

From octacalcium phosphate (OCP) to fluorapatite, a new method for defluoridation of drinking water

Idini A. *, Dore E., Fancello D., Ghiglieri G. & Frau F.

Dipartimento di Scienze Chimiche e Geologiche, Università degli Studi di Cagliari

* Corresponding email: alfredo.idini@gmail.com

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Geogenic contamination of fluoride (F⁻) in ground water is one of the major problems of the water crisis of the 21st century, affecting about 200 million people over 24 countries (Kumari & Khan, 2017). The World Health Organization recommends concentration of F⁻ < 1.5 mg/L for drinking water, in that higher concentrations cause several diseases, such as the most common mottled enamel, osteoporosis and crippling skeletal fluorosis (WHO, 2010).

The aim of this work, in the framework of the FLOWERED project (a Horizon2020 European funded project: Grant Agreement - N. 690378) (www.floweredproject.org), is to develop a low-cost defluoridation technique addressed for rural populations of the East African Rift Valley.

The octacalcium phosphate (OCP), a calcium phosphate with general formula Ca₈(HPO₄)₂(PO₄)₄ · 5H₂O, is a precursor of apatite group which includes hydroxylapatite Ca₅(PO₄)₃OH (HAP) and fluorapatite Ca₅(PO₄)₃F (FAP).

OCP is a very unstable phase in aqueous solutions that, in the presence of F⁻ or at pH > 7.4, transforms in an epitaxial growth of HAP-FAP through sub-solidus reaction (Zhan et al., 2005). The stoichiometric fluoride uptake capacity of the reaction OCP → FAP is 34.4 mg F⁻/g OCP.

The potential of OCP in fluoride removal from both synthetic solution and natural water has been tested through sorption experiments performed in batch mode: vials of 50 ml with 200 mg of OCP and different initial concentration of fluoride (40, 60, 80, 120, 140 mg/L F⁻) have been placed on a rotor at 40 rpm for different time of reaction (from 0.5 to 24 hours). The possible effect of existing co-anions in solution was tested repeating the removal experiment with fluoride molar equivalent of Cl⁻, OH⁻, HCO₃⁻.

The results show that the equilibrium of the reaction is reached within 8 hours; the empirical removal capacity (Q_e) ranges between 25.7 and 28.6 mg F⁻/g OCP. No significant variations of Q_e are observed, neither in the presence of Cl⁻ and HCO₃⁻, nor at different pH conditions (pH = 7, 8, 11.25). The experimental data, fitted with the Langmuir isotherm model and the pseudo-second-order kinetic equation, provide a theoretical maximum sorption capacity (Q_{max}) of 29.6 mg F⁻/g OCP at 20 °C. All the solutions after the treatment reach a circum-neutral pH of 7.01-7.26.

Further development of this research will be focused on the realization of effective, low-cost filters to be tested in the rural areas of the East African Rift Valley.

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