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Conversion of natural phosphate rock into mesoporous hydroxyapatite for heavy metals removal from aqueous solution

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ABSTRACT

A macroporous natural phosphate rock and its converted mesoporous hydroxyapatite material were evaluated for heavy metal (Pb^{2+}, Cu^{2+}, Zn^{2+}) remediation. The modified phosphate was found to show better sorption capacities than natural rock, due to its larger specific surface area. However, the presence of organic matter within the natural phosphate influences its affinity for the different metal ions, suggesting that this sorbent may find applications for the removal of specific elements.

1. Introduction

The removal of organic and inorganic pollutants from wastewaters is a major environmental issue related to the continuous development of industrial activities [1,2]. Activated carbons are currently considered as the most effective organics sorbents due to their high surface areas [3]. In the case of heavy metal ions, materials exhibiting cation exchange properties such as kaolinite [4] or bentonite [5] can be used. However, these sorbents are often too expensive to be utilized at a large scale [6] and may even present some ecotoxicological effects [7]. Thus, it is necessary to identify new sorbents that are cost-effective, environmental friendly.

Preliminary experimental studies performed for the adsorption of heavy metal ions on various low-cost minerals revealed that natural phosphate could remove limited quantity of metals from environmental aqueous solution, contrary to synthetic apatites [8–17], but the used chemical precursors of calcium and phosphorus in preparing of apatite are relatively expensive at industrial scale. Recently, a natural phosphate mineral was used as a raw material to prepare a novel and efficient adsorbent by a dissolution and precipitation method [18]. This converted apatite material was developed as a new adsorbent for the removal of organic and inorganic pollutants from aqueous environments. To check the potentiality of this approach, we have selected a natural phosphate rock from Bengurir deposits (Morocco), an important source of phosphate [19]. Noticeably, no detailed information on the heavy metal sorption properties by this Bengurir phosphate deposit in Morocco is available so far. Therefore its capacity for the removal of common metal pollutants (Pb^{2+}, Cu^{2+} and Zn^{2+} ions) was investigated and compared to the performance of the its converted mesoporous phosphate.

2. Experimental

2.1. Materials

Two adsorbents were used in this study: (i) natural phosphate (noted NP) and (ii) modified natural phosphate as mesoporous synthetic apatite (noted MNP). The phosphate rock sample used in this work originates from the Bengurir region (Morocco) [19] The sample was washed and then sieved to give a 100–400 μm size fraction using ASTM standard sieves. The choice of this material is based on its low cost, considering its abundance in the Morocco ores. The second MNP sorbent was prepared using recently reported procedure [18]: a complete dissolution of the natural phosphate from Bengurir was slowly performed with 1 M HNO_3 solution at pH = 2 under vigorous stirring to obtain calcium and phosphorus precursors. The filtrated solution was then precipitated with concentrated solution of NH_4OH at room temperature and aged for 24 h. The products were collected by filtration, washed, dried at 100 °C overnight.

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2.2. Adsorption procedure

Stock solutions (2000 mg L^{-1}) were prepared from analytical grade lead nitrate, copper nitrate, and zinc nitrate using double distilled water. The test solutions (100 mL, C_0 = 0–1500 mg L^{-1}), obtained by serial dilution of stock solutions at pH = 5 ± 0.1, were equilibrated in a thermostatic water bath at 25 °C before adding 200 mg of adsorbent under stirring (250 rpm). Since contaminated waters often contain several metal ions, competition experiments were also performed to study the sorption capacity of the both sorbents in the presence of copper, zinc and lead salts at equal concentrations, in the 100–1500 mg L^{-1} range. During kinetics experiments, the suspensions were sampled through direct filtration using a 0.45 μm membrane filter. Metal concentration was determined by inductively coupled plasma (ICP) emission spectroscopy (ICPS-7500, Shimadzu, Japan). All experiments were performed in triplicate and experimental errors were found below 5%.

The quantity of metal ions adsorbed on apatite q_t was calculated as the difference between the initial C_0 and the instant concentration $C(t)$:

$$q_t = \frac{C_0 - C(t)}{m} V \quad (1)$$

where m and V are the adsorbent mass and the volume of the contaminated solution, respectively.

3. Adsorbent characterization

As recently published [19], natural phosphate NP from Bengurir (Morocco) is a carbonaceous fluoroapatite. Its chemical composition was determined as: Ca(37.84%), P(15.03%), F(2.84%), Si(1.78%), S(0.78%), Na(0.79%) and other trace elements, that contains ca. 7 wt% of organic matters. Its specific surface area is ca. 20 m^2 g^{-1}, that is a low value considering possible application in sorption processes. To overcome this limitation, we have recently developed a novel route to prepare a mesoporous apatite materials from this natural phosphate (noted MNP as modified natural phosphate), involving a dissolution–precipitation reaction [18]. For more structural information, Fig. 1 shows the XRD patterns of the as-received and calcined MNP compared to those of the NP reference, all of which indicate the presence of apatite. However, the NP sample presents additionally impurities such as quatz–SiO_2. In addition, Fig. 2 depicts the IR-spectra of the phosphate rock and its derivative

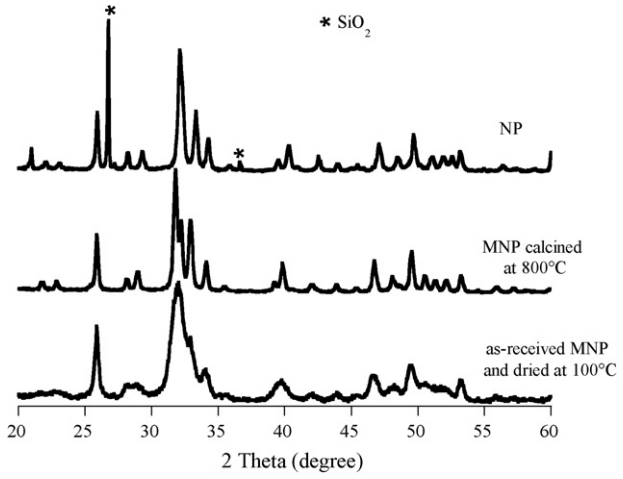

Fig. 1. XRD patterns of the as-prepared MNP and heated at 800 °C, compared to natural phosphate NP (as reference). The fluorine and silica are recuperated in residual solid after dissolution process of NP.

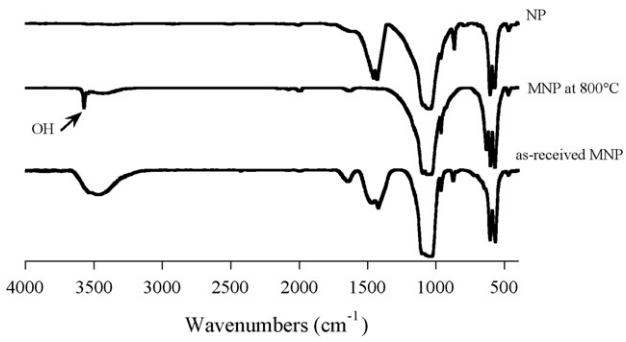

Fig. 2. IR-spectra of as-prepared MNP and heated at 800 °C compared to NP as reference.

apatite MNP. For the both materials, the strongest bands between 1100 and 900 cm^{-1} are attributed to PO_4 groups, the peaks at 500–600 cm^{-1} are assigned to P–O mode. In addition, the bands at 875 and 1425–30 cm^{-1} are assigned to carbonate vibrations. However, for MNP calcined at 800 °C, additional bands appear at 3625 and 630 cm^{-1} corresponding to OH vibration in an ordered apatite structure, demonstrating that MNP is a pure hydroxyapatite phase, in contrast to the NP sample. These results are confirmed by chemical analyses (Fig. 3), where Ca/P molar ratio for MNP is equals to 1.95 while no fluorine and silica are present, as a result of filtration after the dissolution of the natural phosphate. The nitrogen sorption isotherms of MNP and NP are shown in Fig. 4 and exhibit a typical type IV shape. In the high P/P_0 pressure domain, the MNP isotherm is characterized by a well-defined plateau indicating a closed mesoporosity whereas the NP mineral does not exhibit such a plateau, suggesting the presence of an open mesoporosity. The specific surface area of MNP can be estimated to be ca. 150 m^2 g^{-1} by the BET method. The calculated pore size distribution (Fig. 5) using BJH method indicates that the modified natural phosphate exhibits a pore population distributed around ca. 10 nm, whereas

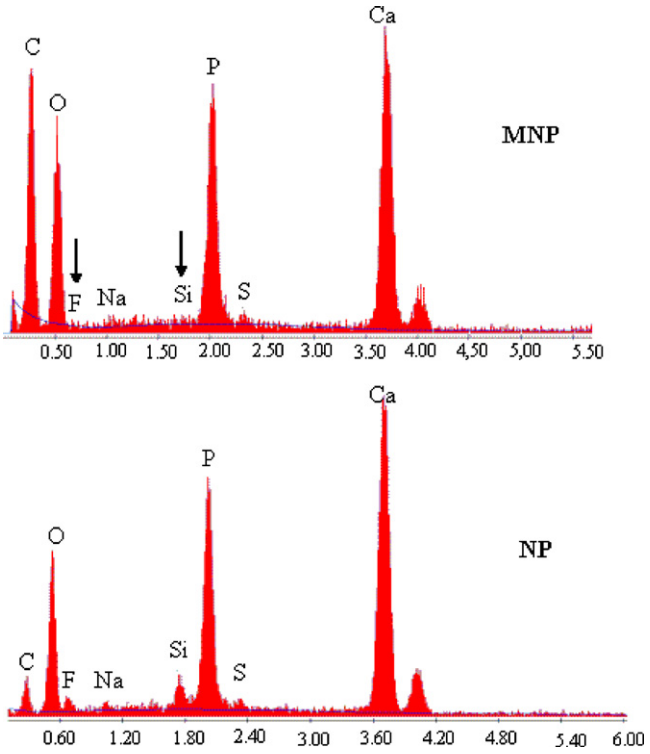

Fig. 3. EDAX spectrum of the MNP compared to that of NP as reference.