



Natural zeolites from Ethiopia for elimination of fluoride from drinking water



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ABSTRACT

Zeolites and fluoride-rich groundwaters are both usually associated to volcanic regions, and hence in this work we study natural zeolites as fluoride-adsorbents in order to develop a cheap and locally-available fluorosis mitigation technology. The defluoridation capacities of eleven samples originally from Ethiopia are studied as raw materials, without any treatment. Results show that one of the samples, containing mainly analcime and mordenite zeolites, has a maximum defluoridation capacity of 0.47 mg(F⁻)/g; interestingly, this adsorbent is able to reduce the fluoride concentration beyond the safe limit established by the World Health Organization of 1.5 mg/L. In addition, desorption of fluoride from the adsorbent is easily and quantitatively achieved by subjecting the fluoride-loaded solid to a mild treatment of NaOH 0.001 M; such regenerated adsorbent retains 56% of the initial defluoridation capacity. Experiments carried out with real groundwaters show that this sample preserves its high defluoridation capacity in an actual case. Therefore, our study reports a promising cost-effective and locally-available new adsorbent for defluoridation of fluoride-rich groundwaters.

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1. Introduction

Fluoride (F⁻) is one of the most abundant anions in groundwaters all over the world. The occurrence of fluoride in groundwaters comes from the partial dissolution of fluoride-containing rocks, the most important minerals being fluorite (CaF₂), cryolite (Na₃AlF₆) and fluoroapatite (Ca₅(PO₄)₃F). The presence of fluoride in drinking water can be beneficial or harmful for human health depending on the concentration. At concentrations in water ranging between 0.4 and 1.0 mg/L, fluoride is beneficial, especially in young children, for the calcification of the dental enamel. In contrast, a too high ingestion of fluoride can lead to dental and/or skeletal fluorosis. Because of the higher stability of fluoroapatite ($K_{ps} = 3.16 \times 10^{-60}$) with respect to hydroxiapatite ($K_{ps} = 2.34 \times 10^{-59}$) and the same charge and similar ionic radii of fluoride and hydroxide anions, fluoride shows a great trend to isomorphically substitute hydroxide within the apatite network that conforms bones and teeth. Up to a certain level, substitution of hydroxiapatite by the more resistant fluoroapatite strengthens the dental enamel, contributing for the prevention of caries. However, a massive presence of fluoroapatite makes teeth, and in extreme cases of exposition, bones, denser, harder and more fragile, provoking yellowish or brownish striations or

mottling of the enamel and crippling skeletal fluorosis. Therefore, the World Health Organisation (WHO) established the maximum limit for the concentration of fluoride in drinking water in 1.5 mg/L, beyond which ingestion of water is harmful for human health [1]. Hence, the development of technologies, preferably low-cost and environmentally-friendly, capable of reducing the fluoride concentration below the limit established by the WHO represents nowadays a world-wide crucial target [2,3].

At present, a series of technologies exists for the removal of fluoride from water below such limit [2]. Existing defluoridation technologies include precipitation-coagulation, membrane-based processes, ion-exchange methods, and adsorption methods. Of these, adsorption is the preferred technique because of its low cost and ease of operation, high efficiency, easy accessibility, environmental benignity, and because adsorbents can in principle be re-used and recycled [2,4].

In adsorption methods, fluoride is removed by adsorption on different types of solid materials (adsorbents), by means of ion-exchange or surface reactions. A fundamental question for the implementation of adsorption methods is the proper choice of the material to be used as adsorbent. Evaluation of an adsorbent involves, in practical terms, considering its adsorption capacity in dilute solutions, pH, time required for fluoride removal, stability, regeneration capacity, possible interferences with other ions, and especially, cost and accessibility. Through the years, an intense effort has been applied for the development of synthetic, natural and

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waste materials for removal of fluoride from water. A large variety of materials has been studied, including impregnated and activated alumina [5,6], rare earth oxides [7], clays and other soil materials [8], impregnated silica [9], carbon materials [10,11], calcium-based materials [12,13], bone char [14], zeolites [15] and natural biomaterials [16,17]. However, when the concentration of fluoride in water is reduced to actual concentrations present in groundwaters, generally below 10 mg/L, many of these materials partially lose their defluoridation capacity.

Zeolites represent a class of materials that can be effectively used as adsorbents. Indeed, they are world-wide used as cation-exchangers, even as adsorbents in water and wastewater treatments [18]. Zeolites are crystalline microporous aluminosilicates with a defined three-dimensional structure composed by Si and Al oxide tetrahedra which share oxygen vertices. The three-dimensional arrangement of these tetrahedral units gives place to a wide diversity of open-framework topologies, conforming channels and cavities of well-defined dimensions. Zeolites are found in nature, in volcanic areas all over the world. The inorganic network is exclusively composed of Si and Al, with different relative ratios depending on the particular framework topology. The incorporation of Al^{3+} in the inorganic framework generates a negative charge on the network which needs to be balanced by the presence of cationic species, which are hosted within the channels and cavities. These cationic species (extra-framework cations) are not directly bonded to the inorganic network, but are retained by steric effects and electrostatic interactions, and hence can be exchanged by other cations, triggering one of the main applications of zeolites in industry as cation-exchangers.

Due to their cationic-exchange properties, zeolites have rarely been used for the removal of anions as fluoride. Nevertheless, worth is noting that zeolites have a volcanic origin, and therefore are abundant in countries with volcanic regions. Interestingly, one of the main sources of fluorine in the Earth Crust comes from volcanic activity, which releases magmatic fluorine usually as hydrogen fluoride through volcanic degassing. However, hydrogen fluoride, being one of the most soluble gases in magmas, desorbs only partially (<20%) during volcanic activity [19]. Volcanic rocks thus usually show high levels of fluoride, which are transferred to groundwaters through water–rock interaction processes. At the same time, such volcanic areas are often rich in zeolites; in fact, countries with severe problems of endemic fluorosis, such as China, Mexico or Ethiopia, have large deposits of zeolites [20]. Based upon these grounds, it would be very interesting to develop a defluoridation technology based on zeolites in order to provide a sustainable, accessible, locally-available and cost-effective fluorosis mitigation solution.

The limited use of zeolites as fluoride adsorbents is probably due to the fact that zeolites usually have negative surface charges at all pH values, which provides them with high adsorption capacities for cations, but low for anions because of electrostatic repulsions when anions approach the negatively-charged zeolite surface. However, it has been shown that the adsorption capacity of zeolites can be increased by modifying their surface with multivalent metallic cations [21], taking advantage of their high cation-exchange properties. In this way, Na^+ ions usually present as extra-framework cations can be exchanged by Al^{3+} or La^{3+} , giving place to active sites for the removal of fluoride [15]. The exchange of Al^{3+} and La^{3+} cations involves the appearance of a point of zero charge (PZC) for these zeolites, at 8.15 and 4–5.25, respectively, indicating that at pHs below these values, the zeolites are positively-charged, thus resulting in an increased attraction of the negatively-charged F^- anions, and a consequent higher defluoridation capacity. Defluoridation was found to be higher for the Al-treated zeolite since in this case F^- was observed to be removed by chemical adsorption, while for the La-treated zeolite adsorption was by Coulomb

interactions. Other studies have also shown that similar exchanges with multivalent cations, not only Al^{3+} and La^{3+} but also Zr^{4+} , Fe^{3+} or Ca^{2+} , result in an increased defluoridation capacity of the zeolites [20,22–25]. In summary, these studies show that zeolites can be effectively used for the removal of fluoride, especially if subjected to suitable pre-treatments, resulting in high-fluoride removal capacities, with the additional advantages of the zeolite characteristic physical properties, especially in terms of high surface area and chemical and thermal stability, low-cost and easy accessibility.

Fluoride contamination in the Rift Valley area, in south Ethiopia, and the associated occurrence of dental and even skeletal fluorosis, has become a national problem that requires attention at all country levels [26–28]; 41% of the drinking-water sources in the Ethiopian Rift Valley have a fluoride concentration exceeding 1.5 mg/L [29]. Despite several attempts to reduce the total fluoride concentration in potable waters, the mitigation activities in Ethiopia and in Africa at large are still at the initial stages. On the other hand, zeolites are a vast natural resource in Ethiopia that remains so far unexploited; in this context, zeolites offer a complementary approach to the reduction of fluoride in water in the Rift Valley area by using natural local and so far unexploited resources. Based on these grounds, the main objective of the present work is to test the potential use of several samples of naturally-occurring zeolites of the country in fluoride removal. Our main purpose is to use them as raw materials, without any treatment, to reduce the cost as much as possible in view of their potential use in countries with less economic resources.

2. Experimental details

2.1. Characterisation of solid samples

11 Samples of different minerals were collected in the North of the country, in the Tigrae region [30]. Samples were grounded with a disc mill, and characterised by X-ray diffraction (PanalyticalX'Pro diffractometer using $\text{Cu K}\alpha$ radiation), ICP-AES elemental analyses (Fluxy-30, Claisse), Thermogravimetric Analyses (TGA)/Perkin-Elmer TGA7), Scanning Electron Microscopy (FE-SEM FEI Nova NANOSEM 230) and ^{27}Al MAS NMR spectra, which were recorded at room temperature using a Bruker AV-400-WB spectrometer with a 4 mm probe spinning at 10 kHz. The ^{27}Al NMR spectra were measured using a $\pi/4$ pulse of 3 μs , contact time of 3 ms and recycle delay of 2 s operating at 40 MHz.

2.2. Evaluation of the defluoridation capacity of the samples

The 11 samples were tried as raw materials, without any treatment, as adsorbents for the removal of fluoride. In principle, large doses of 100 g(adsorbent)/L were studied. Defluoridation was carried out at room temperature, with a contact time of 20 h under continuous agitation in order to ensure complete exhaustion of the adsorbents. The concentration of fluoride in the initial solution and after equilibrium upon the addition of the adsorbent was measured by the Ion Selective Electrode technique with a pH & Ion-meter GLP 22 CRYSON; TISAB III (CRYSON) was used as buffer. Due to its more promising defluoridation properties, a more complete study for sample 3, constituted of analcime and mordenite, was carried out.

Desorption experiments were carried out by subjecting the samples (after an initial defluoridation treatment) to a basic treatment with NaOH solutions of 0.1, 0.01 or 0.001 mol/L concentrations for 3 h, with a solid-to-liquid ratio of 1 g/50 mL. Desorption of fluoride was determined by measuring the fluoride concentration of the resulting solution.

The possibility of regenerating the adsorbent was tested by first exhausting the defluoridation capacity of the raw material (after 6 consecutive cycles) with a fluoride solution of 21.9 mg/L, then subjecting the solid to a mild desorption treatment (with NaOH 0.001 mol/L), and reusing the resulting solid as adsorbent with a dose of 50 g/L and an initial fluoride concentration of 22.1 mg/L.

3. Results

3.1. General characterization of the samples

Identification of the phases present in the different samples was carried out by XRD (Table 1). We focus on sample 3 which, as we will see below, gave the best defluoridation ability. Sample 3 contains a mixture of mordenite and analcime. Mordenite (MOR type-structure) is a high-silica large-pore natural zeolite whose framework is composed of three channel systems, two in the [001] direction, limited by 12-($6.5 \times 7.0 \text{ \AA}$) and 8-($2.6 \times 5.7 \text{ \AA}$) membered rings, and a perpendicular 8-membered ring channel along the [010] direction ($3.4 \times 4.8 \text{ \AA}$), making it a very interesting material for catalytic applications. The general formula of mordenite is $(\text{Na}_2, \text{Ca}, \text{K}_2)_4(\text{H}_2\text{O})_{28}[\text{Al}_8\text{Si}_{40}\text{O}_{96}]$, although the non-framework cation compositions are mostly Na dominant. Analcime (ANA type-structure) is richer in Al (general formula of $\text{Na}(\text{H}_2\text{O})[\text{AlSi}_2\text{O}_6]$), and its framework contains a porous system composed of irregular channels formed by highly distorted 8-membered rings, with dimensions of $4.2 \times 1.6 \text{ \AA}$ [31]. Regarding the Si/Al composition (Table 1 in the Supporting information), EDX–SEM analyses (not shown) did reveal a distinction between ANA and MOR phases; some of the particles were richer in Al, which should correspond to ANA, while others, less abundant, were richer in Si, which should belong to the MOR phase. A higher proportion of Si/Al ratios was found between 1 and 2 (typical for ANA) than between 4 and 6 (typical for MOR), suggesting a major presence of the former zeolite phase.

The eleven samples were tested as raw materials as fluoride adsorbents. In this initial screening, a high dose of 100 g/L and high fluoride initial concentration of 22.1 mg/L were used. Results are shown in Fig. 1, which displays the defluoridation capacity (in black, left axis) and the fluoride removal percentage (in grey, right axis) of the different solids. Results clearly show that out of the 11 samples, sample 3 was able to actually reduce the fluoride concentration to a considerable extent (with a fluoride removal of 80%);

Table 1
Identification of phases by XRD of the different samples. *General formula of the zeolite phases taken from [32]; “?” indicates an ambiguous phase identification. ↓ indicates a minor presence, and † indicates a major presence of the phase.

Sample	Si/Al	Phases identified by XRD			
		Zeolite phases			Non-zeolite phases
		Mineral	IZA code	General formula*	Mineral
1	3.28	Stilbite	STI	$[(\text{Ca}_{0.5}, \text{Na}, \text{K})_9(\text{H}_2\text{O})_{30}][\text{Al}_9 \text{Si}_{27} \text{O}_{72}]$	–
2	59.13	–	MOR(↓)	–	Quartz
3	2.44	Mordenite	MOR	$[\text{Na}_2, \text{Ca}, \text{K}_2]_4(\text{H}_2\text{O})_{28}[\text{Al}_8\text{Si}_{40}\text{O}_{96}]$	–
		Analcime	ANA(†)	$[\text{Na}(\text{H}_2\text{O})][\text{AlSi}_2\text{O}_6]$	–
4	3.16	Mordenite	MOR	$[\text{Na}_2, \text{Ca}, \text{K}_2]_4(\text{H}_2\text{O})_{28}[\text{Al}_8\text{Si}_{40}\text{O}_{96}]$	Celadonite
5	3.77	–	–	–	Anorthite vermiculite
6	1.88	Natrolite	NAT	$[\text{Na}_2(\text{H}_2\text{O})_2][\text{Al}_2\text{Si}_3\text{O}_{10}]$	–
		Analcime	ANA(↓)	$[\text{Na}(\text{H}_2\text{O})][\text{AlSi}_2\text{O}_6]$	–
7	4.89	Mordenite	MOR	$[\text{Na}_2, \text{Ca}, \text{K}_2]_4(\text{H}_2\text{O})_{28}[\text{Al}_8\text{Si}_{40}\text{O}_{96}]$	Quartz
		Stilbite?	STI?	$[(\text{Ca}_{0.5}, \text{Na}, \text{K})_9(\text{H}_2\text{O})_{30}][\text{Al}_9 \text{Si}_{27} \text{O}_{72}]$	–
8	18.22	–	–	–	Quartz
9	25.08	–	–	–	Quartz
10	2.44	Analcime	ANA	$[\text{Na}(\text{H}_2\text{O})][\text{AlSi}_2\text{O}_6]$	Vermiculite
		Thomsonite?	THO?	$[(\text{Ca}_2\text{Na})(\text{H}_2\text{O})_6][\text{Al}_5\text{Si}_5\text{O}_{20}]$	–
11	2.35	Stilbite	STI	$[(\text{Ca}_{0.5}, \text{Na}, \text{K})_9(\text{H}_2\text{O})_{30}][\text{Al}_9 \text{Si}_{27} \text{O}_{72}]$	–
		Scolecite	NAT	$[\text{Ca}(\text{H}_2\text{O})_3][\text{Al}_2\text{Si}_3\text{O}_{10}]$	–

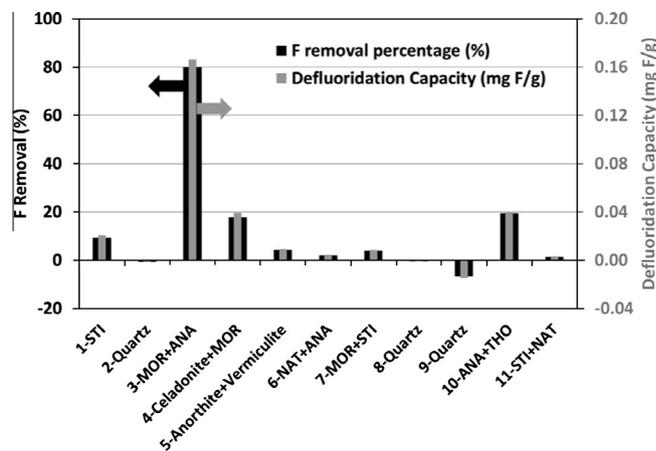


Fig. 1. Defluoridation capacity of the eleven samples studied (in $\text{mg}(\text{F}^-)/\text{g}$). Defluoridation conditions: $[\text{F}]_0 = 22.1 \text{ mg/L}$; adsorbent dose = 100 g/L. Time = 20 h. Agitation.

samples 1, 4 and 10 also showed a non-negligible fluoride-removal ability (9%, 18% and 19%, respectively), although low.

3.2. Study of the defluoridation capacity of sample 3

Fig. 2 (top) shows the defluoridation capacity of sample 3 as a function of the adsorbent dose (from 0 to 200 g/L), using an initial fluoride concentration of 18.3 mg/L. We observed that at this high concentration, sample 3 was able to reduce the fluoride content down to 1.9 mg/L (at a dose of 200 g/L), close to the threshold value established by the WHO, reaching a fluoride removal of 90%. The typical behavior of fluoride adsorbents is observed, where the defluoridation capacity decreases upon an increase of the dose. At this initial fluoride concentration, the defluoridation capacity of sample 3 ranged from 0.21 (at 20 g/L) to 0.08 (at 200 g/L) $\text{mg}(\text{F}^-)/\text{g}$.

We next tried sample 3 for defluoridation in a more-demanding process, from water with an initial concentration of 5.0 mg/L (Fig. 2-bottom). Interestingly, we observed that sample 3 is able to reduce the fluoride concentration beyond the WHO limit at an adsorbent dose slightly lower than 60 g/L. A further increase of the dose to 100 g/L does not involve a strong additional reduction of the fluoride concentration, remaining at a value close to

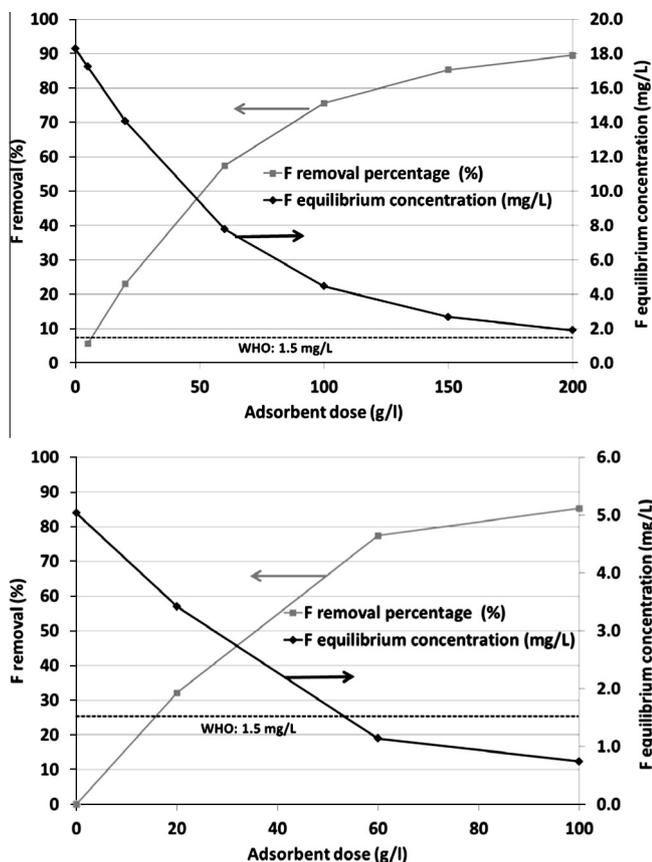


Fig. 2. Fluoride removal percentage (grey, left axis) and fluoride concentration in equilibrium (in mg/L, black, right axis) after defluoridation treatment as a function of the adsorbent dose using sample 3 as adsorbent and an initial fluoride concentration of 18.3 (top) or 5.0 (bottom) mg/L (Time = 20 h).

0.7 mg/L, which represents an optimum value for fluoride concentration to avoid fluorosis while maintaining at the same time the beneficial health effects of fluoride in the organism.

Fig. 3 shows the dependence of the defluoridation capacity as a function of the initial fluoride concentration, using an adsorbent dose of 100 g/L. The typical behavior of fluoride adsorbents is observed, where the capacity increases with an increase of the initial fluoride concentration, from 0.04 to 0.15 at initial concentrations of 5.0 and 21.9 mg/L, respectively. This behavior shows that defluori-

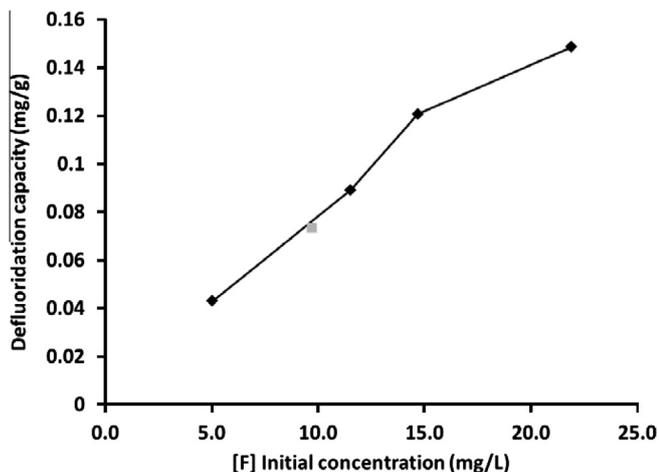


Fig. 3. Fluoride removal capacity of sample 3 as a function of the initial fluoride concentration. The grey point indicates that defluoridation was performed on a real water sample (Bofo). Defluoridation conditions: adsorbent dose = 100 g/L. Time = 20 h. Agitation.

ation of less-concentrated solutions is a more-demanding process. However, worth is noting that sample 3 is able to reduce the fluoride concentration beyond the WHO limit of 1.5 mg/L, as observed in Fig. 2, although the capacity at this concentration is lower.

When studying fluoride adsorbents, it is very important to analyze the possibility of desorbing fluoride from the adsorbent after a defluoridation treatment, both for determining the eventual disposal of fluoride and the possibility of regeneration of the adsorbent. Desorption of fluoride adsorbents is usually carried out by subjecting the samples after defluoridation to a basic solution. Sample 3 was initially used for defluoridation at an adsorbent dose of 100 g/L with an initial fluoride concentration of 11.5 mg/L. After this, the resulting solid was submerged in 0.1, 0.01 or 0.001 mol/L solutions of NaOH for 3 h; XRD (not shown) showed that the phases resisted the basic treatment. Desorption of fluoride was determined by measuring the fluoride concentration in the resulting solutions; the theoretical fluoride concentration if all the fluoride adsorbed in the solid was released would be 1.78 mg/L. The percentage of fluoride desorption is displayed in Fig. 4. Interestingly, we observed a very high desorption after treatment with 0.001 mol/L NaOH, which is a relatively mild process (pH around 11). This means that fluoride is not very strongly adsorbed on sample 3. Surprisingly, we observed that an increase on the NaOH concentration involved a reduction of the fluoride desorbed, especially when the NaOH concentration is 0.1 mol/L, in contrast to what was expected. This result is not clear at the moment; however, we think that the lower desorption at higher NaOH concentrations could be misleading, since treatment of zeolites with highly concentrated basic solutions usually provokes a disruption of the framework, which could explain the inefficient desorption. Indeed, TGA analyses (Fig. 1 in the Supporting Information) showed the presence of a weight loss at 630 °C in the sample treated with NaOH 0.1 M which is usually assigned to dehydroxylation processes commonly ascribed to a partial disruption of the zeolite framework and consequent formation of OH-connectivity defects. Reuse of this regenerated sample (with NaOH 0.1 M) showed a negligible defluoridation capacity, evidencing that the defluoridation ability has been cancelled by this strongly basic treatment.

We studied the possibility of using this solid for defluoridation in successive treatments (without any regeneration treatment) in order to ensure a complete exhaustion of the adsorbent (Fig. 5). Results clearly show that the defluoridation capacity was not exhausted after the first defluoridation treatment, indeed the capacity in the second use-cycle is only slightly reduced (from 0.15 to 0.13 mg(F⁻)/g). Sample 3 still shows a notable defluoridation capacity up to cycle 5, where the capacity is reduced to less

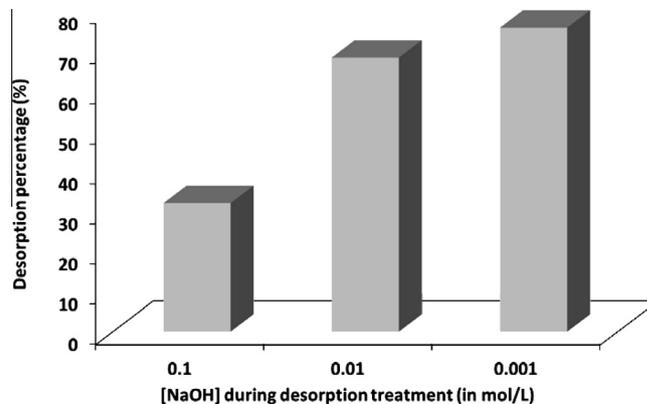


Fig. 4. Desorption of fluoride from sample 3 after defluoridation treatment. Initial defluoridation treatment conditions: adsorbent dose = 100 g/L; [F]₀ = 11.5 mg/L; contact time = 20 h. Desorption conditions: ratio = 1 g/50 mL; contact time = 3 h.

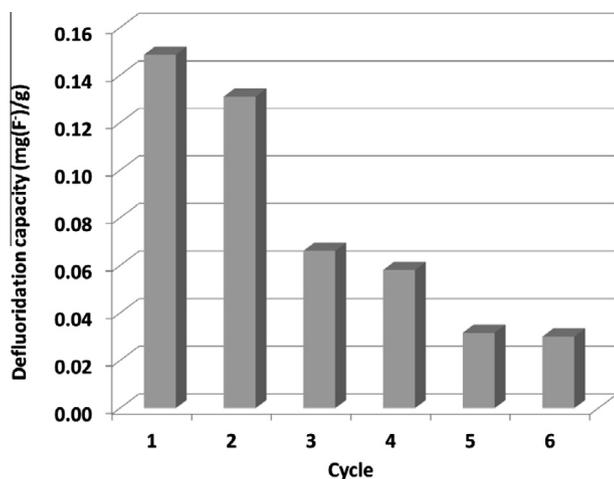


Fig. 5. Defluoridation capacity of sample 3 in consecutive use-cycles (without regeneration treatments). Defluoridation conditions: adsorbent dose = 100 g/L; $[F^-]_0 = 21.9$ mg/L; contact time = 20 h.

than 0.05 mg(F⁻)/g. In sum, the total defluoridation capacity after these 6 cycles was 0.47 mg(F⁻)/g. The exhausted adsorbent was subjected to the same desorption treatment as before, with a mild basic treatment in an NaOH 0.001 mol/L solution for 3 h, which rendered a very high desorption of 87% of the fluoride loaded. The defluoridation capacity of this exhausted and then regenerated material was tested, and a 56% recovery of the initial capacity was observed.

Finally, defluoridation of real waters (kindly provided by OSHO, collected from a village called Bofo, in the Ethiopian Rift Valley), which showed an initial fluoride concentration of 9.7 mg/L and a pH of 8.5, was studied. When this water was subjected to a defluoridation treatment with sample 3 under a dose of 100 g/L and a contact time of 20 h, 76% of fluoride was removed, giving a final pH of 8.5 and a final fluoride concentration of 2.4 mg/L, resulting in a defluoridation capacity of 0.07 mg(F⁻)/g. This defluoridation capacity falls well within the trend of sample 3 as a function of the fluoride initial concentration, which means that our adsorbent is also efficient for defluoridation in a real case.

4. Discussion

In contrast to usual observations of the negligible defluoridation capacity of raw natural zeolites, we have found that one of the eleven samples tested, sample 3, shows a considerable defluoridation capacity, without subjecting it to any treatment. Interestingly, our experiments demonstrate that a zeolite based in analcime and mordenite is indeed able to reduce the fluoride concentration beyond the safe limit of 1.5 mg/L imposed by the WHO. Indeed, our observations showed that most of the initial defluoridation ability of this sample is achieved after the first 30 min of treatment (see Fig. 2 in the Supporting information). In addition, most of the fluoride (87%) can be easily desorbed from the adsorbent by using a very mild treatment (NaOH 0.001 M for 3 h), hence facilitating the final disposal of fluoride; in fact, the final pH of this desorption solution is 9.15, thus facilitating the neutralization of this desorption solution for disposal. Besides, such desorption (regeneration) treatment leads to a recovery of 56% of the initial defluoridation capacity when recycling the adsorbent.

Sample 3 showed a maximum defluoridation capacity of 0.47 mg(F⁻)/g, after several consecutive uses. We should remark that this material is used as adsorbent as a raw material, without any treatment, what reduces dramatically the cost of the prepara-

tion of the adsorbent. The not very high defluoridation capacity might be a consequence of the negative surface charge typical of zeolites, and consequently, there is scope to greatly increase it by subjecting the sample to the usual treatments that are undertaken to zeolites, especially the impregnation of their surface with multivalent cations like Ca²⁺, Fe³⁺ or Al³⁺, to reverse the polarization of the zeolite surface charge, what will potentially enhance the defluoridation capacity of these samples. However, the study of such treatments is out of the scope of the present work since our main purpose is to develop fluoride-adsorbents based on natural zeolites without any treatment in view of their potential use in countries with less economic resources.

In an attempt to unravel the defluoridation mechanism of this solid, and due to the considerable amount of Ca found in this sample (2.9 wt% found by ICP, Table 1-SI), we tried its removal capacity at a dose of 100 g/L, but this time increasing the Na concentration from 22 mg/L (in an NaF solution with fluoride concentration of 18.3 mg/L) to 400 mg/L (by adding the required amount of NaCl). A similar defluoridation capacity (around 0.15 mg(F⁻)/g) was found in both cases. This result suggests that the defluoridation mechanism is not associated to a Na(solution)–Ca(adsorbent) exchange, and consequent CaF₂ precipitation, since an increase of the removal capacity would be expected for the solution with a higher Na concentration. Besides, such a CaF₂ precipitation mechanism would only reach a minimum concentration of fluoride of 8 mg/L, given by the solubility product of CaF₂, in the absence of additional Ca in the solution. Even if a considerable amount of Ca is released to the solution by ion-exchange, such amount should be higher than 500 mg/L to reduce the concentration of fluoride beyond 1 mg/L, which was ruled out by the Ca content found in water after desorption (4.7 mg/L, ICP). In addition, analyses of the defluoridated water showed no Al, indicating that no Al from the mineral is leached to the water, in contrast to the case of alumina that might do under certain conditions. On the other hand, we observed a notable increase of the defluoridation capacity when pH decreased (results not shown), which seems to indicate that the negatively-charged zeolite surface can be detrimental to the defluoridation capacity.

ANA is an Al-rich zeolite (Si/Al = 2). Therefore, the defluoridation capacity of this material might be associated to the presence of Al sample, either in framework or extraframework positions. Often zeolites have connectivity defects which results in the presence of Al–OH and Si–OH sites; this type of Al–OH defects could be responsible for the fluoride removal by OH ↔ F ligand exchange and formation of Al–F bonds, the same as occurs in alumina adsorbents. We analyzed the chemical nature of Al in our material by ²⁷Al NMR (Fig. 3-SI), and we observed the presence of not only tetrahedral Al typical of framework positions in zeolites (band around 60 ppm) but also of octahedral Al in a considerable amount (band around 3 ppm). At this moment the origin of such octahedral Al is not clear; it could come from the presence of extra-framework Al present as charge-compensating cations (coordinated to H₂O or OH groups) within the zeolite frameworks or from the presence of some other octahedral-Al-containing phase not detectable by XRD (either because of a low concentration or an amorphous nature). Anyway, it is possible that this type of octahedral Al might be responsible for the defluoridation capacity of our adsorbent.

5. Conclusions

Zeolites represent ideal candidates to be used as fluoride-adsorbents since usually zeolites and fluoride-rich waters, both generally of volcanic origin, are geographically associated. In this work we have found that one (sample 3) out of the eleven samples studied displays a maximum defluoridation capacity of 0.47 mg(F⁻)/g

when employed as raw material in several consecutive uses, without any treatment, reducing dramatically the cost of preparation of the adsorbents. Interestingly, our results clearly show that desorption of fluoride from the exhausted adsorbent is rather easy and can be achieved up to 87% by a mild basic treatment with NaOH 0.001 mol/L. Besides, such treatment leads to a partial regeneration of the adsorbent, which recovers up to 56% of the initial defluoridation capacity, although this regeneration treatment is susceptible of being optimised. The defluoridation capacity of analcime based sample was also tested with a real water sample with an initial fluoride concentration of 9.7 mg/L, and we observed a similar capacity as in simulated NaF solutions. All these observations make analcime based zeolite a good candidate to be used as fluoride-adsorbent, especially in regions with low economic resources and where it is easily found in nature such as in Ethiopia.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.seppur.2013.10.006>.

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