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Hydroxyapatite materials: from remediation of heavy metal pollution to new catalytic applications

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Among all the calcium phospates, hydroxyapatite (HAP, $Ca_{10}(PO_4)_6(OH)_2$) has proven through the years to be a versatile material, able to play a role in different fields of the applied science, from medical engineering[1] to pollution remediation[2]. In environmental applications, as solid adsorbent, HAP as gained attention because of its unique characteristics of chemical stability, low cost, large availability, and water insolubility. HAP has proven its ability to permanently immobilize polluting (or toxic) metallic cations, with interesting yield of removal from aqueous phase in respect to the most known adsorbents[2-3]. Previous and actual studies, conducted in our laboratories, confirmed the massive and stable immobilization of several heavy metal cations, such as Cu, Pb, Cr, among others, on different HAPs[4].

HAP has even found a role in catalysis because its easy functonalization[5]. Different metallic species of catalytic interest (Cu, Co, Mn, and others) can be deposited on the HAP surface with assured uniform dispersion of the metallic centers. Such catalytic materials show a double functionality; acid-basic sites typical of bare HAP are summed to the electron transfer ability and catalytic feature of the metal ions. Until now, HAP catalysts have found a modest implementation in the field of electrocatalysis, in reactions of industrial (such as ethanol oxidation[6]) and sensoring/environmental interest (sensing/degradation of organic pollutants[7]).

In view of a more sustainable industrial chemistry, this study proposes to employ HAP material at first as sorbent of polluting metallic species and then to re-use the metal-loaded-HAP as electrocatalyst. To explore this feasibility, HAP has been charged with different metals species in tests of simulated polluted water containing given concentration of metallic species (i.e., Cu, Co, and Ni) and then the metal-loaded-HAP has been tested as electrocatalyst for glucose to gluconolactone oxidation, a model reaction of carbohydrates oxidation. Electrocatalytic effect, activity and robustness of such materials have been evaluated. Electrochemical testing (principally, cyclovoltammetric and chronoamperometric analyses) of electrodes modified with the electrocatalysts permitted to estimate the catalytic contribution of the materials to the reaction; yield and selectivity of the electrocatalysts have been also investigated. Comparison with more conventional catalysts and laboratory functionalized HAPs (*ad hoc* impregnated/charged) have been employed in the same model redox reaction, allowing to evaluate the catalytic usefulness of the re-used HAP catalysts.

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