Controlled Growth of nano-Hydroxyapatite on Stilbite: Defluoridation Performance

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Abstract

In Ethiopia, fluoride-contaminated groundwater used for drinking has become a matter of great concern, particularly in the Rift Valley region, due to its serious health hazard (fluorosis). In the present work, we present a systematic study related to the optimization of the synthesis of a composite material having a high defluoridation capacity, consisting of nanohydroxyapatite crystals growth on the external surface of a natural Stilbite zeolite (nHAST) of sizes between 74 and 105 μm . In order to control the growth of significantly small crystals of hydroxyapatite with higher fluoride removal capacity, the most important synthesis parameters, crystallization pH and crystallization time, have been carefully optimized. The obtained materials have been characterized by X-Ray Diffraction, Elemental Analysis, Thermogravimetric Analysis, Infrared Spectroscopy, ^{31}P Nuclear Magnetic Resonance, and Transmission Electron Microscopy; in addition, the defluoridation capacity of the materials has been determined. Interestingly, unlike most adsorbents, nHAST-144h (prepared after 144 hours of crystallization) shows significantly high fluoride-removal efficiency in a wide range of pH with maximum F-removal of 86 % and minimum of 79 % fluoride removals at pH 3 and 10, respectively. Besides, nHAST-144h adsorbent maintains its high defluoridation capacity in the presence of other ions, in particular chloride, sulfate and bicarbonate. In a real situation, nHAST-144h was found to be efficient as well; from real groundwater from the Ethiopian Rift Valley, with a fluoride concentration of 8.2 mg/L and a dose of 10 g/L, nHAST-144h reduced the fluoride concentration down to 1.40 mg/L, below the limit established by World Health Organization (WHO).

Keywords

Fluoride; Fluorosis; Defluoridation; Zeolites; nano-Hydroxyapatite

1. Introduction

Fluoride at a fairly low level is beneficial to the human body for the calcification of dental enamel, prevention of dental decay and maintenance of healthy bones. However, excessive fluoride intake is harmful for human health, leading to dental and skeletal fluorosis, lesion of endocrine glands, thyroid, liver and other organs [1-3]. According to World Health Organization (WHO) guidelines, the acceptable fluoride concentration in drinking water must be in the range between 0.5 to 1.5 mg/L [4]. Despite its frequent high fluoride content, groundwater is widely distributed, and a significantly large number of population, more than 260 million all over the world, consume drinking water with a fluoride concentration higher than 1.0 mg/L. The majority of these people live in tropical regions, fourteen countries in Africa, eight in Asia, and six in the Americas [5, 6], and many of them are confronted with problems due to endemic fluorosis, either dental or skeletal. For instance, in the Rift Valley (Ethiopia) as well as in the North of Mexico, the fluoride content may reach as much as 36 mg/L [7, 8] and 8 mg/L [9,10] , respectively. Thus, the problem is severe and needs immediate solution.

For many years [11], a large number of adsorbent materials have been tested in fluoride removal. Among them, hydroxyapatite (HAp), one of the most extensively investigated defluoridating adsorbents, is of great importance because of the similarity in chemical composition with human bone and the potential for fluoride retention [12]. Many researchers studied HAp-based adsorbents and indicated their potential for fluoride-removal [13-16]. Although HAp has shown an excellent potential towards the retention of fluoride from water, current research is applied in an attempt to further enhance its fluoride-removal capacity through the production of nanosized HAp materials, which in recent years have gained much attention for their unique properties. In this context, a significant number of nano-hydroxyapatite (nHAp) adsorbents have been

synthesized and studied [17-21]. In fact, these nanosized materials showed a much higher defluoridation capacity because of the small crystal size, and consequently the reduction of problems related to diffusion limitations of the ions in larger crystals. However, the potential application of these materials in the field is not easily achievable, due to the cost associated with their production and significant pressure drops during filtration owing to the small particle size. To overcome such permeability problems and at the same time utilize the advantages of nHAp, it is essential to prepare adsorbents based on nHAp in a usable form by combining them with other high-surface materials [22-24], on which the HAp nanoparticles are supported. By having the HAp nanoparticles supported on the external surface of a material with a large particle size, it would be possible to avoid pressure drops associated with the nanosize of nHAp, as well as to prevent the potential toxicity typical of nanoparticles and possible sintering (and loss of efficiency) during defluoridation treatments. In our previous studies, we have reported the potential use of nano-hydroxyapatite (nHAp) crystals grown on the surface of natural stilbite (STI) from Ethiopia as F^- adsorbents (nHAST) [25]. In the current work, different synthesis conditions have been systematically studied aiming to yield an optimum synthesis method that may allow for a scale up synthesis. Among the most relevant parameters, the synthesis pH is a crucial factor in the formation nano hydroxiapatite with significantly higher efficiency. Therefore, this manuscript includes the effect of the growth of nHAST without pH adjustment (autogenous pH value of 8) and crystallization at room temperature, unlike the common precipitation methods of HAp which in most cases is carried out at basic pH (> 9) together with high temperature conditions. The effect of several defluoridation-process parameters, water pH, presence of co-ions, contact time, adsorbent dose and initial fluoride concentration, on the defluoridation performance of nHAST composites has been studied. Finally, equivalent nHAST

composites showing the same properties have been synthesized using different natural stilbite samples from alternative deposits located in Northern Ethiopia.

2. Experimental Part

2.1. Adsorbent preparation

Natural stilbite (zeolite) samples were provided by the School of Earth Sciences, Addis Ababa University. The main stilbite sample used in this work was collected from the Hashenge basalt formation in the Tigray region, and the rest of the samples were collected in the localities of Korem and Maychew in the same region. The nHAST composite is prepared as follows: 2 g of STI zeolite powder of average particle size between 74 and 105 μm was mixed with 30 ml of 1 M $(\text{NH}_4)_2\text{HPO}_4$ and stirred for 2h. The solution pH was then adjusted at different values (from 7 to 10), either with 0.1 M HCl or 0.1 M NaOH. Optimization of the crystallization pH (from 7 to 10) was performed at a fixed crystallization time of 19 hours, and optimization of the crystallization time was studied for periods ranging from 2 to 144 hours at the optimized crystallization pH; both crystallization studies were performed at room temperature conditions. The adsorbent was filtered, washed and dried in open air at room temperature overnight.

2.2. Characterization

Powder X-Ray Diffraction (XRD) patterns were collected with an X'pert Pro PANalytical diffractometer equipped with an X'celerator detector using a Cu K_α radiation and Ni filter, which has a wavelength of 1.54056 Å. The stilbite phase identification was done using the ICSD database for X'Pert Highscore Plus with Reference code 00-044-1479. The chemical inorganic composition has been determined by Inductively Coupled Plasma Optical Emission

Spectrometry (ICP-OES, Optima 3300 DV model). The content of HAp (wt %) in the nHAST composite material is calculated from the P content obtained from this elemental analysis (wt %), according to eq. 1.

$$\text{HApwt\%} = \text{P wt \%}_{(\text{ICP})} \times \frac{502}{93} \quad \text{Equation 1}$$

where 502 is the total molecular mass of HAp, $(\text{Ca}_5(\text{PO}_4)_3\text{OH})$ and 93 is the molecular mass of P in HAp.

Thermogravimetric (TGA) analyses were performed on a thermogravimetric analyzer PERKIN ELMER TGA7; samples were heated at a rate of $20\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ up to a maximum temperature of 900°C under air flow. Infrared measurements were carried out using an Attenuated Total Reflectance spectrophotometer (ATR, PIKETECHNOLOGIES) in the range of $500\text{--}4000\text{ cm}^{-1}$, using quartz as detector. ^{31}P MAS-NMR was used to confirm the presence of HAp in these adsorbents; the spectra were recorded at room temperature using a Bruker AV-400-WB spectrometer and a recycle delay of 20 s, while spinning the samples at 162 MHz. Furthermore, in order to study the atomic structure and the nature of the composite, Transmission Electron Microscopy was applied. Scanning Transmission Electron Microscopy (STEM) was chosen, as it is less damaging to electron-beam sensitive materials. The observations were performed on selected nHAST composite samples, prepared with crystallization times of 19 and 144 hours. STEM studies were performed with a spherical aberration corrected FEI Titan XFEG, which was used at 300 kV, equipped with a corrector for the electron probe allowing a maximum resolution of $0.8\text{ \AA}$; the microscope was also equipped with an EDS detector (Energy Dispersive Spectroscopy) and a Gatan Tridiem energy filter for EELS (Electron Energy Loss Spectroscopy).

measurements. Prior to observations, the samples were crushed, dispersed in ethanol or acetone and placed onto a holey carbon copper micro grid. The point of zero charge (PZC) was measured by potentiometric mass titrations technique [26, 27], using 665 Dosimat (Metrohm, Switzerland) machine. The pH was measured using a digital pH meter standardized by buffers (WTW Inolab pH/ION Level 2, Germany).

2.3. Fluoride-removal experiments

Fluoride-containing solutions of two initial F concentrations (C_o), 5 and 10 mg/L, have been prepared from sodium fluoride (NaF, Sigma-Aldrich), in accordance with the most frequently reported values from real polluted drinking water samples, from 1.5 up to 11.6 mg/L, in the Rift Valley region in Ethiopia [28]. In particular cases, different initial fluoride concentrations and adsorbent doses were studied. Defluoridation experiments were carried out at room temperature (23 ± 2 °C), with a contact time of 20 h under continuous agitation. 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, after addition of a total ion strength adjustment buffer (TISAB III, CRISON). All experiments were repeated in order to test the reproducibility and mean values are reported. The adsorption efficiency (Q_t), and defluoridation capacity (Q_e) were calculated following eq. 2 and 3:

$$Q_t = \frac{C_o - C_t}{C_o} \times 100 \quad \text{Equation 2}$$

$$Q_e = \frac{C_o - C_t}{\text{dose}} \quad \text{Equation 3}$$

where C_o is the initial F^- concentration, C_t is the equilibrium F^- concentration (both in mgF^-/L), and the dose is expressed in g/L .

In this study, apart from the total defluoridation capacity (Q_e), which is referred to the total mass of the composite material, including the zeolite and the HAp (calculated following eq. 3), the intrinsic capacity of HAp ($Q_{e(HAp)}$), which is referred only to the percentage of HAp in the composite material, was used to describe the relative activity of the adsorbent material with respect to the amount of HAp, and was calculated following eq. 4:

$$Q_{e,HAp} = \frac{C_o - C_t}{\text{Total dose} \times \frac{(\text{wt \% HAp})}{100}} \quad \text{Equation 4}$$

Studies were also conducted in order to investigate the effect of process parameters during fluoride adsorption by nHAST. The effect of the adsorbent dose on fluoride removal was studied by varying the dose from 4 to 12 g/L . The effect of the initial fluoride concentration and contact time on nHAST composite was investigated by varying initial fluoride concentrations and contact time from 5 to 200 mg/L and from 0 to 28 hours, respectively. The effect of the water pH on the adsorption of fluoride on nHAST adsorbent was studied by varying the water pH from 3 to 10; again the pH was adjusted to the desired value either with 0.1 M NaOH or 0.1 M HCl. The effect of co-existing anions (HCO_3^- , SO_4^{2-} and Cl^-) on fluoride adsorption by nHAST composite was also studied in the presence of anions that commonly exist in groundwater [29]. A series of solutions with different concentrations of each target anion (0-500 mg/L) was prepared by dissolving the sodium salts of the respective anions in de-ionized water containing the desired concentration of fluoride.

3. Results and Discussion

The synthesis of the composite material based on the growth of nano hydroxiapatite on the surface of natural stilbite involves an initial exchange of NH_4^+ present in the synthesis solution by the exchangeable Ca^{2+} cations from the STI zeolite; these released Ca^{2+} ions then crystallize as HAp nanoparticles on the external surface of the zeolite in the presence of PO_4^{3-} from the synthesis solution at a given pH. In this cation exchange process the slow release of Ca^{2+} ions acts as determining factor for the nucleation of hydroxyapatite, therefore time, crystallization time has to be studied in order to reach an optimum exchange. Furthermore, the pH of the PO_4^{3-} from solution will determine the growth of the HAp nanoparticles. Therefore, different synthesis conditions have been systematically studied aiming to yield an optimum equilibrium between the nucleation and the growth of the aimed nanohydroxyapatite.

The particle size of the natural zeolite used here varied in three main regimes: smaller than 74 μm , within 74 and 105 μm and larger than 125 μm . Crystals at the larger size regime did not show HAp crystallization while the smallest ones were too difficult to handle due to turbidity effects they created in the suspensions. The sizes of the stilbite crystals used throughout this work were in the range from 74 to 105 μm .

3.1. Optimization of Crystallization pH

The effect of crystallization pH on the growth and amount of HAp crystallized on the STI surface was initially investigated by XRD (Figure 1). As can be clearly observed, all the nHAST composite samples synthesized from different crystallization pHs as well as the original STI zeolite showed very similar X ray diffraction patterns. The main peaks of the STI framework are

clearly observed in all the materials, confirming the stability of the zeolite under the synthesis conditions; however, no XRD reflections due to the growth of nHAp could be appreciated. The quantitative chemical compositions of the nHAST samples synthesized from different crystallization pHs were determined by ICP and are presented in Table 1. As observed, ICP analysis detected a constant amount of Ca^{2+} on the different materials. No P was detected at all in the original STI, while a constant amount of P was also observed in the nHAST composite samples. Thus, the wt % of HAp grown on the STI surface (as calculated from the content of P determined by ICP, eq. 1) is also constant, irrespective of the crystallization pH.

Batch-mode defluoridation tests were used to analyze the fluoride-removal capacity of nHAST composite samples at two initial fluoride concentrations: 5 (Figure 2A) and 10 mg/L (Figure 2B), using 10 g/L of adsorbent dosage for a contact time of 20 hours at room temperature. Figure 2 plots the variations in F^- removal capacity among the samples as a function of the crystallization pH. The defluoridation capacities of nHAST samples synthesized with a crystallization pH of 7.0-7.5 were slightly lower. Similarly, the nHAST samples prepared at basic crystallization pH conditions (pHs of 8.5, 9 and 10) showed lower defluoridation capacities (in the same order), which might be associated to the formation of larger HAp particles at basic crystallization pH conditions. On the other hand, very efficient (and probably smaller) HAp particles are formed at an intermediate pH of 8, yielding the highest defluoridation capacity so far. Interestingly, at this pH the nHAST composite shows about 89 and 67 % of F^- removal efficiency, from initial concentrations of 5 and 10 mgF/L, respectively; these capacities were notably higher than that of nHAST obtained at a pH of 9, with a removal efficiency of about 76 and 61 %, respectively, from water with the same initial fluoride concentrations (Figure 2). Therefore, the best

performing (optimized) crystallization pH for further preparation of nHAST composites was considered as the autogenous pH of 8, and hence not involving additional chemicals.

3.2. Optimization of Crystallization Time

In order to investigate the effect of the crystallization time on the defluoridation performance by nHAST composites, a series of samples were prepared at various crystallization times ranging from 2 to 144 hours, at the optimized autogenous pH of 8. In this case, a close inspection of the diffraction patterns showed slight variations in the region between 23 and 25° 2 θ (Figure 3). In this region, the initial STI mineral showed three clearly distinguishable peaks characteristic of monoclinic stilbite, while the nHAST composite samples showed a single diffraction (marked by a downward arrow in Figure 3), evidencing a progressive change of the space group of STI to orthorhombic [30, 31]. This is caused by the exchange of Ca²⁺ and Na⁺ of the original stilbite by NH₄⁺ ions during the preparation of the composites. The identification of the characteristic crystalline peaks that confirm the formation of HAp on the STI surface by XRD was again not possible, probably due to the low concentration of HAp in the composite, its small (nanometric) crystal size and/or the overlapping with the more abundant and intense STI zeolite diffractions.

Figure 4 shows the thermogravimetric analysis results of the STI zeolite support and of nHAST composite samples. In the temperature region up to 350 °C, several differentiated weight losses can be observed in both the STI and the nHAST composite samples. In STI, a first weight loss at temperatures below 130 °C is assigned to loosely bound water, while a second strong weight losses with maximum desorption rates at around 170 °C and at 260 °C are due to the desorption of strongly retained water molecules within the STI framework by coordination with exchangeable Ca²⁺ ions. A progressive shift of the maximum desorption rate of these weight

losses associated to dehydration to lower temperatures can be clearly observed in the case of nHAST samples, possibly due to the weaker interaction of water molecules with monovalent NH_4^+ ions exchanged for Ca^{2+} ions, as compared to the stronger interaction with divalent Ca^{2+} ions in the original STI sample. Indeed, this decrease to lower temperatures is gradual upon an increase of the crystallization time. Hence, these shifts to lower temperatures are an indication of the progressive exchange of the more-interacting (with water) Ca^{2+} divalent cations by the less-interacting monovalent NH_4^+ cations with increasing crystallization times. In both situations the water desorption intensity decreases significantly with the crystallization time until nHAST-144h composite sample (prepared with 144 h of crystallization), suggesting no more exchange of Ca^{2+} by NH_4^+ ions would occur beyond this time. In line with this, the amount of loosely-bound water (weight loss below 130 °C) increases accordingly with the crystallization time. In addition, nHAST composite samples showed an additional broad weight loss at around 450 °C due to deammoniation, indicating the release of NH_3 as NH_4 -STI (after exchange of Ca^{2+} by NH_4^+) transforms into H-STI [30]. The deammoniation band shows a higher intensity with increasing the crystallization time, indicating the release of a higher amount of NH_3 and thus, again indicating the progress of the ion-exchange, Ca^{2+} by NH_4^+ ions, with the crystallization time. Therefore, we can conclude that the amount of Ca^{2+} ions released to the solution has increased as a function of the crystallization time, leading to the crystallization of a proportionate increasing amount of HAp on the STI surface. Nevertheless, the deammoniation peak of nHAST-144h sample occurred at a slightly higher temperature of about 465 °C, possibly due to the phase transition of the STI zeolite from monoclinic to orthorhombic, due to the total exchange of Ca^{2+} in STI by NH_4^+ ions in nHAST-144h sample.

ATR -Infrared studies (Figure 5) show IR features at about 565, 606 and 1020 cm^{-1} , which are consistent with the presence of PO_4^{3-} groups (marked with blue arrows) [32], whose intensity increases with the crystallization time, suggesting again the formation of a higher amount of HAp on the STI surface with longer times. Additionally, a new band arises at about 1430 cm^{-1} (marked with black arrow) due to the presence of NH_4^+ ions during the HAp crystallization (after exchange with Ca^{2+}). This contributes to confirm what was suggested by XRD and TGA that the chemical treatment with ammonium phosphate caused a progressive (with time) cation exchange of Ca^{2+} by NH_4^+ .

Studies on the point of zero charge (Figure SI-1) were conducted using potentiometric mass titration to determine the modification of the surface charge properties of the parent STI zeolite upon modification with HAp. The PZC of the nHAST-144h composite was determined to be 10, significantly high as compared to the very low PZC of the parent STI zeolite support of only 2.1, indicating that below pH 10 the surface of nHAST-144h is positively charged. This finding indicates an inversion of the adsorption properties of the zeolite, which is now turned into a positively charged surface at almost all range of pH, thus promoting a successful adsorption of an anion like F^- via electrostatic interactions on the external surface.

ICP analysis (Table 1) shows a constant amount of Ca^{2+} in the final composites, whilst the amount of P gradually increased; this confirms that the amount of HAp grown on the zeolite surface is also increasing with the crystallization time, as can be clearly observed in Figure 6-left (black line). Interestingly, the defluoridation capacity of the resulting composites (red line in Figure 6-left) increases also with the crystallization time and thus with the content of HAp in the composite (although the increasing trends (slopes) are not exactly equivalent at long crystallization times), reaching a significantly high fluoride-removal efficiency (about 86 % in

the nHAST composite crystallized for 144 h, from water with 10 mg/L of fluoride concentration and 10 g/L dosage). The corresponding final equilibrium F^- concentration was 1.60 mg/L, almost the same as the maximum permissible WHO limit, 1.5 mg/L (higher doses clearly overpass this threshold), giving a total defluoridation capacity of 0.86 mg/g for composite nHAST-144h. Interestingly, at the same adsorbent dose, if the initial fluoride concentration lowers to 5 mg/L (Figure SI-2), the fluoride-removal efficiency is higher, about 95 %, yielding in this case the final equilibrium F^- concentration of 0.25 mg/L, significantly lower than the WHO safe range.

If we normalize the fluoride-removal capacity to the amount of HAp present in the adsorbent (determined from ICP P content, Table 1), to give the corresponding HAP intrinsic capacity, calculated as mg of F^- per gram of HAp following eq. 4 (Figure 6-left, blue line), we observe an extremely high intrinsic capacity for the HAp in the nHAST composite obtained at low crystallization times (nHAST-2h, with a HAp capacity of 17.28 mg/g of HAp). Given that the theoretical maximum value for a full exchange of F^-/OH^- would be 37.8 mg/g of HAp, this value is extremely high. Indeed it is significantly higher than that of other adsorbents based on Hydroxyapatite such as organic bone char [33], evidencing that the HAp nanocrystals are extremely small in this composite; however, the total capacity of this composite is not very high (0.32 mg/g) because of the low amount of HAp grown. When the crystallization time increases, and hence the amount of HAp grown on the zeolite surface, the intrinsic capacity of the resulting HAp nanocrystals gradually decreases from ~17 down to a plateau value of ~10 mg/g of HAp (Figure 6-left, blue line), indicating that these nanocrystals are slightly less effective for defluoridation (though still much more active than usual HAp materials). Indeed, a direct relationship between the amount of HAp grown on the surface and the intrinsic capacity of the resulting HAp is clearly appreciated (Figure 6-right). This indicates that longer crystallization

times involves a higher amount of HAp nanocrystals but slightly less efficient because of the enlargement of the nHAp crystals. Hence, these observations indicate two opposite trends, low crystallization times involve the growth of a low amount of extremely small and extraordinarily efficient HAp nanocrystals, yet resulting in a low total defluoridation capacity because of the small amount of HAp. Longer crystallization times result in the growth of more and larger nanocrystals, being slightly less efficient for defluoridation, but this is widely compensated by the higher amount of HAp, resulting in very efficient nHAST composites for defluoridation, with capacities reaching up to 0.86 mg/g.

In order to fully understand the nature of the nHAp crystals grown on the surface of the zeolite and how it affects the fluoride removal performance, further studies of selected samples, nHAST-19h and -144h, were carried out using ^{31}P MAS-NMR and Advanced Electron Microscopy Techniques. ^{31}P MAS-NMR spectra of the composites nHAST-19h (green line) and nHAST-144h (blue line) synthesized at pH 8 are plotted in Figure 7. Two other NMR spectra, nHAST-19h at crystallization pH of 9 (red line) taken from our previous work [25], and a typical HAp (dotted black line) sample, were included for comparison purposes. In all the samples the same P resonance is observed at around 2.85 ppm, characteristic of P in HAp, confirming the formation of HAp in the composites [34, 35]. However, in nHAST-19h (green line) and nHAST-144h (blue line) composites synthesized at crystallization pH of 8 in the present study, the band is broader as compared to the typical HAp materials (dotted black line); furthermore, a shoulder at around 0 ppm is observed, both being features related to the nanometric nature of HAp crystals [25,36]. Interestingly, the NMR spectra of the two composites, nHAST-19h and nHAST-144h, synthesized at crystallization pH 8 were even broader than the nHAST-19h composite

synthesized at crystallization pH 9 (red line), suggesting the presence of smaller HAp particles in nHAST composites prepared at pH 8.

Spherical aberration (Cs) corrected scanning transmission electron microscopy (STEM) coupled with High Angular Annular Dark Field (HAADF) detector was chosen to study nHAST-19h and nHAST-144h composite samples in order to fully comprehend the evolution of the HAp crystallized on the STI surface as a function of the crystallization time. Cs-STEM high-resolution imaging allowed observing the growth of small particles of nHAp (Figure 8a) that grew forming very thin fibers decorating the surface of the STI crystals in nHAST-19h. These high resolution observations allowed investigating the HAp crystals over the STI surface. HAp nanocrystals are clearly appreciated in the images as very thin hairy crystals protruding from the STI homogeneous surface. The layered structure of these fibers can be identified with a d-spacing of $2 \text{ \AA}$ (Figure 8b) which is the highest resolution ever reported for HAp structure. As crystallization time increases to 144 hours, the growth of HAp fully covers the surface of the STI crystals in a heterogeneous manner but yet, linked to the zeolite crystals, i.e. no separate HAp crystals are observed, which means that the surface of the stilbite acts as source of nucleation points; the crystals grow to connect these nuclei leading to a fully-covered surface, as shown in Figure 8c. In other words, longer times lead to a higher release of Ca^{2+} from the zeolite, as previously shown, and these cations promote the growth of a very thin layer of nHAp wrapping up the STI crystals as shown in Figure 8c. Indeed, significantly higher amounts of HAp crystals are clearly observed in nHAST-144h sample (Figure 8c) as hairy needles, while at shorter crystallization time, nHAST-19h, the images reveal abundant number of particles in which the smooth surface of the zeolite crystals could still be observed (Figure 8a). The chemical composition of these nanocrystals could be extracted using Electron Energy Loss Spectroscopy

(EELS). STEM/HAADF/EELS mapping (Figure 8d) analysis performed over the area marked with a white rectangle (Figure 8d) clearly shows the crystallization of HAp on the external surface of the STI zeolite, distinguishable by its main constituent element P (Figure 8e), in blue colour (not present in the STI zeolite), attached to the surface of the zeolite crystals, whose identifying element is Si (red colour). As can be observed in nHAST composite samples, red color follows a sharp surface corresponding to the STI crystal, whereas green (Ca) and blue (P) colors of HAp draws thin irregular forms on the surface of STI zeolite.

In summary, the nanometric nature of the crystallized HAp relies on the slow release of Ca^{2+} from the zeolite leading to a much higher F⁻-removal efficiency of HAp on the composite. However, larger extent of Ca exchange and consequently larger amounts of HAp also involves slightly lower intrinsic defluoridation capacities of the HAp crystals as they grow. Therefore, a crystallization time of 144h is considered as an optimum compromise time between both opposite trends to perform further adsorption studies.

3.3. Effect of the defluoridation parameters on the adsorption capacity of nHAST

The influence of the adsorbent dose on the fluoride-removal efficiency of nHAST-144h adsorbent was studied at 4, 6, 8, 10 and 12 g/L doses. Batch adsorption studies were performed using initial fluoride concentrations of 5 and 10 mg/L, a contact reaction time of 20 hours and at room temperature. As described in Figure 9, the fluoride-removal efficiency notably increases with increasing the adsorbent dose up to 10 g/L due to the availability of a higher number of fluoride binding sites. Fluoride removals of about 95 and 84 % were found at doses of 10 g/L from 5 and 10 mg/L initial fluoride concentrations, respectively. Because the equilibrium

fluoride concentration falls within the WHO limit, a dose of 10 g/L was considered as an optimum dose for further adsorption experiments.

In order to identify the dynamics of the adsorption process, batch experiments were carried out using different contact times, with the optimized dose of 10 g/L and 10 mg/L of initial fluoride concentration at room temperature. As shown in Figure 10A, a rapid fluoride removal was observed up to 8 hours, reaching about 81 % of F⁻-removal. The reaction proceeds slowly until 20 hours where the equilibrium is reached, giving a fluoride-removal efficiency of about 84 %. Since there is no significant increase of the fluoride adsorption beyond, a contact time of 20 hours was fixed for further studies. Composite nHAST-144h adsorbent shows significantly high performance due not only to the presence of new active sites, but the high efficiency of nanometric size HAp crystals, as evidenced by ³¹P MAS-NMR and Cs-STEM analyses. Most probably, in the first 8 hours the driving force for defluoridation is the anion exchange of fluoride in solution with surface hydroxyl ions of the nano-HAp. Later on, the slow adsorption is probably the result of the diffusion of the adsorbed external fluoride to the inner adsorbent surface, providing then new F-binding sites on the external surface.

The effect of initial fluoride concentration was studied using fluoride concentrations ranging from 2 to 200 mg/L (Figure 10B). The defluoridation capacity increases with increasing the initial fluoride concentration, up to a value of ~4 mg/g from an initial fluoride concentration of 200 mg/L.

The effect of the water pH was investigated with an initial fluoride concentration of 10 mg/L, adsorbent dose of 10 g/L, contact time of 20 hours and at room temperature conditions; water pH was varied from 3 to 10, using 0.1 M HCl or 0.1 M NaOH. Figure 10C shows that, in contrast to other adsorbents, no strong effect is observed on the F⁻-removal ability as a function of the water

pH. A very soft decrease in the F^- -removal is observed when increasing the water pH from 3 to 8, and then a slightly stronger reduction occurs at very basic pHs of 9 and 10, but still reaching about 79 % fluoride-removal at pH 10, being only 7 % lower than the maximum efficiency at pH 3. Hence, our composite is quite robust against modifications in the water pHs. The small effect of the water pH in fluoride removal of nHAST adsorbent may be attributed to the nature of its surface charge, as evidenced by its high PZC. Anyhow, the slightly higher efficiency at pH less than 6.5 may be due to the gradual increase in attractive forces, whereas the relatively lower efficiency in alkaline medium can be explained by the competition between the OH^- and F^- ions for the adsorption sites. It is known that most adsorbents used in fluoride-removal have narrow working pH ranges, and usually show optimum performance in acidic pH range. However, the pH of natural groundwater with high fluoride content is in the range of 7.6 to 8.6 in most cases [37, 38]. Within this pH range, unlike most other defluoridation adsorbents, nHAST-144h composite shows high performance, about 84 % of F-removal efficiency. Interestingly, the performance remains comparably high in the pH range under investigation: the F-removal varies between 79 % at pH 10 to 86 % at pH 3 (at a dose of 10 g/L and initial fluoride concentration of 10 mg/L).

A wide variety of other anions is generally present in groundwater, and may compete with fluoride ions for adsorption on nHAST composite. In order to investigate their effect on the fluoride removal, batch adsorption experiments were performed in the presence of 100–500 mg/L concentrations of chloride, sulfate and bicarbonate in solutions with 10 mg/L of fluoride concentration; Figure 10D describes their effect on the fluoride-removal efficiency of nHAST-144h. When no competing ions were present, about 84 % of fluoride was adsorbed; the final residual solution pH in this case was about 7. In the presence of bicarbonate ions, the fluoride-

removal efficiency decreases while increasing the concentration. This effect is significant at concentrations higher than 300 mg/L: the efficiency decreased significantly from about 84 % to 65 % in the presence of 500 mg/L HCO_3^- ions, possibly due to the change in pH as well as the strong competing effect of HCO_3^- ions. However, other ions such as chloride and sulfate showed no significant effect within the concentration range tested. In general, the change in removal efficiency when the coexisting ion concentration is below 300 mg/L is almost insignificant, again evidencing a high robustness of our adsorbent against changes in the chemical composition of the water.

3.4. Defluoridation of real groundwater from Ethiopian Rift Valley using nHAST-144h

Finally, the defluoridation potential of nHAST-144h with fluoride-containing real groundwater samples (samples 1 and 2 in Figure 10B), collected from a village near Maki town, in the Ethiopian Rift Valley, was tested; Table 2 lists the chemical composition of the water before and after the treatment. When untreated water of samples 1 and 2 were subjected to a defluoridation treatment at a dose of 10 g/L of nHAST-144h and a contact time of 20 hours, about 83 % of fluoride was removed in both cases; the corresponding final fluoride concentrations were found to be 1.2 and 1.4 mg/L, respectively (below the WHO threshold), giving the same final pH of about 8.1. The defluoridation capacities obtained for groundwater samples 1 and 2 were found to be 0.6 and 0.68 mg F⁻/g, respectively, which falls well within the trend of nHAST-144h as a function of the fluoride initial concentration (Figure 10B); their defluoridation capacities were found to be only slightly lower than that in lab-made fluoridated water solution, possibly due to the presence of various competing ions in real groundwater. In fact, chloride and sulfate concentrations are also reduced during the defluoridation treatment (Table 2), whilst pH remains

practically the same. In sum, these results with real groundwater support the potential use of nHAST-144h as adsorbent for defluoridation in a real case.

3.5. Reproducibility using other Stilbite samples

Reproducibility of the optimized synthesis procedure for the preparation of nHAST adsorbents was successfully tested using other similar natural stilbite zeolites (labeled Z4-Z9) collected from different parts of the country by the School of Earth Sciences (Addis Ababa University). The main stilbite sample used in this work was collected from the Hashenge basalt formation in the Tigray region, and the rest of the samples were collected in the localities of Korem and Maychew in the same region. All zeolite samples (Z4-Z9) involved in the preparation of nHA/zeolite composites were first studied by XRD and ICP in order to identify the zeolitic structure and composition. All the samples were identified as stilbite minerals, and the ICP analyses confirmed a high Ca content (Table 3). For Z4-Z9 zeolite samples, the corresponding nHA/Z4-Z9 composites were synthesized following the optimized synthesis procedure (autogeneous pH of 8, crystallization time of 144 h at room temperature). The composites were characterized and then tested in fluoride-removal, and their performances were compared with the nHAST-144h composite reported above. The X-Ray diffraction patterns of the synthesized nHA/Z4-Z9 composite samples show very similar diffraction patterns (Figure SI-3), suggesting that the crystalline structure of all the zeolites did not change after the growth of HAp on the zeolite surface. Similarly, the presence of HAp was confirmed by the P content in the final composites, as determined by ICP elemental analysis (Table 3). Again, the amount of HAp (calculated by the P content using eq. 1) grown on the zeolite surfaces was in the range between 5.4 % in nHAZ9 to 10.8 % in nHAZ4 and nHAZ5. This confirms the reproducibility of the synthesis procedure.

However, the amount of HAp crystallized is not exactly the same, which might be associated to a different roughness of the zeolite surface involving a different amount of nucleation points for the HAp growth.

Defluoridation tests were performed using 10 mg/L of initial fluoride concentration at 10 g/L dose. The fluoride-removal efficiencies of all the nHA/zeolite composites were significantly high, indicating the formation of a high amount of active nHA sites on the zeolite surface. Maximum fluoride-removal of 93 % was recorded for nHAZ4, whereas the minimum 75% removal was observed for nHAZ7 composite (Table 3). Interestingly, all the composites were able to reduce the fluoride concentration below or at least close to the WHO maximum limit of 1.5 mg/L from an initial fluoride concentration of 10 mg/L. Thus, this study corroborates the reproducibility of the no-energy demanding synthetic procedure proposed, which can be reproduced with different stilbite zeolite samples from different potential mineral deposits.

4. Conclusions

In this study, the optimization of the synthesis parameters allowed a strict control of the crystal growth of nanometric Hydroxyapatite on the surface of the natural stilbite zeolite. Interestingly, an autogenous pH of 8, and a crystallization time of 144 hours at room temperature enabled the crystallization of nano-sized hydroxyapatite crystals in a very sustainable manner. Cs-STEM and ³¹P NMR analyses provide evidences for the formation of nano-crystals of HAp, which explains their high F⁻-removal activity. Defluoridation tests confirm the high potential of nHAST composites for fluoride-removal under very demanding conditions, in solutions with 5.0 and 10 mg/L of fluoride initial concentration, overpassing the WHO limit with a dose of 10 g/L. Even with real groundwater, the optimized nHAST-144h composite has shown a high fluoride-uptake

capacity. Fluoride adsorption was very modestly influenced by the presence of co-ions and shows a minimal effect of the water pH, both of which add value to the use of nHAST composites for F⁻-removal from groundwater. The intrinsic HAp capacity of nHAST, normalized to the amount of HAp on the adsorbent, is significantly high (9.15 mg/gHAp), showing the high F⁻-removal efficiency of HAp on these composites. These results foresee a potential of nHAST-144h composite towards fluoride-removal implementation, particularly under the constraint of low energy demanding environments like Ethiopia.

Acknowledgments

The authors acknowledge Dr. Asfawossen Asrat, Prof. Solomon Tadesse, and Dr. Dereje Ayalew, School of Earth Sciences, Addis Ababa for providing the natural zeolites from Ethiopia. Spanish Government, MINECO MAT2012-31127 project and the Spanish Research Council CSIC I-COOP-H₂O (2013CD0009), are acknowledge for funding. LGH acknowledges the Spanish Ministry of Economy and Competitivity for Ramón y Cajal (RYC-2012-11794) contract.

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Table 1: ICP elemental analysis results of the original STI zeolite and of nHAST composites synthesized as a function of crystallization pH and time.

Sample	Al(% wt)	Si (% wt)	Si/Al	Ca (% wt)	Na (% wt)	P (% wt)	HAp%
STI	8.0	20.4	2.4	4.9	0.50	0.0	—
nHAST 7.0	7.7	22.2	2.7	4.7	0.3	0.9	4.9
nHAST 7.5	7.7	22.6	2.7	4.8	0.3	0.8	4.3
nHAST 8.0	7.3	20.9	2.7	4.7	0.2	0.9	4.9
nHAST 8.5	7.5	20.4	2.5	4.7	0.2	0.8	4.3
nHAST 9.0	7.5	20.2	2.5	4.7	0.2	0.9	4.9
nHAST 9.5	7.7	20.5	2.5	4.7	0.3	0.9	4.9
nHAST 10.0	7.7	20.2	2.4	4.8	0.3	0.9	4.9
nHAST, 2h	8.2	19.4	2.2	5.4	0.4	0.3	1.6
nHAST, 6h	8.5	20.6	2.3	5.5	0.4	0.6	3.2
nHAST, 19h	8.2	19.3	2.2	5.6	0.4	0.9	4.9
nHAST, 72h	8.2	20.4	2.3	5.6	0.2	1.4	7.6
nHAST, 96h	8.4	20.1	2.2	5.6	0.2	1.6	8.6
nHAST, 144h	8.5	20.5	2.2	5.5	0.2	1.7	9.2

Table 2: Physicochemical parameters of groundwater samples before and after treatment with nHAST-144h adsorbent at a dose of 10 g/L and a contact time of 20 hours.

Parameter	Water Sample-1		Water Sample-2	
	Untreated	Treated	Untreated	Treated
Fluoride, mg/L	7.2	1.2	8.2	1.4
Chloride, mg/L	24.1	8.1	19.5	7.9
Sulphate, mg/L	72.0	48.0	76.0	49.0
pH	8.3	8.1	8.3	8.1

Table 3: ICP elemental analysis results of nHAZ4-nHAZ9 composite samples synthesized at the optimized procedure, and fluoride removal (F-Rem%) from water with 10 mg/L of F initial concentration (dose of 10 g/L and contact time of 20 h).

Sample	Al wt %	Si wt %	Na wt %	Ca wt %	P wt %	HAp %	F-Rem%
nHAST144h	8.5	20.5	0.2	5.5	1.7	9.2	84.0
nHAZ4	7.2	20.2	0.1	5.1	2.0	10.8	93.3
nHAZ5	7.3	20.6	0.1	5.1	2.0	10.8	82.8
nHAZ6	7.6	21.8	0.1	5.2	1.2	6.5	82.3
nHAZ7	7.2	20.7	0.1	4.9	1.9	10.3	74.7
nHAZ8	7.3	21.4	0.1	5.2	1.1	5.8	78.8
nHAZ9	7.1	21.0	0.1	5.1	1.0	5.4	76.5

Figure 1: XRD profiles of the original STI zeolite and nHAST composite samples as a function of the crystallization pH.

Figure 2: Defluoridation performance of nHAST composites as a function of crystallization pH, from water with a) 5 mg/L (green line) and b) 10 mg/L (blue line) initial fluoride concentrations; cross signs are for F^- removal efficiency (right axis), and triangles for defluoridation capacity (left axis).

Figure 3: XRD profiles of the original STI zeolite and nHAST composite samples as a function of the crystallization time. Right: detail of the 23-25 2θ region.

Figure 4: TGA (doted lines) and DTG (solid lines) of STI and nHAST composite samples.

Figure 5: IR-ATR spectra of STI and nHAST composites as a function of crystallization time.

Blue arrows indicate PO_4^{3-} bands and black arrow NH_4^+ bands.

Figure 6: Left: percentage of HAp (as determined from the P content, black line), total defluoridation capacity (in mg/g, red line), and intrinsic HAp defluoridation capacity (in mg/g of HAp, blue line) as a function of the crystallization time. Right: Intrinsic HAp defluoridation capacity as a function of the amount of HAp grown on the STI zeolite surface.

Figure 7: ^{31}P MAS-NMR spectra of nHAST-144h prepared at pH 8 (blue), nHAST-19h prepared at pH 8 (green), nHAST-19h prepared at pH 9 (red line), and a sample of HAp (dotted black line).

Figure 8: STEM/HAADF/EELS results on nHAST-19h and nHAST-144h composites. a) Low-magnification image of nHAST-19h. b) Closer observation of the layered materials, where the structure can be distinguished (inset). c) Low-magnification image of nHAST-144h. d) Magnified region where the Spectrum imaging was performed (dashed rectangle). e) Chemical map extracted from the Si (red) and P signals (blue) with the correspondent EELS spectra of the regions denoted as 1 and 2.

Figure 9: The effect of adsorbent dose on fluoride-removal efficiency (dotted lines) and fluoride equilibrium concentrations (solid lines) by nHAST-144h composite.

Figure 10: A) Fluoride removal efficiency as a function of contact time of nHAST-144h composite ($C_o = 10$ mg/L). B) Effect of initial fluoride concentration on the nHAST fluoride-removal capacity (contact time of 20 hours). C) Effect of water pH on fluoride removal of nHAST composite ($C_o = 10$ mg/L and contact time of 20 hours). D) Effect of coexisting ions on fluoride removal of nHAST composite ($C_o = 10$ mg/L and contact time of 20 hours). All studies were performed with a dose of 10 g/L and at room temperature.