Composite materials based on zeolite stilbite from Faroe Islands for the removal of fluoride from drinking water

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ABSTRACT

In this work, three samples of the zeolite stilbite from the Faroe Islands have been used to prepare zeolite/hydroxyapatite composite materials that have been tested for the removal of fluoride present as geogenic contaminant in underground water. The Faroe Islands are an archipelago in the North Atlantic that have volcanic origins of Paleocene and early Eocene age. Early reports on the presence of zeolites in the Faroe Islands indicate abundance of chabazite, analcite, mesolite, heulandites, and stilbite, with heulandite and stilbite dominant in the northern and northwestern part of the islands. Further investigations of the Faroese Geological Survey yielded zeolitic phases in Vestmanna, Streymoy, Morkranes, and Eysturoy, as well as in the sea tunnel that connects the island of Eysturoy with the island of Borðoy. Three stilbite samples coming from these locations have been used with the aim of producing composite materials for fluoride removal. For this purpose, the samples were exposed to a phosphate solution at room temperature for selected periods of time, in such a way that a hydroxyapatite layer develops on the surface of the zeolite crystals. The resulting composites consist of approximately 93% zeolite and 7% nano-hydroxyapatite, which is the active phase for fluoride removal. Excess fluoride (above 1.5 mg/L according to WHO) in drinking waters provokes dental or skeletal fluorosis, an endemic health problem in more than 25 countries. The defluoridation studies in our work are performed using real waters from Spain with initial [F⁻] of 7.1 mg/L. The capacity of the Faroe Islands stilbite-based adsorbent reaches 0.3 mg F⁻/g, showing similar behavior regardless of the stilbite sample used. The impact of the particle size of stilbite in the final defluoridation capacity is remarkable. An increase in the particle size leads to a dramatic decrease in the surface area, affecting the growth of the nano-hydroxyapatite on the zeolite surface and hindering, as a result, its capacity to remove fluoride. Interestingly, electron microscopy and X-ray powder diffraction results clearly show that nano-hydroxyapatite grow on the zeolite surface with a preferential orientation that maximizes the exposure of the (001) face containing the active sites for defluoridation, thus explaining the high F-removal efficiency of these materials.

Keywords: Natural zeolite, stilbite, hydroxyapatite, defluoridation; Microporous Materials: Crystal-Chemistry, Properties, and Utilizations

INTRODUCTION

The occurrence of fluoride in excessively high concentration in groundwater used for human consumption is a matter of great concern by health care organizations all over the world (Chinoy et al. 1991). The reason for this is the capacity of this anion to accumulate on teeth and bones, producing an irreversible illness known as fluorosis. This is a strong deterioration of the teeth and bones that could ultimately lead, in the most severe cases (and in addition to the suffering associated to the illness) to disabling people from normal life. Moreover, not only hard but also soft tissues are targeted by fluoride (WHO 1996). For these reasons, the World Health Organization (WHO) estimated in 1984 that at least 260 million people would be at risk of being affected by this illness due to their consumption of water with a concentration of fluoride higher than 1 mg/L (WHO 1984; UNICEF’s Position on Water Fluoridation, http://www.nofluoride.com/Unicef_fluor.cfm, consulted on April 7, 2019); as a consequence, WHO strongly recommends the reduction of the concentration of this anion in drinking water below 1.5 mg/L (Fawell et al. 2006). The fluoride present in groundwater comes from the leaching of fluoride-rich minerals, mainly fluorite (Ca₂F), criolite (Na₃AlF₁₀), and hydroxyapatite [Ca₅(PO₄)₃F], and there is no method to mitigate the occurrence of this natural dissolution phenomenon (Johnson and Bretzler 2015). Therefore, two alternatives have been envisaged to avoid population exposure to excessive ingestion of this harmful anion. The use of alternative fluoride-free water resources looks initially to be the best action, but it is not effective if one considers that in most cases extensive areas are affected by this problem, particularly in developing countries in which the supply of fresh water coming from distant sources (piped water) is beyond their funding capabilities. The problem is getting worse as in many cases the population is scattered in little villages covering large areas.