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Research article

Characterization of nano-hydroxyapatite synthesized from eggshells for absorption of heavy metals

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ABSTRACT

This paper presents the synthesis of nano-hydroxyapatite using the deposition process on eggshells as a cost-effective starting material. This study investigates the potential of nano-hydroxyapatite as an effective adsorbent for heavy metals. Various analytical techniques, including X-ray diffraction (XRD), X-ray fluorescence spectroscopy (XRF), Fourier transform infrared (FTIR), surface area measurement (BET), and scanning electron microscopy (SEM), were used to characterize its composition and microstructure. The main objective of this study is to evaluate the suitability of synthesized hydroxyapatite as a heavy metal adsorbent in aqueous solutions. The attained results showed that hydroxyapatite with particle size in the range of nanometers and a specific area of 150 m^2/g, and the necessary properties for absorption, was successfully processed. The results showed that the prepared samples had a uniform mesopore distribution between 2 to 3 nm and an explicit size of 9 nm.

KEYWORDS

Nano-hydroxyapatite
Eggshells
Synthesis
Adsorbent
Mesopores

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1. Introduction

Among the contaminants, heavy metals have a serious function in industries like battery production, mining, porcelain enameling, metal finishing, and industries. Dissemination of these pollutants in rivers has negatively affected animals and plants [1–3]. Photosynthesis inhibition by mercury and copper, reduction of chlorophyll production and growth by tentacles, and activity limitation of enzymes by chromium are the harmful influences of heavy metals on plants. On the other hand, the dangerous effects of mentioned metals on animals are organ damage, nervous system damage, reduced body growth, sleeplessness, cancer, and even death [4, 5]. To solve this environmental problem, various technologies have been employed to remove the heavy metals from wastewater involving membrane separation [6, 7], adsorption [8–10], chemical oxidation [11], ion exchange [12, 13], precipitation [14, 15], ozonation [16, 17], and photocatalysis [18, 19].

Among the aforementioned methods for the treatment of wastewater, adsorption has some benefits over other techniques such as simplicity, cost-effectiveness, higher removal efficiency, and feasibility. In addition to the mentioned advantages, the used absorbents can be recovered by using proper desorption methods [20]. All of these aforementioned superiorities have made the adsorption method grow the researchers' attention. In past decades, various components like agricultural waste, natural waste, biomass, industrial waste, and synthetics have been used to eliminate different pollutants [21, 22]. Nevertheless, studies to develop more effective adsorbents are still ongoing.

The mineral hydroxyapatite and its derivatives are favorable materials as an adsorbent for the absorption treatment of wastewater contaminated with dye and heavy metals due to their capability in ion exchange, thermal stability, high tendency to absorb many pollutants, and low water solubility. This component, which is composed of

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calcium, phosphorus, oxygen, and hydroxyl groups, has gained increasing attention because of its unique properties and structure [23–25].

The use of eggshells for the synthesis of hydroxyapatite has garnered a great deal of interest in academic research according to the existence of calcium carbonate ($CaCO_3$) (>95%) in the shell structure. $CaCO_3$ obtained from eggshells has the potential to be employed in producing nanoscale hydroxyapatite through a range of physicochemical and biological methods. Scientists from a range of fields, including chemistry, materials science, and bioengineering, have been actively investigating the production of hydroxyapatite using eggshells as a precursor through dissolution-precipitation [26], UV radiation [27], hydrothermal [28], and chemical precipitation with calcination [29]. Using eggshells for hydroxyapatite synthesis can decrease the disposal and, consequently, the environmental influence of eggshells. Globally, thousands of tons of eggshells are discarded into the environment, making them one of the serious agricultural wastes as per EU regulations [30, 31].

To be the best material for absorbing heavy metals, a material must be biodegradable, environmentally stable, non-hazardous, and have a porous structure and a large and economical surface. Reasonable costs must be incurred for this substance's production, use, and recovery. Eggshells that are thrown away may be converted into hydroxyapatite, as demonstrated by several research works that employ the synthesis methods mentioned above. The impact of hydrothermal conditions on both the structure and properties of the produced hydroxyapatite (HA) was explored by Wu et al. [32]. The findings indicate that the crystallinity of hydroxyapatite (HA) was improved by the hydrothermal reaction. Nano-sized crystals were observed in all conditions of hydroxyapatite (HA) synthesis, with the hydrothermal method yielding larger crystallite sizes than the precipitation method, and the size increasing with prolonged hydrothermal time.

Lee et al. [33] conducted a comparative study to evaluate the adsorption effectiveness of hydroxyapatite obtained from eggshells and bone in the removal of heavy metals. The findings show that hydroxyapatite obtained from eggshells shows a higher absorption efficiency for heavy metals compared to hydroxyapatite derived from bone. The results show that eggshell-derived materials have the potential to act as a cost-effective and sustainable adsorbent for the removal of heavy metals.

Amalia et al. [34] synthesized hydroxyapatite from eggshells through both calcination and non-calcination processes, followed by a reaction with Na_3PO_4. They demonstrated the formation of highly pure crystalline hydroxyapatite from calcined eggshells and amorphous HA from uncalcined eggshells, emphasizing the effectiveness of HA synthesized from chicken eggshells, particularly those subjected to calcination, as a promising adsorbent for Cd (II) ions with an absorption efficiency of 99.85%.

In this scholarly article, the synthesis of hydroxyapatite from eggshells and its potential application in the sequestration of heavy metals were examined. The findings indicated that the hydroxyapatite derived from eggshell possesses favorable structural and functional characteristics, rendering it a promising adsorbent for heavy metals in water and wastewater treatment, as well as for metal reclamation processes.

2. Materials and methods

In this work, hydroxyapatite was synthesized through the precipitation method, employing eggshells as the raw material. Chicken eggshells serve as the calcium source, and phosphoric acid (H_3PO_4) was utilized as the phosphate source. The initial step involved collecting and preparing the eggshell, which was washed with deionized water to remove any surface impurities. The eggshells were subsequently dried and then cut and crushed into small pieces employing a mortar and pestle to increase their surface area for improvement of chemical interactions. Then the obtained materials were sieved through a 20-grain sieve. Synthesis of hydroxyapatite from eggshell was achieved by using a heating process and acidic phosphoric acid (H_3PO_4) solution. For this purpose, the remaining eggshells were dissolved in a molar ratio of 1:2 in a commercial H_3PO_4 solution. The obtained solution was stirred and heated at 300 rpm via the hot plate magnetic stirrer for 4 hr at a temperature of 300–330 °C. During the heating process, efforts were made to maintain the pH in the range of 1–3. By adding $Ca(OH)_2$ to the solution, it was heated to 450 °C for 8 hours. The pH was gradually adjusted to 9–12 during this period by adding drops of 0.1 M sodium hydroxide (NaOH) solution. After separation, the hydroxyapatite was thoroughly washed with clean water to remove any acidic residue. The resulting hydroxyapatite can then be dried at room temperature or at a lower temperature, such as using cold air infiltration. The suspension is subsequently dried to obtain a powder. Finally, obtained samples are passed through a 30-mesh sieve.

In this research, the elemental compositions were determined using a Philips X-ray fluorescence (XRF) test, model PW1410, manufactured in the Netherlands. X-ray diffraction patterns are generated to recognize crystalline phases using a Siemens with a voltage of 30 kV and a current of 25 mA. The produced Hydroxyapatite is examined using a Perkin-Elmer infrared spectrometer in the range of 1400–400 cm^{-1}. In addition, a Coxem scanning electron microscope manufactured in South Korea is used to examine the morphology of the produced hydroxyapatite. Specific surface area and pore volume were studied by BET (Micromeritics ASAP 2020, USA). In this research, the specific surface area, the volume of pores, and the size distribution of porosity in synthesized samples were determined using data obtained from the absorption and desorption curves of nitrogen at the temperature of liquid nitrogen (K4/77), measured with the Belsorp mini-II device and the corresponding Barrett-Joyner-Halenda (BJH) pore size distribution, respectively.

3. Results and discussion

Table 1 shows the result of the XRF analysis of as-heated eggshells. As it is known, CaO is the primary component needed to produce hydroxyapatite, making up more than 96% of the eggshell. As is well-known, CaO is the primary component required for hydroxyapatite production, constituting over 96% of the as-prepared eggshells after calcination. As evident from Table 1, the presence of this chemical

Table 1. XRF analysis of as-heated eggshells.

	Wheight (%)			
Chemical composition	K_2O	P_2O_5	MgO	CaO
As-heated eggshells	0.29	2.41	0.53	96.77

compound in the as-heated eggshell structure was confirmed by XRF analysis to the extent of 96.77%.

In the heating process, eggshells are transformed into calcium oxide through the release of carbon dioxide (CO_2) based on the following reaction:

$$CaCO_3 \rightarrow CaO + CO_2 \quad (1)$$

X-ray technology was utilized to conduct a structural and phase analysis of the eggshell. Fig. 1 shows the XRD patterns of eggshell powder and as-synthesized hydroxyapatite. As expected, Fig. 1a reveals the presence of calcium carbonate peaks. During the synthesis process, the entirety of the calcium carbonate within the eggshell served as a precursor for the generation of hydroxyapatite. The XRD pattern of hydroxyapatite typically exhibits several distinct peaks that are associated with its crystalline structure. The most prominent peaks in the XRD pattern of hydroxyapatite occur at 2θ angles of approximately 25.9 °, 31.8 °, 32.2 °, 32.9 °, 39.8 °, and 46.6 °. These peaks correspond to the (002), (211), (112), (300), (310), and (222) crystallographic planes of hydroxyapatite, respectively. It can also be found that the strongest peak has appeared at the angle of 31.8 ° in the plane of (211). The XRD patterns displayed distinct peaks corresponding to the nanocrystalline hydroxyapatite and calcium carbonate as depicted in Fig 1b. The resulting XRD patterns exhibited broad diffraction peaks, indicating the nanocrystalline nature of the hydroxyapatite.

The result of the BET curve analysis is displayed in Fig. 2. The surface area of a material is subject to modification during both processing and synthesis. The division (milling) of a particle into smaller particles generates further surfaces, increasing in the surface area. Similarly, the creation of pores within the particle's interior, whether through decomposition, dissolution, or other physical or chemical means, also results in an increased surface area [35]. The absorption rate of heavy metals is directly influenced by the specific surface area of the adsorbent material. The number of heavy metal adsorption sites in adsorbent materials increases with increasing specific surface area. In addition, heavy metals and adsorbents physically and chemically interact more with increasing specific surface area, and absorption increases.

The BET curve shown in Fig. 2 shows the textural characteristics of nano-hydroxyapatite, including the specific surface area of particles (150 m^2/g). This measurement provides additional verification of the porous characteristics of hydroxyapatite, which possesses a high surface area. The most of previous reports of hydroxyapatite nanoparticles with a high surface area have been achieved either through high-temperature calcination or prolonged digestion periods [36, 37]. However, a long digestion period has been employed for our present study. Kamieniak et al. [38] have successfully produced mesoporous hydroxyapatite with a surface area of 242.20 m^2/g, utilizing porous carbon nanorods as a rigid template for the first time. In their investigation, initially, they created porous silica and then produced porous carbon employing the previously prepared porous silica. Finally, they synthesized mesoporous hydroxyapatite on the produced porous carbon matrix. Hence, their applied procedure is considerably more complicated in comparison to our approach. Kumar et al. [39] manufactured mesoporous hydroxyapatite (MPHA) by diverse soft templates. Notably, when the soft template used is ascorbic acid, the resultant MPHA shows a surface area of around 107.40 m^2/g. In addition, Zhou et al. [40] employed vitamin C as a soft template, yielding mesoporous hydroxyapatite with a surface area of 88 m^2/g. Chen et al. [41] synthesized mesoporous hydroxyapatite with a surface area of 190 m^2/g by employing a soft template. Hence, a large portion of research work is performed using synthesis routes that rely on soft templates. As a result, the discussion that was done here collectively displays the successful synthesis of mesoporous hydroxyapatite with a reasonably specific surface area through the utilization of this calcium carbonate template-based technique.

Fig. 3 shows a scanning electron microscopy image of as-synthesized hydroxyapatite powder obtained from eggshells. As can be seen from Fig. 3, a nanometer-scale structure with a high specific surface area has been attained for hydroxyapatite particles. Due to their small size and high surface-to-volume ratio, nanoparticles are excellent for absorbing heavy metals that can be dangerous to the environment and human health. Because particle size significantly affects the surface activity of hydroxyapatite powder, ultra-small (< 200 nm) HA nanoparticles might exhibit encouraged adsorption capability for heavy metal ions.

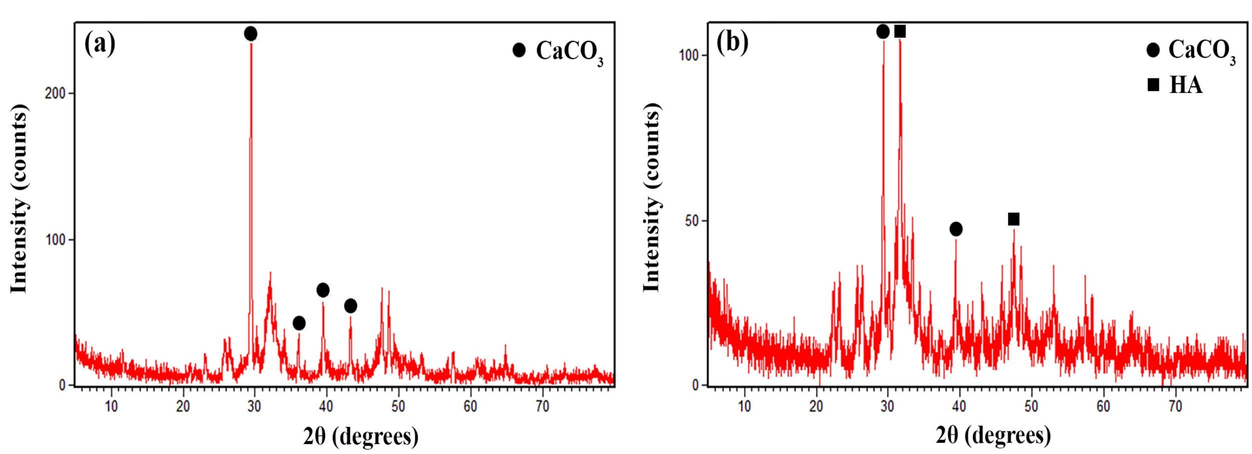

Fig. 1. a) XRD patterns of eggshell powder and b) synthesized hydroxyapatite.

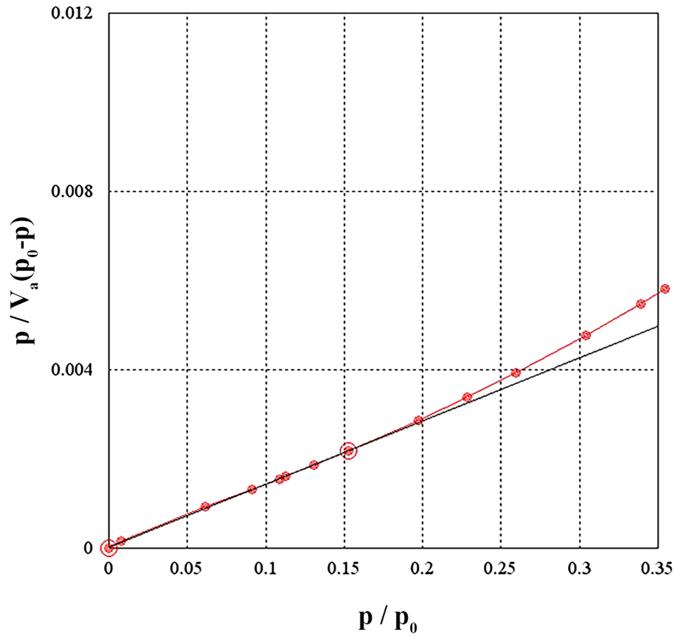

Fig. 2. BET curve of hydroxyapatite sample.

Fig. 4 demonstrates the corresponding Barrett-Joyner-Halenda (BJH) mesopores size distribution of the synthesized hydroxyapatite powder. The pore size distribution, as depicted in Fig. 4, is observed to be in the range of 2 to 3 nm and includes a distinct size of 9 nm. This pore size distribution is crucial for heavy metal adsorbents. The increased pore sizes likely result from spaces or gaps between the particles of hydroxyapatites.

The porous structure increases the effective surface area in the absorption of heavy metals and thus increases the absorption capacity of heavy metals. The mesopore in hydroxyapatite increases the stability and capacity of the compound to absorb heavy metals. Due to these pores, heavy metals have easier access to the absorbent surface, which improves the absorption efficiency of contaminated chemicals.

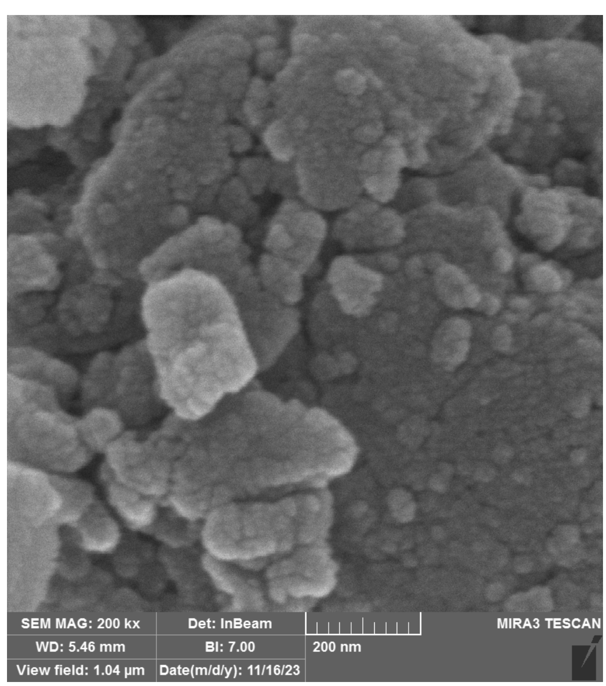

Fig. 3. Scanning electron microscopy image of nano-hydroxyapatite powder made from eggshells.

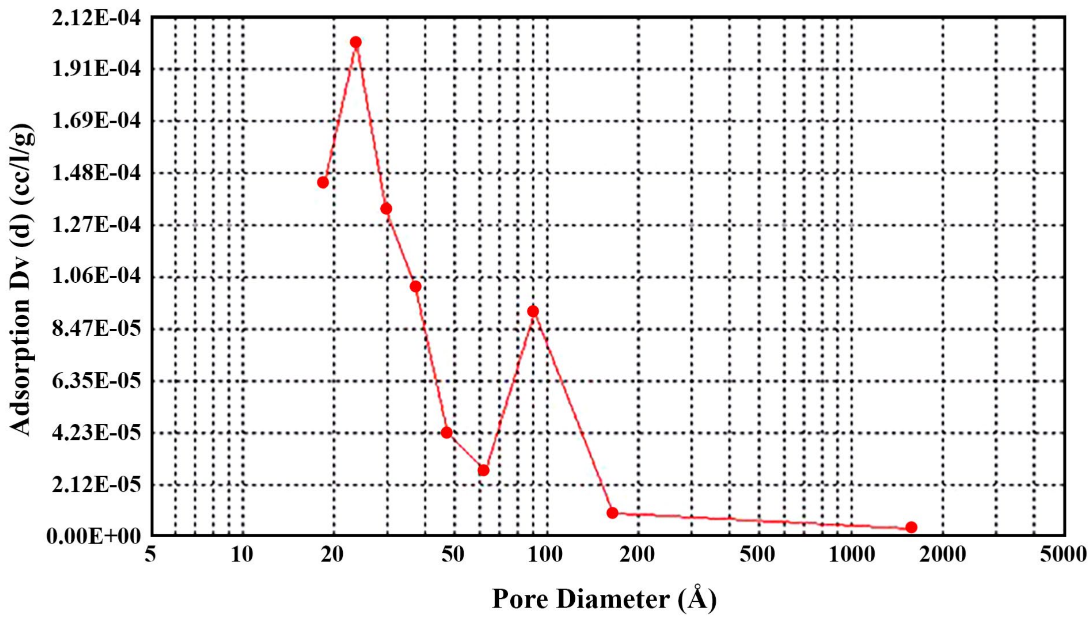

Fig. 4. The absorption curve (BJH) of hydroxyapatite sample.

The findings of hydroxyapatite-related infrared spectroscopy are displayed in Fig. 5. FTIR spectroscopy operates on the principle that the interference of radiation between two beams results in an interferogram. This signal is generated based on the change in the length of the path between two beams reflected from mirrors within the interferometer block. The two domains, frequency, and distance can be converted into each other through the mathematical procedure of Fourier transformation; hence the term Fourier transform infrared spectroscopy. A characteristic feature of a typical hydroxyapatite FTIR spectrum is the presence of an absorption band around 3415 cm^{-1}, corresponding to hydroxide. This band has been attributed to the bending vibrations of bound water within the hydroxyapatite lattice. Experience has shown that when the crystallinity of the investigated calcium phosphate increases, the bifurcation of the phosphate double-bending peak increases. The bands centered at 1083 cm^{-1} are obtained due to the stretching vibrations of the P–O bond of hydroxyapatite. The band located at 542 cm^{-1} also bending of the phosphate groups in the synthesized hydroxyapatite. The bands observed at 1393 cm^{-1} have been assigned to the C–O bond of carbonate (CO_3) groups present in the eggshells. However, these bands exhibited reduced intensities in the FTIR spectrum of the eventual hydroxyapatite product, obtained after the elimination of CaO using sucrose. The distinctive band of carbonate ions at 1393 cm^{-1} is recognized in the precursor of the $CaCO_3$/HA composite as well [42].

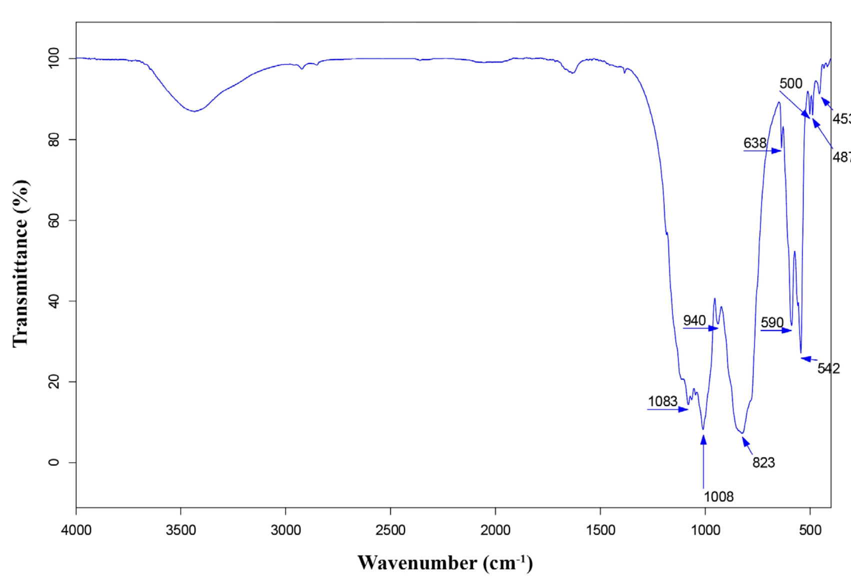

Fig. 5. Fourier transform infrared spectroscopy results related to hydroxyapatite.

One of the features of the hydroxyapatite structure, inter-network water, is indicated by the bands in the 1636 cm^{-1} range. Hydroxyapatite is known as a strong adsorbent for heavy metals. Due to the presence of hydroxyl groups and phosphate groups, this compound has a high absorption capacity for heavy metals. The main surface performances, as revealed by FTIR investigations, are associated with hydroxyl, phosphate, and carbonate groups. Using FTIR and XRD analyses, it has been found that Ca^{2+} undergoes substitutions with different metal cations like Cd^{2+}, Zn^{2+}, Pb^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, etc. Substitutions including phosphate occur with several oxyanions such as VO_4^{3-}, AsO_4^{3-}, PO_4^{3-}, NO_3^-, SO_4^{2-}, CO_3^{2-}, etc. while hydroxyl substitutions take place with anions such as Cl^- and F^- [23, 43].

4. Conclusions

The findings indicated the successful production of hydroxyapatite with particle size in the nanometer range and a specific surface area of 150 m^2/g, possessing the requisite properties for adsorption. Furthermore, evenly distributed mesopores, ranging in size from 2 to 3 nm and a distinct size of 9 nm in the prepared samples, were observed. The use of hydroxyapatite synthesized from eggshells in the absorption of heavy metals creates an opportunity to valorize waste. Eggshell waste is abundantly available and often thrown away, causing environmental problems. This research provides a sustainable solution to waste management challenges by converting eggshell waste into valuable absorbent materials. In addition, the production of hydroxyapatite from eggshells can help to develop circular economy methods, improve resource efficiency, and reduce the environmental impact of waste disposal. More research has been done to optimize hydroxyapatite synthesized from eggshells in water treatment systems. In addition, further research is necessary to investigate the adsorption process and reusability of hydroxyapatite adsorbent to develop a sustainable and cost-effective water treatment solution.

CRediT authorship contribution statement

Leyla Karamzadeh: Investigation, Methodology. Writing – original draft.
Esmaeil Salahi: Conceptualization, Supervision, Writing – review & editing.
Iman Mobasherpour: Funding acquisition, Validation.
Armin Rajabi: Data curation, Writing – review & editing.
Masomeh Javaheri: Supervision, Writing – review & editing.

Data availability

The data underlying this article will be shared on reasonable request to the corresponding author.

Declaration of competing interest

The authors declare no competing interests.

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