

A Green Approach for Nanoparticle Synthesis for Bioremediation: A Review

Mihir Iyer¹, Heta Patel², Surabhi Kulkarni³

^{1, 2, 3}Interdisciplinary School (IDS) Science, Savitribai Phule Pune University
Corresponding author: [mihiriyer07\[at\]gmail.com](mailto:mihiriyer07[at]gmail.com)

Abstract: *Bioremediation is the need of the hour with concerning reports of environmental degradation surfacing. Traditional routes of bioremediation involve displacing contaminated materials to a different location or attempting to eliminate the contaminated materials. However, with the rise of nanomaterials and nanotechnology, there has been tons of research on using nanomaterials for bioremediation. This article delves into green chemical and biological strategies for the synthesis of various nanomaterials for bioremediation via two mechanisms – (1) sorption and (2) photocatalysis.*

Keywords: nanotechnology, bioremediation, nanochemistry, nanobiotechnology

1. Introduction

Over the years, concerning reports regarding the degradation of our environment have come to light. Every year, around 10 million tons of untreated hazardous chemicals are emitted from factories into the environment [1]. Numerous cases of complicated infections due to pollution have come forth. The World Health Organization (WHO) estimates 7 million deaths per year due to indoor and outdoor air pollution [2]. The cause for such death is particulate matter, especially trace metals. Rapid industrial development increases the amount of trace metals. Sediments often contain trace elements such as mercury (Hg), lead (Pb), cadmium (Cd), arsenic (As), chromium (Cr), zinc (Zn), copper (Cu), and nickel (Ni) [3]. Water pollution is another leading cause of a plethora of diseases suffered by humans. Most threats to safe water include chemical pesticides, heavy metals, petroleum oil, pesticides, hydrocarbons such as aliphatic, aromatic, and polycyclic aromatic hydrocarbons, nitroaromatic compounds, chlorinated hydrocarbons such as polychlorinated biphenyls (PCB) and perchloroethylene, organophosphorus compounds, organic solvents (phenolic compounds), and phthalates [95]. Thus, eliminating these from air and water is the need of the hour.

Conventional techniques for remedying water and land – remediation – include removing contaminated sources and separating them by either placing them in a landfill, disposing of contaminated water into the ocean, or capping and containing the contaminated areas of a site. [94]. These methods are interim; they only work for a short amount of time as they pose risks to the new sites where they are deposited. A better approach than these traditional methods is to destroy the pollutants if possible, or at least to transform them into innocuous substances [94]. Certain technologies that have been utilized include high-temperature incineration and various forms of chemical decomposition such as base-catalyzed dechlorination and UV oxidation [94]. These methods have proven to be highly effective in reducing the levels of various contaminants. However, they do have their downsides, such as being complex, costly for small-scale applications, and not being widely accepted by the public [94]. In particular, incineration may increase exposure to contaminants for both workers and nearby residents, thereby

raising safety concerns [94]. Thus, to combat this, bioremediation was introduced as an alternative.

Bioremediation is a process that utilizes natural biological activity to eliminate or neutralize different types of contaminants. It involves using low-cost and low-technology techniques that are generally well-received by the public and can be conducted on-site. Bioremediation makes use of living organisms, mainly microorganisms or plants, to detoxify hazardous pollutants [96]. Conventionally, multiple in situ and ex situ methods for bioremediation have been reported. They include bioventing, biosparging, bioaugmentation, biostimulation, landfarming, biocompositing, biopiles, and bioreactors [96]. However, these methods are plagued by a variety of disadvantages, stemming from competition, growth rate, and other technical factors. Thus, researchers have employed techniques from the field of nanobiotechnology to combat this.

Nanomaterials possess a unique advantage as they possess significantly more properties than their bulk counterparts [4]. The property exploited the most for absorption and adsorption is size. Nanomaterials are exceptional absorbents and catalysts, due to their larger specific areas, lower temperature modification, customizable pore size, shorter inter-particle diffusion width, high number of related adsorption sites, and diverse surface chemistry when compared to other options [5]. Nanoparticles that have a higher fraction of surface area, increased surface energy, precise dimensions, and spatial confinements are showing potential benefits in fields such as catalysis, magnetism, electronics, and optics [4].

There are lots of physical and chemical processes used for the synthesis of nanoparticles. However, most of them take up immense amounts of energy, are often connected with dangerous substances, and are less sustainable and cost-effective [1]. Biological or bio-mimetic processes [3] for the synthesis of such nanomaterials are environmentally more sustainable, require less energy, and do not produce any hazardous by-products. Moreover, fabrication of nanomaterials via living organisms tend to use up ions from their surroundings and either reduce or oxidize them [4].

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This review encompasses different strategies used to synthesize nanomaterials using green synthesis methods for nanobioremediation. The nanomaterials covered in this review can be classified into two; (1) Nanomaterials synthesized via uptake of contaminants and; (2) Nanomaterials synthesized ex vivo and introduced into the system for uptake. Nanomaterials covered in the second category perform bioremediation via two mechanisms – sorption and photocatalysis – which we will cover further.

Reduction of metal ions to form nanoparticles via biogenic methods

Nanoparticles are biosynthesized when the microorganisms grab target ions from their environment and then turn the metal ions into the elemental metal through enzymes generated by the cell activities [51]. It can be classified into intracellular and extracellular synthesis according to the location where nanoparticles are formed [52, 53]. Such a process can directly aid bioremediation since these organisms can obtain metal ions directly from the source where we aim to perform bioremediation.

The inherent constraints of chemical and physical methods in nanoparticle synthesis underscore the potential advantages offered by biological approaches. Biogenic synthesis, utilizing microorganisms, presents a dependable, sustainable, safe, and environmentally friendly technique for nanoparticle production. Bacterial, algal, fungal, and yeast cells have demonstrated the capability to extract metals from their surroundings and transform them into elemental nanoparticle forms, either accumulating or secreting them.

Biogenic nanoparticles are usually synthesized via either intracellular or extracellular mechanisms [52, 53]. The intracellular method consists of transporting ions into the microbial cell to form nanoparticles in the presence of enzymes whereas the extracellular synthesis of nanoparticles involves trapping the metal ions on the surface of the cells and reducing ions in the presence of enzymes [51, 54].

Nanoparticles of bacterial origin

Researchers have shown the successful synthesis of Ag, Au, Fe, Ni, Zn and other significant nanoparticles using bacteria, namely *Bacillus licheniformis*, *Pseudomonas deceptionensis*, *Pyrococcus furiosus*, *Pyrobaculum islandicum*, and *Pseudomonas aeruginosa* [55]. These nanoparticles have also shown good efficacy in terms of bioremediation.

Cyanobacteria, known for their photosynthetic capabilities, have garnered significant attention as a phylum of bacteria with immense potential in nanoparticle synthesis. A study done by someone showed that aqueous extracts from the cyanobacterium *Oscillatoria limnetica* have proven effective in synthesizing silver nanoparticles through reduction processes, followed by subsequent stabilisation [56]. The size of the nanoparticles ranged between 2.9 to 21.23nm [56]. Other cyanobacterial strains used for nanoparticle synthesis are *Scytonema* sp., *Nostoc* sp., *Phormidium* sp., *Desertifilum* sp. and more [57, 58].

Apart from metal nanoparticles, other organic nanoparticles have also been studied. A study by Chen et al. showed the synthesis of exopolysaccharide self-assembled nanoparticles using *L. planatarum*-605 strain from Chinese fermented

pickles [50]. It showed a record biosorption capability for Pb^{2+} , Cu^{2+} , Cd^{2+} , and methylene blue [50].

Nanoparticles synthesised by Actinomycetes

Actinomycetes possess properties of both fungi and prokaryotes like bacteria. They can produce secondary metabolites intracellularly and extracellularly with varied biological activities [59].

Silver nanoparticles produced from Actinomycetes have been shown to possess significant antibacterial activity. Silver nanoparticles (AgNPs) synthesized using *Streptomyces* sp. BDUKAS10 showed 16-, 15- and 13-mm zones of inhibition against *Staphylococcus aureus*, *P. aeruginosa* and *Bacillus cereus*, respectively [60]. Another study by Selvakumar et al. showed the successful synthesis of AgNPs extracellularly from *Streptomyces rochei* using 10^{-3} $AgNO_3$ and 10^{-4} $AgNO_3$ [61].

For the biosynthesis and characterization of gold nanoparticles, only a few of the genera such as *Thermomonospora*, *Nocardia*, *Streptomyces*, and *Rhodococcus* have been identified from actinomycetes [62].

Nanomaterials synthesised by Yeast

Yeast strains of several genera are known to employ different mechanisms for nanoparticle synthesis resulting in significant variations in size, particle position, monodispersity, and other properties. In the context of bioremediation, we know that most yeast genera can accumulate significant amounts of heavy metal ions [63] and their detoxification mechanism involves glutathione, metallothioneins and phytochelatin [63]. Once yeast cells accumulate heavy metal ions, they synthesize nanoparticles which may accumulate for easy removal.

A study shows the synthesis of stable gold nanoparticles by *Pichia jadinii* by reduction of gold ions via enzymes present in the cell wall and cytoplasm [64]. Two patents were granted to Correa et al. for the synthesis of copper nanoparticles for bioremediation. In brief, the process involves using the dead remains of *Rhodotorula mucilaginosa* yeast, and the filamentous fungi *Hypocrea lixii* and *Trichoderma koningiopsis* in an aqueous solution containing copper to remove the metal and to simultaneously create metallic copper nanoparticles. The process is carried out under optimal physio-chemical conditions [65, 66]. The end product is nanoparticles of metallic copper that help to absorb the copper pollutants from the affected area [65, 66]. Thus, this and similar techniques can be used to formulate nanoparticles to help with bioremediation.

Nanoparticle synthesis by Algae

The use of algae for the biosynthesis of nanoparticles for bioremediation is also increasingly becoming common. Algae are renowned for their capacity to hyper-accumulate heavy metal ions and remodel them into more malleable shapes by performing bioreduction, similar to yeast, intracellularly and extracellularly [67].

Algae can synthesize various metal oxide nanoparticles, such as gold, silver, platinum, palladium, copper oxide and zinc oxide [63]. For example, *Chlorella vulgaris*, *Dunaliella*

salina, and *Nannochloropsis oculata* can produce silver nanoparticles of less than 15 nm size inside the cells within 48 h [68]. The metal ions can attach to the cell surface through electrostatic interactions with negatively charged carboxylate groups. Subsequently, enzymes can reduce the ions, leading to nuclei formation and growth with metal ion reduction [69].

Nanoparticle Synthesis by Viruses

Viruses have emerged as promising candidates as nanoparticles for biomedical applications, owing to their biocompatibility, biodegradability, capacity for mass production, programmable scaffolds, and ease of genetic manipulation for desired characteristics. It has been reported that viruses are used for the synthesis of inorganic nanoparticles, such as cadmium sulphide, silicon dioxide, iron oxide and zinc sulphide [63]. The challenge of synthesizing inorganic nano-crystals has been observed in bacteria and fungi. This is because of the limitations posed by protein frameworks, DNA-recognizing linkers, and surfactant-assembled pathways [63]. However, these restrictions can be overcome by using modified viruses that can produce self-assembling surfaces with quantum dot structures [63]. This approach yields nanoparticles of uniform size, shape and length. The incorporation of unnatural amino acids as unique handles for subsequent chemical reactions is also possible using similar recombinant expression strategies [63].

Wastewater management via sorption of target molecules over nanomaterials

Polychlorinated biphenyls (PCBs) and Polycyclic Aromatic Hydrocarbons (PAHs) are hydrophobic. Hence, their solubility in water is limited. However, their toxicity is determined by their accumulation in tissues over time [6], especially in fatty tissues [7]. Conventional water treatments fail to remove these compounds.

PAH are hydrocarbons formed by 2 or more aromatic hydrocarbons, present abundantly in the environment [10]. PAH have a wide range of applications, including manufacturing pigments, dyes, and plastics, as well as wood preservation, agrochemical production, and use in the pharmaceutical industry [10]. Humans are at risk of exposure to PAHs primarily by breathing in polluted air, consuming contaminated water, and eating fish and other contaminated food [8]. PAHs exhibit remarkable stability, which enables them to be efficiently transported over long distances in gaseous form. They are resistant to degradation when attached to atmospheric particles and can eventually settle into ecosystems, including water bodies [11]. Exposure to PAHs is even more harmful owing to their carcinogenic and mutagenic nature [12]. Examples include benzo[a]pyrene, naphthalene, chrysene, and benzo[b]fluoranthene [10].

PCBs are relatively heat stable and can withstand both acids and alkalis, which renders them of value in an extensive variety of applications including transformers, capacitors, and lubricants [9]. These were commonly used in various products such as plasticizers, coatings, inks, adhesives, fireproof materials, insecticides, and paints. [6]. Due to their heat-stability and resistance towards acids and alkalis, environmental accumulation of PCBs causes severe contamination [14]. Ecological exposure to PCB has been

reported to cause carcinogenic, endocrinal reproductive neurotoxic, pathological, and immunological complications [15] and hence require immediate attention.

There have been multiple reports of different kinds of nanomaterials synthesised for this process.

Carbon nanotubes act as efficient nano adsorbents, useful for the removal of most organic contaminants from wastewater [13]. They show exceptional uniqueness with their massive surface area, external volume, and high mesoporous volume [16]. Both single-walled and multi-walled carbon nanotubes have been tested for the removal of PCBs and PAHs from water [17]. Moreover, the functionalization of these nanotubes with groups like -OH, -NH₂, -COOH, etc. improves their adsorption capabilities [18].

Traditional chemical synthesis methods include laser vaporisation, laser ablation, arc discharge, pyrolysis, and chemical vapour deposition methods. However, most of these strategies require complex process control, high reaction temperature or a long synthesis time [27]. This is, however, impractical, and environmentally harmful.

Multiple reports regarding greener methods of synthesis of carbon nanotubes have been published. Multi-walled carbon nanotubes (MWCNTs) were synthesised by using green catalysts synthesised from garden grass (*Cynodon dactylon*), rose (*Rosa*), neem (*Azadirachta indica*) and walnut (*Juglans regia*) plant extracts [25]. MWCNTs especially grown with walnut extract showed 8-15 nm diameter and 3600 µm length [26].

Another method devised by Kang et al. [27] is the one-step quenching method of synthesis using graphite. Hakim et al. used burnt coconut shells as graphite sources for this method [28]. The obtained graphite was heated at 700°C and then immediately submerged in cold distilled water for some hours [28]. This was heated at 60°C to remove all the water for 24 hours to obtain the nanotubes [28].

The applications of carbon nanotubes are immense. Reports suggest a high sorption rate, independent and even dependent on some factors, that are promising.

A study done by Shao et al. (2011) grafted methyl methacrylate on multi-walled carbon nanotubes (MWCNT) using the N₂ plasma technique [19]. The study aimed at the removal of 4,4'-dichlorinated biphenyl under ambient conditions. The results indicate that adsorption on the grafted nanotubes was much higher than regular nanotubes - more than 95% removal of PCB in 24 hours [19]. This makes them efficient materials for immobilization of these PCBs. However, this material is pH dependent. The removal efficiency works best in a medium of pH 2–10 and decreases as pH exceeds 10 [19].

In another study by Shao et al. (2010), β-cyclodextrin was grafted on multi-walled nanotubes [20]. Cyclodextrins have been reported to form inclusion complexes with PCBs and PAHs [21]. Moreover, their hydrophilic periphery is highly convenient for the removal of such organic compounds from aqueous media [22]. The synthesized nanomaterial exhibited

high removal efficiency toward PCB (>95%) at an adsorbent content of 0.04 g/L for 50 h contact and equilibrium time [20]. This indicates that this nanocomposite has a very high adsorption capacity toward PCB, and it is pH-independent.

A significant study done by Mahdavian and Mousavi studied the removal of PCBs by using single-walled carbon nanotubes [23]. The results showed a complete removal of PCB at ambient conditions. Results also show that the increased diameter in the armchair SWCNTs improves the detection and degradation potential of the tube to PCBs [23].

An interesting study done by Velzeboer et al. compared the sorption of PCBs of fullerenes, MWCNTs, micro-polyethylene, and nano-polystyrene [24]. The results show 3-4 degrees higher sorption of PCBs on MWCNTs than the rest [24]. The more interesting result is that salinity decreases the sorption rate of PCBs on MWCNTs [24].

A study done by Paszkiewicz et al. showed that helical multi-walled carbon nanotubes exhibit high sorption abilities, up to 99%, toward PAH removal at very low concentrations [30].

A relatively novel material used in this field is graphene oxide. It has gained significant attention due to its unique properties, especially the fact that it can be functionalized by different groups [29]. Most uniquely, it possesses surface O-functionalities which help it maintain stability whilst maintaining its hydrophilicity under common environmental conditions [31]. Moreover, colloidal graphene oxide proves to be a good contaminant carrier [32].

A study done by Ren et al. (2018) explored the adsorption characteristics of sulfonated graphene (SG) for a widespread PCB called PCB28 [33]. Adsorption isotherm of PCB28 to SG fitted best with the Langmuir model and the Polanyi-Dubinin-Manes (PDM) model, with the maximum adsorption capacity (Q_{max}) calculated as around 530 mg kg⁻¹ [33]. This suggests that PCB28 might be mainly adsorbed to SG in the monolayer through a strong π - π conjugation interaction between the benzene ring of PCB28 and the benzene skeleton of SG [33, 34]. The efficiency can also be attributed to the large surface area of the material [6]. However, it was found that the adsorption is temperature dependent; lower temperatures favour adsorption [35].

Tian et al. studied a hybrid of graphene oxide (GO) and amino-functionalized polypropylene nonwoven graphene oxide (PP-g-DMAEMA/GO) with a dual-scale channel structure, for fast removal of PCB from water [36]. The intertwined structure of PP-g-DMAEMA/GO with many channels allows for smooth water permeation and efficient capture of organic pollutants in both batch and filtration processes. [36]. The PP-g-DMAEMA/GO obtained can retain 74.3% of GO's adsorption performance, indicating that both sides of GO provide accessible binding sites. [36]. This structure also achieved more than 85% removal of PCB from water with a concentration of 1 mg/L of PCB [6, 36]. The kinetics fit pseudo-first-order kinetics and the material could easily be recovered by simply washing it with an ethanol solution [36].

Iron-based nanomaterials are usually found naturally in the environment. Due to their size, they show high adsorption [37] and selectivity [38]. Thus, they can be used in settings of wastewater management. A variety of iron nanoparticles are used for bioremediation, namely zero-valent iron nanoparticles, iron hydroxide nanoparticles, iron ox-hydroxide nanoparticles, and iron oxide nanoparticles [44]. Overall, the action of iron nanoparticles can be classified into two mechanisms – adsorption and photocatalysis.

Adsorption involves electrostatic interactions, ligand-ion interactions, and other forces due to which wastewater pollutants can bind to iron NPs [45]. More notably, iron NPs (FeNPs) synthesized using green methods show adsorption via redox, complex formation, and ion exchange tendencies towards pollutants [46, 47].

Iron-oxide nanoparticles (IONPs) act as strong adsorbents due to their small size, higher surface area and sorption sites, and the ability to tune their surface chemistry for enhanced selectivity [38]. Core-shell IONPs consist of an iron core and an organic, inorganic or both organic and inorganic shell. The choice of materials for the shell depends upon its application. The shell tailoring allows for the development of nanocomposite materials that have a high affinity for specific contaminants and can be readily used in the environment [38].

Phenolic compounds within water sources are deemed extremely harmful due to them causing changes within endocrine functions [41]. Moreover, the cause of human disorders due to these compounds can be chalked to their biorefractory and hydrophobic properties [42]. In a study, Zhou et al. synthesized a dual-responsive nanomaterial with ultrafine Fe@SiO₂ as a magnetic core and poly(N-isopropylacrylamide) (PNIPAM) as a thermosensitive outer shell [43]. The results showed that the high adsorption rates were due to the hydrophobic effect, hydrogen-bonding interaction, and electrostatic attraction. The adsorption process followed a pseudo-second-order kinetics model and nonlinear isotherms, indicating that it was a heterogeneous adsorption process. When using Fe@SiO₂@PNIPAM, the adsorption efficiency of 4-NP was more than 90% within 2 hours under optimized conditions. The maximum adsorption amounts were found to be 2.43 mg/g for BPA, 6.83 mg/g for TBBPA, 24.75 mg/g for 4-OP, and 49.34 mg/g for 4-NP [43].

Owing to the high efficacy of iron-based nanoparticles in the context of nanobioremediation, extensive research has been carried out into green synthesis methods for synthesizing these nanoparticles. Plant-mediated preparation of iron nanoparticles is inexpensive and eco-friendly. A study done by Devatha et al. shows the synthesis of FeNPs along with capping molecules via extracts of leaves from *Mangifera indica*, *Murraya koenigii*, *Azadiracta indica* and *Magnolia champaca* [48]. Moreover, these nanoparticles were tested for simultaneous removal of total phosphates, ammonia nitrogen, and chemical oxygen demand. Among the different plant-mediated synthesized FeNPs, *Azadiracta indica* FeNPs showed the removal of 98.08% phosphate, 84.32% ammonia nitrogen and 82.35% chemical oxygen demand removal. Another study conducted by Shah et al. showed the successful synthesis of iron nanoparticles using *Spinacia oleracea* (spinach) extract [49]. The COD has reduced from 405 mg/L

to 85 mg/L and the BOD reduced from 56 mg/L to 22 mg/L [49].

This proves the strong efficacy of the adsorption mechanism of iron-based nanoparticles in the context of wastewater management. We shall discuss the photocatalytic mechanism of iron nanoparticles in the upcoming section.

Nanomaterials employing photocatalysis for bioremediation

Photocatalysts are outstanding materials that can easily alter solar energy for use in oxidation and reduction activities. These materials have attracted great interest because of their potential for eliminating toxic and dangerous compounds from the environment.

Heterogeneous photocatalysis is a process that involves diverse chemical reactions initiated by a photocatalyst in a different thermodynamic phase than the reactants, it requires semiconductors with broad light absorption, suitable energy band positioning, and long charge carrier diffusion paths. Achieving these in semiconductors is challenging [70, 71]. Photocatalytic materials, illuminated with light-balancing valence and conduction bands during the photolysis process, create electronic holes that combine with organic pollutants, producing reactive oxygen species. The size of nanoparticles is crucial in photocatalysis, with water molecules capturing holes generated by electron-hole pairs. The release of hydroxyl radicals (OH^\cdot) from water molecules enables the degradation of various microbial cells and organic pollutants.

Environmental concerns have elevated due to newly emerging pollutants in water resources and rising levels of air contaminants. Aromatics, dyes, phenols, insecticides, pesticides, solvents, and numerous other organic pollutants with possibly cancer-causing intermediates have become much more prevalent in natural resources because of the development of industrialization. Aquatic and human life are at risk due to the widespread pollution of water caused by wastewater from a variety of industries, including food packaging, leather tanning, textiles, and dye manufacturing that uses organic dyes [73-75]. As such, eliminating these organic-coloured dye compounds before release into the environment represents a significant challenge for researchers across the globe [72]. Water bodies receive approximately 10% to 15% of the coloured dyes released. Because of the increased turbidity and decreased penetration of sunlight, this poses a threat to marine life [73]. Synthetic dyes are used to permanently colour fabrics because they are resistant to chemicals, perspiration, sunlight, and other factors. Most synthetic dyes used in the textile industry are azo dyes, which make up 70% of them. Reactive azo dyes are dyes with heterocyclic rings that substitute halogens and create a covalent bond with the cellulose's functional groups. Due to their electronegative nature, these reactive dyes undergo nucleophilic substitution. After reactive dye hydrolyzes and becomes resistant to chemical, physical, and environmental agents, this attack results in the fixation on fabric [76].

TiO_2 is the most widely used photocatalyst, and it is used in the majority of published research on the subject. Because of its large bandgap energy (3.2 eV), the particle must be excited by UV light to cause charge separation. In the study by

Muniandy et al. [77], TiO_2 nanoparticles were produced using a green chemistry technique in ideal circumstances, and they demonstrated a successful photodegradation of Methylene Blue solution in the presence of sunlight. Using a low-temperature precipitation method, titanium tetraisopropoxide (TTIP) as the precursor, water as the solvent, and starch as the template, active mesoporous anatase TiO_2 NPs with small crystallite size (9 nm) were successfully synthesized. The prepared TiO_2 photocatalyst's photocatalytic activities were assessed using a 6 ppm aqueous solution of methylene blue (MB). The optimum condition for photodegradation of MB solution at 6 or 10 ppm MB solution is by using 0.1 g TiO_2 NPs synthesized using 0.01 mol TTIP under basic conditions. Besides, synthesized TiO_2 NPs revealed high stability against the photodegradation process as they can be recycled for up to 10 cycles [77].

The synthesis of TiO_2 nanoparticles by chemical and environmentally friendly methods using ethanol and jasmine flower extract is reported in another intriguing work [78]. The nanoparticles are spherical, in the rutile phase, and range in size from 31 to 42 nm on average. They exhibit strong antibacterial activity against both gram-positive and gram-negative bacteria as well as high photocatalytic activity for the degradation of methylene blue. The performance of the green-synthesised nanoparticles is superior to that of the chemically-synthesised ones. TiO_2 nanoparticles show promise for use in biomedical and environmental applications [78].

Using mulberry plant extract as a bio-reductant, this work reported a straightforward and environmentally friendly method to create TiO_2 nanoparticles with an anatase phase and wide bandgap [79]. With a 96% removal efficiency in 120 minutes, the TiO_2 nanoparticles demonstrated exceptional photocatalytic activity for the degradation of methylene blue. Additionally, the nanoparticles showed excellent stability and five cycles of reusability [79].

The use of green synthesized silver nanoparticles (AgNPs) has also gained significant attention in various fields due to their unique properties and potential applications in bioremediation. Using the fruit extract of *Crataegus pentagyna* as a reducing and capping agent, Ebrahimzadeh et al. [80] synthesized silver nanoparticles (AgNPs) by the green synthesis method to degrade the organic contaminant dyes in wastewater. Green synthesized silver nanoparticles were used under various conditions to eliminate organic dyes. The test results demonstrate that, in the presence of sunlight, the CP-AgNPs eliminate organic contaminant dyes with degradation efficiencies of 85, 70, and 78%, respectively, for rhodamine b (Rhb), eosin (EY), and methylene blue. These findings demonstrated that CP-AgNPs have a great deal of potential for photocatalytic activity-based organic pollutant degradation [80].

Silver nanoparticles produced by *Terminalia bellirica* have numerous biological uses and pose no environmental risks. This article reports on the biological synthesis, photocatalytic, and antibacterial activities of silver nanoparticles made from an ethanolic extract of the fruit *Terminalia bellirica* [81]. The synthesis of silver nanoparticles is characterized by UV-Vis spectroscopy and diffraction light scattering. Using UV-Vis

spectroscopy, the photocatalytic degradation of methylene blue is assessed. To identify antibacterial activities, the disc diffusion method is applied. The ethanolic extract of *T. bellirica* fruit was used to create silver nanoparticles, which demonstrated strong antibacterial and photocatalytic properties. The study's findings demonstrated the value of nanobiotechnology in water purification [81].

A green synthesis of silver nanoparticles made from extracts from the leaves of *Moringa oleifera* and *Cadiospermum halicacabum* has been reported [82]. Because silver ions are reduced to silver nanoparticles when exposed to sunlight, it is visible as a colour change. A UV-Vis spectrophotometer was used to examine the same. The distinct phases and structural characteristics of the synthesized nanoparticles were examined using XRD and SEM analyses. With the aid of FTIR, the functional group was located. Using methylene blue dye degradation as a model for photocatalysis, the generated nanoparticles yielded 92.7% after 48 hours of exposure [82].

To develop efficient and scalable methods for the controlled synthesis of zinc nanoparticles, unlocking their full potential for diverse applications. Researchers are investigating novel techniques tailored to the unique characteristics of zinc, such as its reactivity and potential for alloy formation.

Another study reports the green synthesis of ZnO nanoparticles (ZnNPs) using aqueous *Cassia fistula* plant extract as fuel by solution combustion synthesis [83]. The NPs were evaluated for photodegradative, antimicrobial, and antioxidant activities. The extract was found to contain reducing components such as polyphenols (11%) and flavonoids (12.5%). The NPs were found to have a hexagonal wurtzite structure. UV-visible absorption of ZnO NPs showed an absorption band at 370 nm which can be assigned to the intrinsic band-gap absorption of ZnO due to the electron transitions from the valence band to the conduction band. Synthesis of multifunctional ZnO NPs using naturally occurring plant products has been advocated as a possible environment-friendly alternative to chemical methods [83].

Utilizing jackfruit extract, a straightforward combustion process was used to create the ZnO nanoparticles at 400°C [84]. An X-ray diffraction (XRD) pattern showed that the nanoparticles were crystalline. The produced nanoparticles were further characterized using Raman spectroscopy, BET surface area, and scanning electron microscopy (SEM). Moreover, it has been employed as a photocatalyst in the breakdown of methylene blue dye, an organic pollutant. This technique is a more environmentally friendly way to create ZnO nanoparticles with strong photocatalytic activity [84].

The properties of ZnO nanoparticles produced by environmentally friendly synthesis (biomediated methods in microwave irradiation) were investigated in another work [85]. Extracts from *Saponaria officinalis* were utilized in the green nanochemistry synthesis of ZnO as capping and reducing agents. Although the plant extract is not effective in converting zinc precursor in ZnO nanoparticles at a rate that is acceptable without additional thermal processing, it may be used as a capping and structuring agent. The photocatalytic effect of as-synthesized flower-like ZnO nanoparticles was

assessed using the MB degradation process under UV light. Based on their size and morphology, the ZnO nanopowders demonstrate good degradation activities in an aqueous solution of MB. ZnO nanoflowers made without a capping agent had the maximum photocatalytic performance (42%) after 40 minutes of exposure to light, while the addition of CTAB or *S. officinalis* extracts resulted in a decrease of degradation efficiency to 33% and 21%, respectively [85].

Nanomembranes and bioremediation

Nanomembranes are effective methods in modern water treatment technology that effectively remove hazardous materials such as organic, inorganic, and biomedical pollutants and heavy metals. Membrane filtration segregates particles according to their concentration, pressure, size, and pH [86]. The filtration mechanism can be improved by modifying the membrane with chemical solutions. The membrane comprises a precise porous surface, which is important in eliminating heavy metals from polluted water. The materials that make up nanomembranes are divided into two categories - polymer and ceramic. Because of its hydrophobic capacity, ceramic membranes are preferred over polymer membranes for treating industrial effluent. Polypropylene, polyethylene, and polyvinylidene fluoride materials are commonly used in polymeric membranes due to their hydrophobic nature and ability to foul easily [87].

This treatment is a promising technology because it is simple to use, efficient, and requires little space. It also eliminates supplementary organic elements and suspended solids. Organic matter (OM) and dissolved organic matter (DOM) are two major membrane exits. Pretreatment of DOM effluent is recommended to improve membrane performance and remove OM. These methods can grasp the full volume of aqueous liquid for heavy metal elimination [87].

To attain the highest possible separation efficiency membranes should have high permeability, high surface porosity, good pore structure, hydrophilicity, and antifouling properties. Membrane fouling has been the main issue with the filtration process. The hydrophobic surface of the membrane is the source of this issue, which over time causes the permeate flux to decrease and the pressure to rise. Reducing the issue of surface fouling can be achieved by improving the hydrophilicity of the membranes. In this context, it is common practice to employ the following methods: embedding of metal or inorganic particles, incorporating hydrophilic components, and hydrophilic membrane modification [88].

While membranes are recognized for their sustainability owing to low energy consumption, the emphasis now is on how important it is to use green fabrication techniques when creating membranes.

A study conducted by Szekely et al. reports on the fabrication of high-performance Thin Film Composite (TFC) membranes solely from sustainable resources, such as plant-based monomers (priamine, tannic acid), green solvents (p-Cymene, water), and recycled polymer waste (PET) [89]. Unlike conventional TFC membranes produced from petroleum-based materials, this approach aims to minimize energy consumption. The ultrathin selective layer (30 nm) of the

hydrophobic membrane exhibits excellent performance, achieving acetone permeance of up to $13.7 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ with a 90% rejection of styrene dimer (235 g mol^{-1}). Furthermore, the membranes display stability in six solvents and sustain long-term continuous nanofiltration over one week, demonstrating their robustness. Control over membrane selectivity (cut-off between 236 and 795 g mol^{-1}) is successfully achieved by adjusting the conditions of interfacial polymerization [89].

In a different analysis authored by Oh and Bang et al. [90], a polyphenol-based loose nanofiltration membrane was developed successfully through a combination of blending and interfacial coordination strategies. The method involved introducing an iron ion complex into a Polyether sulfone (PES) membrane using the non-solvent induced phase separation (NIPS) technique, with Tannic acid (TA) coordinating with Fe^{3+} to form the loose separation layer. The thickness of the TA layer was adjusted by varying the TA assembly time. Incorporating TA improved surface hydrophilicity and introduced a negative charge. The optimized membrane, assembled for 3 hours (PES/Fe-TA3h), exhibited a pure water flux of $175.8 \text{ L m}^{-2} \text{ h}^{-1}$, along with high dye rejections of 97.7%, 97.1%, and 95.0% for CR, MB, and EBT, respectively, and salt penetration rates exceeding 93.8% for Na_2SO_4 , MgSO_4 , NaCl, and MgCl_2 at 0.2 MPa. Additionally, the PES/Fe-TA3h membrane demonstrated stable dye rejection and salt permeation over a 24-hour continuous test period, with a high FRR of 90.3%, 87.5%, and 81.6% for CR, EBT, and MB, respectively. This study presents a novel approach to fabricating loose nanofiltration membranes for efficient dye and salt fractionation in saline textile wastewater.

Another eco-friendly approach studied involves the development of biopolymeric nanofibrous membranes inspired by fish skin for oil-water separation. These membranes utilize fish gelatin, which is water-soluble and has a low gelation temperature, making it suitable for electrospinning. The process achieves high efficiency, with a maximum flux of $2086 \text{ L m}^{-2} \text{ h}^{-1}$ and over 99% separation efficiency for suspended and emulsified oil. Moreover, the approach employs sustainable practices, including eco-friendly crosslinking methods and gelatin derived from fish waste, thereby enhancing biodegradability and reducing environmental impact [90].

Moreover, within the context of sustainable practices, we explore the composition of starch. It elucidates the presence of two distinct macromolecules - amylose, characterized by linear α -D-glucopyranosyl units linked by α -1,4 bonds, and amylopectin, which comprises highly branched α 1,4-linked glucan chains connected by α -1,6 linkages. It serves as a major energy reserve in a wide range of higher green plants. Starch-based biodegradable plastics are economically viable, abundant, and renewable biomaterials extensively utilized in biomedical and disposal applications. Chemical or physical modifications of starch-based materials are often explored to understand degradation kinetics and enhance drug delivery. In vitro enzymatic degradation using fungal amylase is employed to hydrolyze starch films of various molecular, crystalline, and granular types to investigate the impact of different structures on enzymatic degradation [91-93].

2. Conclusion

Bioremediation is the need of the hour with concerning reports regarding the continuous degradation of the environment. However, conventional methods of bioremediation possess technical disadvantages that can be overcome by using nanotechnology. This review covered different strategies using nanomaterials to eliminate pollutants from air and water. The two mechanisms covered were (1) sorption and (2) photocatalysis. These methods overall showcase an enhanced efficacy towards the elimination of various pollutants and prove to be viable options for future research in the field of nanobioremediation.

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