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A Synthesis of Biogenic Nanoparticles (NPs) for the Treatment of Wastewater and Its Application: A Review

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Abstract: Nanoscience is a rapidly growing science stream that has been one of the cost-effective and energy-efficient approaches with wide applications. Water pollution is a major issue that is increasing continuously due to anthropogenic activities and several organic and inorganic contaminants. To overcome this issue, nanoparticles (NPs) have been successfully used to treat water. These NPs possess many beneficial applications in many fields like agriculture, cosmetics, photoconductors, environmental biotechnology, glass and alloy production, solar cells, nanomedicine and drug deliveries, biosensors, food industries, etc. The properties comprising high surface area, greater chemical reactivity, and mechanical properties play a vital role in imparting such beneficiary properties. As a result, there has been an increasing demand for the synthesis of NPs. However, excess usage of NPs further creates toxic by-products. Therefore, scientists and researchers are now focussing on the biogenic synthesis of NPs. The biological routes of NP synthesis have been crucial because they are eco-friendly and environmentally safe. This chapter highlights the usage of different approaches and biogenic sources for the production of NPs. It also discusses the recent advancement in the use of biogenic NPs with respect to applications for wastewater treatment.

Keywords: nanoparticles (NPs); biogenic/green synthesis; wastewater treatment; water pollutants

1. Introduction

In recent years, the escalating global concern over water pollution has driven intensive research into novel and sustainable solutions for wastewater treatment. Among these solutions, the synthesis of biogenic nanoparticles (NPs) has emerged as a promising avenue of exploration. Nanomaterials (NMs) are substances with at least one dimension as ≤100 nm. They could be of various shapes which are particles, tubes, rods, and fibres. Nanoparticles (NPs) are categorized into four types. These are: (1) inorganic (2) organic (3) carbon-based and (4) composite-based (Bhardwaj *et al.*, 2022a). Various R&D and industries have focussed on the synthesis of NPs for many purposes. The synthesis of NPs broadly follows two approaches: a top-down approach, and a bottom-up approach (Baig *et al.*, 2021). During the process of the top-down approach, the bulk materials are divided to produce nanostructured substances; while during the process of the bottom-up approach, NPs are synthesized by means of chemical reactions involving atoms/ions/molecules (Singh *et al.*, 2020; Baig *et al.*, 2021). There have been few studies that have reported the side effects and challenges due to excessive NPs usage (Buzea *et al.*, 2007; Verma and Kumar, 2019). The conventional routes of NPs synthesis have been observed to be associated with hazardous and volatile chemicals; thus NPs further create secondary pollution (Gautam *et al.*, 2019). For example, use of chemicals like sodium borohydrate

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($NaBH_4$), hydrazine hydrate (N_2H_4), amines (RNH_2), and thiols (R–SH) during the synthesis of NPs have been utilized as agents for reduction, capping and stabilization. These chemicals have also been reported to be causing hazardous impacts on the environment and the health of living beings (Hannah and Thompson, 2008). Toxic hydrazine compounds have been reported to cause disruption to the aquatic ecosystem, while affecting organs and body systems like liver, central nervous system (CNS), kidneys, and cardio-vascular system of animals (Oh and Shin, 2015).

Studies have, therefore, now focussed on the biosynthesis of NPs using plants, microbes, etc. Biogenic NPs are synthesized using biological organisms. Such organisms could be cultured easily and have high metal uptake intracellularly. The metabolic activities of such microorganisms enable extracellular/intracellular synthesis of NPs utilizing a different route of synthesis (Khan and Jamil Khan, 2017). The biogenic methods provide an ecological and economically feasible way and replace the hazardous chemicals used with the natural products (Vaseghi *et al.*, 2018). These natural compounds such as amino acids, classes of vitamins, polyphenols, carbohydrate moieties, etc. are derived from plants, and microbes like bacteria, fungi, yeast, etc. The synthesis, processing and application of biogenic NPs have been considered to be safe, simple, cost-effective, sustainable as well as eco-friendly techniques for fabrication of NPs that would comply with "green chemistry" objectives (Iravani and Varma, 2020). These biogenic NPs have been observed to exhibit remarkable efficiency in removing a wide range of contaminants, including heavy metals, inorganic pollutants, pharmaceutical residues, and organic compounds. According to the study of Klaus-Joerger and team, the usage of biological organisms to be utilized as potential bio-nano factories has been a novel approach for the production of various nano-sized particles (Klaus-Joerger *et al.*, 2001). For example, a cadmium sulfide nanoparticle (CdS-NPs) of the dimension range of 20-200 nm were produced inside the cells of *Klebsiella aerogenes* bacterium. Similarly, gold (Au) and silver (Ag) nano-sized particles were amalgamated by using *Verticillium* sp. and fungus *Fusarium oxysporum*, and Ag nanocrystals of specific size and morphology were amalgamated by using *Pseudomonas stutzeri* bacterium (Klaus-Joerger *et al.*, 2001).

Previous research studies have been carried out to tackle water pollution problems using NPs as they possess beneficial properties like high surface area, high chemical reactivity, low cost, lesser energy, effectively regenerating for reusage (Gautam *et al.*, 2019). The applications of biogenic NPs for treatment of wastewater have been a rapid escalating area of research. A study reported tin oxide-NPs (SnO_2-NPs) were synthesized from bacterial biomass *Escherichia. harbicola* effectively sequestrate dyes such as methylene blue, erichrome black T, methyl orange, from samples of wastewater through the process of photocatalytic degradation (Srivastava and Mukhopadhyay, 2014). Similarly, a study comprised of removing 98 % of toxic organic dyes bromophenyl blue within approx. 12 minutes of treatment of Ag-NPs of size 8-10 nm which were synthesized using aqueous extract of *Cercidiphyllum japonicum* (Khan *et al.*, 2016). Similar works have been carried out with marine algae (*Lemanea fluviatilis)*, it can biosynthesised Au-NPs of size 5.9 nm and these NPs have been utilised for water purification (Rauwel *et al.*, 2015; AlNadhari *et al.*, 2021). Plant extracts of *Mentha spicata* L. have been used to synthesize iron-nanoparticles (Fe-NPs) of size 20-45 nm that effectively sequestered arsenic (As III & V) from wastewater (Prasad *et al.*, 2014). Similarly, the leaves of mango (*Mangifera indica)*, have been used to biosynthesize polycrystalline Fe-nanorods that effectively treated 38-49 % of heavy viscosity of oil (Al-Ruqeishi *et al.*, 2019).

Such studies have highlighted the successful applications of biogenic NPs for treatment of wastewater. This review provides an insight about biosynthesis of various NPs using plants, bacteria, fungi, yeast, and its potential applications for wastewater treatment. This synthesis aims to provide an in-depth exploration of biogenic NP synthesis techniques, their applications in wastewater treatment, and the challenges and opportunities inherent in their commercialization. By delving into the cutting-edge research and potential of biogenic NPs, we embark on a journey towards cleaner and more sustainable water resources for our planet. The authors have suggested some recommendations for successful application of biogenic NPs for wastewater remediation purposes.

2. Routes of Synthesis of Biogenic Nanoparticles (NPs)

Many physical, biological, and chemical techniques have been studied and employed to synthesize NPs. Biological techniques utilize plants, bacteria, fungi, yeasts, and viruses to synthesize metal as well as metal-oxide NPs (Akhtar *et al.*, 2013). The brief procedure of biosynthesis of NPs has been depicted in Figure 1.

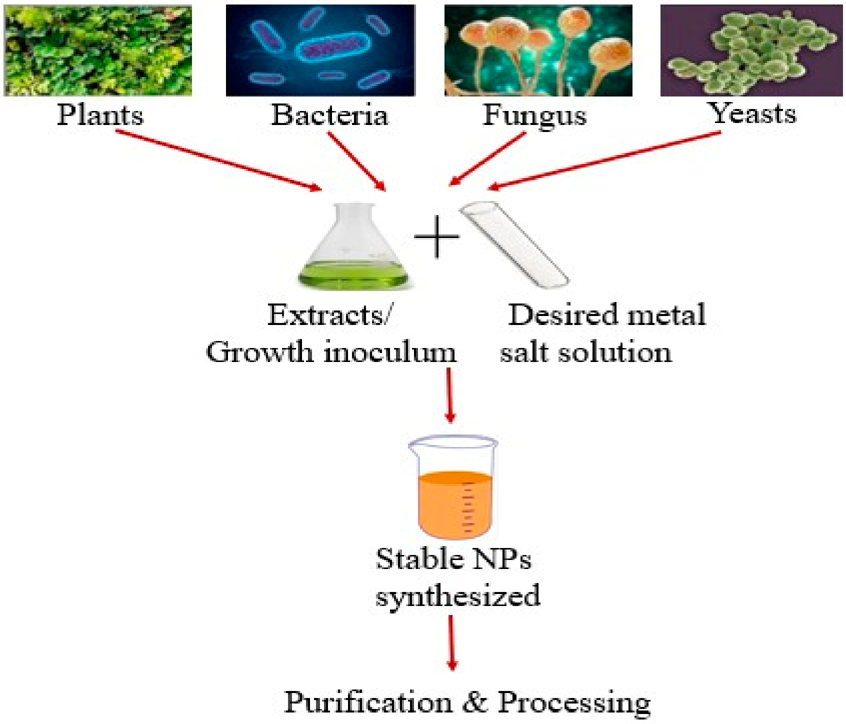

Figure 1: Procedure for Synthesis of Biogenic Nanoparticles (NPs)

2.1. Plants

As an eco-friendly and reliable method of synthesis of NPs, plants have successfully been explored for quick and extracellular bio-synthesis of metal-NPs such as Au- and Ag-NPs (Akhtar *et al.*, 2013). Synthesis of NPs of platinum (Pt), palladium (Pd) has been synthesized using the extracts of various parts of different plant species. Sugar-derived moieties undergo cross-coupling reactions in the presence of isopropanol under controlled thermal and microwave heating conditions to yield metal-NPs. Addition of 5 mol % (or calculated as mole fraction of a compound multiplied to 100 times) of glucose into the above reaction mixture leads to an increase in yield of the products (Camp *et al.*, 2014). A recent study has highlighted the synthesis of Ag- and Au-NPs from extracts of lemongrass leaf. For example synthesis of Au-NPs by using leaves/stem extracts of *Hyptis capitata* with aqueous tetrachloroaurate ($AuCl_4^-$) ions (Revathy *et al.*, 2022). Similarly, Ag-NPs were prepared using 10 mL of the leaf extract with 90 mL of aqueous silver nitrate ($AgNO_3$) solution and subjecting to microwave irradiation (Revathy *et al.*, 2022). Stable and crystalline Au-NPs (16-40 nm) were synthesized by exposing the aqueous extracts of the leaves of geranium and fruit extracts of amla (*Embalica officinalis)* with $AgNO_3$ solution (Tu *et al.*, 2022). Similarly, leaf extracts of tamarind, neem (*Azadirachta indica)*, geranium, aloe vera have been observed to reduce Au ions into Au-NPs, and Ag ions into Ag-NPs (Jannathul Firdhouse and Lalitha, 2022).

2.2. Microorganisms

Researchers are focussed on synthesis of NPs using microbial sources and have emerged as a promising field in nanobiotechnology. Microorganisms, like bacteria, fungi, yeasts and viruses, have been studied to possess intra- and extra-cellular potentiality to produce metal-NPs and are therefore considered as bio-factories (Zambonino *et al.*, 2023). Biosynthesis of NPs by using microbes is a rapid,

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multistep, and comparatively costlier process as it includes microbial isolation, culturing process, and maintenance, etc.

2.2.1. Bacteria

Bacterial cells have been studied to possess properties related to biomineralization, bioaccumulation, bioleaching, etc. The biotransformation of metals by bacteria has been observed by researchers and has generated interest in fabrication of NPs using bacteria (Ramanathan *et al.*, 2013; Bhardwaj *et al.*, 2019). A study conducted on *Lactobacillus* sp. and *Sachharomyces cerevisae* successfully synthesized titanium nanoparticles (Ti-NPs) of size 8-35 nm under controlled pH, partial pressure of hydrogen gas, and redox potential possessed by culture solutions (Jha *et al.*, 2009). Biosynthesis of NPs of Pd, Ag, Fe, cobalt (Co), rhodium (Rh), nickel (Ni), Pt, lithium (Li), etc. has been achieved using the bacterial strain *Pseudomonas aeruginosa*. To obtain respective NPs, the species were grown under static conditions in uniform solutions of 0.001 M of sodium tetrachloropalladate (Na_2PdCl_4), $AgNO_3$, iron(III)nitrate ($Fe(NO_3)_3$), cobalt(II)chloride hexahydrate ($CoCl_2.6H_2O$), rhodium sodium chloride ($Na_3RhCl_6.2H_2O$), nickel(II) chloride hydrate ($NiCl_2.6H_2O$), ammonium hexachloroplatinate ($(NH_4)_2PtCl_6$), and lithium chloride (LiCl) (Srivastava and Constanti, 2012).

Similarly, bacterial species like *E. coli*, *Staphylococcus aureus*, Enterobacteria, *P. stutzeri*, *Geobacter metallireducens* GS-15, etc have been reported to synthesise metallic-NPs of various sizes (Mandal *et al.*, 2006; Narayanan & Sakthivel, 2010; Jiang *et al.*, 2020). For example *E. coli* K-12 strain was utilized for synthesizing Au-NPs that were used for catalytically degrading 4-nitrophenol pollutants from water bodies (Srivastava *et al.*, 2013). A study established a simple method for synthesizing Au-NPs from *Aspergillum* sp. WL-Au strain was incubated with different concentrations of chloroauric acid ($HAuCl_4$) in phosphate-buffered saline (PBS) systems at 30°C, 150 rpm for 7 days (Zhang *et al.*, 2021).

2.2.2. Fungi

Myco-nanotechnology has been used for synthesizing NPs from kingdom fungi. Fungi possess diversity, tolerance to high metals, ability to accumulate metal ions, etc. (Moghaddam *et al.*, 2015). Mechanisms of biosynthesis of NPs are intracellular/extracellular. During intracellular mechanisms, metal precursors are mixed with fungal culture. It then gets internalized by biomass and is synthesized. The NPs are subsequently extracted using chemical treatments, centrifugation, and filtration, etc. (Molnár *et al.*, 2018). During extracellular synthesis, desired metal precursors are mixed with aqueous filtrate that consists of fungal biomolecules, which results in formation of free-formed NPs in dispersion/solution (Costa Silva *et al.*, 2017; Gudikandula *et al.*, 2017).

Filamentous fungus, *Verticillium* sp., *Fusarium oxysporum*, etc. have been utilized for the biosynthesis of metallic NPs, such as Ag-NPs of dimensions 25±12 nm. This was achieved by growing the biomass in respective metallic ion solutions (Priyabrata Mukherjee *et al.*, 2001). Similarly, *Aspergillus fumigatus* has been used for synthesizing zinc oxide nanoparticles (ZnO-NPs), and *Rhizopus*, *Fusarium*, *Schizophyllum radiatum*, *Candida albicans*, etc. have been used for synthesizing Au- and Ag-NPs (Moghaddam *et al.*, 2015; Naraian and Abhishek, 2020). Nicotinamide adenine dinucleotide (NADH) as well as its dependent enzymes such as nitrate reductase have been studied to be one of the key steps in biosynthesis of metallic-NPs (Baymiller *et al.*, 2017). The proposed method includes pathways of NADH dependent reductases along with shuttle quinone extracellular procedures. It was reported that depending upon the quantity of NADH formed, the synthesis of alloy of Au-Ag NPs with a variety of compounds was possible (Mubarakali *et al.*, 2012; Bhardwaj and Naraian, 2021). The size of NPs formed has been observed to be dependent on synthesis conditions like fungal species used, temperature, pH, dispersion medium, etc. (Lee and Jun, 2019).

2.2.3. Yeast

Marine yeast species *Yarrowia lipolytica* has been observed to biosynthesize Au-NPs upon exposure to chloroauric acid ($HAuCl_4$) (Agnihotri *et al.*, 2009). In another study, a marine yeast strain *Rhodosporidium diobovatum* has been studied to synthesize lead sulphide nanoparticles (PbS-NPs) of size 2–5 nm with a ratio of 1:2::Pb:S (Seshadri *et al.*, 2011). Various strains of *Saccharomyces* genus have been used to synthesize NPs of zinc sulfide (ZnS), Ag, and titanium dioxide (TiO_2) (Sandana Mala and Rose, 2014). Research conducted by Venkat and team successfully synthesized intracellular phytochelatin-coated cadmium sulphide nanoparticles (CdS-NPs) of size 50-60 nm by using *C. albicans* and CdS solution. The synthesized CdS-NPs showed antibacterial activities against bacterial species *Salmonella typhi* and *S. aureus* (Kumar *et al.*, 2019). Biogenesis of selenium nanoparticles (Se-NPs) was obtained using yeast derived extracts of *Magnusiomyces ingens* LH-F1 by growing it in 2 mM SeO_2, 500 mg/L protein at pH 7 (Lian *et al.*, 2019). *Saccharomyces cerevisiae* has been studied to synthesize NPs of ZnS, TiO_2, CdS, using solutions of zinc sulphate ($ZnSO_4$), titanic acid ($TiO(OH)_2$), cadmium chloride ($CdCl_2$) with hydrogen sulfide (H_2S) respectively (Patel *et al.*, 2021). Another study was conducted on baker's yeast *S. cerevisiae* biosynthesized Ag-NPs of size 3-60 nm using cell extracts. The synthesized Ag-NPs were observed to possess antimicrobial activities against pathogens such as *E. coli*, *S. aureus*, *P. aeruginosa*, *Bacillus subtilis*, *C. albicans* (Bhardwaj *et al.*, 2022b; Salem, 2022).

3. Applications of Biogenic Nanoparticles (NPs) for the Treatment of Wastewater

Biogenic NPs have broad applications in context to chemical engineering, manufacturing of textiles, tissue engineering, clinical diagnostics (nanobots), nanomedicines, electronics, as well as organ implantations (Santhoshkumar *et al.*, 2011) biosensors (Probin Phanjom *et al.*, 2012), biological imaging (Nagaraj *et al.*, 2021), biomarkers, cell labelling, etc. (Le *et al.*, 2011; Singh and Nalwa, 2011). Gautam and team studied the removal of inorganic/organic pollutants, pharmaceutical pollutants, and toxic heavy metals found in wastewater by using biogenic NPs (Gautam *et al.*, 2019; Singh *et al.*, 2021). The diagrammatic representation of the use of NPs for the treatment of wastewater is shown in Figure 2.

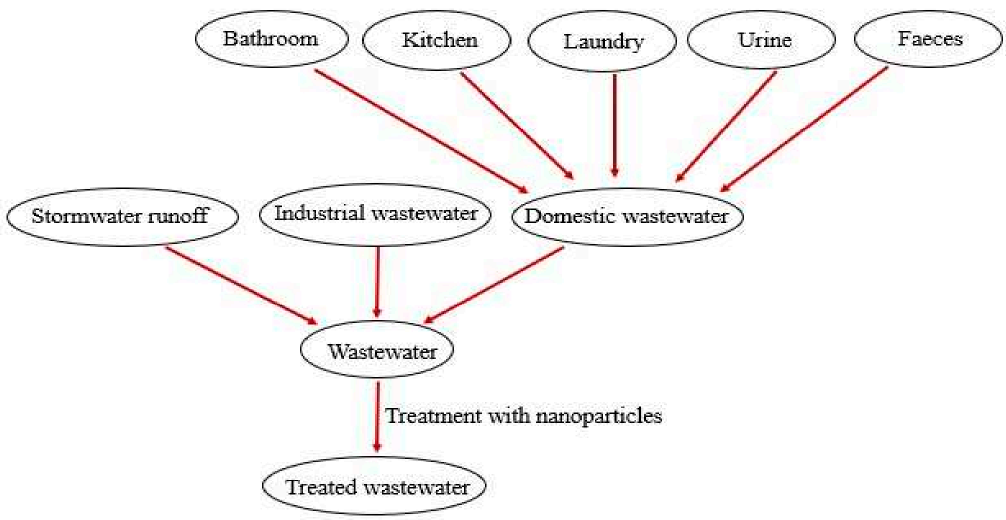

Figure 2. Use of Nanoparticles (NPs) for the Treatment of Wastewater

3.1. Removal of Organic Pollutants

Due to the expansion of urbanization, and the activities of industries and agriculture, water is polluting (Gupta *et al.*, 2023). Organic pollutants are made up of mostly carbon and hydrogen. These pollutants are pesticides, insecticides, synthetic dyes, polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), as well as phenols (Lapworth *et al.*, 2012). Persistent organic pollutants (POPs) are harmful in nature and have been reported as hazardous to the environment (Bhardwaj and Jindal, 2019; Bhardwaj *et al.*, 2020; Bhardwaj *et al.*, 2021). These organic pollutants enter aquatic bodies through agricultural runoff, industrial effluents, as well as sewages of domestic sectors. After that these pollutants enter the food chain and accumulate in the tissue of aquatic plants and animals and then human beings.

Nanotechnology (NT) is an emerging technique for the removal of various pollutants from different commodities (Bhardwaj et al., 2022a). Nano-adsorbents, nano-films, as well as nano-catalysts are NT based products that are used to remove organic pollutants. Wastewater contaminated with monochlorobenzene, for example, was treated using degradation techniques based upon fenton like oxidation that were mediated by Fe-NPs that were simultaneously reduced or capped by polyphenols from tea (Kuang *et al.*, 2013). Research showed synthesis of Fe and Fe/Pb bi-metallic NPs using tea extracts. The formed NPs are sized between 20-30 nm (Smuleac *et al.*, 2011). The NPs were used for eliminating highly toxic pollutants, trichloroethane (TCE) from wastewater through the reductive degradative mechanisms. Biogenic Ag nanocatalysts have substantiated their potency in removing/degrading many organic pollutants. Besides Ag, and other biogenic NPs have also been studied for their effectiveness in disassembling some toxic organic contaminants found in wastewater (Smuleac *et al.*, 2011).

Photo-catalytically removing naphthalene found in aqueous phase was carried out using biologically fabricated NPs doped with Fe and Zn (Muthukumar *et al.*, 2017). The photo-catalytic efficiencies of Fe/Zn-NPs were observed to be superior as compared to Zn-NPs. Aqueous extracts of fungal strains *Trichoderma viride* and *Hypocrea lixii* were utilized for synthesizing extracellular Au-NPs for treating 4-nitrophenol present in wastewater (Mishra *et al.*, 2014). Au-NPs were used to convert 4-nitrophenol into 4-aminophenol. A research study developed biocompatible Au-NPs from *Aspergillum* sp. for effectively removing the presence of aromatic water pollutants such as *o*-nitroaniline, 2-nitrophenol, *m*-nitroaniline 3-nitrophenol, and 4-nitrophenol (Qu *et al.*, 2017).

Arora and team studied phenolic pollutants and their toxicity and stated that they are carcinogens and can damage the liver as well as red blood cells (RBCs) (Arora *et al.*, 2014). After interaction with the microorganisms, they may generate other compounds that could be similarly toxic to the original compound. Wang and team described the mechanism of the production of manganese oxides (BioMnOx) nano-biocomposite from green algal species *Desmodesmus* sp. WR1 and reported that it is helpful for removing bisphenol from samples of wastewater (Wang *et al.*, 2017). A study reported synthesizing manganese nanocatalysts using manganese (Mn)-oxidizing bacterial species *Pseudomonas* sp. G7 and it is helpful in the oxidative degradation of 2,4-dichlorophenol, 2,4,6-trichlorophenol, and 2-chlorophenol (Tu *et al.*, 2015). A list of different sources of biogenic NPs which were used in various applications have been highlighted in Table 1.

Table 1. Different Sources (Bacteria/Fungi/Algae) of Biogenic Nanoparticles (NPs) with their Applications

S. No.	Biogenic Sources (Bacteria/Fungi/Algae)	Nanoparticles (NPs)	Applications	References
		Bacteria		
1	*Lactobacillus kimchicus*	Gold	Drug delivery, cancer diagnostic	Mathivanan *et al.*, 2019
2	*Staphylococcus epidermidis*		Catalysts	Pantidos and Horsfall, 2014
3	*Paracoccus haeundaensis*		Antioxidants	Srinath and Rai, 2015
4	*Cupriavidus* sp.	Silver	Antibacterial	Markus *et al.* 2016
5	*Bacillus subtilis*			Patil *et al.*, 2019
6	*Staphylococcus aureus*	Zinc oxide		Rauf *et al.*, 2017

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7	*Bacillus subtillis*		Synthetic dyes	Dhandapani *et al.*, 2020
8	*Bacillus* sp.	Nanoselenium	Biomedical	Bharathi *et al.*, 2020
9	*Desulfovibrio vulgaris*	Platinum and palladium	Catalysts	Martins *et al.*, 2017
		Fungi		
10	*Aspergillus niger*	Iron oxide	Wastewater treatment	Mughal *et al.*, 2021
11	*Aspergillus terreus*	Silver	Antibacterial, anticancer	Hulikere and Joshi, 2019
12	*Cladosporium cladosporioides*		Antioxidant, antimicrobial	Zhang *et al.*, 2020
13	*Aspergillus niger*	Copper	Antidiabetic and Antibacterial	Zhang *et al.*, 2019
14	*Mariannaea* sp. HJ	Selenium	Medicinal and electronics	Vijayanandan and Balakrishnan, 2018
15	*Aspergillus nidulans*	Cobalt oxide	Energy storage	Joshi *et al.*, 2017
16	*Cladosporium cladosporioides*	Gold	Antioxidant, antimicrobial	Bhargava *et al.*, 2016
17	*Cladosporium oxysporum*		Catalysis	Srivastava *et al.*, 2019
18	*Fusarium oxysporum*	Platinum	Nano medicine	Chatterjee *et al.*, 2020
		Algae		
19	*Botryococcus braunii*	Silver	Catalysis	Manikandakrishnan *et al.*, 2019
20	*Portieria hornemannii*		Antibacterial	Arya *et al.*, 2019
21	*Colpomenia sinuosa* and *Pterocladia capillacea*	Iron oxide		Colin *et al.*, 2018
22	*Caulerpa racemosa*	Gold	Biomedical	Salem *et al.*, 2019
23	*Egregia* sp.			Gonzalez-Ballesteros *et al.*, 2017
24	*Cystoseira baccata*		Cancer	Mourdikoudis *et al.*, 2018

3.2. Removal of Pharmaceutical Pollutants

Several pharmaceutical compounds such as hormones, antibiotics, endocrine disrupting compounds (EDCs), and steroids might create problems for the health of the wildlife and humans if these compounds enter in the water supply system (Kim *et al.*, 2007). Malik and team suggested the nano-based approach for the removal of these compounds (Malik *et al.*, 2017). A team led by Forrez developed biogenic bio-palladium (Bio-Pd) and manganese oxides (BioMnOx) which were nano-sized particles and are being use for removing different pharmaceutical compounds from wastewater (Forrez *et al.*, 2011). There are various pharmaceutical pollutants that were reported in sewage runoff and were successfully removed by BioMnOx-MBR like diclofenac (86 %), triclosan (78 %), iopromide

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(68 %), codeine (93 %), clarithromycin (75 %), N-acetyl-sulfamethoxazole (92 %), sulfamethoxazole (52 %), diuron (94 %), mecoprop (81 %), iomeprol (63 %), naproxen (95 %), ibuprofen (95 %), iohexol (72 %), and chlorophene (89 %) (Forrez *et al.*, 2011). Martins and team synthesized bio-Pd and bio-Pt using *Desulfovibrio vulgaris* for the removal of 17 β-estradiol, ciprofloxacin, and sulfamethoxazole (Martins *et al.*, 2017).

De Corte and team synthesized bio-Pd-NPs from the metal-reducing bacteria and used in the treatment of diclofenac-bearing water (De Corte *et al.*, 2012). De Gusseme and team synthesized Pd-NPs using *Shewanella oneidensis* for the removal of Diatrizoate from the effluent (De Gusseme *et al.*, 2011). Au/Pd nanocatalyst was prepared using *S. oneidensis* and used to purify trichloroethylene and diclofenac contaminated water (De Corte *et al.*, 2012). De Corte and team reported that bio-Au and bio-Pd nano catalysts are failed to remove the pollutants individually while the combined effectiveness of Au and Pd nano catalysts was notable and remove > 78 % of pollutants (De Corte *et al.*, 2012). Furgal and team synthesized Bio manganese oxide nanoparticles (MnO_2-NPs) using *P. putida* for the elimination of various micropollutants from aquatic samples (Furgal *et al.*, 2015). Xu and team studied the combined effectiveness of bio-synthesized Pd-NPs, that were chemically developed MnO_2, and iron oxide (Fe_3O_4) NPs for degrading various pharmaceutical pollutants (Xu *et al.*, 2018).

3.3. Removal of Inorganic and Radioactive Pollutants

Due to several nuclear activities, the aquatic bodies have been contaminated by radioactive waste. These wastes may pollute the surface water as well as ground water through leaching from mines and run off from nuclear reactors and nuclear power plants. These wastes can cause chronic and acute toxic effects on living beings (Gawande and Jenkins-Smith, 2001). Researchers studied the contamination level in the PET bottled drinking water and lake water (Bhardwaj and Sharma, 2021; Bhardwaj, 2022). Handley-Sidhu and team developed biogenic hydroxyapatite materials (Bio-HAPs) using *Serratia* sp. for the remediation of such waste (Handley-Sidhu *et al.*, 2011a). The remediation efficiency of Bio-HAP for strontium (Sr^{2+}) was higher than commercial HAP. Bio-HAP-NPs successfully scavenged some biohazard materials such as Sr, Co, uranium (U), and europium (Eu) from samples of groundwater (Handley-Sidhu *et al.*, 2014). Handley-Sidhu and team used Bio-HAP-NPs (20 to 90 nm) for the elimination of Sr^{2+}, Co^{2+}, etc from the water (Handley-Sidhu *et al.*, 2011b). The surface area of Bio-HAP-NPs was found to be more than commercial HAP-NPs. Bio-HAP-NPs with a size < 40 nm and a surface area > 70 m^2g^{-1} showed greater removal of radioactive waste. It was stated that calcium ions (Ca^{2+}), magnesium ions (Mg^{2+}), and sodium ions (Na^+) showed a minimal impact on removing the ability of Bio-HAP-NPs. Nano-scale Bio-HAP-NPs was also described for the elimination of radionuclides from the water (Gangappa *et al.*, 2017). Choi and team synthesized biogenic Au-NPs (Bio-Au-NPs) using a bacterial species, *Deinococcus radiodurans* for eliminating radioactive iodine ($^{125}I^-$) (Choi *et al.*, 2017).

Nitrate (NO_3^-) contamination in samples of water is a serious problem because of its great solubility and persistent nature. Higher concentrations of NO_3^- can cause methaemoglobinaemia, malformations in congenital, and cancers (Fewtrell, 2004). NO_3^- can enter water bodies through agricultural activities and cause eutrophication which is harmful to aquatic ecosystems (Camargo *et al.*, 2005). A research study stated that various nanotechnological approaches are present to remove the contamination of NO_3^- from samples of wastewater (Tyagi *et al.*, 2018). Wang and team studied the batch adsorption method and synthesized iron nano adsorbents from extracts of eucalyptus leaves and green tea (Wang *et al.*, 2014). Copper nanoparticles (Cu-NPs) synthesized from the flowers extract of *Hibiscus sabdariffa* and were impregnated with activated carbon which was prepared using the biomass of babassu coconut. These carbon complexes were utilized for removing NO_3^- at varying temperatures (Paixão *et al.*, 2017). The capacities of adsorption of the nano-carbon complexes were expected by Langmuir and Freundlich isotherm and were superior than simple activated carbon. Katata-Seru and team synthesized eco-friendly Fe-NPs from the leaf and seed of *Moringa oleifera* for the elimination of NO_3^- from the ground water and surface water samples (Katata-Seru *et al.*, 2017).

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Phosphorus (P) is also known to cause eutrophication by promoting algal growth. Yong and team synthesized hydroxyapatite crystalline nano material using *Serratia* sp. for the remedy of phosphate (PO_4^{3-}) present in wastewater (Yong *et al.*, 2004). Cao and team synthesized Fe-NPs treated with a cationic surfactant (CTAB) from Eucalyptus leaf extract for the elimination of PO_4^{3-}. The PO_4^{3-} elimination efficiencies of CTAB-coated NPs were higher as compared to uncoated NPs (Cao *et al.*, 2016). Gan and team reported the efficient elimination of PO_4^{3-} via Fe_3O_4-NPs which were synthesized from the extract of Eucalyptus leaf (Gan *et al.*, 2018).

3.4. Removal of Heavy Metals

Heavy metals are well acknowledged for their toxic effect on human health and the environment. Lead (Pb), mercury (Hg), nickel (Ni), arsenic (As), cadmium (Cd), and chromium (Cr) are extremely toxic and poisonous due to their affinity for bioaccumulation (Chipasa, 2003; Sadre Alam *et al.*, 2023; Bhardwaj *et al.*, 2023a; Bhardwaj *et al.*, 2023b). Domestic and industrial effluents, agricultural run-off, and acid mine drainage are the main contributors to heavy metals pollution of the aquatic environment. Mukherjee along with team synthesized Fe_2O_3-NPs by using *Aloe vera* leaves extract for the removal of As from the aqueous phase (Mukherjee *et al.*, 2016). A study organically synthesized magnetic Fe_3O_4-NPs from tea waste for the elimination of As (III) and As (V) (Lunge, Singh and Sinha, 2014). Martinez-Cabans and team manufactured Fe_3O_4-NPs by using eucalyptus extract for the elimination of As from the wastewater (Martínez-Cabanas *et al.*, 2016). Andjelkovic and team extracted Fe_3O_4 nanowires from a chemoautotrophic bacteria *Mariprofundus ferrooxydanson* for the removal of As (V) and As (III) (Andjelkovic *et al.*, 2017).

Cr is well acknowledged for its lethal effects on living beings. Rao and team synthesized Fe-NPs using *Punica granatum* extract for eliminating Cr (VI) from the wastewater. The NPs surface was altered by two strains (NCIM 3590 and NCIM 3589) of yeast and *Yarrowia lipolytica* used for the removal of Cr (VI) present in aqueous solution (Rao *et al.*, 2013). Fe-NPs sized between 50-80 nm were synthesized using the leaves extract of Eucalyptus for eliminating Cr (VI) from samples of wastewater (Madhavi *et al.*, 2013). Fe-NPs were synthesized using the extracts of fruit and plant (eg: *Mentha spicata*, *P. granatum*, *Syzygium aromaticum, and Camellia sinensis*) for the elimination of Cr (VI) from the aqueous phase (Mystrioti *et al.*, 2016). Xiao and team reported that the sorption of Cr was greater in acidic medium because of the charge on the surface of Fe-NPs (Xiao *et al.*, 2016). Lingamdinne and team synthesized Fe-NPs from the seed extract of *Cnidiummonnieri* (L.) Cuss for eliminating Pb (II) and Cr (III) from the aqueous medium (Lingamdinne *et al.*, 2017).

Cd toxicity in water may be the source of itai-itai and other medical or health concerns by damaging the normal acting of the cardiovascular system, liver, and kidney (Nordberg, 2004). Biogenic NPs have been extensively used to clean the water from toxicity of Cd. Raj and team synthesized CdS-NPs from a marine bacterium *P. aeruginosa* JP-11 for the elimination of Cd from samples of wastewater (Raj *et al.*, 2016). Another study reported the elimination of Cd from the aqueous phase through the Fe-NPs which were synthesized from the extract of tangerine peel (Ehrampoush *et al.*, 2015).

Some heavy metals like Zn and Cu are considered micro-nutrients but they may become poisonous for aquatic life and humans at high concentration. Jain and team reported biogenic Se-NPs by mixing and incubating Se with cultured anaerobic sludge for minimizing Zn (II) in samples of wastewater (Jain *et al.*, 2015).A team led by Kandasamy, synthesized biogenic Fe-NPs from *Streptomyces thermolineatus* for the elimination of Cu ions from the effluents of the pigment industry (Kandasamy, 2017). A group of researchers engineered Se-NPs from bacterial extracellular polymeric substances (EPS) for removing elemental Hg from groundwater (Wang *et al.*, 2018). Srivastava and team synthesized MgO-NPs by utilizing biocompatible acacia gum for eliminating Cd (II), Mn (II), Pb (II), Ni (II), Zn (II), Cu (II), and Co (II) from synthetic wastewater (Srivastava *et al.*, 2015). Zhou and team informed the synthesis of BMO-NPs by using *P. putida* MnB1 for removing Zn (II), Cd (II), as well as Pb (II) (Zhou *et al.*, 2018).

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4. Conclusions and Future Recommendations

The escalating and persistent increase in water body pollution, stemming from various organic and inorganic pollutants, is a growing source of concern. Novel technologies have been extensively researched to combat water pollution, with a particular focus on wastewater treatment. Traditional methods of NP synthesis often involve the use of volatile and hazardous chemicals, leading to the generation of secondary pollution. Consequently, there is a strong emphasis on exploring the biogenic synthesis of NPs, known for their environmental safety and cost-effectiveness. Biogenic NPs are synthesized using natural compounds such as carbohydrates, polymers, proteins, flavonoids, alkaloids, polyphenols, and more, sourced from fungi, plants, yeast, and bacteria. These compounds have demonstrated their efficacy as stabilizing and capping agents during NP synthesis. This study highlights the significance of and recent advancements in biogenic NP synthesis. It explores various biosynthesis routes utilizing plants, bacteria, fungi, and yeast, showcasing the potential applications of these NPs in wastewater treatment. Biogenic NPs show promise in the removal of heavy metals, inorganic and radioactive pollutants, pharmaceutical residues, and organic contaminants from wastewater. While this field of research is rapidly expanding, the commercial application of these techniques remains underexplored. Challenges, primarily related to cost-effectiveness, hinder their large-scale implementation for wastewater purification. Additionally, there is a pressing need to develop modified NPs that are more efficient, easily manageable, sustainable, and environmentally friendly. In summary, the rise in water pollution necessitates innovative solutions. Biogenic NPs, synthesized from natural compounds, hold great potential for addressing this issue. Although their applications in wastewater treatment are still emerging, their environmental benefits are substantial. However, scaling up and commercializing these techniques present challenges that must be addressed to fully harness their potential for sustainable water purification.

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