

Organophosphonate-modified hydroxyapatites for Zn(II) and Pb(II) adsorption in relation of their structure and surface properties



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ABSTRACT

The grafting of nitrilotris(methylene)-triphosphonate (NTP) molecules can provide an effective route to modify the surface properties of apatite materials. The higher specific surface area for the modified hydroxyapatite is around 160 m²/g compared to the pure hydroxyapatite (HAp) (120 m²/g). The nitrogen and phosphonate groups are responsible to remove the heavy metals by complexation reactions, suggesting that these low cost sorbents may find applications for the detection of specific metals elements and limited environmental impact.

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1. Introduction

Mining and foundry activities steel production, and solid waste incineration contribute most significantly to environmental Zn(II) and Pb(II) pollution [1,2]. Depollution of wastewater involves a series of treatment methods such as sorption and ion exchange, precipitation and membrane technologies. Among them, sorption processes are considered to be more promising due to their cost-efficiency factor. The first limitation can be addressed using low cost materials with high immobilization capacities. Among these, hydroxyapatite is particularly well-suited for the immobilization of metallic cations. Several sites of P—OH groups on the hydroxyapatite surface are responsible to adsorb the mineral and organic species. Despite the large number of data already accumulated on this subject, an overview of the current literature indicates that the incorporation of organic moieties increases the efficiency of the sorption phenomenon [3–6]. In addition, few studies showed the possibility of ionic exchange between phosphate ions of the apatite and organic ions such as phosphonate, carboxylate and amino groups as agents for surface modifying hydroxyapatite nanoparticles [7–10]. In fact, Kandori et al. [7] succeeded in grafting oleylphosphate molecules onto the surface of hydroxyapatite by precipitating Ca(OH)₂—H₃PO₄ in presence of disodium oleylphosphate affecting the hydrophilic–hydrophobic surface. Other studies were devoted to increase the active sites at solid surface able to fix many organic and mineral

pollutants [8–10]. In this context, we have evaluated an amino-phosphonate molecule, nitrilotris(methylene)triphosphonic acid (NTP), as potential additives to prepare a modified hydroxyapatites with high capacity for metal sorption. Nitrilotris(methylene) triphosphonic (NTP) acid has a strong affinity for a wide range of inorganic cations [11–13] and bears three phosphate groups (Fig. 1). Moreover, these three molecules have the advantage of being water soluble, cheap and environmental-friendly [12]. This study shows that NTP molecules can be reacted in reasonably amounts with Ca²⁺ ions to have a modified apatite and very significantly increase the material sorption rate and efficiency for Zn²⁺ and Pb²⁺ ions.

2. Experimental

2.1. Material

The ungrafted HAp was prepared by a modified chemical wet method [9]: 1.667 mol. of Ca(OH)₂ was dissolved in 200 ml of deionized–distilled water and stirred for 1 h 30 min at 25 °C. Soluble NH₄H₂PO₄ phosphate was dissolved in 100 ml of deionized water and then added to the calcium solution in the stoichiometric ratio corresponding to Ca/P = 1.67. The final suspensions were aged for 48 h at room temperature (23–25 °C), filtered and thoroughly washed with deionized water. The recovered precipitate was dried overnight at 100 °C.

The grafted hydroxyapatites (NTP-HAp) were obtained following a similar procedure except for the phosphorus-containing solutions that were prepared by mixing (1 – x) moles of NH₄H₂PO₄ with x/3 mol of nitrilotris(methylene)triphosphonic acid (NTP) in

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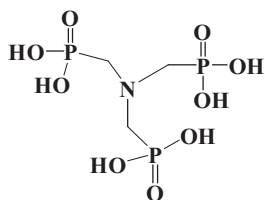


Fig. 1. Chemical structure of nitrilotris(methylene)-triphosphonic (NTP).

considering the reactivity of the three $-\text{PO}(\text{OH})_2$ functions containing in NTP molecule (Fig. 1). The percentage of organic NTP phosphorus in the total phosphorus (organic + inorganic) was chosen as 0; 2.5; 5 and 10 noted HAp, 2.5NTP-HAp, 5NTP-HAp and 10NTP-HAp, respectively. The final equilibrium pH of the mixture slowly decreased with NTP content in the mixture from pH 12 to 10 values.

2.2. Adsorption experiments

Stock solutions of Pb(II) and Zn(II) ions (2000 mg L^{-1}) were prepared from analytical grade $\text{Zn}(\text{NO}_3)_2$ and $\text{Pb}(\text{NO}_3)_2$ salts dissolved distilled water. The test solutions ($V = 100 \text{ ml}$, $C_0 = 0\text{--}2000 \text{ mg L}^{-1}$ and $0\text{--}1000 \text{ mg L}^{-1}$ for Pb and Zn respectively), obtained by serial dilution of stock solutions at $\text{pH } 5 \pm 0.1$, were equilibrated in a thermostatic water bath at 25°C before adding 200 mg of adsorbent under stirring (250 rpm). The pH was adjusted at pH 5 with 0.1 M NaOH or 0.1 M HNO_3 . For kinetic study, aliquots of the supernatant solution were taken with a 2 ml propylene syringe equipped with a 0.45 mm filter. The amount of adsorbed metal per gram of sorbent q_t (in mg g^{-1}) at time t was calculated as follows: $q_t = (C_0 - C_t/m) \times V$ where C_0 and C_t are the metal ion concentration (in mg L^{-1}) in the liquid phase initially and at any time t respectively, m is the mass of adsorbent (in g) in the solution, and V is the solution volume (in L). All measurements were performed in triplicate and experimental errors were found below 5%. Zn^{2+} and Pb^{2+} ions were chemically analyzed by inductively coupled plasma (ICP) emission spectroscopy (ICPS-7500, Shimadzu, Japan).

3. Results and discussions

3.1. Structure characterization of modified HAp

The crystalline phases were characterized by using the X-ray powder diffraction (Philips PW131 diffractometer, $\text{CuK}\alpha$ radiation). A good ability of the three functions $\text{PO}(\text{OH})_2$ of NTP molecule with Ca^{2+} ions is confirmed by series of experiments considering that one, two or three $\text{PO}(\text{OH})_2$ functions containing in NTP molecule can react with Ca^{2+} ions in the presence of inorganic phosphorus PO_4^{3-} ions. XRD results show that the formation of a unique apatite phase needed to consider all the three $\text{PO}(\text{OH})_2$ functions of NTP during the preparation of the grafted NTP-HAp samples. X-ray diffraction patterns of the prepared powders reveal a poorly crystalline apatite structure, but depend on the NTP content in the apatite powder (Fig. 2a). Even after heat-treatment at 800°C , the apatite phase became well-crystallized and a second phase attributed to $\beta\text{-Ca}_3(\text{PO}_4)_2$ ($\beta\text{-TCP}$) appears at high NTP content (Fig. 2b). Contrary to our previous results using natural phosphate as calcium and phosphorus precursors [14,15], two main phases are present indicating that NTP molecules are also extremely effective to inhibit HAp crystal growth. To characterize better the phosphorus environment in the apatite structure, ^{31}P Solid State NMR measurements were performed on an Avance III 500 Bruker spectrometer. Experiments were carried out at a frequency of

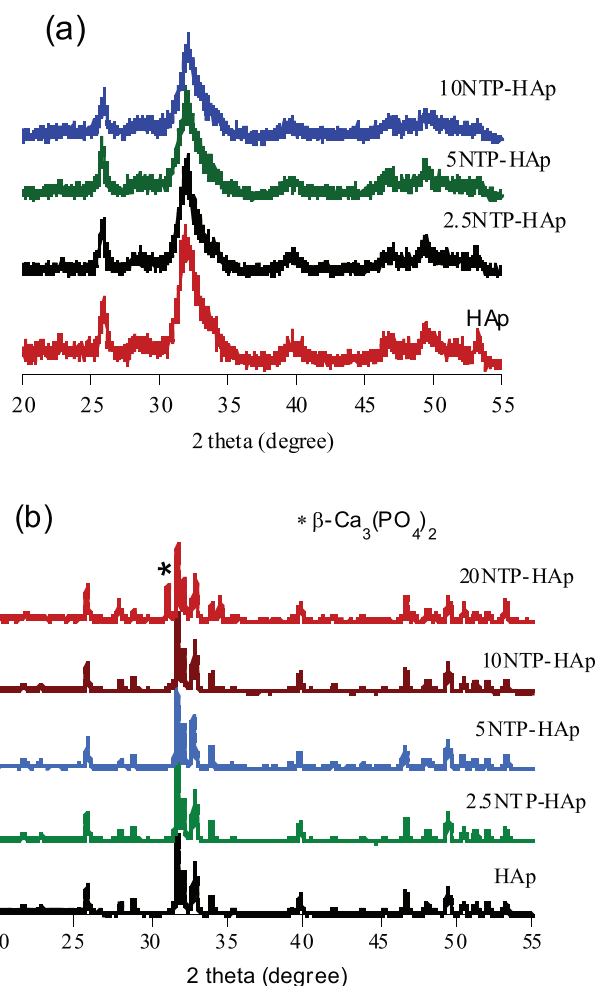


Fig. 2. XRD patterns of NTP-HAp treated with various NTP agents as received (a) and after heating at 800°C (b).

202.49 MHz using 30° pulse; recycle delays of 10 s and 128 scans. Fig. 3a shows the ^{31}P NMR spectra of NTP-HAp samples. In pure HAp, a single peak of phosphorus is observed at 2.9 ppm vs. $85\% \text{ H}_3\text{PO}_4$, indicating that one phosphorus site is available in the structure similar to that found in synthetic apatites as well as in bone and teeth [16]. Additionally to this sharp resonance, one broad resonance at 12.2 ppm is observed in grafted NTP-HAp especially for high NTP content. The later peak is characteristic of organophosphorus linked to Ca^{2+} ions such as demonstrated elsewhere [9,17,18]. To better confirm NTP grafting of NTP in HAp structure, ^{13}C NMR experiments were carried out at a frequency of 75.51 MHz using 90° pulse, ^{13}C NMR spectra (Fig. 3b) clearly show that the carbon peak related to $-\text{CH}_2-$ from NTP molecule found at 85.8 ppm , which is absent in ungrafted HAp spectrum. In addition, the NTP-grafting has also proved by IR spectroscopy, in which infrared bands are observed at $1090, 1030, 962, 603, 565 \text{ cm}^{-1}$ related to PO_4 groups (Fig. 4a). Additionally, the fine peaks in the $3600\text{--}3700 \text{ cm}^{-1}$ range correspond to the constitution OH groups of the ungrafted apatite, whereas a broad spectral band appears at 3500 cm^{-1} for all grafted hydroxyapatites, explaining a possible interaction of the hydroxyl OH linked to calcium with NTP species. Other absorption bands of CO_3^{2-} vibration at 1460 and 875 cm^{-1} and new vibration modes also appear essentially at 1540 and 1480 cm^{-1} related to the N-C and C-P bonds where their intensities increase when the NTP content is more added. Fig. 4b shows that a pure hydroxyapatite was obtained when the thermal treatment of NTP-HAp powders at 800°C has realized related to

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