

Synthesis of hydroxyapatite derived from agricultural waste and its applications as an adsorbent for heavy metal removal from wastewater

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The presence of heavy metals in aquatic systems can be harmful to all living species. Heavy metals are not biodegradable, and their tendency to accumulate in living organisms often causes different undesirable consequences. Therefore, removing these impurities from wastewater has become one of the key issue related to environmental protection. There are many methods developed to remove heavy metals from wastewater and adsorption is one of the most popular one. Despite of the diversity of these technologies there is still a need to develop methods that do not require a large financial input.

The most important features that determine materials used as adsorbent are their low cost, biocompatibility and environmental friendly nature. Hydroxyapatite presents all of them. Moreover, hydroxyapatite particles are characterized by high specific surface area and simple method of synthesis. It is also reported that it can be obtained from agricultural waste based on calcium like eggshells.

The aim of this paper is to show and compare different methods of hydroxyapatite synthesis using eggshells as a source of calcium and its sorption capacity due to different metal cations from aqueous solution.

1. INTRODUCTION

Hydroxyapatite as the main inorganic component of human bones and teeth is a naturally occurred material of composition $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$. Hence, this compound is of scientist interest in order to medical, especially orthopedical and dental applications [1]. Besides the medical usage, the features such as pH and temperature resistance, highly developed surface area, insolubility in water and possibility of a number of modification makes this material interesting and promising combination from ecological point of view [2]. There are known different crystalline forms of calcium phosphates, but hydroxyapatite exhibits the best qualities in the case of heavy metal removal from contaminated water. It can be noticed that calcium phosphates are widely employed in many fields what is listed in the Table 1 [3–5].

Table 1. Comparison of calcium phosphates [3–5].

Name of compound and its formula	pH stability	Ca/P ratio	pK _a value	Applications
Monocalcium phosphate monohydrate MCPM $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$	0.0–2.0	0.5	1.14	Component of phosphorous containing fertilizers
Monocalcium phosphate anhydrous MCPA $\text{Ca}(\text{H}_2\text{PO}_4)_2$		0.5	1.14	Component of fertilizers, artificial bone graft
Dicalcium phosphate dihydrate (brushite) DCPD $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	2.0–6.0	1.0	6.59	Component of dentistry products (as protector against caries), fertilizers, in glass production, food supplement and water soluble drugs delivery
Dicalcium phosphate anhydrous (monetite) DCPA CaHPO_4		1.0	6.90	Component of calcium phosphate cements, polishing agent, diet supplement
Amorphous calcium phosphates ACP $\text{Ca}_x\text{H}_y(\text{PO}_4)_z \cdot n\text{H}_2\text{O}$ n-3-4.5; 12-20% H_2O	5.0–12.0	1.2–2.2		Component of calcium phosphate cements, dentistry and surgery applications of its bioactive composites

cont. Table 1.

Name of compound and its formula	pH stability	Ca/P ratio	pKa value	Applications
Octacalcium phosphate OCP $\text{Ca}_8(\text{HPO}_4)_2(\text{PO}_4)_4 \cdot 5\text{H}_2\text{O}$	5.5–7.0	1.33	96.6	Bone implants material
α - Tricalcium phosphate α -TCP α - $\text{Ca}_3(\text{PO}_4)_2$		1.5	25.5	Component of calcium phosphate cements and fertilizers
β - Tricalcium phosphate β -TCP β - $\text{Ca}_3(\text{PO}_4)_2$		1.5	28.9	Component of calcium phosphate bone cement, bone- substitution ceramics, fertilizers, polishing and dental powder, porcelain, pottery and animal nutritional supplement
Calcium-deficient Hydroxyapatite CDHA $\text{Ca}_{10-x}(\text{HPO}_4)_x(\text{PO}_4)_{6-x}(\text{OH})_{2-x}$ ($0 < x < 1$)	6.5–9.5	1.5–1.67	85	Promising compound for manufacturing of artificial bone substitutes
Hydroxyapatite HA, HAp $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$	9.5–12	1.67	116.8	Coating for orthopaedic (e.g. hip-joint prosthesis), dental implants, component of calcium phosphate cements, repairing of hard tissues
Fluorapatite FAp $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$	7.0–12.0	1.67	120	Fluorine source in pharmaceutical products
Tetracalcium phosphate TTCP $\text{Ca}_4(\text{PO}_4)_2\text{O}$		2.0	38–44	Component of various self-setting calcium phosphate cements, coatings in metallic implants

The main sources of synthetic hydroxyapatite is synthesis from synthetic reagents or from natural sources of calcium. There are a lot of papers about obtaining hydroxyapatite material from materials such as: fish [6–8], poultry e.g. turkey [9] and mammalian bones (bovine or porcine) [10, 11]), corals [12, 13], sea shells [14, 15], plants [16] or eggshells [17–22].

Eggshells are wastes produced as a residues of eggs during a food preparation in households, restaurants, bakeries and so on. They are built with characteristic 3-layer structure: the rich in the proteins

cuticle layer placed on the outside, middle layer with a sponge-like structure and the inner one with a predominance of lamellar shape [23].

The largest amount of hen eggs are produced in China. In 2017 there were released more than 31 million of tonnes, what was less than 50 % of total world production [24]. It gives an enormous amount of available shell wastes every year. Eggshell consist of calcium carbonate (94%), organic substances (4 %), magnesium carbonate (1 %) and others (1%) [25]. Many potential and practical applications of eggshells are presented in the literature [26–29]. Because of many advantages it was considered to obtain commercial products using raw or processed egg wastes what is shown in the Fig. 1.

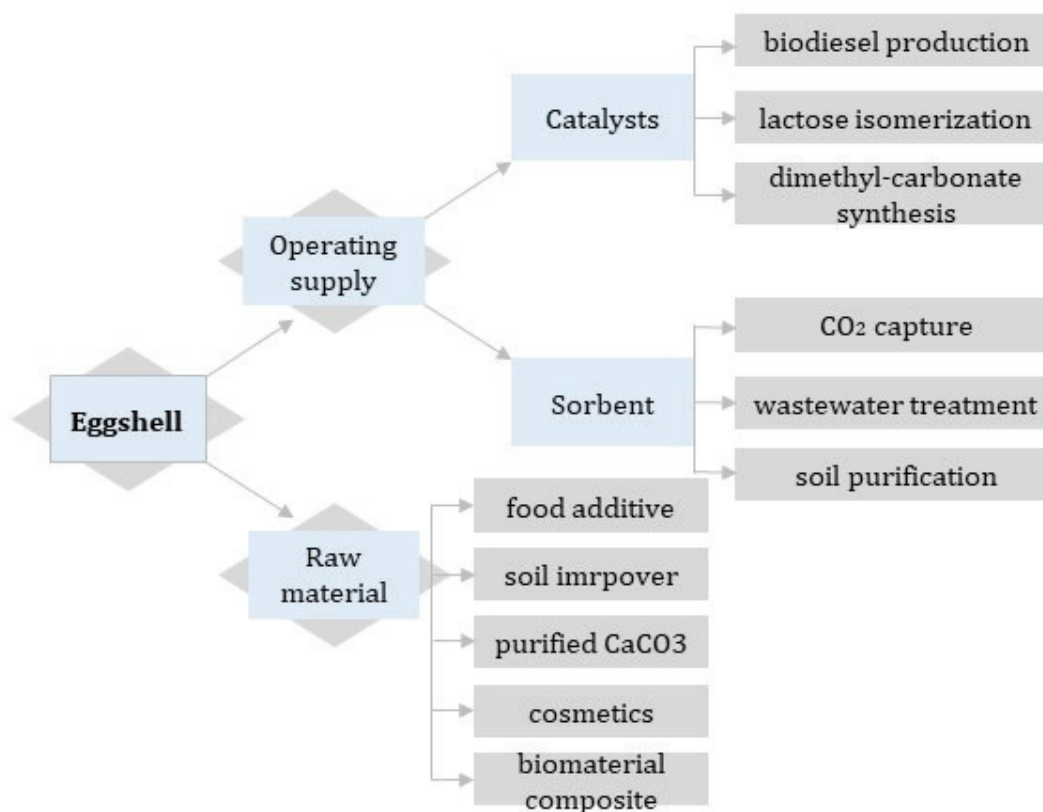


Fig. 1. Potential applications of eggshells.

2. THE SYNTHESIS OF HYDROXYAPATITE FROM EGGSHELLS

A standard path of hydroxyapatite synthesis from eggshells include calcium oxide extraction and its mixing with phosphorous

precursors. In the most common published procedure the shells was firstly washed and boiled (or steamed) to remove dirt, dried and crushed to fine powder. To obtain calcium oxide from calcium carbonate the eggshells were calcined in high temperature (usually at 900°C). Calcination was also employed to remove organic residues such as proteins, amino acids or glycoproteins. As-prepared powder was dissolved and mixed with phosphate source solution and stirred rigorously. The reactions can be presented as follows [3]:



It is easy to change the structure and porosity of received material by controlling synthesis conditions such as: temperature, molar ratio of components, time, pH of solutions etc. All this factors have impact on the obtained form of calcium phosphate and its mechanical properties. Fig. 2 shows general steps during synthesis and most important in every step factors.

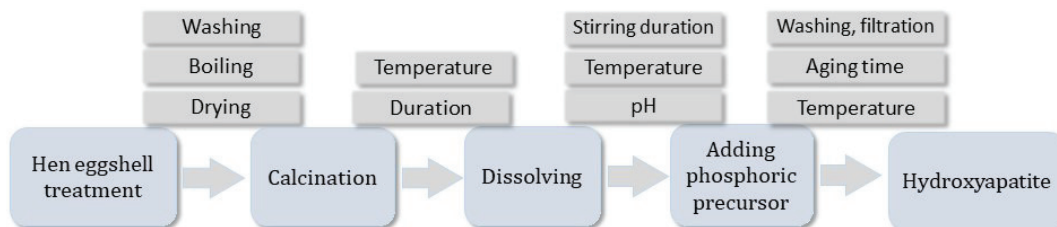


Fig. 2. Schematic pathway of synthesis hydroxyapatite from eggshells.

Moreover, the presence of additional groups such as carbonate one in the crystalline structure has significant impact on the morphology and improves its biochemical activity due to medical applications [3].

Two phased material consisting of hydroxyapatite and β -TCP can be obtained from calcined eggshells and phosphoric acid (1:1.1 ratio) through ball milling (24h) according to Lee and Oh procedure [30]. It was shown that phase purity of the material depends on CaO and H_3PO_4 ratio during the milling.

Nanosized HA (18 nm) was received by microwave irradiation of washed and calcined eggshells and diammonium hydrogen phosphate [18]. Nontoxic nature of the product was proved on the

basis of increasing MG-63 osteoblast cells size during the biological studies.

Synthesis of hydroxyapatite was carried out also without calcination. It was proved that reaction of crushed and washed raw eggshells with hydrochloric acid and DAHP leads to formation of satisfying product. Furthermore, the presence of organic residues was considered as helping factor in shape and size control. On the other hand, it was underlined that presence of biomolecules is undesirable due to biomedical application [21].

Nanosized HA derived from eggshells was also prepared using calcined chicken eggshell material and potassium dihydrogen phosphate during sol-gel reaction [19]. Polycrystalline form of received material was deduced from TEM analysis while results of XRD pattern interpretation allowed to notice one phase formation. In cited studies elongated spheroidal shaped crystals with average size of 35-50 nm were observed.

The hydroxyapatite powder originated from eggs wastes were also synthesized and used to modify the electrodes. For this purpose the hydrothermal method of preparation was employed [22]. Powdered eggshells were treated with DAHP in the temperature range from 80°C to 160°C for 2 days. It was proved that at low temperature product was 3-phase mixture consisting of monetite, whitlockite and hydroxyapatite and the increase of heating temperature to 160°C caused prevailing formation of HA. It was also noticed that the changes of temperature during the calcination had a significant influence on the morphology of particles. The small, laminar-like plate structures were characteristic for the material treated at 80°C. At 140°C flower-like clusters and small prisms with smoot surfaces were observed as well as jagged micro-sheets at 160°C.

Another work showed possibility of production the flower-like hydroxyapatite nanocrystallites (~78nm) from microwave stimulated reaction of eggshells and DAHP mixture in the presence of EDTA. Presence of hydroxyapatite was established according to the FTIR spectra. The spectra exhibited characteristic for B-type substituted cHA peaks positions at 1459, 1415 and 875 cm^{-1} . It was also found the trace amount of magnesium ions using EDX analysis [31].

More developed flower-like structure was the result of reaction between calcined eggshells and dihydrogen ammonium phosphate

using hydrogen peroxide/*N,N*-dimethylformamide solvent [32]. Synthesis was carried out at 120°C for 24 hours. It was underlined that under listed conditions partial crystallization of the product occurred and the morphology of the product was closely connected with the temperature and the component ratio in the mixed solvent. The potential applications of the product in pharmaceutical industry, as an adsorbent or luminescent factor, were also suggested.

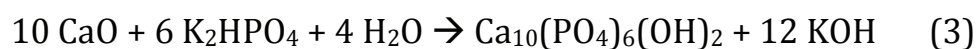
Hydrothermal synthesis between calcium oxide derived from eggshells and calcium dibasic phosphate (CaHPO_4) was used to produce hydroxyapatite-based material [33]. Authors decided to carry out the shells calcination at lower temperature (700°C) for 5 hours and initial pH of the synthesis equal to 5. Results of the synthesis showed that the product is not pure hydroxyapatite and there was found also amorphous component. Moreover, the XRD patterns showed that the crystalline form consist mostly of hydroxyapatite (75%), but there was also significant amount of CaHPO_4 (25%). It was observed that received hydroxyapatite had mainly whiskers form and this structure was considered as desirable according to medical applications.

The impact of temperature and duration of eggshells heating on the purity of hydroxyapatite was analyzed for the material produced by solid state reaction of prepared CaO with dicalcium phosphate dehydrate (DCPD) [23]. According to received results, one phase of calcium phosphate, i.e. pure hydroxyapatite can be produced at 1100°C for 3 hours. Calculated Ca/P ratio was higher than the literature value for hydroxyapatite and it was equal to 2.20. It was linked with presence of B-type carbonate group in the crystal lattice.

Other way to obtain nanosized particles of HA using eggshells was synthesis using precipitation technique [34]. In this case calcinated eggshells was dissolved in pure water at 100°C and left to reached room temperature. As-prepared solution of $\text{Ca}(\text{OH})_2$ was titrated using 0.6M phosphoric acid H_3PO_4 solution. pH and anneal temperature were controlled. It was noticed that the synthesis did not require special condition to receive satisfying product, but the impact of pH on the phase purity and temperature resistance of the received product was proved. The XRD patterns and FTIR spectra allowed to confirm one-phase crystalline structure of the product, but when the pH value was lowered during the synthesis, secondary phase formation was also observed. It was shown that there is the dependence between the calcination temperature and the received

particles size. The average size of the particles was determined about 30 nm and increased to ~150 nm according to increasing the calcination temperature from 400°C to 900°C. Moreover, product derived from eggshells calcined at a higher temperature presented higher ability to agglomeration.

Pure hydroxyapatite was obtained using self-assisted chemical reaction of calcined eggshells and hydrogen dipotassium phosphate K_2HPO_4 [17]. The reagents were mixed in proper ratio and kept in 37°C for different periods of time (24h-168h). The pH of the suspension was maintained using ammonium hydroxide at the value of 12. The reaction proceeded according to following equation:



The confirmation of the composition of the received material was made using FTIR and XRD patterns. In both cases characteristic peaks positions for hydroxyapatite were found. It was underlined that the product was very pure and the method used can be also available for the industrial scale.

Hydroxyapatite was received by 3 step microwave- assisted wet chemical precipitation and used as a component during biopolymer synthesis [20]. Firstly, collected eggshells was boiled to remove organic residues and dissolved in nitric acid. In the next step the diammonium hydrogen phosphate, received by mixing phosphoric acid and ammonium hydroxide in the proper molar ratio, was added to the solution.

The pH value of the solution was adjusted to 11. As-prepared reaction mixture was treated by microwave irradiation at 80°C for 15 min. Centrifuged and washed precipitate was characterized using XRD method. Modification of the product by defatted soybean residues allowed to obtain environmentally friendly nanocomposite. Received HA particles were proved to be in the shape of needle with nanoscale size (4-14 nm in diameter and 5-100 nm of length). All described methods are summed in Table 2.

Table 2. Comparison of eggshell- derived hydroxyapatite synthesis method.

Method	Synthesis way	HA size	Secondary phase	Shape	Ref.
Ball milling	Calcined eggshells mechanically mixed with P precursor using ball-milling		β -TCP	Grape-type granular	[30]
Microwave irradiation treatment	Activation of eggshell-derived Ca precursors with microwave irradiation	18 nm	CaO	spherulite	[18]
Sol-gel method	Material modification using traces amount of biomolecules for searching new properties	50 nm	-	rectangular	[21]
Sol-gel method	decreasing temperature of heating during calcination to 700°C	35-50 nm	-	Prolate spheroidal	[19]
Hydrothermal treatment	Soaking the eggshells in $\text{NH}_4\text{H}_2\text{PO}_4$ at different temperature for 2 days (80°C, 110°C and 160°C, respectively)	400-600 nm	Mostly monetite	Laminar-plate	[22]
		200-500 nm	Miluti-phase product	Flower-like/tiny particles	
		1-2 μm	monetite	hashed micro-sheets	
Microwave assisted sol-gel method	Microwave activation of precursor	78 nm	B-TCP	Flower-like	[31]
Solvothermal method	Preparation of flower-like particles	15-35 μm	-	Flower-like	[32]
Hydrothermal method	Synthesis nanosized HA using non modified hydrothermal method	60 nm	CaHPO_4	whiskers	[33]

cont. Table 2.

Method	Synthesis way	HA size	Secondary phase	Shape	Ref.
Solid-state reaction	Employment calcined eggshells and DCPD as precursors	-	B-TCP	Spheroidal	[23]
Precipitation technique	Study the impact of temperature and pH on HA size	35nm	TCP	Globule-like	[34]
Self-assisted reaction method	Study the soaking effect (in K_2HPO_4 for different periods of time) on HA morphology	41 nm	-	Circular	[17]
Microwave assisted precipitation method	Green synthesis of nanocomposite films in biopolymers production	4-14 nm	-	Needle-like	[20]

3. HYDROXYAPATITE AS AN ADSORBENT FOR HEAVY METAL REMOVAL

In recent years many papers regarding the use of eggshells as a precursor to biomaterial synthesis can be found. The scientists are focus not only on pure hydroxyapatite synthesis but mostly on synthesis of the product with proper properties according to intended application.

Heavy metal contamination can come from a variety of sources: petroleum refining, fertilizer industry manufacturing of die, pesticides or batteries etc. [35]. They are completely not biodegradable, which means that there is no natural way to remove them from ecosystem and they are constantly circulating in it. Finding effective way to clear out all traces of heavy metal pollution is the target not only because of environmental, but also human health reason. Heavy metals can cumulate in human body and when the proper concentration is reached they can cause many serious diseases. The most toxic are cations such as Cd^{2+} , Cr^{3+} , As^{3+} , Pb^{2+} , Cu^{2+} , Ni^{2+} or Zn^{2+} . High solubility in aqueous system causes the entering of

metal cations to the food chain [36]. A lot of techniques were used to remove heavy metals from wastewater, such as chemical precipitation, reverse osmosis, reduction, oxidation, ion exchange, electro dialysis or ultrafiltration. However, to apply this technologies to the industrial scale there is still a need to improve efficiency and to reduce cost. Next disadvantages of these methods are inherent limitations like requirement of several pretreatments, generating large amounts of sludge, sensitive operating conditions and so on [35]. It is shown that the most effective technique for heavy metal contaminations removal is adsorption with activated carbon as adsorbent what is not desirable from economical point of view [37].

Using hydroxyapatite originated from eggshells to remove copper, zinc and lead ions from aqueous solution was proposed by Mortada et al. [38]. They used the precipitation method to produce hydroxyapatite based material and investigated its adsorption capacity. The results of morphology studies confirmed crystalline nature of the product with Ca/P molar ratio of 1.685. The XRD pattern allowed to notice the hexagonal form of hydroxyapatite in the sample. TEM and SEM pictures showed the rod-like shape nanocrystals with the size in the range of 22 to 36 nm. Adsorption studies of Cu^{2+} , Zn^{2+} and Pb^{2+} from the aqueous media at different pH, stirring duration and HA amount were investigated. It was shown that all these factors had a strong impact on the adsorption process. The adsorption capacity values of analysed metals was determined using Langmuir model and it was about 2.43, 2.37, 2.53 mmol g^{-1} for copper, zinc and lead, respectively. It was assumed that the monolayer of adsorbed metal is formed during the adsorption process on the sample surface. Optimization of adsorption parameters allowed to notice that in the pH range of 6-9 hydroxyapatite presented the highest efficiency with respect to chosen metal ions. It was also found that the process was fast and adsorption capacity reached the plateau after 30 min. Desorption investigations showed the possibility of recovery once used material without a significant loss of adsorbent efficiency in the next cycles. Comparison of obtained values with certified reference material demonstrated the meaningful difference. Therefore, all this results led to the conclusion that hydroxyapatite originated from eggshells can be presumably used in wastewater treatment according to studied material.

Hydroxyapatite was also employed to remove nickel ions from the aqueous solution [39]. Bioadsorbent were obtained via precipitation method using calcined eggshells and phosphoric acid in alkaline solution. It was shown that received product was composed of 20-40 μm agglomerates of sheet and flower-like structures. The EDS and XRD results also confirmed the presence of hydroxyapatite in the sample. To carry out the adsorption, received material remained in contact with 1000 mg/dm^3 solution of nickel ions for 21 days. The morphology studies were repeated after the process and compared with previous results. The FTIR and their corresponding EDS spectra showed the textural structure modification indicating the important role of dissolution-precipitation phenomena in the mechanism of the adsorption. The additional peak on the EDS spectra derived from Ni was also noticed. Moreover, the presence of the strong signal of Ni was connected with the lower intensity of Ca signal. It was explained that the observed trend results from the substitution of calcium atoms by nickel ones in the crystalline structure. The equilibrium time of the process of 80 min with 91.5% removal efficiency was determined. It was also found that the shape of the plot can be divided into two parts: first 60 min, presenting sharp increase of removal efficiency with the time changes and after 60 min where the changes of efficiency were subtle caused by less amount of free active sites and lower concentration of the ions in the solution. According to the initial concentration changes the adsorption efficiency increased with the Ni^{2+} increase until the system equilibrium was reached. The increase of Ca^{2+} concentration in the solution corresponding to Ni^{2+} decrease was also noticed. It was considered as confirmation of substitution occurrence. Adsorption capacity was determined using Langmuir model according to the highest value of R^2 equal to 0.9999. The value of adsorption capacity of 109 mg/g was determined. The comparison of received data with literature sources showed the possibility of utilizing eggshell waste in the process of bio- adsorbent production.

Cooper ions removal using hydroxyapatite originated from eggshells was also studied [40]. The synthesis of nanosized adsorbent with a medium particle size between 20 and 32 nm was carried out using microwave irradiation. Samples of obtained material were tested due to its adsorption capacity of Cu (II) ions dissolved in aqueous media. The influence of pH of the solution, the contact time and concentration of Cu^{2+} on the removal capacity was also checked.

It was shown that the optimal value of pH is 5. According to time dependence rapid increase at first 180 min was noticed. After that time the slower curve slope was observed with equilibrium reached after 600 min. The adsorption capacity was determined based on Langmuir and Freundlich isotherm models. Better fitting has been achieved for Langmuir model ($R^2= 0.9948$). The calculated value of adsorption capacity equals to 142.86 mg/g, what was considered as a satisfying result. It was also compared with results received for the material modified with alginic acid and calcium chloride, what showed almost doubled value of adsorption capacity for non-modified product.

Hydroxyapatite-based material prepared with respect to Kumar method to remove lead ions from wastewater was considered [41]. The flowerlike structure was confirmed using SEM technique. FTIR spectrum presented characteristic peaks for hydroxyapatite what showed the presence of hydroxyapatite in the sample. The adsorption of lead contamination from aqueous solution on nanostructure adsorbent was studied. Maximum of removal efficiency was noticed at the pH value of 7 and temperature 24°C. There was stated that contact time with the lead solution had a strong influence on the adsorption process. The equilibrium state of the system was observed after 15 min with the removal efficiency equal to 99.8%. To describe the adsorption process Langmuir and Freundlich isotherm models were used. It was proved that better correlation constant (0.994) was achieved in the case of Langmuir model. Received adsorption capacity value was equalled to 322.6 mg/g. The obtained result were compared with others adsorbent originated from natural sources. It gave conclusion that studied material exhibited a high value of adsorption capacity, but not the greatest one. However, the synthesis of used adsorbent was simple, inexpensive and allowed to recycle bio-waste what was underlined as the biggest advantages.

4. CONCLUSIONS

It was shown that there is still a need to search for a new modification of synthesis conditions and reagents introducing additive mechanical and chemical properties into studied materials in order to assumed applications. Despite of the obvious possibilities of using hydroxyapatite for medical application, intensive research is

also in progress due to its application as a bioadsorbent for heavy metal pollution removal from contaminated water. It was proved that hydroxyapatite derived from agricultural wastes has many advantages over conventional, commonly used materials. The possibility to change its properties with non-complicated synthesis procedure modifications makes this product promising in many fields of scientific interest. The products received so far presents satisfying trends, but to introduce the hydroxyapatite- based adsorbents into the industrial scale, there is still a need to improve its adsorption capacity.

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