Deciding geochemical factor for incorporation of metal ions in vacant sites of non-stoichiometric hydroxyapatite

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Sustainability in terms of water demands improved water quality and clean water resources which face anthropogenic inputs with persistent heavy metals as a major hurdle. Incorporation of a metal ion in vacant sites of a mineral can be a good option for its permanent removal and is affected by many factors including ionic radius and charge. Ions with higher Ionic potential, easily partition to solids while vacant sites can handle ions with similar size and charge.

To compare and evaluate the deciding factor between these two, in this work, mineral hydroxyapatite (HAP), $Ca_{10}(PO_4)_6(OH)_2$ was synthesized in laboratory by varying the Ca/P ratio to generate non-stoichiometry and therefore vacant Ca sites [1]. We have synthesized two HAPs with Ca/P=1.67(St-HAP) and Ca/P=1.3 (Non-St-HAP). As the ionic radius of Ca^{2+} is 0.99 Å and therefore two toxic metals i.e. Zinc and Cadmium with similar charge i.e. +2 and different ionic radius i.e. 0.74Å and 0.95 Å were selected as adsorbate. Comparatively evaluation of adsorption efficiency was done by supplying the adsorbate separately while mixture of Cd^{2+} and Zn^{2+} was supplied to compare the selective crystal incorporation of ions.

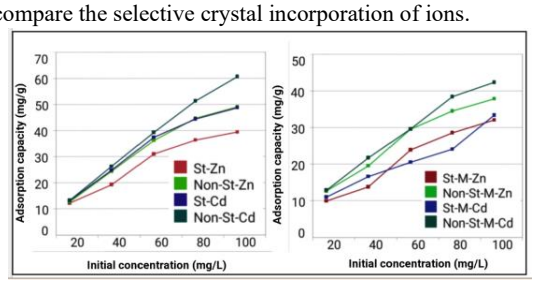

Fig.1 *Adsorption of Zinc and Cadmium separately (left) and in mixture (right) on St-HAP and Non-St-HAP*

Results in figure-1 clearly shows that non-stoichiometry results in increased sorption capacity for both Cd^{2+} and Zn^{2+} due to increased surface area, while similar size of Cd^{2+} as of Ca^{2+} results in higher cadmium removal in the mixture of metal ions even if Zn^{2+} has higher ionic potential and therefore higher affinity towards solid compared to Cd^{2+}.

[1] Y. Sekine, R. Motokawa, N. Kozai, T. Ohnuki, D. Matsumura, T. Tsuji, R. Kawasaki, K. Akiyoshi, Calcium-deficient Hydroxyapatite as a Potential Sorbent for Strontium, Sci Rep-Uk, 7 (2017) 2064.