

## Synthesized materials for decontamination of heavy metals polluted aqueous solutions

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### Abstract:

Heavy metals present in wastewater are a major environmental problem all over the world. Heavy metals are a very serious concern as they are not biodegradable and can be accumulated by organisms, leading to various health problems. The present paper describes the use of a synthesized biomaterials (hydroxyapatite - HAP) for the removal of heavy metals from aqueous environments. The obtained results are promising, as the synthesized material is able to be used as a decontamination tool for wastewaters charged with heavy metals. The synthesized material was characterized using state-of-the-art analytical techniques (X-ray diffraction, energy-dispersive X-ray fluorescence, dynamic light scattering and inductively coupled plasma – atomic emission spectroscopy). These studies have shown that by using synthesized hydroxyapatite, heavy metals ions can be removed from solutions by chemical reaction with hydroxyapatite. The hydroxyapatite has different affinity for selected heavy metals.

**Keywords:** biomaterials, nanomaterials, hydroxyapatite, wastewater, heavy metals, analytical techniques

### 1. Introduction

On the way towards a sustainable development, natural water plays a crucial role, as it represents the basis for food production, trade, human needs and a healthy aquatic ecosystem. Natural water sources are finite, while the water demand is increasing due to human development in the last centuries, leading to action plans at national and international level [1]. Currently, one of the major problems of mankind is pollution. Heavy metals present in wastewater are a major environmental problem. Heavy metals are a very serious concern as they are not biodegradable and can be accumulated by organisms, leading to various health problems [2].

To remove heavy metals from waste waters are known a lot of methods (precipitation method, ion exchange method, adsorption method, biomembrane filtration, reverse osmosis, electro dialysis, membrane electrolysis or electrochemical precipitation) but each of them present advantages and disadvantages [3-7].

Besides these methods, the use of hydroxyapatite seems promising due to its properties and the low cost involved in its synthesis [8-10]. Hydroxyapatite is one of the most studied biomaterials, with a wide range of medical applications in the reconstruction and regeneration of bone structures, for which researchers have shown interest, but it can also be used in environmental purposes to remove different heavy metals from waters or soils [10-12]. Nriagu and Dell [13] firstly suggested phosphate for removing soluble Pb from the aqueous phase,

but hydroxyapatite, has been proposed as a inexpensive but efficient adsorbent for removal/remediation from soils polluted by Pb [14, 15].

The apatites are a family of compounds with similar structure but different compositions. They can be represented by the following general formula:  $M_{10}(XO_4)_6Z_2$ , where M is usually a divalent cation,  $XO_4$  - most often a trivalent anion, and Z - is generally, but not necessarily, a monovalent anion. The "M" positions are generally occupied by a divalent cation ( $Ca^{2+}$ ,  $Sr^{2+}$ ,  $Pb^{2+}$ ,  $Mg^{2+}$ , etc.), monovalent cations ( $Na^+$ ) and trivalent cations ( $La^{3+}$ ). Positions groups " $XO_4$ " are occupied by trivalent anions ( $PO_4^{3-}$ ) and other divalent anions ( $SO_4^{2-}$ ,  $HPO_4^{2-}$ ,  $CO_3^{2-}$ ) or tetravalent ( $SiO_4^{4-}$ ). "Z" positions can be occupied, usually, by monovalent anions such as ( $OH^-$ ,  $F^-$ ,  $Cl^-$ ,  $Br^-$ ,  $I^-$ ), bivalent anions ( $CO_3^{2-}$ ,  $O^{2-}$ ,  $S_2^{2-}$ ) or neutral molecules ( $H_2O$ ,  $N_2$ ,  $O_2$ ) [16].

Hydroxyapatite is the most common apatite, corresponding to the formula  $Ca_{10}(PO_4)_6(OH)_2$ . Hydroxyapatite is the most stable phosphocalcic compound in aqueous solutions. Solubility of this material is influenced by several factors such as: Ca/P ratio, degree of crystallinity, porosity, particle size distribution, the presence of impurities in the crystalline structure (i.e. carbonate groups, chloride, fluoride or magnesium ions etc.).

The present paper describes the use of hydroxyapatite (HAP) for the removal of heavy metals from aqueous environments. The obtained results are promising, as the synthesized material is able to be used as a decontamination tool for wastewaters charged with heavy metals, thus offering a facile route for depollution, through the use of a easy-to-synthesize biomaterial.

## 2. Methodology

### 2.1 Materials

Hydroxyapatite (HAP) was obtained as follows: 0.25 mol  $Ca(NO_3)_2 \cdot 4H_2O$  (Merck KGaA, Germany) were dissolved in 250 mL distilled water; 0.25 mol of  $(NH_4)_2HPO_4$  (Merck KGaA, Germany) were dissolved in 250 mL distilled water; the calcium containing solution was put into a flask and heated to the temperature of 80 °C. The phosphorus containing solution (with the pH adjusted to 10 with  $NH_4OH$  – Chimreactiv, Romania) was added into the calcium containing solution under vigorous stirring. The reaction was performed at 80°C for 3 h, with the pH constantly kept at 10. After the reaction, the deposited mixtures were washed with distilled water, filtered, and rinsed with ethanol (Merck KGaA, Germany). The ethanol-containing gel was dried in a vacuum oven at 45 °C [17].

The heavy metals removal experiments were performed in diluted stock solutions: Mercury ICP standard (Merck, CertiPUR)- concentration 1000 mg/L and mono-element stock solutions prepared *in house* from salts of used metals (spectrographically standardised substance – Johnson Matthey &Co, LTD).

### 2.2 Methods

Energy dispersive X-ray fluorescence analyses (EDXRF) were performed using a PW4025 MiniPal 2 spectrometer (PAnalytical). X-ray diffractions (XRD) were obtained by the use of a DRON UM1 diffractometer, operating at 32 kV and 25 mA, using Co  $K_\alpha$  radiation (1.79021 Å). The XRD and EDXRF results were processed using professional data processing software. The DLS (Dynamic light scattering) measurements were performed using a Malvern NANO ZS (RED BADGE) apparatus.

For ICP-AES (inductively coupled plasma atomic emission spectrometry) analyses was used a Varian, Liberty 110 spectrometer for quantitative determinations of heavy metals from aqueous solutions. The instrument has a 40.68 MHz RF Generator and a 0.75 m Czerny-Turner Monochromator with a 1800 grooves/mm Holographic grating. Instrument operating

parameters are: plasma gas flow 12 L/min, V-Groove nebulizer, 15 rpm pump rate, 10 sec integration time, and automatic background. The wavelength used for the measurement of metals were Co-228,616 nm; Cu-324.754 nm; Zn- 213,856 nm; Cd – 228.802 nm; Ni – 231.604 nm; Hg-253.652 nm.

### 3. Results and discussions

XRD pattern of the sample HAP-showed the structure of the prepared sample was similar to the hydroxyapatite standard ASTM 9-432 (fig. 1). There is a high consistency between the data of HAP and that of the standard, with lattice dimensions of  $a = b = 0.9434$  nm,  $c = 0.6876$  nm. No other impurity was observed in the XRD pattern.

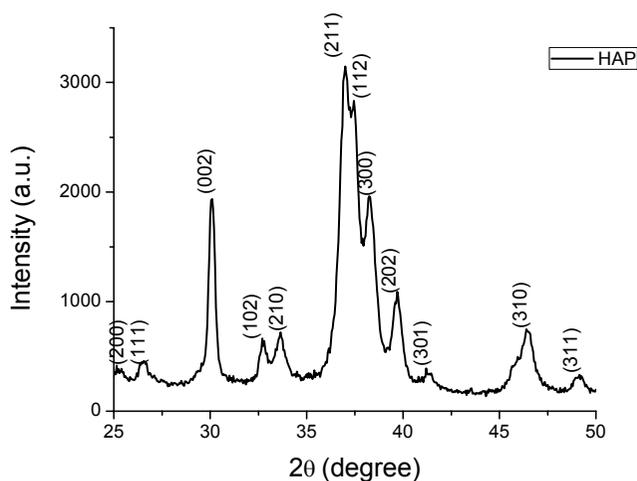


Figure 1. XRD pattern of the synthesized hydroxyapatite

The DLS measurements (figure 2) reveal the small dimensions (in the nanometric range) of the synthesized material.

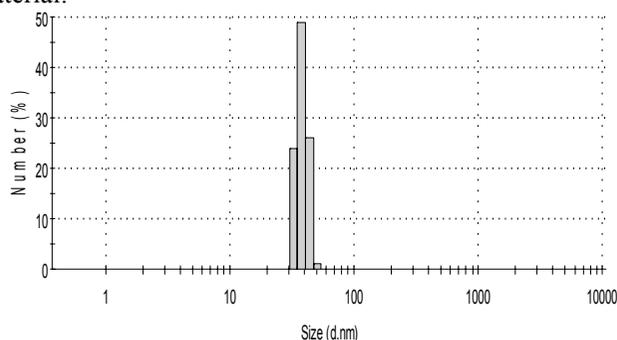


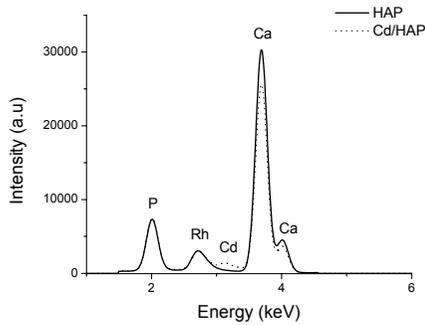
Figure 2. DLS measurements of the hydroxyapatite

In order to evaluate the capacity to remove heavy metals from wastewater, standard solution of selected heavy metals (Cd, Co, Cu, Hg, Ni, Pb and Zn) were separately prepared, each having a concentration of 500 ppm (mg/L). The synthesized powder (0.25 g) was immersed in a volumetric flask containing 50 mL of solution and shaken for 24 hours using a Laboshake

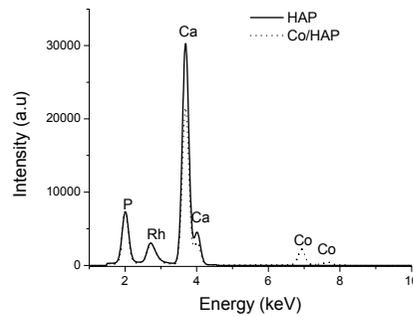
(Gerhardt) shaker. The experiments were carried out in triplicate. After this period, the solutions were filtered; the filtered solutions were measured by ICP-AES (table 1), while the solid parts were washed with distilled water, dried and measured by EDXRF (figure 3). The results are the mean value of the three determinations.

Table 1. ICP-AES results for heavy metals removal. The results are expressed in mg/L and represents the mean value of the three determinations

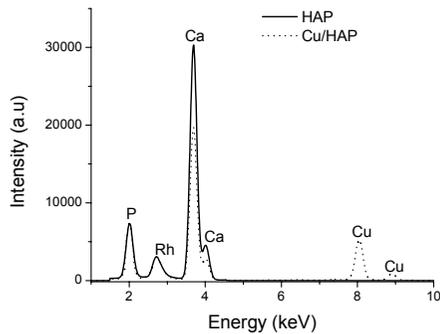
	Cd	Co	Cu	Hg	Ni	Pb	Zn
Before treatment	500	500	500	500	500	500	500
After treatment	193	297	203	321	341	<0.6	313



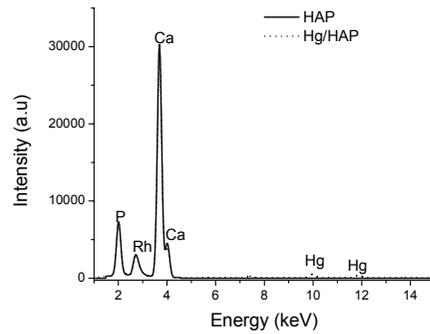
a



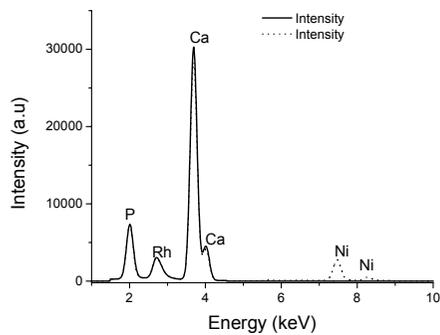
b



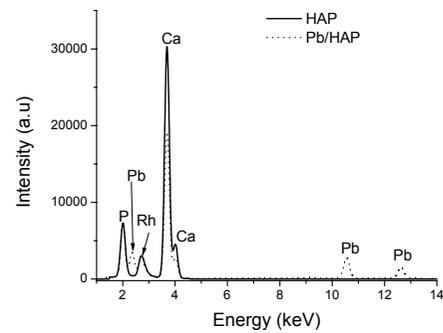
c



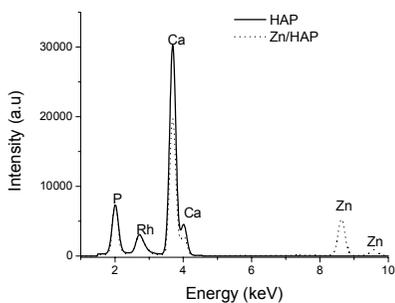
d



e



f



g

Figure 3. EDXRF results of the apatite powders after treatment

The EDXRF results presented in figures 3a to 3g suggests that the heavy metals removed from the aqueous environment are intimate linked to the apatite structure, through a ion-exchange process (suggested by the decrease in calcium content, correlated with the uptake of heavy metal), in good concordance with literature data [18].

The corroborated ICP-AES and EDXRF results suggest the following affinity of hydroxyapatite for heavy metals uptake:



To confirm this conclusion, a multi-element 500 ppm (mg/L) solution was prepared (containing Co, Cu, Pb, Hg) and treated as above. The ICP-AES results after treatment are:  $\text{Pb} < 0.6 \text{ mg/L}$ ,  $\text{Cu} = 362 \text{ mg/L}$ ,  $\text{Co} = 413 \text{ mg/L}$ , while for Hg, no uptake was noticed. The EDXRF results presented in figure 4 confirms the uptake of these three metals.

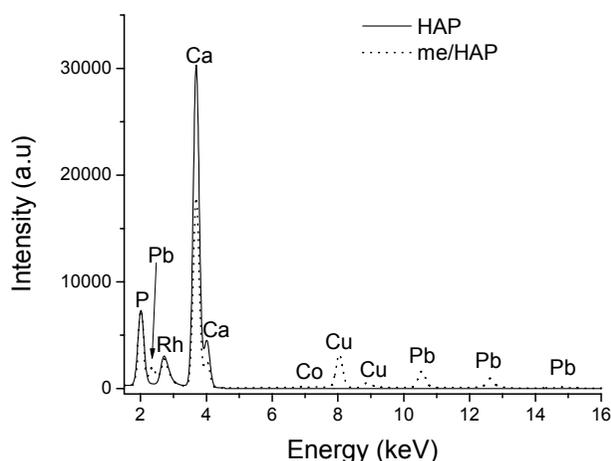


Figure 4. EDXRF results of the apatite powders after treatment of the multi-element solution

#### 4. Conclusions

Material nanoparticles (hydroxyapatite) were synthesized and analytical characterized and their applications in environmental protection (removal of heavy metals from wastewaters) were studied. These studies have shown that by using synthesized hydroxyapatite, heavy metals ions can be removed from solutions by chemical reaction with hydroxyapatite. The hydroxyapatite has different affinity for selected heavy metals.

The synthesized material offer better results for wastewaters containing single pollutants; for wastewater containing multiple pollutants hydroxyapatite tends to selectively remove the pollutants (in our case, it firstly completely removed lead and then removed smaller quantities of the other pollutants). From the results presented above, it can be observed that removal of contaminants using biomaterials like hydroxyapatite can be an valuable method for wastewater treatment.

The proposed solution could be successfully used, either by itself, or in combination with other techniques (as zeolites or activated carbon). As it is a relatively cheap decontamination method, it could be applied (either as filters or granules) in underdeveloped or even emerging countries.

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