

Structurally and morphologically tailored hydroxyapatite materials for effective immobilization of polluting heavy metal species from wastewaters

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In the present study, several calcium hydroxyapatite powders ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, HAP) have been tested for their known ability in removing heavy metal ions from aqueous solutions ^[1]. HAP samples have been synthesized under different conditions (varying Ca/P stoichiometry and morphology) to tune the properties of the obtained materials and comparing their removal efficiency towards several polluting metal species (Cr(III), Pb(II), Ni(II), Cu(II), Co(II)). HAPs have been batch-tested in simulated polluted waters, containing both single and multi-metal species, with different concentrations, molar ratios and pH. The experiments have given knowledge on the removal efficiency/selectivity of the different HAP samples, as well as on the adsorption mechanism. Leaching tests have also been performed to confirm the permanent confinement of the entrapped metal species. The prepared materials have been characterized by various physical-chemical techniques: FT-IR spectroscopy, XRPD, TEM-EDX, and N_2 -adsorption/desorption analyses. The analyses were carried out on bare and metal-loaded HAPs. The results have revealed that different mechanisms are involved in the metal species uptake by HAP; for example, Cu(II) and Cr(III) were mainly removed by surface complexation and/or ion-exchange ^[1] with Ca^{2+} , while Pb(II) was immobilized through the formation of stable hydroxypyromorphite phase ($\text{Pb}_{10}(\text{PO}_4)_6(\text{OH})_2$).^[2] Results obtained with multi-metal species disclosed a more complex behavior, with variation of the efficiency and selectivity of HAPs towards a given target cation depending on the molar ratio among the species in solution, and pH. Structural and morphological properties of HAPs effectively influence the adsorption process. Further studies are being conducted to achieve a full understanding of the role of the material properties in the metal immobilization process.

[1] A. Corami, S. Mignardi, V. Ferrini, in: "Copper and zinc decontamination from single- and binary-metal solutions using hydroxyapatite", *Journal of Hazardous Materials*, vol. 146, 2007, 164-170.

[2] S. Campisi, C. Castellano, A. Gervasini, in: "Tailoring structural and morphological properties of hydroxyapatite materials to enhance the capture efficiency towards copper(II) and lead(II) ions", *New Journal of Chemistry*, vol. 42, 2018, 4520-4530.