Synthesis and Characterization of Hydroxyapatite Nanoparticles for Environmental Applications

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Abstract - The present research presents the synthesis of nanoparticles of hydroxyapatite (Nps-Hap) and its potential uses for cadmium and chromium removal from contaminated effluents. The Nps-Hap obtained by chemical reaction were characterized with Scanning Electron Microscopy-Energy Dispersive X-Ray Spectroscopy (SEM-EDAX), X-ray Diffraction (XRD), Transmission Electron Microscopy (TEM) and Brunauer–Emmett–Teller (BET) isotherm analysis. The Ca/P calculated from EDAX analysis was 1.78. The synthesized nanoparticles show a surface area of 140.5 $m^2.g^{-1}$ and a pore radius of 7 nm. The results of XRD analysis showed the presence of Hap phases. TEM images show semispherical and elongated nanoparticles with mean diameter of 36.7 nm $\pm$ 13.5 nm. The removal kinetics showed that cadmium is removed more effectively than chromium, at pHs of 3 and 5 respectively.

Keywords: cadmium, chromium, hydroxyapatite, metal removal, nanoparticles.

1. Introduction

In recent years, issues and challenges associated with heavy metal contamination of water have become more relevant [1]. In fact, contamination of water by the presence of heavy metals, especially in areas close to extractive industries, represents a serious threat to humans and the environment [2]. Heavy metals in these matrixes can be removed by precipitation; it is also possible to use adsorption or ion exchange methods. For this reason, new adsorbents have been sought, specifically targeting cadmium and chromium as these two species pose the highest risks to the environment and human health. In recent investigations, hydroxyapatite (Hap) is shown as a promising material to remove heavy metals, either by adsorbing them on its surface or through ion exchange mechanisms [3-6]. Also, the advantage of Hap is that this material can be easily synthesized from waste resources, such as waste shell [7], providing a sustainable source of adsorbent material.

In the literature, many methods have been reported for synthesizing Hap, including sol–gel [8] reverse microemulsion [9], hydrothermal [10], microwave-hydrothermal [11-12], precipitation [13-15] and solid-state reaction [16] methods. Weakly agglomerated and nano-sized Hap particles have been obtained through hydrothermal and reverse microemulsion strategies [10]. The precipitation process is the most reported method for preparing particles of Hap. This process is simple, low cost and suitable for scaled-up industrial production. In this sense, a chemical reaction can be a good possibility to obtain well dispersed Nps-Hap for environmental application in a single step [3, 5].

2. Experimental section

2.1 Preparation of Nps-Hap

Calcium nitrate tetrahydrate, $Ca(NO_3)_2.4H_2O$ ($\geq$ 98%) and Ammonium dihydrogen phosphate, $(NH_4)H_2PO_4$ (97%), were purchased from Sigma-Aldrich Peru (Lima, Peru). All chemicals were of analytical purity and used as received without further purification.

A 0.6 M $Ca(NO_3)_2.4H_2O$ solution, and 0.5 M $(NH_4)H_2PO_4$, solution were used to prepare NPs-Hap at pH = 10. Aqueous solution of calcium nitrate was vigorously stirred at room temperature. A solution of ammonium hydrogen phosphate was slowly added dropwise to the calcium nitrate solution. Once the reaction was done, we centrifuged the colloids containing nanoparticles at 2,000 rpm for 7 minutes (three times) using a micro centrifuge (Eppendorf 5804). To remove excess calcium and phosphates ions, the colloids of nanoparticles were washed with deionized water two times. A dried nanopowder of Nps-Hap was obtained by drying at 40°C overnight.

2.2 Characterization techniques

2.2.1 Elemental Composition Analysis

Chemical compositions of the samples were analyzed by SEM using a FEI Quanta 650 in the secondary electron mode at an accelerating voltage of 3-10 kV (FEI Europe BV; Eindhoven, The Netherlands). EDAX analysis was performed with an Ametek EDAX TEAM system coupled to the SEM microscope.

2.2.2 Structural Characterization

XRD analysis have been carried out using a BRUKER D8 ADVANCE (Karlsruhe, Germany) X-ray diffractometer equipped with a copper anticathode (λ Cu Kα= 1.54056˚A). Data were obtained over the range $2\theta = 5°–70°$ using a step size of 0.03° and counting time of 10 seconds per step. Reference intensity ratios methodology from XRD was used in order to assign the phases observed in the X-ray pattern. The crystallite size measurements were also carried out using the Scherrer equation, $D=k\lambda/\text{ß}\cos\theta$, where D is the crystallite size, k is a constant (=0.9 assuming that the particles are spherical), λ is the wavelength of the X-ray radiation, ß is the line width at half maximum intensity of the peak and θ is the angle of diffraction.

2.2.3 Morphology Analysis

The size and morphology of Nps-Hap were performed by TEM using a LVEM5 microscope (Delong Instruments-Check Republic). Histograms of size distribution were calculated from the TEM images by measuring the diameters of at least 50 particles using ImageJ software. A small amount of nanopowder was dispersed in ethanol (98%) by sonication during 3 min. Then 5 µL solution containing Nps-Hap were placed on carbon-coated TEM copper grid.

2.2.4 Surface Area and Pore Size Distribution

Nitrogen adsorption isotherms for Brunauer–Emmett–Teller (BET) isotherm analysis of the materials was performed using a Quantachrome Autosorb 1C. Specific surface areas SBET were measured using a 15-point isotherm at 77.4 K for N_2 activities less than 0.35, after outgassing the sample under dynamic vacuum at 423 K for at least 8 hours. Pore volume was measured at an activity of 0.99.

2.3 Metals removal

For the metal removal tests, stock metal solutions (50 mg.L^{-1}) were prepared with deionized MilliQ water and $CdCl_2$ or $CrCl_3$. The effect of pH on the metal adsorption process was studied over the pH range 2 – 8, and the initial metal ion concentration was fixed at 50 mg.L^{-1}. The desired pH levels were adjusted with 2 M HCl or 2 M NaOH. Next, 10 mg of Nps-Hap were added to 10 mL of the above-mentioned solution and placed in an orbital shaker at 180 rpm for 24 h. Finally, solutions were filtered through a 0,45 µm membrane filter and measured by atomic absorption spectrometry.

For the adsorption kinetics tests, 10 mg of Nps-Hap were added to 10 mL metal ion solution at 50 mg.L^{-1} at pH 3 for cadmium solutions and pH 5 for chromium solutions. Samples were shaken for designated time periods (5, 10, 30, 45, 60, 90, 105, 120, 240, 360, 1080 and 1440 min). The isothermal adsorption experiments were conducted with metal ion solutions (10 mL, 50 mg.L^{-1}) with different Hap masses (1,0; 2,5; 5,0; 7,50 and 10 mg), at optimal pH and time contact determined in the previous sections (for cadmium solutions were at pH 3 and 2 h and for chromium solutions were at pH 5 and 6 h).

3. Results and discussion

The Nps-Hap obtained by chemical reaction were characterized by the techniques described previously. BET results show that synthesized Nps-Hap have a surface area of 140.5 $m^2.g^{-1}$ and a 7 nm pore radius. These values are higher than those found in a commercial Hap sample ($15.7 m^2.g^{-1}$ and pore radius >40nm).

The EDS spectrum shows all K and L emission peaks for calcium, phosphorus and oxygen (Figure 1). Similar results have been previously reported by *Ragab al.* [17]. The results obtained by the EDS analysis indicate that the synthesized product is composed of Nps-Hap. Furthermore, the average Ca/P ratio =1.78 is very close to 1.67 and 1.80 reported by *Wang et al.* [15] and *Tariq et al.* [18], respectively.

The XRD spectra (Figure 2) reveal diffraction peaks at 2θ = 31.5º, 45.7º and 56.13º which correspond to the hexagonal structure of hydroxyapatite (Hap) according to the JCPDS card no.00-009-0432. The diffraction peaks in each pattern can be well indexed to the phase of hydroxyapatite and no peaks from any other crystalline phases were identified. In order to compare the crystallinity and crystallite size, a commercial Hap powder sample (Hap-C) was analysed by XRD. The crystallite size using the Scherrer equation and considering the 002 family of planes, were 22.7 nm and 23.5 nm for Hap-C and Hap-S respectively.
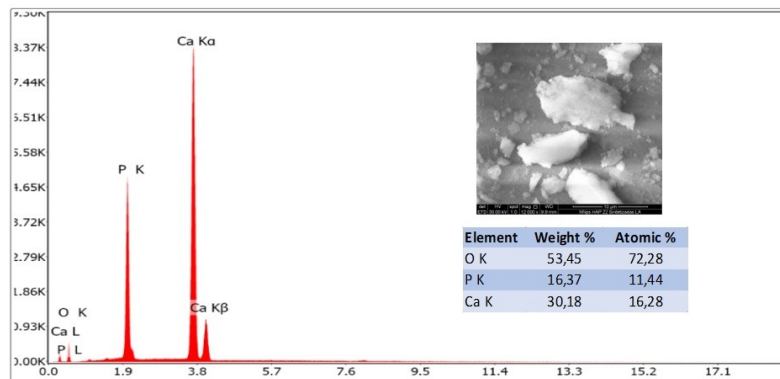

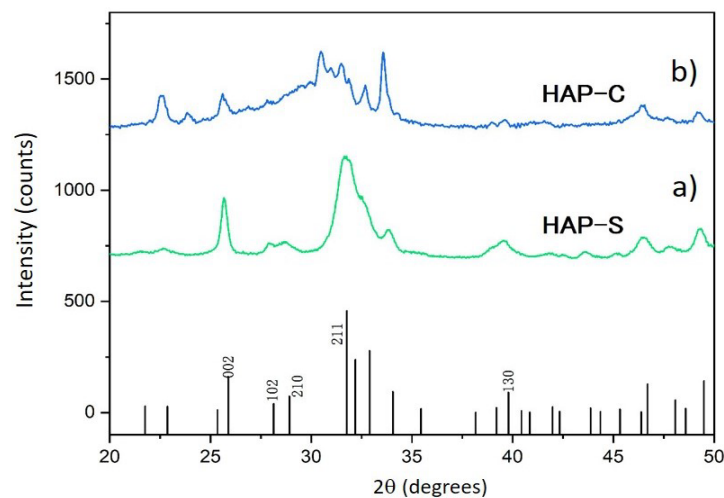Fig. 1: EDS spectrum of hydroxyapatite nanoparticles prepared by chemical reduction.

Fig. 2: XRD patterns of hydroxyapatite nanoparticles prepared at room temperature (HAP-S) a) and commercial product (HAP-C) b).

The average size and morphology of the Nps-Hap were determined by image analysis on TEM photographs (Figure 3). The nanoparticles have an elongated shape, that are in agreement with results reported by *Wang et al.* [15], and the size distribution analysis suggest a size between 6 to 80 nm with a mean diameter of 36.7 nm ± 13.5 nm.
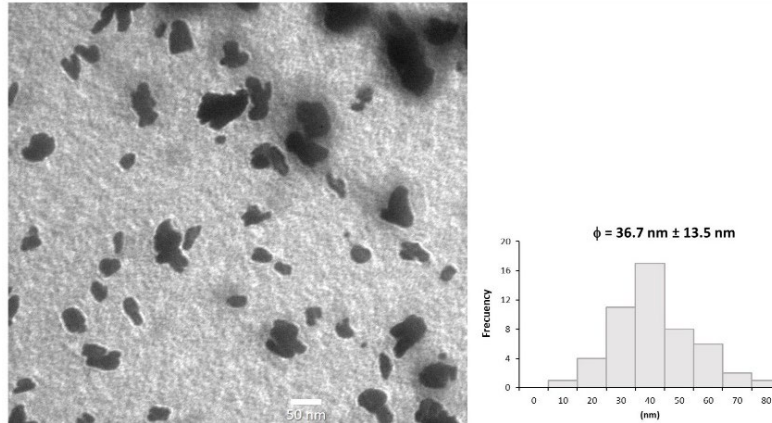
Fig. 3: TEM images and particle size distribution of Nps-Hap.

The adsorption behaviour of Cd^{2+} and Cr^{3+} as a function of pH is observed in Figure 4. It is appreciated that the removal of cadmium is much greater than that of chromium in a wide range of pH. Cd^{2+} becomes almost 100% removed, while Cr^{3+} removal is effective at pH values above 3. Similar results were reported by *Peld et al.* [19] when natural and synthetic apatites as sorbents were used.
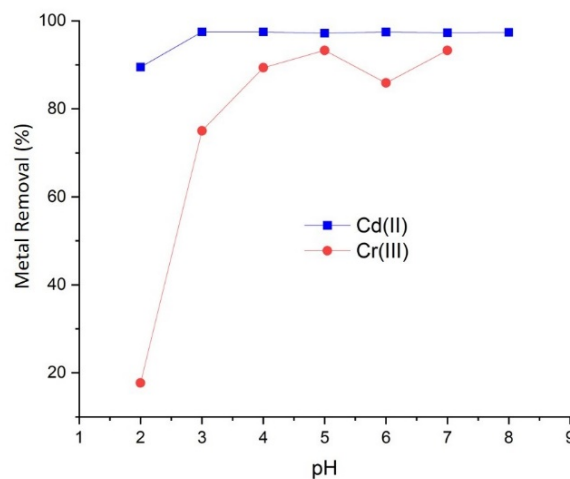

Fig. 4: Variation of cadmium and chromium adsorption as a function of pH.

From the kinetics point of view, the removal tests were carried out at room temperature at the optimum pHs of 3 and 5 for cadmium and chromium respectively (Figure 5). Result shows that the adsorption of Cd^{2+} ions onto the Nps-Hap surface was remarkably fast and equilibrium was reached within 50 minutes in which the removal percentage reached up to 70%. The removal kinetics clearly show that cadmium adsorbs faster than chromium on Nps-Hap. In the first 100 minutes, the Nps-Hap managed to remove 82% of cadmium while approximately 70% of chromium had been removed. A further increase in contact time does not have a radical effect on the percentage removal for either Cd^{2+} or Cr^{3+}.

Previous studies have shown that in regions of pH below 4, hydroxyapatite crystals begin to gradually dissolve [20, 21]. *Peld et al.* [19] shows that the sorption of cadmium at pH values lower than 3 is negligible or close to zero, as the apatite begins to dissolve. At pH higher than 3, the sorption is nearing the apatite sorption capacity, not depending on a further pH increase. *Mavropoulos et al.* [22] proposed that metals as Pb^{2+} may also be removed by Hap through the cation exchange process which took place at the HAp surfaces and controlled by liquid-film diffusion. Then similar behaviour can be taken place when solutions of Cd^{2+} and Cr^{3+} are used [23]. According to *Peld et al.* [19] the estimation of the sorption mechanism is based on the molar ratio (Q) of the cations bound with the Hap to the cations released from

the Hap during sorption as well as on the structural changes caused by the sorption process. If Q is close to one, which allows an assumption that sorption takes place mainly by cation exchange.

On the other hand, it is observed that the maximum removal of cadmium is 91% while in the case of chromium, its removal can reach up to 95%. These values are above the yields reported by *Avram et al.* [24] for the removal of Cd^{2+} (68%) and Cr^{3+} (80%). The sorption process of metal ions involves complex adsorption on the adsorption sites on the Nps-Hap surface [24, 25]. Additional studies to establish the mechanisms of cd and cr removal are under way.
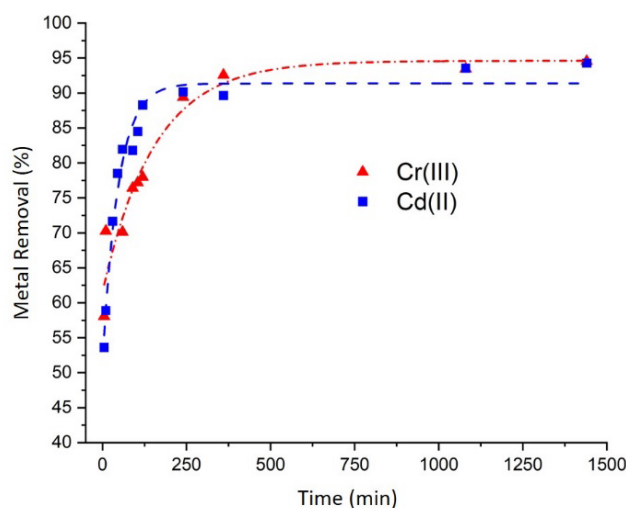

Fig. 5: Adsorption kinetics of cadmium and chromium at optimum pH.

4. Conclusion

In summary, Nps-Hap with hexagonal structure have been successfully synthesized by a chemical reaction. The semispherical or elongated shape of nanoparticles have a mean diameter of 36.7 nm ± 13.5 nm. The synthesized Nps-Hap show a surface area (140.5 $m^2.g^{-1}$) that is 9 times bigger than the commercial Hap (15.7$m^2.g^{-1}$). The pH interferes in the removal of metals, being the optimal values of 3 and 5 for cadmium and chromium respectively. At optimum pHs, the removal of cadmium is faster than that of chromium.

Acknowledgements

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