ L^{-1}}$) could be reached whatever the water treated. Considering the high level of chloride and sulfate in the treated water, efficient post-treatment could be developed in the future.
(7) The desorption study showed that the cuttlefish bone could be reused for fluoride removal by rinsing for 60 min the cuttlefish bone with a solution: 10 g of cuttlefish bone/1000 mL of NaOH solution 3 M. Following regeneration, the adsorbent can be used for further removal of fluoride.

Acknowledgements

Authors are thankful to Pr. Fakhfakh Zouheir, Dr Mezghani Imed, University of Sfax, Fakhfakh Abdelakhallak, technician, Société Nationale de Distribution et d'Exploitation des Eaux, Sonede Sfax and Ben Meftah Nabil, Technician, Division Mineralogy and Rock Mechanics, Companie Phosphate Gafsa CPG, for providing necessary research assistance.

References

[1] W.H.O. (World Health Organization) Guidelines for Drinking Water Quality: Water Safety and Human Health, World Health Organization, Singapore, 2010
[2] M. Pontié, Phénomènes électrocinétiques et transferts ioniques dans les membranes poreuses à faible seuil de coupure. Application au traitement des eaux saumâtres, Thèse, Univ. Tours France, 1996
[3] A. Lhassani, M. Rumeau, D. Benjelloun, M. Pontié, Water Res. 35 (2001) 3260–3264.
[4] S. Meenakshi, R.C. Maheshwari, J. Hazard. Mater. B 137 (2006) 456–463.
[5] R. Desjardins, Le Traitement des Eaux, Editions de l'Ecole Polytechnique de Montréal, 2ème ed., 1990.
[6] X. Fan, D.J. Parker, M.D. Smith, Water Res. 37 (2003) 4929–4937.
[7] H. Lounic, L. Addour, D. Belhocine, H. Grib, S. Nicolas, B. Bariou, N. Mameri, Desalination 114 (1997) 241–251.
[8] A.G. Perrov, E.V. Dudkin, O.A. Sidorenko, V.V. Antipov, S.A. Khakhanov, R.I. Makarov, Desalination 132 (2000) 315–321.
[9] S. Sourirajan, T. Matsurra, Water Res. 6 (1972) 1073–1086.
[10] Z. Amor, B. Bariou, N. Mameri, M. Taky, S. Nicolas, A. Elmidaoui, Desalination 133 (2001) 215–223.
[11] N. Kabay, O. Arar, S. Samayta, U. Yuksel, M. Yuksel, J. Hazard. Mater. 153 (2008) 107–113.
[12] H. Games, F. Persin, J. Sandeaux, G. Pourcelly, M. Mountadar, Desalination 145 (2002) 287–291.
[13] C.K. Diawara, L. Paugam, M. Pontié, J.P. Schlumpf, P. Jaouen, F. Quemeneur, Sep. Purif. Technol. 40 (2005) 3339–3347.
[14] M. Pontié, H. Dach, J. Leparc, M. Hafsi, A. Lhassani, Desalination 221 (2008) 174–191.
[15] K. Vaaramaa, J. Lehto, Desalination 155 (2003) 155–170.
[16] I.B. Solangi, S. Memon, M.I. Bhanger, J. Hazard. Mater. 171 (2009) 815–819.
[17] A. Moufti, S. Jemjami, M. Mountadar, A. Hamdani, Rev. Sci. Eau 17 (2004) 463–470.
[18] K.P. Bulusu, W.G. Nawlakhe, Indian J. Environ. Health 30 (1988) 262–299.
[19] C.L. Yang, R. Dluhy, J. Hazard. Mater. 97 (2002) 239–252.
[20] S. Ayoob, A.K. Gupta, P.B. Bhakat, V.T. Bhat, Chem. Eng. J. 140 (2008) 6–14.
[21] A.K. Chaturvedi, K.P. Yadava, K.C. Yadava, K.C. Pathak, V.N. Singh, Water Air Soil Pollut. 49 (1990) 51–61.
[22] R.P. Gogoi, R. baruah, Indian J. Chem. Technol. 15 (2008) 500–503.
[23] D. Thakre, S. Rayalu, R. Kawada, S. Meshram, J. Subrt, N. Labhsetwar, J. Hazard. Mater. 180 (2010) 122–130.
[24] S. Meenakshi, C.S. Sundaram, R. Sukumar, J. Hazard. Mater. 153 (2008) 164–172.
[25] B.D. Turner, P. Binning, S.L.S. Stipp, Sci. Technol. 39 (2005) 9561–9568.
[26] Y. Min, T. Hashimoto, N. Hosbi, H. Myoga, Water Res. 33 (1999) 3395–3402.
[27] S. Ayoob, A.K. Gupta, Crit. Rev. Environ. Sci. Technol. 36 (2006) 433–487.
[28] M. Mohapatra, S. Anand, B.K. Mishra, D.E. Giles, P. Singh, J. Environ. Manage. 91 (2009) 67–77.
[29] M. Mahramanlioglu, I. Kizilcikli, I.O. Bicer, J. Fluorine Chem. 115 (2002) 41–47.
[30] Y. Cengeloglu, E. Kir, M. Ersoz, Sep. Purif. Technol. 28 (2002) 81–86.
[31] A. Tor, N. Danaoglu, G. Arslan, Y. Cengeloglu, J. Hazard. Mater. 164 (2009) 271–278.
[32] B. Kemer, D. Ozdes, A. Gundogdu, V.N. Bulut, C. Duran, M. Soylak, J. Hazard. Mater. 168 (2009) 884–894.
[33] S.S. Tripathy, J.L. Bersillon, K. Gopal, Sep. Purif. Technol. 50 (2006) 310–317.
[34] J. Rodier, L'analyse de l'eau: eaux naturelles, eaux résiduaires eau de mer, 8ème ed., Dunod, Paris, 2005.
[35] D.M. Moore, R. Reynolds, X-ray Diffraction and the Identification and Analysis of Clay Minerals, 2nd ed., Oxford University Press, 1997.
[36] P. Somasundaran, E. Agar, J. Colloid Interface Sci. 154 (1967) 433–440.
[37] S.L.S. Stipp, Geochim. Cosmochim. Acta 63 (1999) 3121–3131.
[38] P. Fenter, P. Geissbuhler, G. Srajer, L.B. Sorenson, N.C. Sturchio, Geochim. Cosmochim. Acta 64 (2000) 1221–1228.
[39] D.S. Thomson, P.G. Pownall, J. Colloid Interface Sci. 131 (1989) 74–82.
[40] B. Siffert, P. Fimbel, Colloids Surf. 11 (1984) 377–389.
[41] D.S. Cicerone, A.E. Regazzoni, M.A. Blesa, J. Colloid Interface Sci. 154 (1992) 423–433.
[42] Y.C. Huang, F.M. Fowkses, T.B. Lloyd, N.D. Sanders, Langmuir 7 (1991) 1742–1748.
[43] M.G. Sujana, R.S. Thakir, S.B. Rao, J. Colloid Interface Sci. 206 (1998) 94–101.
[44] S.K. Nath, R.K. Dutta, Clean-Soil, Air, Water 38 (2010) 614–622.