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A Review on Sustainable Ways to Make Hydroxyapatite for Wastewater Purification

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ABSTRACT

In this review, hydroxyapatite (HAp) as a promising sustainable adsorbent for wastewater treatment was considered by synthesizing the HAp from bio-waste material sources such as eggshells and fish bones. Of all these different methods, co-precipitation route is easy and amenable to scale up while the sol-gel synthesis route gives high purity and homogeneity of the particles. The metal and metal oxide supported HAp composites (i.e. Fe-HAp-TiO_2-HAp) are reported to exhibit excellent heavy metal and dye impurity removal owing to high surface reactivity and photocatalysis. Nevertheless, the small and small wastewater operating conditions show the prevalence of degradation efficiency with the pH dependency, co-occurring ions, low recyclability. Future research direction should be dominated on low temperature green synthesis, regeneration and multi-cycle stability, and the properties should be evaluated from the techno economic view to determine the commercial sustainability. To achieve this, the proper design of these pathways will help to move from hydroxyapatite from a promising laboratory reagent to a feasible, eco-friendly adsorbent to support circular economy wastewater treatment.

Keywords: Hydroxyapatite, Green Synthesis, Wastewater Treatment, Heavy Metal Ion Removal, Dye Removal.

1. **Introduction**

The resulting high level of industrialization has led to continuous water body discharge of most pollutants, thereby causing enormous public health and environmental challenges. Heavy metals and man-made organic dyes are the most frequently occurring toxins, whose toxicity is species, concentration, and degradation process dependent [1]. As the water is our most essential element required for survival, the requirement of treatment of water is necessary. In this age of industry, tons of wastage are produced and are disposed in water, this leads to a massive water pollution, damaging the ecosystem of aquatic biomes. Rapid urbanisations are also responsible for this same problem and causing climate changes and global warming with contaminating the surface water. If this continues then, there will be the scarcity of pure surface water for regular use, and a destruction may occur in the aquatic ecosystem. To solve the issue, nowadays researchers are trying to find out possible ways to get rid of this menacing problem. Many water treatment procedures like using activated carbon, membrane separation purifying, ion exchange method, adsorption and flocculation etc. are now employed for the treatment of wastewater efficiently. The work is also going on to solve the problem using bio derived absorbent [2].

An advanced adsorbent should exhibit greater selectivity, high adsorption capacity over a broad pH and pollutant concentration scale and fast kinetics. The removal of dyes from contaminated water is crucial because of their harmful results on health of any living being and the environment. The complex molecular structure of dyes makes their elimination challenging.

Hydroxyapatite, whether derived from synthetic or natural waste resources, has shown suitable physical and chemical properties which enable fast and efficient binding to pollutants. Since HAp is composed primarily of calcium and phosphorus that makes hydroxyapatite biocompatible and non-toxic. Hydroxyapatite (HAp) with its chemical formula $Ca_5(PO_4)_3(OH)$ is a calcium phosphate bio ceramic and has been among the most promising adsorbents due to its hexagonal closed pack crystal structure with an appreciable amount of porosity, ion-exchange ability, and high biocompatibility [3]. Hydroxyapatite can easily be synthesized from bio-waste with minimal cost and effort with maximum purity. Utilizing hydroxyapatite can contribute to the recycling of waste materials and to use them in minimizing the waste in water [4]. While HAp synthesis from biogenic wastes has been practiced recently, HAp derived from synthetic waste with comparable performance has not been published. The wastewater treatments need an efficient adsorption performance which needs the highest purity, crystallinity, appreciable porosity, grain size distribution, etc. Owing to such characteristics, HAp and its composite hold potential as excellent water adsorbents for large-scale drinking-water treatment process due to their high efficiency and environmentally friendly nature. In this work, the focus is on natural source of HAp, and its uses for water treatment.

2. Methodology Review

A systematic literature review was conducted to generate transparency and reproducibility. Articles from 2020 to 2025

using keyword hydroxyapatite, green synthesis, bio-waste derived HAp, wastewater treatment, heavy metal removal, dye adsorption were collected from Scopus database, ScienceDirect database, SpringerLink database and Google Scholar.
Inclusion criteria: (i) analytical or experimental study of HAp synthesis or composite for wastewater treatment, (ii) English peer-reviewed articles and (iii) focus on green/biowaste sources.
Exclusion criteria: (i) biomedical alone papers, (ii) non-English or non-peer reviewed articles, and (iii) information from pre 2020 of non-environmental relevance.

3. Sources of HAp

Natural synthesis uses natural wastes to create hydroxyapatite (HAp), which helps cut down on costs while also improving the properties of the nanoparticles.
Natural waste derived hydroxyapatite (HAp) has demonstrated strong adsorption capabilities for these pollutants and is globally preferred because of its cost effectiveness and industrial scalability compared to techniques such as reverse osmosis and electrochemical methods[5].

Fig.1 Schematic Diagram of HAp Sources.

Between natural HAp and synthetic HAp the later exhibits better physical properties, enhancing its performance in various applications[2]. Various natural sources of HAp are shown below.

Table 1 Discussion Table of sources of CaHAp.

Natural Sources	Advantages	Ca/P Ratio	Yield% & Purity	References
Eggshell	Aids reduce costs by recycling natural waste as a calcium source.	1.67	No β-TCP, CaO, or other impuri-ties detec-ted	[6]
Shells (Oyster, seashells, clam)	Produces hydroxyapatite with strong crystalline structure	1.67	-	[7]
Fishbones	Improves the properties of HAp particles,	1.67	contains β-TCP and α-TCP	[8]
Fish scale	Crystalline structure forms well at relatively low temperatures.	1.57	carbonated HAp.	[9]
Animal bone	Improving the quality of hydroxyapatite (HAp) particles.	1.66	High crystallinity	[10]

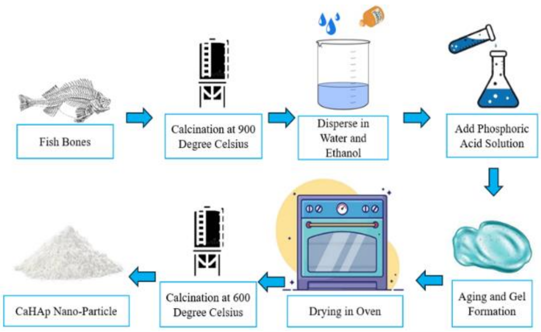

Fig.2 Schematics Flowchart of Synthesis of HAp via Sol-Gel Process.

4. Synthesis of Hydroxyapatite

Various synthesis techniques have been developed to synthesize HAp. Different techniques are commonly employed for the synthesis of hydroxyapatite (HAp) nanoparticles with individual advantages in terms of controlling particle size, morphology, and crystallinity. Calcium phosphate salts are combined with a chelating agent at alkaline pH in the co-precipitation method, followed by stirring, aging, centrifugation, washing, drying, and calcination to produce nanoparticles.For the hydrothermal method, calcium and phosphate salts are treated at elevated temperature using an autoclave or microwave, facilitating crystallinity. Sol-gel, at the Ca/P ratio of 1.67, consists of precursor mixing, aging, cleaning, and drying, where ultrasonic agitation can further develop mechanical and morphological characteristics. Sono chemicals are attained by ultrasonic irradiation under basic conditions to increase the rate of HAp synthesis, with nanoparticles harvested after centrifugation and drying. Lastly, the ultrasound–microwave process integrates ultrasound and microwave irradiation, with the incorporation of phosphate to provide a 1.67 Ca/P ratio, subsequently followed by ultrasound treatment and microwave reflux, ultimately synthesizing HAp nanoparticles[5].

5. Synthesis of HAp Synthesis

Hydroxyapatite combined with other materials to enhance its characteristics is called a HAp composite. Current research has been focused on improving the physicochemical and mechanical characteristics of HAp through such mixtures.

The synthesis processes are summarized in table below.

Table 2 Analysis of HAp synthesis process

Method	Relative Energy Use	Key Features	References
Co-precipitation	Low	Simple, cost-effective, good scalability; may form agglomerates	[5]
Hydrothermal	High	Produces highly crystalline HAp; requires autoclave and higher pressure	[11]
Sol–gel	Moderate	High purity and homogeneous nanoparticles; suitable for composite formation	[5], [12]
Sonochemical	Moderate	Accelerated reaction rate under ultrasonic irradiation; fine particle control	[5]
Ultrasound–Microwave Hybrid	Moderate	Combines rapid heating and nucleation; improved crystallinity and yield	[5]

5.1. Metal/Metal-Oxide-Based HAp Composite

Adamu et al. synthesized Fe-doped hydroxyapatite by co-precipitation using a slow addition of a metal solution to a solution of phosphate at 80°C and 800 rpm under pH 10, then aged for 15 hours, washed, and dried at 110°C for 24 hours [13]. Khalid et al. synthesized Cu-HAp and Ni-HAp by proper blending of HAp powder with copper or nickel sulfate and subsequent calcination for 1 hour at 800°C to obtain the final bio-composites [9]. Hui et al. synthesized magnetic hydroxyapatite via co-precipitation by first forming an iron-based precipitate under nitrogen, then gradually adding calcium and phosphate solutions at pH 11, followed by heating, aging, magnetic separation, washing, drying, and grinding into fine powder[11]. Electron transfer is enhanced by metal doped HAp (Fe, Cu, Ni) so that the dye degradation efficiency is enhanced.

5.2. Polymer/Biopolymer-HAp Composite

Akartase et al. synthesized a hydroxyapatite/chitosan (HAp/CTs) composite, preparing HAp alongside chitosan, and used high-purity chemicals and distilled water. Stock solutions of Cd^{2+} and Zn^{2+} ions (1200 ppm) were prepared and diluted to various concentrations for experimental use [14]. Iji et al. synthesized Kaolin–HAp–starch composites by mixing the raw materials with water, cold-pressing the powders into cylindrical green bodies at 10 MPa and air-drying for three days. The samples underwent a two-stage thermal treatment: first heating to 500°C to remove starch, then sintering at 800–1000°C with controlled heating rates and holding times, producing pellets for physical and mechanical testing[15]. Polymer/HAp composites have enhanced mechanical strength and ion-exchange capability.

5.3. Graphene /Titanium-HAp composite

Bhuvaneshwari and Sonia prepared hydroxyapatite from turkey femur bones by boiling to remove soft tissue, treating with NaOH to eliminate proteins, drying, and calcining at 900°C for 4 hours, yielding purified HAp suitable for further synthesis or coating applications raw bone into a purified, hydroxyapatite enriched material that could be used in synthesis and coating [10]. ZnO-doped nano-hydroxyapatite and graphene oxide were mixed in a 9:1 ratio and ground for 1 hour to produce a homogeneous nHAp/ZnO/GO ternary nanocomposite, which was then stored in a desiccator to prevent moisture absorption[16]. The HAp-TiO_2 composite was prepared by mixing hydroxyapatite powder with anatase TiO_2 in various weight ratios, stirring in deionized water for 24 hours, allowing precipitation for 48 hours, and then filtering and calcining at 700°C for 2 hours to obtain a crystalline product, precipitated during 48h, filtered and calcined at 700°C for 2 hours to obtain the crystalline product [12]. Graphene/TiO_2-HAp composites possess synergistic photocatalytic and adsorption properties.

6. Heavy Metal Ion Removal

Heavy metal ions like Cd^{2+}, Cr^{3+}, Pb^{2+}, etc are produced by various industrial processes, especially through battery manufacturing as they are main components of battery. They enter into the ecosystem due to inadequate waste treatment practices[17]. Moreover, since they are not biodegradable, even small concentrations can be toxic and cause long-term environmental damage[18].

In another study HAp-Sb nanoparticles were successful in removing 99% lead ion from water[19]. In another study Ca-HAp, Ba-HAp, Sr-HAp, and Pb-HAp removed Cr^{3+}, Pb^{2+}, Cu^{2+}, Cd^{2+}, Co^{2+}, Mn^{2+}, Zn^{2+}, Fe^{2+}, Ni^{2+} ions from water[20]. Kaolin -HAp-starch removed 98.74% Cr^{3+} ion from water[15]. HAp- nanoparticles and $CaCO_3$/HAp composite were successful removing multiple heavy ions such as Cd^{2+}, Pb^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+}, Zn^{2+} which are very poisonous[18], [21]. Fluoride ion is a common water pollutant which infects naturally in soil and water sources. Fe-HAp & HAp composites removed 89.8%–71.5% F^- ion from water[13]. These were the most important cases, but we studied some other cases which are shown below in a table in detail.

Table 3 Analysis of Heavy Metal Ion Removal Using Hap

Absorbent	Impurities removed	Initial Concentration (IC) Adsorbent dose (AD)	Efficiency	References
HAp-Sb nanoparticles	Pb^{2+}	IC:100 mg/L/ AD: 0.2 g/L	99%	[19]
Fe-HAp & HAp	F-	IC:10 mg/L AD:0.5g/L	89.8%–71.5%	[13]
HAP-nanoparticles	Pb^{2+}	IC:0.2-8 mg/L AD: 0.1-0.4 g/L	98.94%	[22]
Kaolin - HAp - starch	Cr^{3+}	IC: 15 mg/l AD: 75-600 mg/L	98.74%	[15]
HAp-nanoparticles	(Ca^{2+})	AD: 15 mg/L	99.9%	[23]
$CuFe_2O_4$-HAp	Fe^{2+} and Al^{3+}	AD: 1 g/L	72.5 - 98.9%	[24]

7. Dye Removal

Even small amounts of synthetic dyes in wastewater can be very harmful on aquatic life and ecosystems, as many of these dyes are carcinogenic. Therefore, it is essential to remove dye molecules from wastewater[25]. Electrostatic attraction plus ion exchange is the prevalent mechanism for the removal of cationic dyes (e.g. methylene blue, rhodamine B) while surface complexation and photocatalytic degradation mechanism is increasingly important for the removal of anionic dyes (e.g. Congo red).

HAp-$MnFe_2O_4$ removed 88% methylene blue dye[25]. Cu-HAp and Ni-HAp removed 94% Malachite Green (MG) dye[9]. HAp-Titanium dioxide (TiO_2) removed both organic dye (methylene blue) and textile dyeing effluents with 67.69%-91.38% efficiency[26]. HAp/TiO_2 removed 94% Remazol Red RB textile dye[12].
HAp-TiO_2-SnO_2-Al_2O_3. removed 98% Rhodamine B (RhB) dye[6]. These were the most important cases, but we studied some other cases which are shown below in detail.

Table 4 Analysis of Dye Removal Using Hap

Absorbent	Impurities removed	Efficiency	References
HAp-nanoparticles	Congo Red (CR) dye	85%	[7]
$MnFe_2O_4$-HAp	methylene blue dye	88%	[25]
HAp/ZnO/GO	methylene blue	99%	[16]
TiO_2-HAp	organic dye (methylene blue) and textile dyeing effluents	67.69%-91.38%	[26]
Cu-HAp and Ni-HAp	Malachite Green (MG) and Cd^{2+}	94%	[9]
Cu-HAp	Congo Red (CR)	99%	[27]
HAp-TiO_2-SnO_2-Al_2O_3.	Rhodamine B (RhB) dye	98%	[6]
Ag-HAP	Methylene Blue, 4-Nitrophenol, & 4-Nitroaniline	99%	[28]

8. Practical, Physical and Operation Limitations and Constraints

Even with claimed efficiencies in the high range, real life performance is usually limited by other factors such as narrow pH functional range (i.e. 6-8), ion competition and kinetics. Main hindrances constraining the industrial exploitation are regeneration and reusability.

9. Discussion and Research Prospect

This review identifies the sol-gel process and co-precipitation as the most sustainable synthesis processes. Precursor costs and requirement for energy to be calcinated are limiting factors in the overall large-scale utilization. Regeneration cycles, mechanical strength of HAp composites, and techno-economical aspects should be the priority in future studies.

10. Conclusion

This review identifies hydroxyapatite (HAp) as an effective and sustainable adsorbent for removing wastewater especially when synthesized from bio-waste materials sources like eggshells and fish bones. Among the different routes, co-precipitation route provides the simplicity and scale up while sol-gel synthesis provides the high purity and homogeneity of particles. The HAp composites based on metal and metal oxides (e.g. Fe-HAp-TiO2-HAp) have a high removal of heavy metal and dye impurities due to high reactivity at the surface and photocatalytic activities. But operational wastewater conditions have tendency of breakdown efficiency to the basis of pH sensitivity, co-present ions and poor recyclability. Subsequent research should mainly focus on low temperature green synthesis, regeneration and multi-cycle stability, and techno economic evaluation to establish feasibility for industrial applications. Development of these fronts will assist in changing from hydroxyapatite as a promising laboratory material to a pragmatic, environmentally friendly adsorbent to facilitate circular economy wastewater treatment.

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