REMOVAL OF PHENOL AND NON-STEROIDAL ANTI-INFLAMMATORY DRUGS FROM WATER MATRICES USING DOPED HYDROXYAPATITE

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Emerging pollutants have become a worldwide problem of great concern for decades. Water pollution with organic compounds such as phenols and NSAIDs (non-steroidal anti-inflammatory drugs) represents an alarming problem of the whole world, with hazardous environmental consequences. Hydroxyapatite has gained significant attention from scientific groups for its promising adsorbent properties in the removal of pollutants from water, but also for the possibility of its recovery. The present study investigates the adsorption of ibuprofen and phenol using tuned apatitic materials, namely hydroxyapatite in which calcium is partially substituted with Ni or Zn, in order to improve hydroxyapatite's properties and enhance the final applications.

Keywords: water pollution; NSAIDs; phenol; adsorption; apatitic materials.

1. Introduction

Different types of pollutants have occurred in water bodies because of the rapid increase in human and industrial activities. These pollutants are mainly classified in two types: organic compounds, such as dyes, pesticides, pharmaceuticals, endocrine disruptors and aromatic hydrocarbons, and inorganic pollutants, like metal ions, nitrates and phosphates [1]. Their toxic effects on the

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environment differ from one pollutant to another, based on their type, concentration, and degradation pathways in the water bodies [2].

One example of a well-known class of pollutants is pharmaceutics (PCs), which are formulated to exhibit bioactivity at low doses and maintain stability to facilitate extensive interaction with the target species. Numerous studies consistently reveal the presence of PCs at minimal concentrations, ranging from ng/L to µg/L, in surface or ground water, as well as in the wastewater effluents from hospitals, pharmaceutical production facilities or in urban areas, as a result of human usage abuse [3-4].

Ibuprofen (IBU) falls within a contemporary category of frequently encountered water pollutants known for their biological activity, having a pronounced impact on the environment even at lower concentrations. Despite being present in low concentrations, the by-products of ibuprofen persisting in the aquatic environment can still pose risks to both humans and animals [5]. Because of the acidic groups derived from both carboxylic acid and hydroxyl groups attached to aromatic rings, non-steroidal anti-inflammatory drugs (NSAIDs) exhibit strong organic acidity, with pKa values ranging from 3.2 to 4.0. Their broad polarity and limited degradability have posed challenges in achieving the complete removal of NSAIDs from wastewater treatment plants and environmental water [6].

Phenol is identified as an organic, colorless pollutant prevalent in wastewater, primarily originating from ceramic, leather, and petrochemical industries. Its presence is also observed in wastewater from several types of industries (including textile, pharmaceutical, paints and varnishes, plastics, oil refineries, wood manufacturing, and many others). The discharge of phenol into water, soil, and air adversely affects the environment. Additionally, in ocean environments, chemical spills pose a potential risk of releasing phenol, contributing to ecological damage in aquatic ecosystems due to its high solubility and toxicity [7-10]. A variety of technologies are used for extracting phenol from aqueous solutions, categorized into chemical, physical, and biological methods [11].

Recognized for its environmental friendliness and cost-effectiveness in comparison to conventional methods such as chemical precipitation, advanced oxidation, electrochemical, and membrane technologies, adsorption stands out as a promising tertiary treatment technology [2]. The efficacy and speed of adsorption technology relies on the careful design of the adsorbent material. Traditional adsorbents that are commonly used include commercial activated carbons, clays, and polymeric materials. Nevertheless, innovative materials derived from industrial, agricultural, and biomass waste have been engineered and demonstrated excellent adsorption properties for a diverse range of pollutants in water bodies [1].

Hydroxyapatite (HAP), characterized by the chemical formula $Ca_{10}(PO_4)_6(OH)_2$, is known as an eco-friendly material due to its non-toxicity, biocompatibility, and potential applications in environmental protection processes [12]. Beyond these properties, it can be synthesized through biological waste, such as animal bones, fishbones, eggshells, seashells, and limestones, or synthesized through various cost-effective methods [13].

Considering its excellent thermal and chemical stability, structural flexibility, and remarkable water insolubility (with a solubility product constant, Kps, approximately 10^{-59} at 25 °C) [13], HAP has been widely and effectively selected for the decontamination of different pollutants from wastewaters [12].

Therefore, this study was focused on investigating the adsorption of ibuprofen and phenol using tuned apatitic materials, namely hydroxyapatite partially substituted with two different metal ions, Ni^+ and Zn^+, in order to improve hydroxyapatite's properties and enhance the final applications.

The present paper describes the synthesis and characterization through modern analytical methods. Furthermore, there are presented preliminary studies regarding its' potential application in environmental protection, especially adsorption of a non-steroidal anti-inflammatory drug – ibuprofen and phenol.

2. Experimental

2.1. Materials and methods

The reagents used were analytical-grade reagents (purity > 98%), supplied by Merck KGaA (Darmstadt, Germany), NH_4OH was supplied by CHIMREACTIV (Bucharest, Romania), ibuprofen and acetonitrile (ACN) were acquired from Sigma-Aldrich (Baden-Württemberg, Germany).

2.2. Synthesis and characterization

Hydroxyapatites substituted with Ni and Zn were prepared according to a recipe developed within the ICECHIM Laboratory [14], using $Ca(NO_3)_2 \cdot 4H_2O$ and a salt of Ni^+ or Zn^+ (solution 1) and 0.25 mol $(NH_4)_2HPO_4$ (solution 2), dissolved in distilled water. In a 1 L flask, solution 1 was brought to a temperature of 80ºC, with the help of an Biobase heating mantle, over which solution 2 was added dropwise, under continuous mechanical stirring. For 3 hours after the end of the dripping, the pH=10 was maintained with the help of an ammonia solution and a temperature of 80ºC. After the end of the reaction time, the obtained precipitate was repeatedly washed with ethanol to remove traces of ammonia. The final material resulted from mixing the solid phase with ethanol to form a gel and then drying it at 45ºC under vacuum for 48 hours. In order to obtain the targeted materials, the maintenance of the synthesis parameters (temperature and pH) represents a key aspect.

The table below shows the abbreviations of the synthesized materials:

Table 1

Encodings for the synthesized materials

Synthesized material	Encoding
Hydroxyapatite substituted with Zn, Ca:Zn molar ratio 1:1	ZnHAP 1:1
Hydroxyapatite substituted with Ni, Ca:Ni molar ratio 3:2	NiHAP 3:2

The characterization of the obtained materials aimed to confirm the obtaining of the metal-oxide apatitic materials, by means of X-ray diffraction (XRD), X-ray fluorescence (XRF) and Fourier transform infrared spectroscopy (FTIR) analyses. Thermal analysis (AT) was used to study the thermal stability of the materials, while the morphology of the materials was evaluated by scanning electron microscopy (SEM).

For the X-ray diffraction analyzes, a Rigaku SmartLab diffractometer (Rigaku Corporation, Tokyo, Japan) was used, operating under the conditions: 45 kV, 200 mA, $Cu_{K\alpha}$=1.54059 Å radiation, parallel beam configuration; the obtained diffractograms were analyzed using Rigaku Data Analysis Software PDXL 2 (Rigaku Corporation, Tokyo, Japan), and comparisons were made with the International Center for Diffraction Data (ICDD) database PDF-5+ for interpretation. To assess the metal content in the synthesized materials and identify potential impurities in their structure, X-ray fluorescence analysis was employed, namely Vanta C Series Handheld XRF, equipped with a 40 kV X-ray tube, rhodium anode and Silicon Drift Detector. Each beam had a 60-second acquisition time during the analysis process.

The apatitic materials' FTIR spectra were captured using a Jasco FTIR 6300 spectrometer (Jasco Corporation, Tokyo, Japan) coupled with a diamond crystal attenuated total reflection accessory (KRS5 lens). The measurements were conducted within the 400–4000 cm^{-1} range, involving 30 scans, with 4 cm^{-1} resolution. Thermal stability was assessed using a Q5000IR instrument (TA Instruments, New Castle, DE, USA). The heating rate was 10 °C/min, ranging from room temperature to 700 °C, in platinum vessels under a synthetic air atmosphere (99.999%) and a flow rate of 50 mL/min. The obtained isotherms were compared with those of pure hydroxyapatite, a material acknowledged for its excellent thermal stability [16].

For the morpho-structural characterization of the obtained phosphatic materials, they were analyzed by scanning electron microscopy (SEM) using an instrument Hitachi TM4000plus II (Hitachi HiTech), coupled with an energy dispersive X-ray spectrometry accessory (EDX - Oxford Instruments). The technical operating parameters, such as the detector type (secondary electrons – SE, backscattered electrons – BSE), the acceleration voltage (5kV, 10 kV, 15 kV

or 20 kV) and the resolution range between x500÷x1500, were diversified, in order to obtain the most detailed results.

2.3. Adsorption tests

The obtained materials underwent assessment for their adsorption capacities of phenol and one non-steroidal anti-inflammatory drug, namely ibuprofen. First of all, in order to select the optimum dosage of adsorbent material, plastic tubes with 15 mL volume were prepared with 0.05, 0.1, and 0.2 g of the adsorbent, along with 10 mL of pollutant solution at concentrations ranging from 1 to 100 mg/L. The next step implied shaking them in a GFL 3025 shaker (Gesellschaft für Labortechnik Mbh, Burgwedel, Germany) for 24 hours to reach equilibrium, and a temperature of 20 °C. Stock solutions were prepared by dissolving phenol and ibuprofen in distilled water to a concentration of 1 g/L. Subsequently, the tubes underwent centrifugation, and samples were extracted from the supernatant was analyzed using a HPLC L-3000 system (Rigol Technologies Inc., Beijing, China). The analysis conditions included a Kinetex EVO C18 column (150 x 4.6 mm), injecting 10 µL of sample. The system performed in the following conditions: two solvents H_2O:Acetonitrile (v/v = 50/50) in isocratic mode, 220 nm wavelength and 1 mL/min flow rate.

Each experiment was carried out in triplicate, and the average values were used as results. The following equation was used to quantify the pollutants retained on solid surface:

$$q_e = \frac{(C_0 - C_e) \cdot V}{m} \tag{1}$$

In this equation, C_0 and C_e are the initial pollutant concentration and the pollutant concentration at equilibrium in the solution (mg/L), V is the volume of phenol solution (L), and m represents the quantity of apatitic adsorbent (g).

3. Results and discussions

The syntheses of apatitic materials were firstly confirmed through X-ray diffraction. Our group previously reported the characteristic peaks for hydroxyapatite and metal-substituted hydroxyapatites, namely 25.87 degrees, which corresponds to the (002) plane, 31.22 degrees—(211), 32.17 degrees—(112), and 32.77 degrees—(300), compared with the ICDD card no. 01-074-0565 (for hydroxyapatite) [14]. In case of ZnHAP 1:1, a secondary phosphate phase resulted from the diffractograms (Fig. 1), consisting of parahopeite—($Zn_3(PO_4)_2(H_2O)_4$), ICDD card no. 01-070-1908. The corresponding peaks for this type of material are: 19.74 degrees— (1-10), 20.20 degrees— (110), 33.51 degrees— (12-1), 35.02 degrees – (002) and 36.45— (01-2), respectively. As for NiHAP 3:2, the diffractogram showed that, beside hydroxyapatite, the second phase was represented by calcium nickel phosphate, ICDD card no. 01-071-0645.

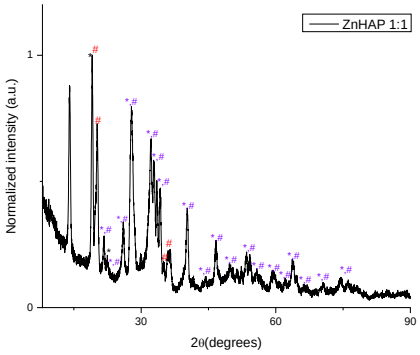

Fig. 1. Diffractogram for ZnHAP 1:1 (* - hydroxyapatite; # - parahopeite)

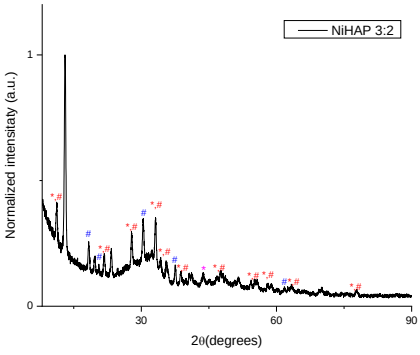

Fig.2. Diffractogram for NiHAP 3:2 (* - hydroxyapatite; # - calcium nickel phosphate)

In order to detect any potential impurities, the second step in materials characterization consisted of analyzing them by X-ray fluorescence. From the below XRF spectra (Figure 3 and 4), it can be noticed that the obtained materials do not exhibit any impurities. The presence of the metal ions used for the substitution is demonstrated by the appearance of the distinct peaks for zinc and nickel (K_α, K_β).

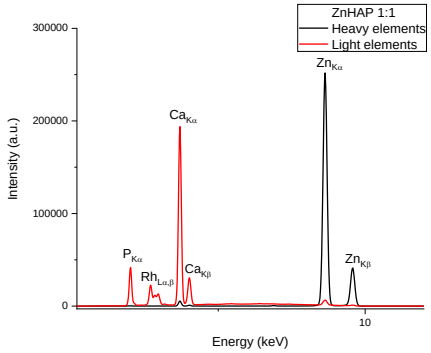

Fig. 3. X-ray fluorescence spectra of ZnHAP 1:1.

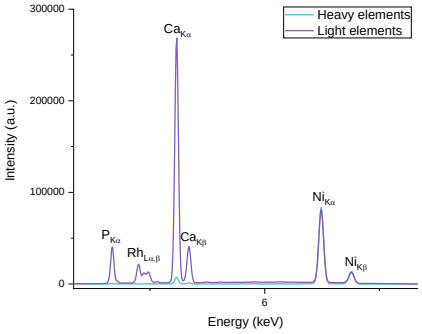

Fig. 4. X-ray fluorescence spectra of NiHAP 3:2.

Fig. 5 and 6 present the FTIR spectra of the samples, showing all the characteristic bands of these types of solids: 1024 and 562 cm^{-1} for ZnHAP 1:1, and 1016 and 548 cm^{-1} for NiHAP 3:2, respectively, being associated with the phosphate group. The peaks observed at 3034 and 3046 cm^{-1} are attributed to the vibrational stretching of the hydroxyl structural groups, being one of the bands designated for hydroxyapatite by the literature data, while the deformed vibration is visible at approximately 1697 and 1636 cm^{-1} [16].

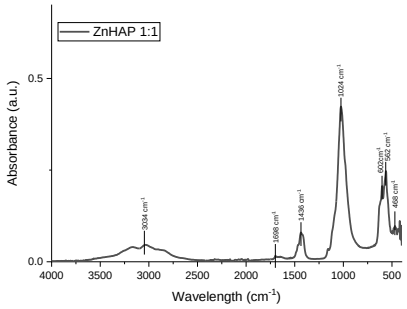

Fig. 5. FTIR spectra of ZnHAP 1:1.

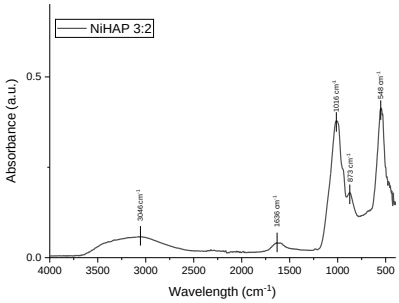

Fig. 6. FTIR spectra of NiHAP 3:2.

The thermal analyses of the obtained materials are presented in Figs. 7 and 8. The thermogram for ZnHAP 1:1 indicates a residue of approximatively 87% at 700 °C, while for NiHAP 3:2, the residue is approximatively 82%. The mass losses obtained for the materials can be categorized into 4 phases: phase 1—from room temperature to about 150 °C with a mass loss around 2,50% (for ZnHAP 1:1) attributed with the water desorption from the powders' surface; phase 2—from 150 to 290 °C, with a mass loss about 7%, attributed with the loss of bonded water and decomposition of unreacted precursors. The primary weight loss for the nanomaterials occurred in this phase, because of the appearance of other phenomena, including the dihydroxylation of the phosphorous-hydroxyl groups [17], which continues also in phase 3 with a mass loss of approximately 2,40%; phase 4 comes with a mass loss approximatively 0,8%, due to the beginning of the decarbonization process. In the case of NiHAP 3:2, the first phase of mass loss is higher than for ZnHAP 1:1 (approximatively 12%), phenomena which will be further studied.

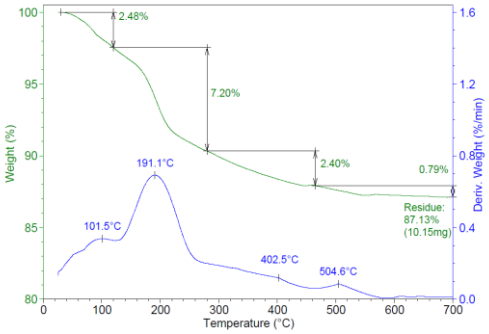

Fig. 7. Thermogram of hydroxyapatite substitued with Zn (ZnHAP 1:1).

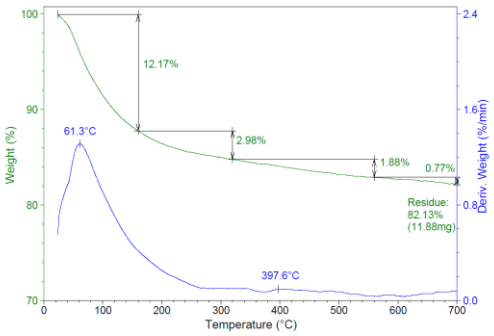

Fig. 8. Thermogram of hydroxyapatite substitued with Ni (NiHAP 3:2).

Scanning electron microscopy characterization method provides essential data regarding the morphology of the nanomaterials, and the size of the formed particles. Furthermore, the compositional analysis of the numerous elements present in the samples was conducted with the help of energy dispersive X-ray

spectroscopy (EDX), through the compositional evaluation of the characteristic X-rays of the elements.

Fig. 9. SEM image of ZnHAP 1:1.

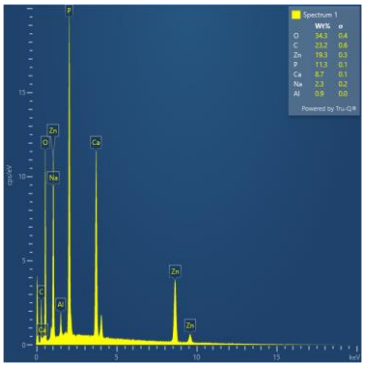

Fig. 10. EDX spectra of ZnHAP 1:1.

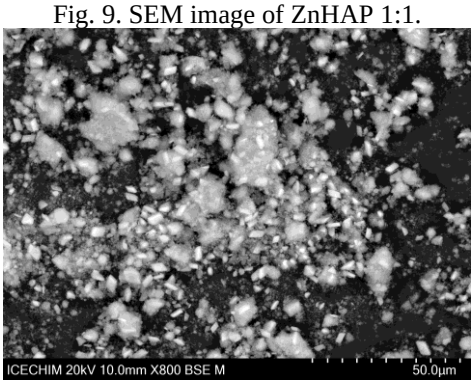

Fig. 11. SEM image of NiHAP 3:2.

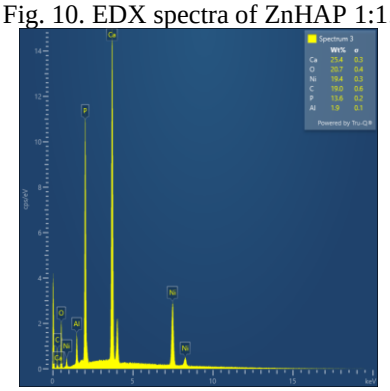

Fig. 12. EDX Spectra of NiHAP 3:2.

The SEM images (presented in fig. 9 and fig. 11) suggest similar morphologies of the analyzed materials, as well as the formation of large aggregates (with dimensions in the micrometer range). There are also visible spherical shaped particles with clumped distributions. The EDX spectra (fig. 10 and 12) of the samples also demonstrate the presence of the metal ions used for the synthesis of hydroxyapatite partially substituted.

Regarding the adsorption studies, from the graphics below, it can be concluded that the optimum dosage of apatitic adsorbent used is 10 g/L. The equation was used to determine the amount of pollutants adsorbed onto the solid surface when reaching equilibrium:

$$q_e = \frac{(C_0 - C_e) \cdot V}{m} \qquad (1)$$

Figs. 13 and 14 illustrate the impact of the type and quantity of adsorbent on the adsorption process of ibuprofen and phenol, respectively. According to the graphs, the optimal dose of adsorbent for both pollutants is 10 g/L. The best results for ibuprofen adsorption were achieved using apatitic materials substituted

with $Ni2^{+}$ ions, while for phenol adsorption, composites with Zn^{2+} ions showed the most effective performance.

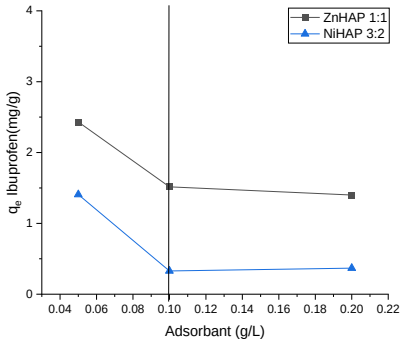

Fig. 13. Effect of the type and amount of adsorbent in the ibuprofen adsorption process.

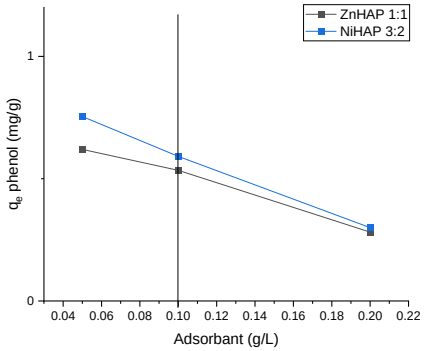

Fig. 14. Effect of the type and amount of adsorbent in the phenol adsorption process.

4. Conclusions

The work provided results regarding the synthesis and characterization of four apatitic materials, doped with metallic ions of Ni^{+} and Zn^{+}, in order to enhance the adsorbent properties. The adsorption capacity of the composite materials was evaluated towards harmful organic pollutants such as ibuprofen and phenol. It was demonstrated that, in order to obtain an equilibrium on the adsorbent surface, the optimum dosage used is 10 g/L, for each pollutant. Developing nanomaterials with controlled morphologies and customizable size and shape is crucial. This approach facilitates the use of environmentally friendly and cost-effective purification methods with great potential for an effective removal of various types of contaminants from wastewater. Further studies will be provided regarding the mechanisms of adsorption, and also the possibility of composites' regeneration, in order to integrate these materials in a depollution technology.

Funding

This work has been funded by the Ministry of Research, Innovation and Digitization through INCDCP-ICECHIM Core program PN 23.06.01.01 (AQUAMAT). The authors also gratefully acknowledge the support of gratefully acknowledge the financial support provided by a grant of the Ministry of Research, Innovation and Digitization, CCCDI—UEFISCDI, project number PN-III-P2-2.1-PTE-2021-0309, contract 81PTE/2022, within PNCDI III. The SEM-EDX analyses on Hitachi TM4000plus II equipment were possible due to the project "Supporting the competitiveness and excellence of research and innovation in INCDCP-ICECHIM in the bioeconomy and related fields (NeXT-BExcel)", contract 15PFE/2021, funded by the Ministry of Research, Innovation

and Digitization through Program 1 - Development of the national research-development system, Subprogram 1.2-Institutional performance Projects to finance excellence in RDI, Contract no. 15PFE.

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