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Review
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Recent Advances in Wastewater Treatment by Utilisation of Bio-waste-derived Hydroxyapatite

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Abstract

Hydroxyapatite (HAp) is basically calcium phosphate and the main inorganic component in natural bone and teeth structure. Animal bones and eggshells are mass-generated bio-wastes, and their calcium-rich structure makes them suitable precursors for bioactive HAp synthesis through biomimetic mineralisation. Industrial wastewater discharge is a worldwide alarming problem due to high-capacity industrial-scale processes, and their adverse effects on human health and environment will be encountered long term. Adsorption is the most widely used separation process in wastewater treatment, in which HAp particles can be used as bio-adsorbents for wastewater treatment processes due to their bioactive nature. Utilisation of bio-waste-derived HAp particles for wastewater treatment applications would be a step towards sustainable development and circular economy concepts. It promotes the reuse and recycle rate of bio-wastes as bio-adsorbents through an effective waste management strategy and increases the circularity of the material in the production chain. This study offers a brief overview of articles published in 2023 on the use of bio-waste-derived HAp particles for wastewater treatment.

Keywords

Hydroxyapatite, bio-adsorbent, bio-waste, adsorption, wastewater treatment, sustainable development

1 Introduction

The consequences of global population growth have established a cause-and-effect relationship involving rising food and energy demand, industrialisation, global warming, climate crisis, urbanisation, and destruction of arable lands, namely, environmental degradation. Potential negative consequences of environmental degradation on urban life and environment have led to increased awareness regarding the widespread adoption of the cyclic flow of materials and reduction in dependence on non-renewable resources through the introduction of recycling applications.

Environmentally friendly technologies and waste management strategies through circular economy (CE) applications have been emerging to achieve sustainable development goals and provide sustainable economic growth.[1,2] However, the current rate of population growth and existing resource utilisation is not sustainable, and current actions in these fields are not adequate to provide sustainability in the next 50-year period.[3] The task of providing food and energy to increasing population and protection of the environment is a challenge; however, a solution is urgently required to shape a better future for next generations. In this manner, waste management strategies have an important role to provide sustainable resource consumption, and would be a tool to mitigate environmental degradation. Developed economic and life cycle assessment models have shown that it is essential to employ appropriate waste management algorithms through proper and innovative routes for specific waste streams to maximise the performance of waste management systems.[4,5] This review provides a brief approach to the utilisation of bio-waste-derived hydroxyapatite (HAp) as bio-adsorbent for wastewater treatment applications. Theoretical studies published in 2023 are discussed to set an overview of the recent developments in the focused area. The high amount of bio-waste generation would provide a sustainable resource for bio-waste-derived HAp production, which would further be used for wastewater treatment applications. The waste management route suggested in this review would be an efficient tool to develop a CE model and have a high industrial potential when scaled-up.

2 An overview of bio-wastes

The annual generation rate of municipal solid waste, household waste and organic residue has significantly increased due to the global population growth. Further utilisation of these wastes and organic residues through bioprocessing industries has also increased the bio-waste generation rate. Approximately 34 % of generated municipal solid waste is estimated to be bio-waste, most of which is disposed of in landfill areas as a mixture of household waste.[6,7] Direct dumping is a conventional waste disposal method; however, the continuous accumulation of bio-wastes could pose ecological challenges. Bio-waste decays, such as methane or carbon dioxide released over an extended period, have adverse effects on living and non-living components of the environment, and contribute to the consequences of global warming.[8,9] Current challenges in achieving sustainable development goals require effective waste management strategies rather than direct dumping, and processing bio-waste into value-added functional materials is a promising tool to combat environmental degradation.

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Bio-waste generation is exponentially increasing, resulting in challenges related to management and disposal strategies, with utilisation rates remaining significantly limited compared to the generation rate. The untreated volume of bio-wastes poses a potential risk to the environment and public health, since their biological origin could lead to diseases.[10] To prevent such risks, it is necessary to implement a CE model for resource recovery from bio-wastes, which would also serve as a tool to meet current economic and environmental demands. In this manner, bio-wastes become important resources in the production of value-added biologically derived products, which may have potential industrial application. There are various treatment processes for the conversion of bio-wastes into value-added materials, such as hydrothermal treatment, pyrolysis, and exfoliation techniques.[11–14] Bio-derived functional materials have different application areas, such as separation processes, drug delivery or tissue engineering applications, development of energy storage devices, and environmental remediation studies.[15–20] Development of these bio-derived functional materials for various applications would provide environmentally friendly protection advantages.

3 HAp as a bio-adsorbent derived from bio-waste

Rapid urbanisation and industrialisation have had adverse environmental impacts, including effects on aquatic life and contamination of water resources. Along with global warming and climate crisis, the scarcity of water resources is alarming.[21,22] Development of low-cost and energy efficient wastewater treatment technologies has been a research hotspot. Flocculation, ion exchange, adsorption, and membrane separation methods have been suggested for wastewater treatment approaches.[23–25] Among these, adsorption is considered the most effective method due to its feasibility, low cost, precision, and ease of application.[26,27] Recent advances in nanotechnology have also led to the development of adsorbents with enhanced sorption capacity and the widespread availability of commercial sorbent materials for wastewater treatment applications.

HAp, $(Ca_{10}(PO_4)_6(OH)_2$, a calcium-phosphate-based mineral, has attracted great interest as a biomaterial due to its mineral structure's similarity to that of human teeth and bone, along with its biocompatible and non-toxic nature. HAp can be derived from natural or synthetic sources via chemical routes by utilising calcium and phosphate-containing reagents.[28–30] The most widely used production methods for HAp synthesis are mechanochemical routes, wet chemical precipitation, hydrothermal, and sol-gel methods.[31,35] Biogenic sources such as eggshells, corals, fish, pig, or bovine bones are calcium-rich waste materials, and their abundance makes them easily accessible. Utilisation of these biogenic sources as precursors for HAp synthesis has been an area of interest, offering environmental benefits in terms of low-cost raw materials and waste management strategies.

Compared to natural HAp particles, synthetic HAp particles have superior physical properties, such as their hollow structure, stability, high surface area, and high porosity, which make synthetic HAp materials suitable for use as adsorbent materials.[36,37]

Chemically pure HAp maintains its hexagonal structure at room temperature. Hydroxide ions in hexagonal HAp are disordered, causing tensions in the hexagonal lattice, and producing offsets through ion vacancies or substitutions.[38–40] These offsets make HAp effective in adsorption processes, in which the main mechanism can be described as through ion exchange, ion complex formation on the surface, and precipitation.

4 Theoretical studies on utilisation of bio-waste-derived HAp as bio-adsorbent

There has been an increasing demand for an effective strategy to remove heavy metals or organic dyes from municipal or industrial wastewater streams. Bio-waste-derived HAp possesses adequate sorption capacity for heavy metals or organic pollutants, and has been widely preferred due to its cost-effectiveness and industrial-scale applicability compared to reverse osmosis or electrochemical methods.[41–44] Fig. 1 provides a brief schematic illustration of the application areas of bio-waste-derived HAp and their potential positive outcomes.

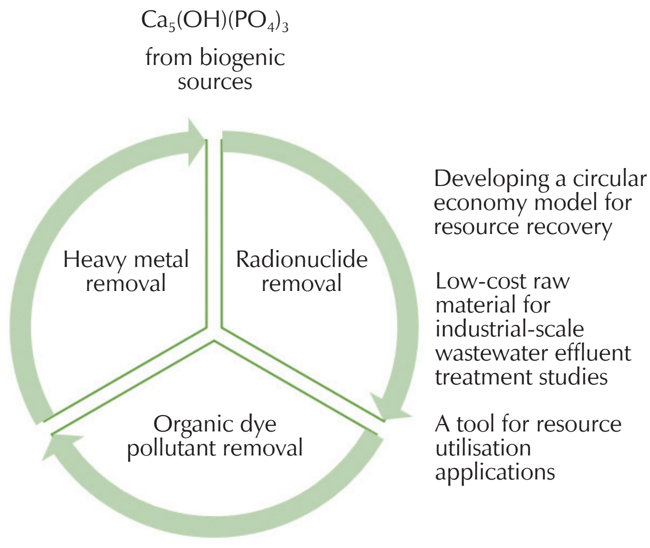

Fig. 1 – Application areas of bio-waste-derived HAp particles

4.1 Heavy metal removal studies

Polymeric materials for wastewater treatment applications are an area of interest. A study conducted by *El Kaim Billah et al.*[45] reported the adsorption performance of chitosan-nHAp (C-nHAp) nanocomposite adsorbent. C-nHAp was prepared for the removal of Cd(II) ions from wastewater. Adsorption mechanism was investigated through pH, dosage rate, contact time, Cd(II) initial concentration, and temperature parameters. Adsorption efficiency of C-nHAp and bare chitosan were compared, and results indicated that C-nHAp composites showed better adsorption performance with a maximum uptake of 126.65 $mg\,g^{-1}$. Adsorption mechanism was fitted to pseudo-second-order model. A simultaneous thermodynamic study also showed that the adsorption mechanism was spontaneous and endothermic. *Yan et al.*[46] also studied the adsorption kinetics together with thermodynamic analysis of straw-derived dissolved organic matter-derived substrate with distiller effluent derived with Ca and $(NH_4)_2HPO_4$, and they also reported that the thermodynamic data showed a spontaneous and endothermic adsorption process for Cd(II) with an adsorption capacity of 222 $mg\,g^{-1}$.

Hubadillah et al.[47] studied arsenic adsorption capacity of bio-derived HAp as in the form of bio-ceramic hollow fibre membrane. This study is reported to be the first in literature in terms of discussing the efficiency of bio-waste-derived hydroxyapatite as hollow fibre membrane through calcination process. As(III) removal performance of synthesized membrane was observed to be up to 99.9 % with a high flux of 250 $kg\,m^{-2}\,h^{-1}$. Equilibrium adsorption capacity was described to be fitted to pseudo-first-order kinetic model.

Jurgelane and Locs[48] utilised activated carbon pellets coated with HAp to investigate the adsorption mechanism of Pb(II), Cu(II), Zn(II) and Ni(II) by observing the effects of pH, initial concentration, and contact time on the efficiency. When compared to uncoated activated carbon pellets, HAp coating enhanced the adsorption capacity for studied heavy metal ions. Highest adsorption capacity was observed for Pb(II) ions at pH 6 for 56, and 47 $mg\,g^{-1}$ for HAp coated and uncoated activated carbon pellets, respectively. Adsorption mechanism was described as pseudo-second-order kinetic model and the best fitted to Langmuir model.

Magni et al.[49] performed an original study by testing Cu(II) and Pb(II) detection performance of high surface-activated carbon and n-HAp composite electrodes. The amount of n-HAp ranged between 84–96 wt%. The results showed that 92 wt% nHAp exhibited oxidation peak intensity of 250 $\mu A\,cm^{-2}$ and 150 $\mu A\,cm^{-2}$ for 50 µM Pb(II) and Cu(II), respectively. These results were reported to be the highest detection performance for carbon-nHAp composites in the literature so far.

Dhanasekaran et al.[50] prepared bio-derived HAp nanorods by chemical precipitation method and investigated radionuclide (U(VI)) removal capacity from aqueous solution. Batch adsorption experiments were performed by observing the effects of pH, contact time, initial concentration, temperature, and ionic strength parameters. Adsorption of U(VI) onto HAp nanorods was monitored by EDS elemental mapping method, FT-IR, and XRD analyses. Adsorption kinetics were best fitted to Elovich model and Langmuir isotherm. Temperature-dependent studies were in accordance with the endothermic adsorption mechanism. A brief summary of theoretical studies on heavy metal removal is given in Table 1 below.

Table 1 – Theoretical studies on heavy metal removal using bio-waste-derived HAp

Adsorbent	Heavy metal	Max. uptake/ flux	Kinetic model/ Isotherm
Chitosan-nHAp[45]	Cd(II)	126.65 $mg\,g^{-1}$	Pseudo-second-order
			Spontaneous, endothermic
Straw-derived n-HAp[46]	Cd(II)	222 $mg\,g^{-1}$	Spontaneous, endothermic
Bio-ceramic hollow fibre membrane[47]	As(III)	250 $kg\,m^{-2}\,h^{-1}$	Pseudo-first-order
Activated carbon coated with HAp[48]	Pb(II)	56 $mg\,m^{-1}$	Pseudo-second-order
			Langmuir

Apart from studies on heavy metal removal from wastewater effluents, drinking water treatment through the defluorination process has also been presented in the literature. *Mehta et al.*[51] utilised calcium and magnesium-rich source derived HAp for fluoride removal from aqueous media. Defluorination studies were performed by preparing HAp pellets, and continuous column defluorination experiments were carried out to define the optimum column parameters. Fluoride concentration, flow rate, pellet size, and absorbent bed parameters were optimised to maximise fluoride removal efficiency. Absorbance data were fitted into Thomas and Yoon-Nelson kinetic models with an optimised removal rate value of 1.21 $mg\,g^{-1}$. The study was applicable for drinking water defluorination studies and suitable for scaling up.

4.2 Dye removal studies

In addition to toxic heavy metal removal studies, organic dye removal studies are also an area of interest. *Vanitha et al.*[52] studied methylene blue (MB) dye adsorption mechanism through bio-waste-derived HAp doped with TiO_2-graphene oxide (GO) to enhance adsorption capacity through photocatalytic route. Prepared composite HAp-TiO_2-GO adsorbent also showed photocatalytic performance, and MB dye removal mechanism was defined by dual adsorption and photocatalytic degradation route. Photocatalytically active HAp-TiO_2-GO adsorbent showed 98 % removal rate for MB with a first order rate constant. Prepared ternary adsorbent showed enhanced removal efficiency when compared to non-photocatalytically active HAp adsorbents.

Aaddouz et al.[53] studied MB removal capacity of hydroxyapatite as bio-adsorbent by investigating the effects of contact time, pH, temperature, and initial concentration parameters. Optimum removal efficiency of 88.88 % was obtained with an initial MB concentration of 45 $mg\,l^{-1}$ within 20 min. Adsorption mechanism was described to be pseudo-second-order kinetic model, and equilibrium adsorption process was described through Freundlich adsorption isotherm.

Vinayagam et al.[54] synthesized eggshell-derived nHAp particles in the presence of *Muntinga calabura* leaf extract as the solvent, and investigated Congo red dye adsorption capacity. Additionally, optimisation studies were also performed by central composite design. A dye adsorption of 89.96 % was reached in the case of initial 33.18 mg l^{-1} load within 137 min. Adsorption kinetics were described as pseudo-second-order model and fitted Freundlich isotherm. Thermodynamic analysis also indicated the spontaneous and exothermic nature of the adsorption process.

Yarahmadi and Sheibani[55] reported $CuSO_4$ promoted HAp derived from eggshells through hydrothermal route. Catalytic degradation performance of organic pollutant dyes, namely MB, 4-nitrophenol and 4-nitroaniline in aqueous media containing $NaBH_4$ was studied. Reaction conversion in equilibrium state for the case of 4-NP, 4-NA, and MB were reported to be 99, 96, and 99.5 %, respectively. This study reports the high catalytic performance potential of bio-waste-derived catalysts for organic dye pollutant removal.

Bin Mobarak[56] utilised chicken eggshells as Ca precursor for HAp through solid state synthesis followed by calcination at 950 °C. Adsorption efficiency of Congo red dye was studied, and the maximum capacity of 9.64 mg g^{-1} was observed, fitted with Langmuir isotherm and pseudo-second-order kinetic model. The study reports the high application potential of eggshell-derived HAp adsorbents for organic dye pollutant removal from wastewater streams.

Weng et al.[57]utilised fish scales as substrates for HAp synthesis through freeze-drying, hot-air drying, and natural draft-drying methods, and compared the surface area of resulting HAp particles. Among the three methods, the highest surface area was obtained by natural draft-drying method. Maximum absorption capacity of 1259.60 mg g^{-1} in the case of acid fuchsin was observed, fitted with Langmuir isotherm, and thermodynamic analysis revealed that the mechanism was exothermic and spontaneous. The study reveals the removal of acid fuchsin from wastewater through HAp prepared by natural draft-drying method, which is a green, low cost, and low energy approach.

Ali et al.[58] performed a novel study based on the removal of gentian violet (GV) dye from aqueous media utilising HAp as the adsorbent. HAp was synthesized through a two-step microwave and precipitation method. Removal studies were conducted through contact time, adsorbent dosage, pH and initial concentration. Obtained experimental data were best fitted with pseudo-second-order kinetic model and Halsey isotherm. Maximum adsorption capacity of 1.035 mg g^{-1} was achieved with 99.32 % removal rate. Thermodynamic analysis of adsorption study revealed that adsorption process was endothermic and spontaneous.

Hai et al.[59] used superparamagnetic iron oxide nanoparticles coated with HAp for removal of Congo red dye. Effects of pH, initial dye concentration, composite adsorbent weight, temperature, and contact time were investigated. Maximum adsorption capacity of 158.98 mg g^{-1} was achieved. Adsorption mechanism was fitted with pseudo-second-order kinetic model and Langmuir isotherm. Preparing a composite with HAp and superparamagnetic iron oxide nanoparticles is suggested to be an efficient route for Congo red dye removal from wastewater effluents.

Kokeb et al.[60] used waste bones as substrates for calcium-phosphate nanopowders. They investigated adsorption capacities in the case of disperse red 1 and DCT reactive blue 109 dyes. Maximum adsorption capacities of 98.65 and 96 % for disperse red 1 and DCT reactive blue 109 dyes, respectively, were observed. Adsorption isotherms show a difference with respect to dye type, namely, Freundlich isotherm for disperse red 1, and Langmuir isotherm for DCT reactive blue dyes. Results show high application potential of bio-waste derived calcium-phosphate nanopowders for high performance azo-dye effluent treatment. A brief summary of theoretical studies on organic dye removal are given in Table 2.

Table 2 – Theoretical studies on dye removal using bio-derived Hap

Adsorbent	Dye	Removal rate / %
HAp-TiO_2-GO composite[52]	MB	98
HAp[53]	MB	88.88
Eggshell-derived nHAp[54]	Congo Red	89.96
Eggshell-derived $CuSO_4$ promoted HAp[55]	4-NP	99
Eggshell-derived $CuSO_4$ promoted HAp [55]	4-NA	96
Eggshell-derived $CuSO_4$ promoted HAp[55]	MB	99.5
HAp[58]	Gentian Violet	99.32

Recent studies in the field of wastewater treatment applications using bio-waste-derived HAp material primarily focus on the removal of heavy metals and organic dyes. Synthesized HAp particles are mostly used in combination with polymeric, paramagnetic, or photocatalytic promoters to enhance the adsorption efficiency. In addition to kinetic model analysis, most of the studies also report thermodynamic analysis of the adsorption process, and describe the adsorption mechanism as spontaneous and endothermic. Results indicate high performance adsorption results, promising for achieving such high efficiency with waste-derived adsorbents. Adsorption-desorption cycles might be employed to further utilise dye and/or HAp particles; however, detailed feasibility studies might be required for the applicability on a large scale. Regeneration cycles might have an adverse effect on the performance of adsorbent after a while. In such a case, safe disposal, burning or recycling can also be applied. Introducing bio-waste-derived HAp particles in industrial wastewater treatment presents an environmentally friendly approach and sustainable solutions to addressing current environmental issues through resource recovery, and provides a better solution mechanism for future generations. Additionally, economic analyses of bio-waste derived adsorbent and composite material synthesis routes should be considered for scaling up these processes.

5 Conclusion

Global population growth and increased industrial activities have resulted in an increased generation rate of municipal wastes and industrial wastewater effluents, respectively. Facile synthesis of bio-derived adsorbents to remove the pollutants from wastewater has been gaining importance. Synthesis of adsorbents from bio-wastes offers an environmentally friendly, low-cost approach, and contributes to the valorisation of ever-increasing waste materials. HAp is a calcium-phosphate material with high structural similarity to that of natural bones and teeth. Bio-waste-derived HAp has high potential as a bio-adsorbent for wastewater treatment applications. "Green" routes for the synthesis of industrially applicable materials have been gaining importance. Valorisation of bio-wastes as precursors for HAp synthesis would provide a framework oriented toward sustainable development goals, and developments in this field would offer a promising alternative for the synthesis of eco-friendly and low-cost materials that can be used to remove impurities, such as heavy metals and organic pollutants originating from aqueous dyes. Utilisation of HAp as bio-adsorbents in wastewater treatment applications is mostly focused on removal of heavy metals and organic dye pollutants from industrial discharges. Batch adsorption studies were also conducted to observe the radionuclide removal capacity of bio-derived HAp nanorods from aqueous solutions. This study offers an overview of recent developments in wastewater treatment using bio-waste-derived HAp as bio-adsorbents, providing brief reviews of articles published in 2023. The findings of this review might benefit municipal waste treatment facilities as well as the textile industry, which discharges large volumes of wastewater effluents.

However, most of the reported studies were conducted at the laboratory scale, highlighting the need for pilot-scale systems for further commercialisation. Another aspect to consider is the intensity of batch applications with effluents containing a single type of heavy metal or organic dye pollutant. Therefore, studies should explore multi-pollutant and heavy metal systems to simulate adsorbent performance with real-time wastewater effluents. Regeneration and maximum number of adsorption-desorption cycles should also be investigated to optimise the adsorption performance. Additionally, potential valorisation areas for HAp particles, such as their use as catalysts, nano-fertilisers or in ceramics production should be thoroughly explored.

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SAŽETAK

Napredak u pročišćavanju otpadnih voda korištenjem hidroksiapatita dobivenog iz biološkog otpada

Cemre Avşar

Hidroksiapatit (HAp) je glavna anorganska komponenta u kostima i zubima, a riječ je o kalcijevu fosfatu. Životinjske kosti i ljuske jaja su bogati izvor biološkog otpada, a njihova struktura bogata kalcijem čini ih optimalnim prekursorima za bioaktivnu sintezu HAp kroz biomimetičku mineralizaciju. Problematika ispusta industrijskih otpadnih voda je globalno alarmantan problem s obzirom na obimne industrijske procese, čije dugoročne negativne posljedice na ljudsko zdravlje i okoliš su neminovne. Adsorpcija je najrašireniji separacijski proces za uklanjanje onečišćujućih tvari iz otpadnih voda. Čestice HAp-a mogu se koristiti kao bioadsorbensi u procesu pročišćavanja otpadnih voda zbog svoje bioaktivne prirode. Korištenje čestica HAp dobivenih iz biootpada dodatni je korak prema održivom razvoju i kružnom gospodarstvu jer promiče ponovnu upotrebu i recikliranje biološkog otpada. Kroz ovaj rad dan je pregled radova objavljenih 2023. na temu primjene čestica HAp-a dobivenih iz biološkog otpada u pročišćavanju otpadnih voda.

Ključne riječi
Hidroksiapatit, bio-adsorbens, biootpad, adsorpcija, pročišćavanje otpadnih voda, održivi razvoj

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Pregled
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