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Original Research Article

Synthesis and Characterization of Hydroxyapatite as a Potential Adsorbent for the Removal of Pollutants in Wastewater

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ABSTRACT

Hydroxyapatite (HAp) is promising adsorbent material for the treatment of contaminated liquid effluents due to its bioactivity, biocompatibility, biodegradability, eco-friendly and cost effectiveness. Water bodies are polluted daily as a result of increase in the activities of man due to global industrialization which poses significant environmental and health challenges, necessitating the development of effective and sustainable treatment strategies. This study is aimed at synthesizing HAp as a potential adsorbent material for the removal of pollutants from waste water via adsorption. Turkey bones was used as a precursor material for the biosynthesis of the hydroxyapatite. A comprehensive characterization analysis was employed using Scanning Electron Microscopy (SEM), Fourier Transform Infrared (FTIR), X-Ray Diffraction (XRD), X-Ray Fluorescence (XRF), Brunauer-Emmett-Teller (BET), Thermogravimetric Analysis (TGA) and Differential Thermal Analysis (DTA) to elucidate the morphological, structural and chemical properties of the synthesized adsorbent. The study revealed the microstructural characteristics of the novel adsorbent and the BET surface area was found to be 41.90 m^2/g while the pore volume and pore diameter were 0.0189 cm^3/g and 1.794 nm respectively. The XRD revealed the crystallinity of the adsorbent with XRF showing the dominance of calcium and phosphate and the FTIR spectrum showed the characteristics peaks, confirming the presence of the functional groups in the adsorbent which contributes to the electrostatic interactions. The study therefore recommends HAp as one of the adsorbents that will facilitate the effective removal of pollutants from waste water.

1. INTRODUCTION

Clean water is an essential resource that that man and other living organisms need to survive. However, our water bodies are been polluted daily as a result of the increase in the activities of man due to global industrialization. The excessive use of dyes in the textile, pulp and paper, cosmetics, pharmaceutical and food industries during the course of its operations is a major challenge (Mahroug and Belkai, 2024).

These dyes effluents when discharged into the water bodies without treatment poses a great health risks to man and the water bodies due to the carcinogenic and mutagenic nature of these dyes.

Researchers have investigated different methods for the treatment of dye-containing liquid effluents such as chemical oxidation, coagulation, flocculation, electrochemical treatments, membrane processes, reverse osmosis, enzyme technology, adsorption using activated carbon etc (Feng et al., 2021; Mcyotto et al., 2021). However, the deployment of these methods is hampered by several limitations bordering on performance and economic attractiveness.

Among the treatment options explored, adsorption has been reported to be the most effective and it has been established to be superior to other treatment strategies on the basis of its ease of operation, simplicity of design, removal efficiency, eco-friendliness and its ability to treat effluents with a wide range of dye concentration (Barakan and Aghazadeh, 2021).

However, liquid effluent treatment via adsorption is usually done using various adsorbents such as activated carbon, silica gel, activated zeolite and many others but conventional activated carbon is the most common and its limitation is because of the cost (Crini and Lichtfouse, 2019).

This has motivated the search for alternative adsorbents with high performance characteristics but low cost and one option is the utilization of waste materials as precursors for adsorbents (Li et al., 2020). The use of treated waste materials as adsorbents has attracted a lot of attention from researchers because of their low cost, abundance, chemical and mechanical resistance (Eletta et al., 2020). Many researchers have investigated the use of agricultural waste materials as precursor for green synthesis of adsorbent for the removal of dyes from aqueous solution. Although these materials offer better process economics compared to the commercially sourced ones, however, they have been reported to suffer from low adsorption capacities as a result of the involvement of the hydroxyl groups of the cellulosic component of these materials in the formation of hydrogen bonds (Silva et al., 2020). Thus, there is a drive to develop adsorbents that are both affordable and potent for dye removal from solution.

Hence hydroxyapatite becomes an effective substitute adsorbent for the adsorptive treatment of wastewater contaminated with dyes and heavy metals. Hydroxyapatite is a member of the apatite family, consisting essentially of calcium and phosphate mineral denoted as $Ca_{10}(PO_4)_6(OH)_2$. is a major constituent of bones and is mainly responsible for their hardness and strength with estimated weights of as high as 70% (Carmen, et al., 2023; Pepla et al., 2014). Hydroxyapatite can be prepared from various animal bones (Ghedjemis et al., 2021), calcined organic matters like a seashell (Ayoub et al., 2023), eggshells (Paziresh et al., 2021), fishbone (Sathiyavimal et al., 2020), fishscales (Sricharoen et al., 2021) calcined organic matters like a seashell (Karunakaran et al., 2021), coral (Zhang et al., 2019), and algae as well as biomolecules from plants (Sadat-shojai et al., 2013).

Hydroxyapatites are attracting attention as cheap, effective and high-performance adsorbents for the removal of pollutants from liquid effluents (Pai et al., 2020). Research studies involving the use of hydroxyapatite as adsorbents have become increasingly popular due to some of its important properties like bioactivity, biodegradable, biocompatibility, eco-friendly nature, non-toxicity, non-inflammatory and non-immunogenicity (Xu et al., 2020; Nayak and Bhushan, 2021). Hydroxyapatite has been demonstrated to possess superior characteristics compared to other adsorbents because it is able to accept large amounts of cationic and anionic compounds (Pai et al., 2019). This makes it versatile as an adsorbent for the removal of numerous pollutants from solution. The superiority of hydroxyapatite is closely linked with its microstructural characteristics such as particle size distribution, shape, crystallinity and porosity (Fihri et al., 2017).

Green synthesis method of hydroxyapatite makes use of waste materials to substitute the phosphate and calcium precursors (Sathiskumar et al., 2019). Limiting the use of toxic chemicals in favour of naturally available waste resources for the synthesis of hydroxyapatite which is used in the treatment of waste water is a way of solving the problem of water pollution which is the aim of this work.

2. MATERIALS AND METHODS

2.1. Biosynthesis of Hydroxyapatite from Turkey Bones

The turkey bones used as precursor material for the biosynthesis of hydroxyapatite were collected from a local restaurant in Benin City, Edo State, Nigeria (Figure 1). The bones were rinsed with clean water several times to remove any adhering dirt and debris. In preparing the base calcium precursor, the turkey bones were first boiled in hot water for a period of 3 hours to remove the spongy organic materials such as tissue residues and bone marrow. The bones were then burned in an open flame for a period of 30 minutes to remove the remaining organic components and residual fat materials. The resulting material was then crushed using a laboratory hammer mill to obtain a powdered material which was subsequently calcined in a muffle furnace at 800 °C for 2 h to obtain the HAp (Esmaeilkhanian et al., 2019).

Figure 1: Turkey bones

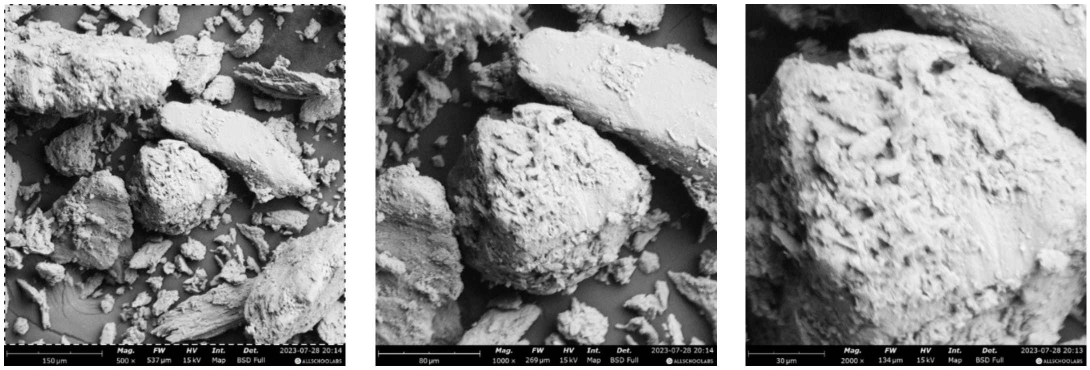
2.2. Characterization of the Adsorbent

The adsorbent was characterized using a high-*resolution* scanning electron microscope (SEM) equipped with a CDU lead detector at 25 kV to determine the surface structure. A Shimadzu FT-IR spectrometer (in the range 400 to 4000 cm^{-1}) was used to examine the synthesized hydroxyapatite adsorbent. The crystallinity of the samples was assessed by X ray diffraction analysis using a Philips X ray diffractometer with Cu-Kα radiation and a radiation wavelength of 1.542 Å. The surface area as well as pore characteristics of the samples were determined using the N_2 adsorption method in a Micromeritics ASAP 2020 BET analyzer at -196°C. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) using a Perkin Elmer thermal analyzer from ambient temperature to 800 °C at a heating rate of 10 °C/min. Nitrogen gas at a flow rate of 20 ml/min was used to ensure inert atmosphere.

3. RESULTS AND DISCUSSION

3.1. Scanning Electron Microscopy

Figure 2 shows the SEM image of the synthesized hydroxyapatite at different magnifications. The image shows an agglomeration of irregular-shaped particles with varying sizes and shapes. The particles exhibit a rough and porous surface morphology, typical of hydroxyapatite (Beh et al., 2020). The particles display a wide range of sizes, with some larger particles appearing to be composed of smaller subunits or agglomerates. This diverse size distribution and irregular morphology are characteristic of hydroxyapatite (Farkas et al., 2023). The image also reveals the presence of voids and pores among the particles, which can contribute to the overall surface area and porosity of the material (Pai et al., 2019). These pores and irregularities on the particle surfaces can potentially enhance the adsorption and ion-exchange properties of hydroxyapatite, making it suitable for applications such as dye adsorption or ion removal from aqueous solutions (Balasooriya et al., 2022). Overall, the SEM micrograph provides valuable insights into the morphological features of the synthesized hydroxyapatite particles, which can influence their performance in various applications, including adsorption and catalysis. These observations are similar to those reported by Sirajudheen et al. (2021) who prepared HAp for the removal of acid blue 113 dye from aqueous solution. Other studies have also reported similar morphological characteristics for HAp used for dye removal (Aaddouz et al., 2023; Sathiyavimal et al., 2023; Vinayagam et al., 2023).



(a) (b) (c)

Figure 2: SEM images of HAp (a) x500 (b) x1000 (c) x2000

3.2. Fourier Transform Infrared Spectroscopy

The FTIR analysis in Figure 3, provides valuable insights into the chemical composition and functional groups present in the hydroxyapatite (HAp). This technique is instrumental in elucidating the interactions between the adsorbent and the adsorbed dye molecules, which ultimately influence the adsorption performance. The HAp spectrum exhibits characteristic peaks at 3394.34 cm^{-1} (stretching vibration of OH group), 2955.77 cm^{-1} (C-H group), 1420 cm^{-1} (asymmetric stretching of COO- group), 1095.73 cm^{-1} (C-H and P-O groups), and 475 cm^{-1} (bending vibration of phosphate ions) (Sirajudheen et al., 2020). The FTIR analysis provides valuable insights into the chemical interactions and mechanisms governing the adsorption process. The presence of various functional groups in the adsorbent, such as hydroxyl, amino, carboxyl, and oxygen-containing groups, contributes to the adsorption of dye molecules through hydrogen bonding, π-π interactions, and electrostatic attractions. These interactions facilitate the effective removal of dye molecules from aqueous solutions.

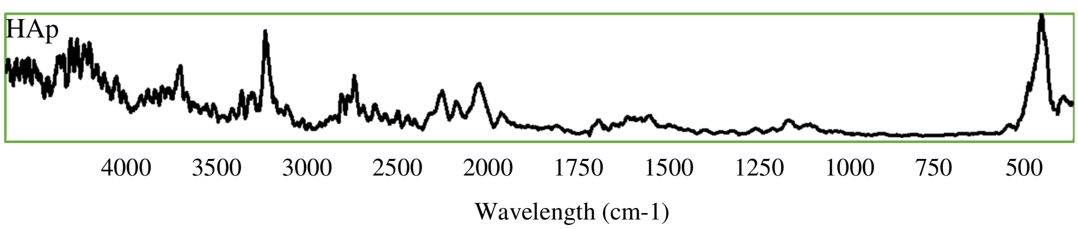


Figure 3: FTIR Spectra for HAp

3.3. X-ray Fluorescence Analysis

By analyzing the oxide composition, it is possible to gain a better understanding of the potential adsorption mechanisms and the suitability of the composite for dye removal applications (Luo et al., 2021).

Table 1: Composition of the hydroxyapatite adsorbent obtained from XRF

Oxide	CaO	P_2O_5	MgO	Al_2O_3	SiO_2	MnO	SnO_2	K_2O	SO_3	Cl
Composition (%)	77.197	14.094	3.697	1.460	1.270	0.000	1.030	0.000	0.207	1.603

From Table 1, the XRF results for hydroxyapatite reveal a high concentration of calcium oxide (CaO, 77.197%) and phosphorus pentoxide (P_2O_5, 14.094%), which are the primary constituents of the hydroxyapatite mineral ($Ca_{10}(PO_4)_6(OH)_2$). The presence of magnesium oxide (MgO, 3.697%) and small amounts of aluminum oxide (Al_2O_3, 1.460%), silicon dioxide (SiO_2, 1.270%), and tin oxide (SnO_2, 1.030%) can be attributed to potential impurities or minor substitutions within the hydroxyapatite structure (Alhassan et al., 2020). These impurities can influence the adsorption properties and ion-exchange capabilities of hydroxyapatite, which can contribute to the removal of anionic dye molecules through electrostatic interactions and surface complexation mechanisms (Fernandes et al., 2020).

3.4. X-ray Diffraction Analysis

The XRD analysis provides valuable insights into the crystalline structure and phase composition of the HAp adsorbent. The analysis of the XRD patterns is important for understanding the structural properties of the composite and their potential implications for dye removal applications. The XRD pattern of HAp in Figure 4, exhibits well-defined and intense peaks, which can be indexed to the characteristic diffraction planes of the hydroxyapatite phase (JCPDS No. 01-083-0557), as reported in the literature (Hosseinzadeh and Ramin, 2017; Sirajudheen et al., 2020). The observed diffraction peaks at 2θ values of 26.16°, 29.19°, 32.07°, 32.49°, 33.17°, 34.34°, 40.11°, 46.95°, 49.75°, and 50.75° correspond to the (002), (210), (211), (112), (300), (202), (130), (222), (213), and (231) planes, respectively, confirming the crystalline nature of

the synthesized HAp.

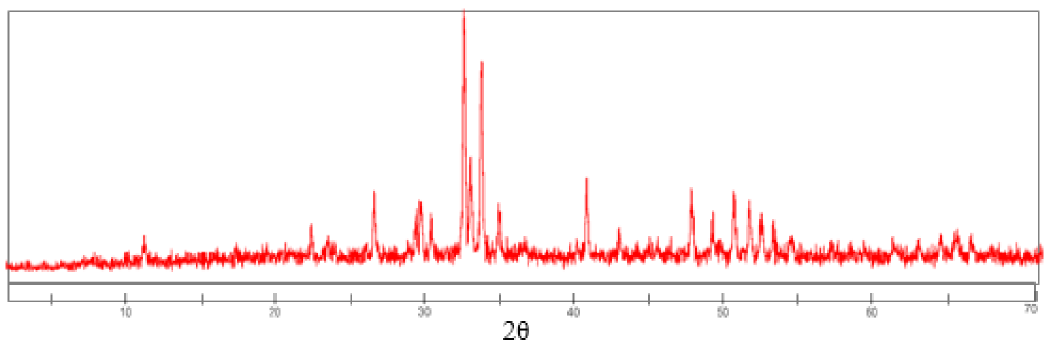


Figure 4: FTIR spectra of HAp

3.5. Surface Area and Pore Analysis

The surface area and pore characteristics of HAp was measured by N_2 adsorption method in a micromeritics ASAP 2020 BET analyzer as shown in Table 2. The surface area and pore characteristics of adsorbents play a crucial role in determining their adsorption performance and capacity. The N_2 adsorption method, coupled with the Brunauer-Emmett-Teller (BET) theory and the Barrett-Joyner-Halenda (BJH) model, provides valuable insights into the specific surface area, pore volume, and pore size distribution of the hydroxyapatite adsorbent. The pore size of 1.794nm signifies a micropore region which is characterized by high surface area (41.90 m^2/g) which enhances the adsorption process.

Table 2: Surface and pore properties of HAp

BET specific surface area (m^2/g)	BJH specific pore volume (cm^3/g)	BJH pore size (nm)
41.90	0.0189	1.794

3.6. Thermal Analysis

The thermogravimetric analysis was used to detect the thermal stability of the adsorbents. From the TGA/DTA profile for HAp as shown in Figure 5, it was observed that the weight dropped gradually to

98% from 30 to 320 ^oC which is due to the evaporation of the water molecules from the surface of the adsorbent. From 320 – 470 ^oC there was a rapid drop the weight to about 18% which could be due to loss of protein, fat tissues and collagen molecular weight from the organic structure (Hernandez-Barretto et al., 2022). From 470 ^oC there was little or no change in the mass.

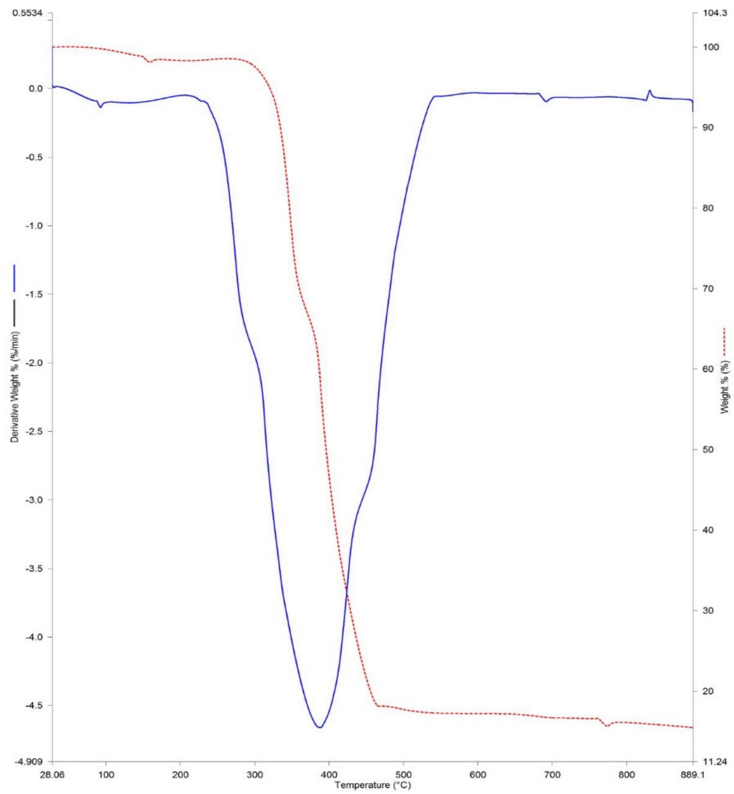


Figure 5: TGA/DTA analysis for HAp

4. CONCLUSION

Green synthesis method of hydroxyapatite makes use of agricultural waste materials to substitute the calcium and phosphate precursors which aid in limiting the economic limitations of the pristine precursors and it is also cost effective. For this study, HAp is synthesized from a naturally occurring biogenic material (turkey bones) which from the characterization of the HAp in this study, it is observed that the crystalline hydroxyapatite properties will be an effective adsorbent for the adsorption of pollutants from liquid effluents and as a result, contributes positively to the quality of our water bodies and the environment. The presence of various functional groups in the adsorbent, such as hydroxyl, amino, carboxyl, and oxygen-containing groups, contributes to the adsorption of dye molecules through hydrogen bonding, π-π interactions, and electrostatic attractions. These interactions facilitate the effective removal of dye molecules from aqueous solutions.

5. ACKNOWLEDGMENT

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6. CONFLICT OF INTEREST

There is no conflict of interest associated with this work.

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