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# Surface properties of Moroccan natural phosphate and its converted hydroxyapatite for adsorption of $Cr^{3+}/Cr_2O_7^{2-}$ ions: Kinetics and isotherms

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## ABSTRACT

Surface of the natural phosphate and its converted hydroxyapatite was evaluated to develop an effective adsorbent suitable for the removal of individual oxymetal of $Cr^{6+}$ and $Cr^{3+}$ ions using batch system at room temperature. The converted hydroxyapatite was prepared from natural phosphate and characterized using various techniques. The experimental results suggest that several active sites exist on natural and synthetic apatite surfaces. They showed a high affinity of natural phosphate for the $Cr_2O_7^{2-}$ ions than c-HAP contrary to that of $Cr^{3+}$ ions related to the presence of silica in natural adsorbent while the converted apatite has a good affinity for $Cr^{3+}$ ions. The difference in adsorptive capacities is also related to the oxidation state of chromium and surface charge, which are effective parameters for Cr uptake on the natural and synthetic apatite.

*Keywords:* Phosphate rock; Converted hydroxyapatite; Surface property; Chromium; Adsorption

## 1. Introduction

Heavy metals have considered as a major toxic elements for the water resources [1]. Among them, chromium with its different oxidation states are considered as priority pollutants detected worldwide in soil, waters and air samples [2]. Its removal from water is a major environmental issue related to the incessant progress of industrial activities. Among the available methods to remediate groundwater-containing chromium, adsorption and ion exchange are efficient alternatives because of their simplicity, easily regeneration of the separation agent and low cost effectiveness [3–8]. The availability and local abundance of the adsorbent are also paramount factors in the choice of such process that they have motivated a large number of scientists to search new adsorbents naturally accessible or easily synthesized [9,10]. In this context, Moroccan natural phosphates appear to be particularly well adapted due to their excellent adsorption properties and to the versatility of structure, composition and modification of the surface [11–13]. As reported by El Asri et al. [13], Moroccan phosphate rock from Bengurir deposits and its derivative synthetic hydroxyapatite have been evaluated for the remediation of lead, zinc and copper metals in aqueous solutions. They demonstrated that the sorption mechanisms are related to the nature of metal and chemical composition of adsorbent, including complexing reactions, ion exchange and dissolution followed of precipitation. In some cases, it has been shown that there is a more favorable mechanism than others, this being linked to the active sites present at adsorbent surface and to the charge of the metal. Few studies are described the hexavalent chromium adsorption onto synthetic hydroxyapatite [14,15]. To our knowledge, no study on the chromium removal by natural and its derivative synthetic apatite has been carried out. One of the originalities of this study is based on the use of phosphate rock as a natural precursor for the preparation of hydroxypatite having a mesoporous surface. However, this study is particularly focused on the influence of oxidation state of chromium, $Cr^{3+}$ and $Cr^{6+}$, on its removal by Moroccan natural phosphate (NP) and its converted

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synthetic hydroxyapatite (c-HAP) working with Cr-contaminated solutions simulate the typical composition of polluted groundwater.

## 2. Materials and methods

### 2.1. Overview of sample preparation

The natural phosphate (named NP) used in this study was sampled from Bengurir region (Morocco), whereas the c-HAP hydroxyapatite was converted from this raw material using the dissolution followed by precipitation reactions [16]. 20 g of NP is dispersed in bidistilled water of 500 mL into a reactor of 2 L and dissolved by adding of 20 mL of $HNO_3$ (65%) under continuous stirring for 3 h at room temperature. A total dissolution of NP was obtained at pH 2 accomplished of completely releasing the $Ca^{2+}$ ions and phosphoric acid $H_3PO_4$. The resulting mixture is filtered and the filtrate is neutralized by ammonia solution ($NH_4OH$ 30%) up pH = 10. The formed precipitate is left to ripen with stirring for 24 h. Thereafter, the precipitate was filtered and dispersed in water under ultrasound irradiation three times to disperse the agglomerated grains. The suspension was filtrated and the final c-HAP product was dried in an oven at 100°C for 24 h.

### 2.2. Adsorption procedure

Stock solutions (1 g $L^{-1}$) of $Cr^{3+}$ and $Cr_2O_7^{2-}$ ions were prepared from reagent-grade chemicals, $Cr(NO_3)_3$,$9H_2O$ and $K_2Cr_2O_7$ in distilled water, respectively. Batch adsorption experiments were performed in glass contactors placed in a multisampler stirrer at 25°C. 200 mg of adsorbent was added to 100 mL of the solution containing different concentrations of chromium, $Cr^{3+}$ and $Cr^{6+}$, at pH 5. During kinetic experiments, suspensions were sampled through direct filtration using a 0.45 μm membrane filter. The Cr concentration in supernatant was analyzed by atomic absorption spectroscopy. All tests were performed in triplicate and experimental errors were found below 5% error. The quantity of the adsorbed $Cr^{3+}$ and $Cr^{6+}$ ions on the apatite $q_t$ was calculated as the difference between the initial $C_0$ and the instantly concentration $C(t)$: $q_t = (C_0 - C(t) \cdot V)/m$, where $m$ and $V$ are the adsorbent mass and the volume of the Cr-contaminated solution, respectively.

## 3. Results and discussion

### 3.1. A syntactic characterization of adsorbents

The thermal stability of the natural phosphate was firstly studied by TG analysis under air atmosphere. Results indicate the desorption of weakly bound water and a progressive loss of weight was observed between 200°C and 800°C, accounting for ca. 6.7 w% of the initial material compared to 3.2 wt% for converted c-HAP attributed to the decomposition of organic or carbonate matter [16,17]. Their specific surface area in the function of temperature is also reported in Fig. 1. The low value of specific area of natural phosphate is related to the variety of shapes of organic and mineral grains and to the organic fraction degraded, but without a strong impact on the NP powder calcined at 500°C (termed NP500). In contrast, the $S_{BET}$ dropped down below 5 $m^2$ $g^{-1}$ for NP calcined 800°C (NP800), suggesting that after full degradation of the organic matter, mineral grain coarsening has occurred. On the other hand, the specific surface of as-received c-HAP is of 150 $m^2/g$, traducing its good porosity. Indeed, the increase of the temperature of calcination improves the degree of crystallinity, which increases the particle size and limits the existence of pores on the solid surface by promoting the granular growth in detriment of nucleation phenomenon.

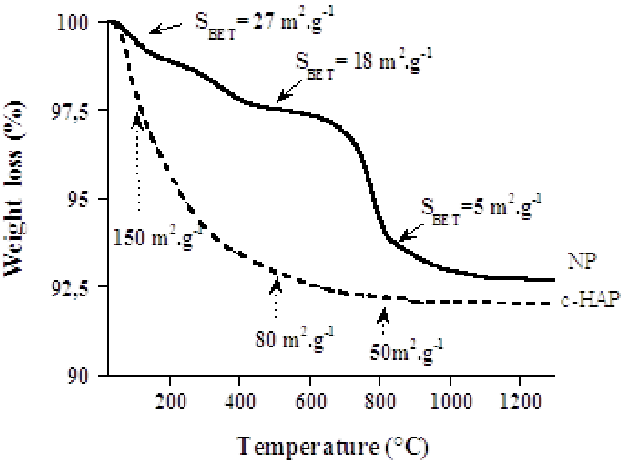

Fig. 1. TG curves of natural phosphate NP and converted hydroxyapatite c-HAP and their corresponding specific surface area at various temperature of calcination.

XRD analyses of the NP100 powder mainly shows the majority of the diffraction peaks are attributed to the apatite phase, with some additional peaks attributable to the quartz-$SiO_2$ and fluorine $CaF_2$ phase (Fig. 2). The XRD diffractogram of NP800 was very similar to that of c-HAP800, demonstrating the insertion of silicates in the apatite structure. In addition, the NP100 powder was also studied by solid-state $^{29}Si$-NMR indicating a main resonance at –107 ppm, corresponding to fully condensed silicon species as expected for quartz. In parallel, no resonance signal of $^{29}Si$ has detected for c-HAP related to un-dissolved quartz at acidic pH of 2. All of these structural and textural characteristics of adsorbents may help us to evaluate their chemical affinity versus chromic species.

### 3.2. Adsorption

Kinetic investigations were carried out to measure the rate of chromium sorption under various experimental conditions and to determine the time required to reach equilibrium of the adsorption process (Fig. 3). Adsorption curves show the same pattern and characterized by a high rate of elimination of $Cr^{3+}$ by c-HaP (90%) slightly higher than those obtained for raw-material NP (70%) for an initial concentration of 100 ppm. Maximum uptake of the both $Cr^{3+}$ and $Cr_2O_7^{2-}$ is reached after ca. 20 min and 30 min for NP and c-HAP, respectively. Noting that the adsorption

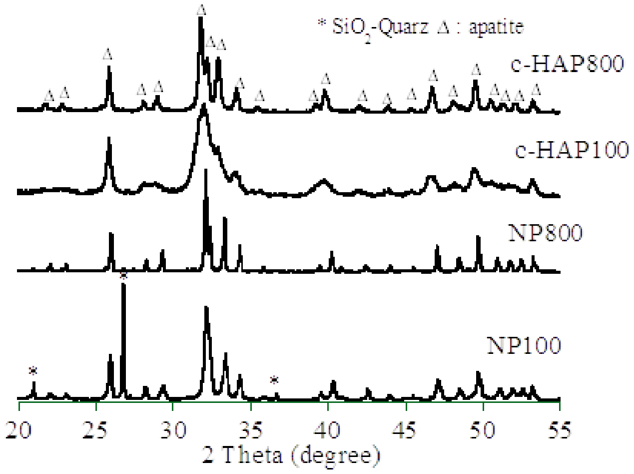

Fig. 2. XRD diffractograms of as-received c-HAP and NP materials and after thermal treatment at 800°C.

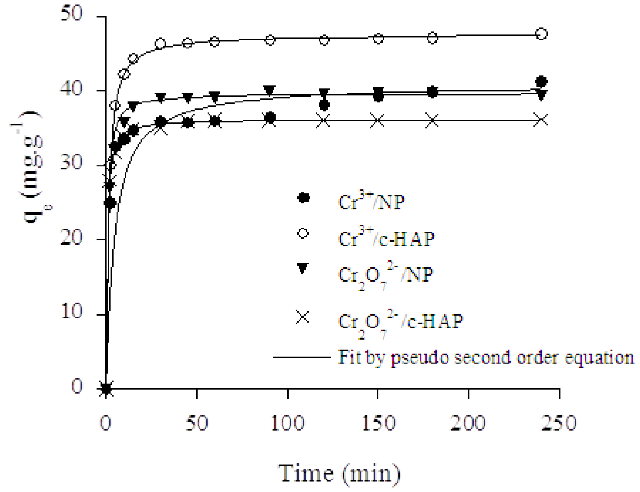

Fig. 3. Effect of contact time on the adsorption of chromium on the Moroccan natural phosphate and its converted hydroxyapatite c-HAP. Lines indicate the result of modeling using the pseudo-second order equation.

capacity of $Cr^{3+}$ is greater than that of $Cr_2O_7^{2-}$ ions related to the nature of the interactions of each oxidation state with NP and c-HAP surfaces. The high retention of c-HAP versus $Cr^{3+}$ species is related to its high specific surface area (150 m²/g), while that of the NP is due to the presence of silica, which may be active sites in its matrix able to more fix the $Cr^{6+}$ than $Cr^{3+}$ ions. The sorption rate constants of the chromium on the two NP and c-HAP adsorbents were determined using Lagergren pseudo first-order and second order models described elsewhere [18]. When applying Lagergren pseudo first-order model, kinetic rate constants $k_1$ are found between 0.014 and 0.076 $min^{-1}$, depending on the chemical composition of adsorbent and the oxidation degree of chromium. However, the values of the calculated equilibrium sorption $q_{e,1}$ are very low compared to the experimental values, in addition to the small correlation coefficients $R^2$ ($0.76 < R^2 < 0.96$) (Table 1). Although better correlation coefficients were obtained using the pseudo second-order model ($R^2 > 0.99$), an overestimation of the $q_{e,2}$ values are in good correlation with experimental data (Fig. 3), where $k_2$ increases while being passed from PN to c-HAP adsorbent or changing $Cr^{3+}$ by $Cr_2O_7^{2-}$ ions.

Based on the kinetic data, sorption isotherms were obtained after 3 h as contact time, showing that c-HAP exhibits a higher $Cr^{3+}$ adsorption capacity than NP contrary to the adsorption of $Cr_2O_7^{2-}$ anions (Fig. 4). The experimental data are fitted using the Langmuir [19] and Freundlich models [20] (Table 2).

Considering Cr sorption, experimental data are less fitted using the both Langmuir and Freundlich equations, suggesting that the sorption reactions occurring in the studied apatite samples are complex. Adsorption on heterogeneous surfaces such as natural phosphate or its derivative apatite is an interesting alternative. The use of unique isotherm is generally not possible in this case. Indeed, adsorption of chromic elements follows a Langmuir model with low site occupancy, but also a Freundlich at higher levels related to the presence of several active sites on the adsorbent surface with different affinities versus $Cr^{3+}$ and $Cr_2O_7^{2-}$ species. The problem of integrating surface heterogeneity may be useful in retaining a variety of organic and mineral pollutants. The chromium-apatite interaction (as indicated by β-Langmuir) is larger for $Cr^{3+}$/c-HAP system, which may related to the porous surface of c-HAP as well as to its

Table 1

Kinetic rate constants ($k_i$) and adsorption capacities ($q_{e,i}$) as obtained by using pseudo-first order and pseudo-second order models for chromium sorption on NP and c-HAP materials. $R^2$ indicate the correlation coefficients for the linear fits

| | Pseudo first order<br>$\log(q_{e,1}-q_t)=\log q_{e,1}-\frac{k_1}{2.303}t$ | | | Pseudo second order<br>$\frac{t}{q_t}=\frac{1}{k_2 q_{e,2}^2}+\frac{1}{q_{e,2}}t$ | | |
|---|---|---|---|---|---|---|
| | $k_1$ ($min^{-1}$) | $q_{e,1}$ (mg $g^{-1}$) | $R^2$ | $k_2$ (g $mg^{-1}$·$min^{-1}$) | $q_{e,2}$ (mg $g^{-1}$) | $R^2$ |
| $Cr^{3+}$/NP | 0.014 | 1.25 | 0.7661 | 0.005 | 40.95 | 0.9988 |
| $Cr^{3+}$c-HAP | 0.058 | 10.15 | 0.9357 | 0.016 | 47.66 | 0.9999 |
| $Cr_2O_7^{2-}$/NP | 0.048 | 7.08 | 0.8890 | 0.036 | 39.70 | 0.9999 |
| $Cr_2O_7^{2-}$/c-HAP | 0.076 | 5.88 | 0.9681 | 0.048 | 36.20 | 1 |

Table 2
Maximum experimental capacity ($q_{e,exp}$) and constants obtained from the modeling of the Cr sorption isotherms using Langmuir and Freundlich equations

| | | $q_{e,exp}$ (mg g$^{-1}$) | Langmuir equation $\frac{C_e}{q_e}=\frac{1}{\beta.Q_{\max}}+\frac{C_e}{Q_{\max}}$ | | | Freundlich equation $\log q_e=\log K_f+\frac{1}{n}\log C_e$ | | |
|---|---|---|---|---|---|---|---|---|
| | | | $Q_m$(mg g$^{-1}$) | β (L·mg$^{-1}$) | R$^2$ | log $K_f$ | 1/n | R$^2$ |
| $Cr^{3+}$ | NP | 105 | 105.3 | 0.065 | 0.97887 | 1.08 | 0.410 | 0.9870 |
| | c-HAP | 155 | 155.8 | 0.118 | 0.9763 | 1.35 | 0.412 | 0.9593 |
| $Cr_2O_7^{2-}$ | NP | 99 | 99.3 | 0.067 | 0.9894 | 0.99 | 0.35 | 0.9904 |
| | c-HAP | 76 | 76.1 | 0.043 | 0.9895 | 1.02 | 0.417 | 0.9846 |

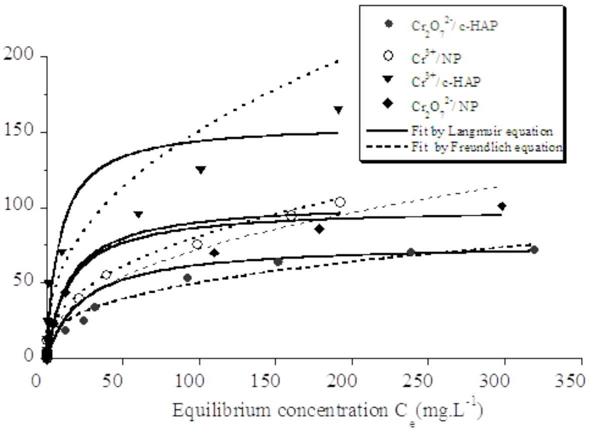

Fig. 4. $Cr_2O_7^{2-}$ and $Cr^{3+}$ sorption isotherms on c-HAP and NP materials. Plain lines and correspond to the simulation of experimental data using the Langmuir and Freundlich models, respectively.

surface acidity. Here again, the sorption variation between the two adsorbents mainly originates from their respective specific surface area, but it is not the only criterion such as demonstrated in several our previous works [11–13]. The high sorption capacities obtained for $Cr_2O_7^{2-}$ anions on NP is related to its heterogeneous surface containing silica as a promising adsorbent for $Cr_2O_7^{2-}$ anions. The fact that the c-HAP apatite was prepared from a phosphate rock is also a key advantage due to its low cost and limited the environmental impact. Moreover, $Cr^{3+}$ adsorption capacity on c-HAP is larger than $Cr_2O_7^{2-}$ species attributed to the electrostatic interactions between the negative charge of the apatite surface and the $Cr^{3+}$ cations, while the sorption mechanism of $Cr_2O_7^{2-}$ is different based on its speciation and the nature of interactions of active functional groups (–OH, –POH) of the apatite and the oxymetal ion ($Cr_2O_7^{2-}$). In fact, the functional groups in NP and c-HAP surfaces are protonated in acidic aqueous media and restricted the approach of cationic or anionic species as result of the repulsive forces [21]. During the sorption reactions, the proton exchange decreases and the functional groups present at solid surface become negatively charged (pH > pKa). Aqueous Cr(VI) exists as five main species: $H_2CrO_4$; $HCrO_4^-$; $CrO_4^{2-}$; $HCr_2O_7^-$, and $Cr_2O_7^{2-}$ where their distribution depends on the pH and $Cr_2O_7^{2-}$ concentration in the aqueous solution. All anionic species can be adsorbed on the protonated active sites at sorbent surface, P-OH or Si-OH, of NP raw material. However, $Cr^{3+}$ mostly occurs in aqueous environment as $Cr^{3+}$, $Cr(OH)_2^+$, and $Cr(OH)^{2+}$, which can be easily fixed onto the electronegative surface of apatite. Based on the chemical composition and surface functional groups, NP and c-HAP contain a large amount of $PO_4^{3-}$ groups that react with aqueous solutions of $Cr^{3+}$ and oxymetal $Cr_2O_7^{2-}$ ions. Consequently, the existence of silica in natural phosphate improves the $Cr_2O_7^{2-}$ retention from aqueous solutions. Comparable results are found using mesoporous zirconia-hydroxyapatite nanocomposites, where $Cr_2O_7^{2-}$ anions are more adsorbed by zirconia-rich phases, while $Cr^{3+}$cations are a good affinity with apatite surface [15]. It is therefore advantageous that the natural phosphate containing silica phase exhibits a combined affinity for both $Cr^{3+}$ and $Cr_2O_7^{2-}$ ions.

In addition, the effect of adsorbent dose was also investigated, showing that the percent removal of $Cr^{3+}$ and $Cr^{6+}$ species by PN and c-HAP gradually increases with the adsorbent dose to 2 g/L. Above this value, the removal percentage of $Cr^{3+}$ rises to a maximum of 74% for NP whereas up to 94% can be removed for c-HAP indicating an ample saturation of their surfaces (Fig. 5). For this purpose, a dose of 2 g L$^{-1}$ has been taken for all sorption tests. To explain the sorption mechanism, the influence of pH on Cr sorption was studied showing that a maximum capacity is observed in acidic pH but the surface of NP appears more basic than that of c-HAP.

The pH evolution of the chromium solution was also monitored during the sorption process (Fig. 6). When the adsorbents are dispersed in water, an increase of pH is observed from 5 to 8.9 and 7.8 using NP and c-HAP, respectively. When a chromium solution at initial pH of 5 is used instead of water, the rise in pH is more limited up to 5.4 and 6.3, suggesting that the release of basic ions is more limited when Cr sorption occurs on the apatite surface.

From Fig. 6, the pH of the mixture gradually increases as a function of time until equilibrium and then remains stable at specific value, which depends on the nature of the adsorbent and solution. When compared to c-HAP, the reactivity of NP is expected to vary for two main reasons: its smaller specific surface area and its chemical composition. In fact, NP is less soluble because it is a fluorinated apatite with low porosity but the presence of organic matter may

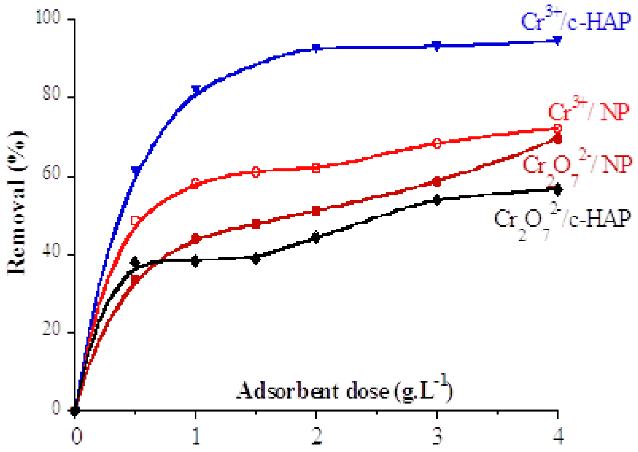

Fig. 5. Effect of adsorbent dose on $Cr^{3+}$ and $Cr_2O_7^{2-}$ removal by NP and c-HAP adsobents.

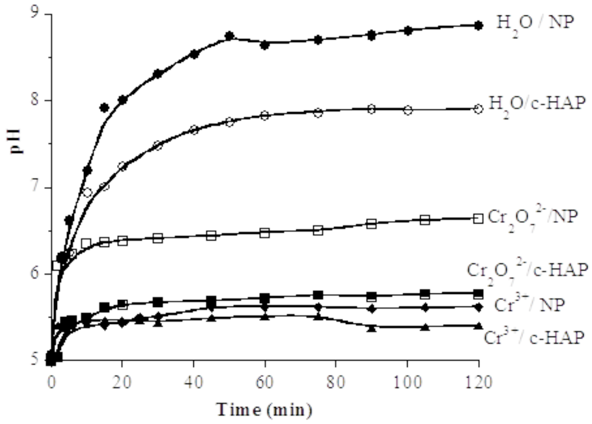

Fig. 6. Equilibrium pH change in the presence of NP and c-HAP with water ($H_2O$) and with added $Cr^{3+}$ and $Cr_2O_7^{2-}$ species.

not only modify the dissolution equilibrium but also contribute to Cr adsorption. For instance, when examining the equilibrium pH of apatite suspensions in water, NP induces an increase of the solution pH up to 8.9 compared to 7.9 for c-HAP. As a smaller surface is accessible for dissolution and hydroxyl release in NP, the natural apatite should be more basic, in agreement with the higher pH of solution and a minimum Cr sorption. Thus, it can be proposed that the organic matter trapped in NP may contribute to the acid-base equilibrium.

As consequently, the experimental data indicate that c-HAP is the most favorable to treat $Cr^{3+}$ in water whereas NP is more adapted for $Cr_2O_7^{2-}$ remediation. However, the c-HAP converted from NP mineral can be advantageous combines a high specific surface area with good affinity for the most heavy metals particularly $Cr^{3+}$ and $Cr_2O_7^{2-}$ ions. Therefore, the current study complete our investigations reported in the literature showed that c-HAP exhibits greater adsorption capacity for various heavy metals particularly chromium species.

## 4. Conclusion

Overall, the natural phosphate has the advantage of a very low cost, low environmental impact and large abundance but exhibits a limited porosity whereas its synthetic derivative was obtained from the former by a dissolution-reprecipitation reaction that would introduce some processing price, but allows obtaining a much higher specific surface area. In terms of sorption properties, the converted apatite c-HAP clearly exhibits better performance both in terms of kinetics and sorption capacities. However, the presence of organic matter does play a role on the relative affinity of natural phosphate for different hazardous species. For this, it might be possible to fill the gap between the both material performances by studying further the role of organic matter or silica in the natural phosphate rock on the Cr sorption. Therefore, the converted hydroxyapatite c-HAP material have a mesoporosity and dual sorption for $Cr^{3+}$ and $Cr_2O_7^{2-}$ species and appeared as interesting adsorbent for metal ion remediation.

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