



## 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 this 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  $\mu\text{m}$ . 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, <sup>31</sup>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 h 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 removal 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).

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### 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 and 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].

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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<sup>-</sup> 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 (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> and stirred for 2 h. 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 h, and optimization of the crystallization time was studied for periods ranging from 2 to 144 h 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<sub>α</sub> 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).

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

where 502 is the total molecular mass of HAp, (Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>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 °C·min<sup>-1</sup> 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 500–4000 cm<sup>-1</sup>, using quartz as detector. <sup>31</sup>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 h. 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 Å; 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<sub>0</sub>), 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

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