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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