



Biogenically synthesized nanoparticles in wastewater treatment; a greener approach: a review

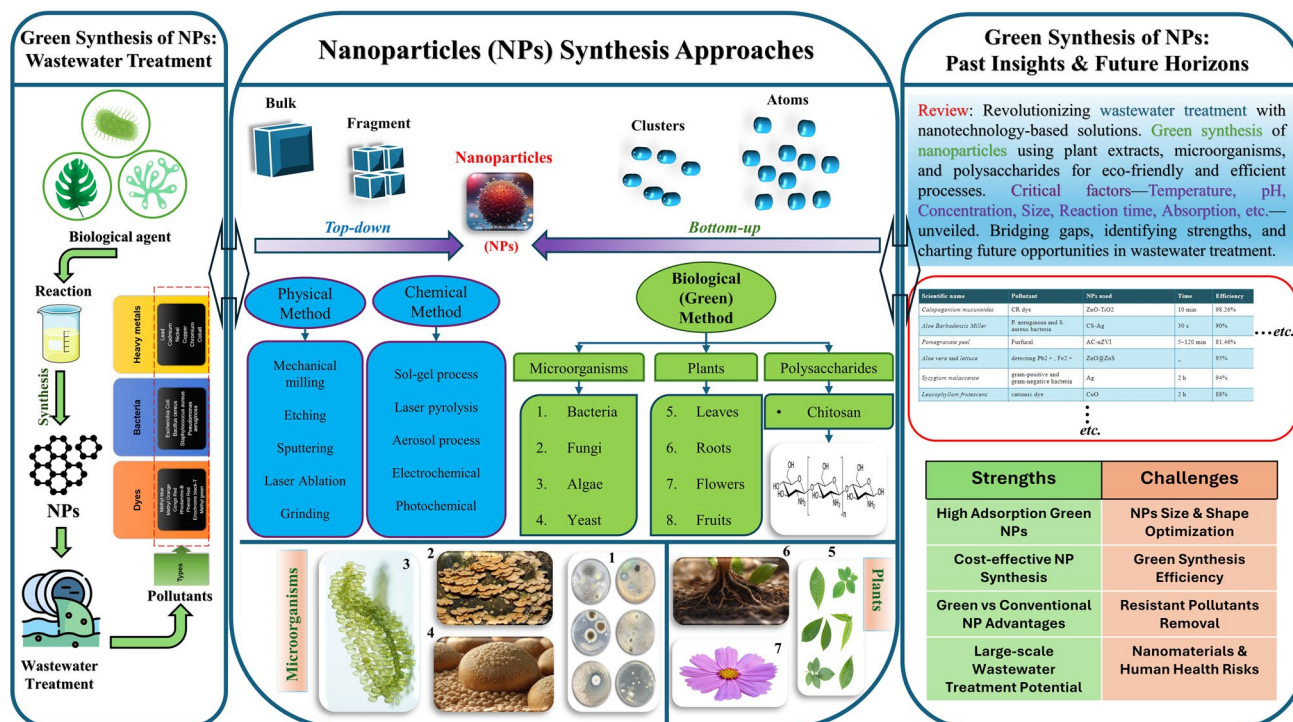
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Abstract

Water resources have been continuously polluted by various wastewaters and cause many risks for humans and living organisms. One of the wastewater treatment solutions is nanotechnology-based approaches that enable wastewater treatment through efficient, flexible, multi-purpose, and cost-effective processes compared to conventional methods. Green synthesis is an environmentally friendly way to produce nanoparticles (NPs), which use biological materials to synthesize. Therefore, using plant extracts, microorganisms, and polysaccharides as stabilizing and reducing agents in the green synthesis of NPs can be an essential component of wastewater treatment in the future. However, there is a gap in the comprehensive review of the biogenic synthesis of NPs in wastewater treatment. In this review, previous research on green synthesis using various plant extracts, microorganisms such as fungi, bacteria, microalgae, and polysaccharides, especially chitosan, were investigated in the treatment of various wastewaters. Factors such as temperature, pH, concentration, and reaction time played a crucial role in the synthesis of NPs, which were investigated separately. Finally, after a complete review of the studies and receiving the strengths and weaknesses of each method, future challenges and opportunities are discussed.

Graphical abstract



Keywords Wastewater treatment · Green synthesis · Microorganism · Plant extract · Polysaccharides

Introduction

Water is the most commonly debated issue on the planet, as it is one of the most necessary prerequisites for the existence of all living forms and the most crucial natural resource for human civilization since ancient times. One of the fundamental concerns of modern society is the constant availability of clean and safe water (Ojha et al. 2021; Zubair et al. 2020). Population growth, economic development, and industrialization contribute to the continued use of hydrological resources worldwide (Gupta et al. 2020; Olvera et al. 2017). Many inorganic pollutants (toxic heavy metals including arsenic, lead, mercury, and cobalt) and organic contaminants (dyes, pesticides, and other items) are produced as a result of anthropogenic causes (González-Poggini et al. 2021; Ghosh et al. 2017; Zunita 2021; Kommu and Singh 2020; Sirés et al. 2014; Ibrahim et al. 2020). The various sources of water pollutants range from industrial wastes to domestic, agricultural, and sanitary effluents, which typically contain dyes, oil, fertilizers, pesticides, pharmaceutical wastes, and other chemicals, affecting water quality (Ojha et al. 2021). Considering the importance of water and its pollution, there are various solutions for water and wastewater treatment, among which nanotechnology is one of the most efficient methods.

Nanotechnology refers to creating new materials on a 1–100 nm scale. Nanotechnology is the synthesis and utilization of minimal materials at the nanoscale for biochemistry, biology, material science, and engineering applications (Gebre and Sendeku 2019; Das et al. 2018; Salem and Fouda 2021). Nanoparticles (NPs) play crucial roles in many critical technologies, including water quality, electronics, biomedical research, mechanics, drug delivery, chemical industries, water treatment, and wastewater treatment. Based on their composition, they are generally divided into three categories: organic, carbon-based, and inorganic NPs. Organic NPs are composed of organic compounds such as carbohydrates, lipids, and polymers. Carbon-based NPs are those NPs that are composed of carbon atoms, and their types include fullerenes, carbon black NPs, and carbon quantum dots (CQD). Inorganic NPs, such as metal and ceramic NPs, include NPs that are not made of carbon or organic materials (Joudeh and Linke 2022). Each of these NPs has wide applications depending on their characteristics.

Nanotechnology's water purification techniques are ideal for delivering highly efficient, flexible, and multifunctional processes that enable high-performance and cost-effective wastewater treatment (Akharame et al. 2021, 2018). Many

researchers and scientists have shown significant interest in their unique characteristics and discovered that they have remarkable uses in various sectors. However, many NPs have exhibited toxicity at the nanoscale. Because of the toxicity, nanotechnology and green chemistry are combined to create environmentally benign NPs using plants, microorganisms, and other natural resources (Sabouri et al. 2022a, b; Sabouri et al. 2022a; Sabouri et al. 2020a, b; Jadoun et al. 2021; Lateef et al. 2016). Researchers have devised several synthetic methods for NPs that have revealed a significant advantage for the environment through clean, nontoxic, and ecologically friendly “green chemistry” processes, including bacteria, fungus, and plants (Duan et al. 2015; Jadoun et al. 2021). NPs synthesized through physical and chemical methods have many losses, and their production is not economically viable. For instance, chemical processes may produce incomplete surface structure materials. Therefore, using biological and green methods is considered an efficient solution (Roy et al. 2013).

The selection of a green solvent, a suitable reducing agent, and a safe substance for stabilization are the three most important parameters for the synthesis of NPs (Nath and Banerjee 2013; Jadoun et al. 2021). Fungi, algae, bacteria, and plants can be used to carry out this synthesis. Plant parts, including leaves, fruits, roots, stems, and seeds, have been employed to synthesize different NPs due to the presence of phytochemicals in their extract that function as a stabilizing and reducing agent (Narayanan and Sakthivel 2011; Razavi et al. 2015; Jadoun et al. 2021). Silver, gold, zinc, titanium, copper, alginate, and magnesium metal NPs have been produced by various microorganisms, mainly bacteria and fungi (Fouda et al. 2017; Salem and Fouda 2021).

Several researchers have investigated the application of biogenic synthesis of NPs in wastewater treatment. They have used green synthesis methods using various plant extracts, microorganisms, and polysaccharides and have investigated the influencing factors in the synthesis. Despite many valuable studies, there is no study that evaluates different methods of biogenic synthesis in the treatment of various types of wastewater. Therefore, this review fills the existing gap in the comparison of different biogenically synthesized NPs in wastewater treatment and points out the advantages and disadvantages of each method. This review first deals with types of wastewater (“Wastewater” section) and synthesis techniques (“Synthesis techniques” section); then, it explains three main categories of green synthesis: microorganism-based (“Microorganism-based synthesis of NPs” section), plant-based (“Plant-based synthesis of NPs”

section), and polysaccharide-based (“Polysaccharide-based synthesis of NPs” section) synthesis of NPs. Since biogenically synthesized NPs are a novel approach in wastewater treatment, “Future challenges and prospective” section describes its future challenges and prospects.

Wastewater

Access to clean water is the most basic human need for health and well-being. Today, the water demand is increasing due to rapid population growth, urbanization, and the development of agriculture, industry, and energy, which continuously pollutes water resources. According to the UNSDG report, it is expected that by 2030, all humans will have fair access to safe drinking water, the release of hazardous chemicals to water sources will be minimized, and the proportion of untreated wastewater will be halved (Sachs et al. 2022). Achieving this goal is not possible unless using green chemistry and synthesis.

Hazardous pollutants such as metal ions, toxic dyes, and bacteria are the main cause of water pollution. Figure 1 shows the types of pollutants in wastewater and their effects and diseases on humans (Baig et al. 2021). Among contaminants, heavy metals are the most critical water pollutants such as Ni, Cr, Zn, Cu, Pb, Co, Hg, Mn. Also, the role of dyes such as methyl orange (MO), methylene blue (MB), and Rhodamine B (RhB) in polluting water has been strongly identified because they play an important role in

various textiles, food, plastic, etc. Approximately 15% of the used dyes are released into water resources after the completion of the process and product production, and due to their aggressive behavior, they produce highly toxic substances (Singh et al. 2018). These materials come from different sources such as urban and agricultural wastes, dye industries, plastic, fossil fuels, etc. (Zhang et al. 2012). Therefore, to have sustainable development and meet basic needs, special attention should be paid to the treatment of existing wastewater with the most optimal methods. Various methods have been used in wastewater treatment, but researchers are trying to find the most optimal ways. They have presented the principles of green synthesis, which must be followed (Fig. 2) as a new approach to preparing affordable, accessible, environmentally friendly filters, as well as with an easy preparation method (Gałuszka et al. 2013). Many studies have been conducted in recent years that have shown the ability of different parts of plants, microorganisms, and polysaccharides, especially chitosan, in wastewater treatment (Tables 1, 2 and 3). The results of the studies show that these green agents are widely used in the green synthesis of processes for removing various organic dyes and heavy metals due to their availability and cheapness. In addition, short reaction time, high efficiency, and reaction in different acidic conditions have made them popular in wastewater treatment. Tables 1, 2, and 3 show a summary of reaction conditions, efficiency, mechanism of treatment, and pollutants removed in wastewater treatment using biogenic synthesis.

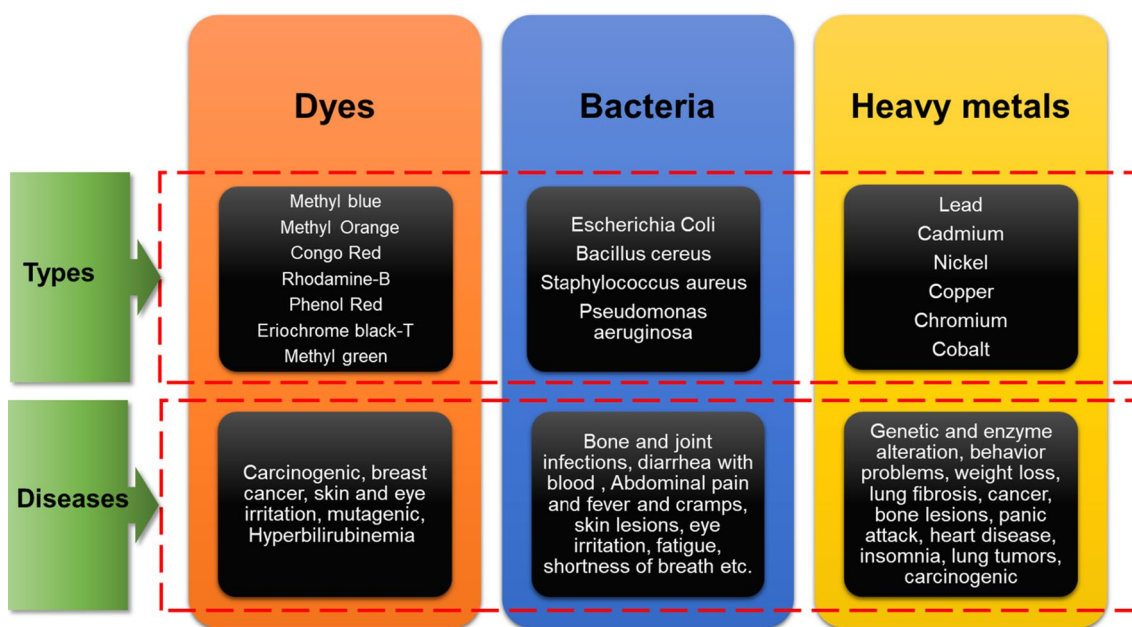


Fig. 1 Hazardous contaminants in wastewater and their effects and diseases (Baig et al. 2021)

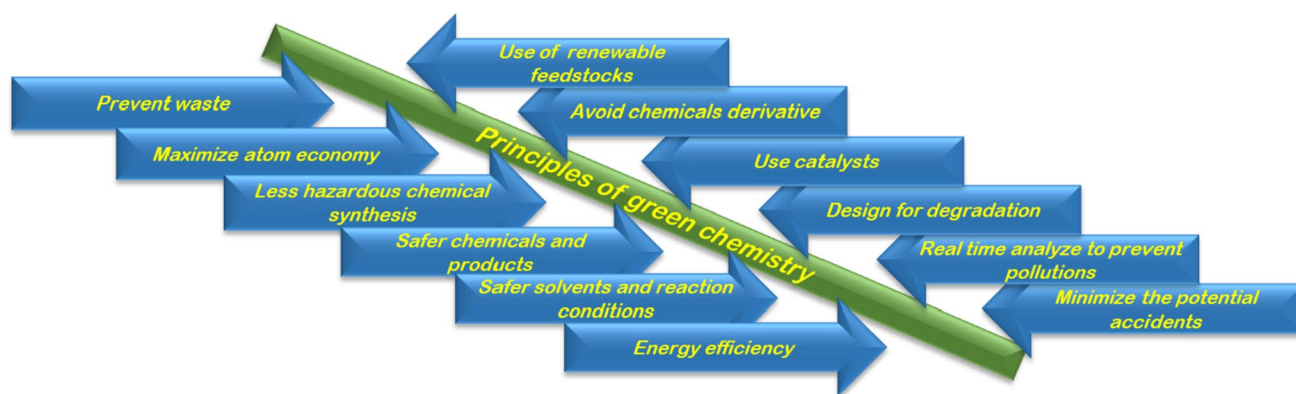


Fig. 2 The principles of green chemistry

Table 1 A brief summary of microorganism-based synthesis of NPs characterization, treatment techniques, and pollutant(s) removed

Scientific name	Pollutant	NPs used	Time	Efficiency	pH	Mechanism of treatment	References
Sludge	Cr(VI)	Fe/Al/Si-bearing oxyhydroxides	–	99.50%	7	hydrolysis process	(Ri et al. 2022)
<i>Lemanea manipurensis</i>	RhB, MO, and MB	MnO ₂	30 min	92%	5	photocatalyst	(Borah et al. 2022)
<i>Shewanella oneidensis MR-1</i>	Cr(VI)	Pd(II)	10 min	97%	2.36	catalytic	(Y. Zhang et al. 2022)
Tea polyphenols-NZVI (TP-NZVI/PE)	nitrate	nZVI	–	79.88%	5	membrane bio-reactor (MBR) filtration	(Zhou and Li 2022)
<i>Bacillus subtilis</i>	Azo dyes	ZnO	18 h	Chemically synthesized: 89.55–88.52% and biosynthesized: 18.46–21.41%	–	decolorization (nanobioremediation processes)	(Swain, Kulkarni, and Manuel 2022)
<i>Purpureocillium lilacinum</i>	dye	CuO	2 h	57.5–63%	9	photocatalytic dye degradation	(Hammad et al. 2021)
<i>Letendreaea</i>	toxic organic pollutants, MO, RhB, and MB	Ag	3–16 min	95.83–98.96%	–	degradation, antioxidant, antibacterial and catalytic activities	(Qiao et al. 2022)
<i>Ulva lactuca</i> and <i>Halopteris scoparia</i>	pathogenic bacteria and fungi	Ag	60 min	reduction between 15 and 21.33 mm in pathogenic fungi growths	11	antibacterial and antifungal activities	(Koçer and Özçimen 2022)
Silver NPs	RhB, MO, and MB	Ag	3–9–16 min	94.94%	–	antioxidant, antibacterial and catalytic activities	(Qiao et al. 2022)
antimicrobial chitosan derivatives	–	Ag	30 min	–	wide range	antimicrobial chitosan	(Abu Elella et al. 2022)

Table 2 A brief summary of plant-based synthesis of NPs characterization, treatment techniques, and pollutant(s) removed

Scientific name	Pollutant	NPs used	Time	Efficiency	pH	Mechanism of treatment	References
<i>Calopogonium mucinoides</i>	CR dye	ZnO-TiO ₂	10 min	98.26%	–	photodegradation	(Rusman et al. 2022)
<i>Aloe Barbadosensis Miller</i>	<i>P. aeruginosa</i> and <i>S. aureus</i> bacteria	CS-Ag	30 s	90%	–	filtration	(Cortes et al. 2022)
<i>Pomegranate peel</i>	Furfural	AC-nZVI	5–120 min	81.46%	5–12	porous in structure (adsorption)	(Rashtbari et al. 2022a, b)
<i>Aloe vera</i> and <i>lettuce</i>	detecting Pb ²⁺ , Fe ²⁺	ZnO@ZnS	–	95%	4,7,10	reaction between ions and sensor	(Ahmadi Bakhtiari, Abdoos, and Karimzadeh 2022)
<i>Syzygium malaccense</i>	gram-positive and gram-negative bacteria	Ag	2 h	94%	6	photocatalyst	(Herbin et al. 2022)
<i>Leucophyllum frutescens</i>	cationic dye	CuO	2 h	88%	–	photocatalyst	(A. Ahmad et al. 2022)
<i>Cleistocalyx operculatus</i>	RhB	nZVI	30 min	95%	3–7	adsorption	(Le et al. 2022)
<i>Syzygium cumini</i>	RhB	ZnO	50 min	98%	9	Photocatalytic	(Rafique et al. 2022)
<i>eucalyptus</i>	17β-estradiol (E2)	Fe–Ni	30 min	98.30%	6	Adsorption	(Gong et al. 2022)
<i>Walnut peel</i>	Eosin Y and Erythrosine B dyes	ZnO	30 min	95.11 and 98.31%	3	adsorption	(Rashtbari et al. 2022a, b)
<i>muskmelon</i>	RhB	CQD	35 min	99.11%	5	Photocatalytic	(Preethi, Viswanathan, and Ponpandian 2022)
<i>Acacia Concinna</i>	(RB-21) dye	MnO ₂	45 min	98%	3	adsorption	(Patra et al. 2022)
<i>Eucalyptus grandis</i>	(DR80) azo dye	nZVI	3 h	≈ 100%	5.5	photo-fenton process	(Puiatti et al. 2022)
<i>Sapindus mukorossi</i>	MB	ZrO ₂	5 h	94%	10	adsorption	(Alagarsamy et al. 2022)
<i>Crataegus ponicica C. Koch</i>	MB	CaO	20 min	98.99%	9	photocatalytic	(Meshkatalasadat, Zahedifar, and Pouramiri 2022)
waste-tea-leaves	Cr(VI)	graphene oxide iron	36 min	99.95%	4	adsorption (diphenylcarbazide)	(Kabir et al. 2022)
<i>Hordeum vulgare L.</i>	MB	Sr ₂ Fe ₂ O ₅ /Dy ₃ Fe ₅ O ₁₂ (SFO/DFO)	–	82%	–	photocatalytic	(Baladi et al. 2022)
<i>L. lucidum</i>	MB, antibacterial	Ag	120 min	70%	6	ultrasound-assisted adsorption	(Sultan et al. 2022)
<i>Prosopis juliflora (Mesquite)</i>	MB	CuO@AC	15 min	97%	7	adsorption	(Farooq et al. 2022)
<i>Date Palm Pits and Eggshells</i>	MB	ZnO, nanohydroxyapatite (NHAP)	100 min	91%	8	Adsorption and Photocatalytic	(Elsayed et al. 2021)
<i>Eucalyptus Globoulus</i>	MO	CuO	180 min	94.10%	6	adsorption (Batch sorption experiment)	(Alhalili 2022)
<i>P. betle</i>	RR141	NiO	100 min	99%	–	photocatalytic	(Arashdeep Singh et al. 2022)

Table 2 (continued)

Scientific name	Pollutant	NPs used	Time	Efficiency	pH	Mechanism of treatment	References
<i>rice straw ashes</i>	Nitrate		10 min	85–90%	7	adsorption	(Robles-Jimarez et al. 2022)
<i>Tea (Camellia sinensis)</i>	MO and RhB	ZVI	60 min	100% and 66.47%	2	fenton degradation	(Eddy et al. 2022)
graphite-based photo-Fenton nanocatalyst from waste tar	RhB	Fe	120 min	–	4.6	photo-fenton catalytic degradation	(D. Li et al. 2022)
green coffee bean	MB	Ag	12 min	96%	–	catalytic activity	(Kordy et al. 2022)
<i>Vinca rosea</i>	MR, EBT, and MO	Mn + Cu	–	78.54 ± 0.16, 87.67 ± 0.06, 69.79 ± 0.36%	–	photocatalytic	(M. M. Ahmad et al. 2022)
<i>Cucurbita pepo</i>	crystal violet (CV) dye	nitrogen modified carbon dots (NCOs)	180 min	99.90%	–	photocatalytic	(Smrithi, Kottam, and Vergis 2022)
<i>Ligustrum lucidum leaf and wheat straw</i>	Phenol	Ag	90 min	78%	3	sono-adsorption	(Khan et al. 2022)
<i>Callistemon citrinus (bottlebrush)</i>	Cr(VI)	hBN-Fe ₃ O ₄	40 min	99.4%	3	adsorption	(Usman et al. 2022)
<i>papaya fruit</i>	microbiological and bacterial removal	Ag	15 min	–	6.31–6.74	filtration of rainwater with sand coated	(Anoob and Meera 2022)
green tea extracts	17 α -estradiol (α E2)	reduced graphene oxide-based iron (rGO@Fe)	–	99.90%	6	adsorption and Fenton oxidation	(L. Liu et al. 2022)
<i>Phyllanthus Niruri</i>	organic dyes	ZnO	2 h	73.60%	12	dye degradation and antioxidant agent	(Ramesh, Rajendran, and Ashokkumar 2022)
<i>Phlogacanthus turgidus</i>	NiPs and RhB	Ag-Au	less than 1 h	68–86%	–	catalytic reduction and degradation	(Dang et al. 2022)
<i>P Nerium oleander</i>	tetracycline antibiotic (TC)	SiO ₂	40 min	99.56%	5	adsorption	(El Messaoudi et al. 2022)
<i>Centaurea cyanus</i>	ketoconazole	TiO ₂	1 h	98.4%	3.5	degradation	(Azizi, Khodabakhshi, and Jamshidifar 2022)
<i>Rosa indica</i>	hexavalent chromium	FeO	–	98%	–	adsorption	(Prema et al. 2022)
<i>Carallita brachiata</i>	Nitrophenol	Au	50 min	more than 90%	6	catalytic application in the reduction	(Chandren et al. 2021)
<i>Moringa oleifera</i>	bisphenol A	Ag	–	95–97%	7	detection, electrochemical sensor for bisphenol A	(Iaballah, Messaoud, and Dridi 2022)
rice husk	industrial dyes, MB and 4-Nitrophenol	Au	30 min	photodegradation of 26%	2–12	degradation, antibacterial and antifungal inhibition	(Harby, El-Borady, and El-Kemary 2022)
<i>Adiantum C.V</i>	MO and Cr(VI)	CuO	60 min	90–92%	6.1	photocatalytic	(Golabiazar et al. 2022)
<i>pomegranate (Pom), Beta vul-garis (V.B), and Seder</i>	MO	TiO ₂	300 min	80%	6	photocatalytic	(Mousa et al. 2022)

Table 2 (continued)

Scientific name	Pollutant	NPs used	Time	Efficiency	pH	Mechanism of treatment	References
<i>Lactuca Serriola</i>	organic contaminant (Crystal Violet)	Nio-NiO	60 min	95%	-	multiple photodegradation mechanisms photocatalytic and antibacterial	(Ali et al. 2022)
<i>Camellia sinensis</i>	acid violet 7 dye	-	120 min	94.21%	6	chitosan-alginate nanocomposite synthesized catalytic activity	(Namrata Roy et al. 2022)
<i>Terminalia arjuna bark</i>	EBT, MO	CuO	100–80 min	98–90%	2–7		(Kumari, Kaushal, and Singh 2022)
<i>Aloe vera</i>	MV6B, MB	Cu	150 min	93%	135	photocatalytic activities	(Ahmaruzzaman 2022)
<i>Aloe vera</i>	MB	MgO-Ag	25 min	90.18–80.60%	-	photocatalytic and antibacterial activities	(Panchal et al. 2022)
<i>Abelmoschus esculentus (Okra)</i>	MB	TiO2	240 min	89%	8	photocatalyst	(Aslam et al. 2022)
<i>areca nut</i>	dye, polyethylene	ZnO	90 min	-	-	antibacterial, antibiofilm	(Raghavendra et al. 2022)
<i>Eucalyptus citriodora and robusta</i>	-	-	45 min	-	-	green synthesis	(Gonçalves et al. 2022)
<i>Hibiscus sabdariffa</i>	MB	Pt-Pd	180 min	83.46%	7.4	photodegradation	(Seckin et al. 2022)
<i>Rosmarinus officinalis</i>	MB	Fe3O4	120 min	98–99%	7.4–7.9	catalytic degradation	(Darezereshki et al. 2022)
onion peel	MB, congo red dye and Cr(VI)	Fe3O4	240 min	90.67% to 96.75% for Cr(VI), 95.41% to 99.42% for MB dye, and 88.71% to 93.89% for CR dye	2,9,3	adsorption photosynthesis and biodegradation	(Kumar Prajapati and Kumar Mondal 2022)
<i>Ganoderma lucidum mushroom</i>	Fe iii ions	Ag-Au	9 min	95–98%	-	catalytic and antibacterial activity	(Nguyen et al. 2022)
<i>Sarcocornia ambigua</i>	-	ZnO	60 min	-	-	photocatalytic activity	(Belén Perez Adassus, Spetter, and Lassalle 2022)
<i>P. roebelenii</i>	organic pollutant and dust	ZnO	105 min	98%	-	photocatalytic and antibacterial activity	(Aldeen, Ahmed Mohamed, and Maaza 2022)
<i>Scrophularia striata</i>	heavy metal ions	NB	120 min	98.2%	6–7.4	phase inversion method	(Dadari, Rahimi, and Zinadini 2022)
<i>Potato starch-assisted</i>	MB	-	90–180–285 min	93–96–99%	-	visible light photocatalytic degradation	(Chandrika et al. 2022)
<i>Nerium oleander</i>	tetracycline antibiotic	SiO2	40 min	-	5	adsorption using dioxide silicon nanoparticle biosynthesized	(El Messaoudi et al. 2022)

Table 2 (continued)

Scientific name	Pollutant	NPs used	Time	Efficiency	pH	Mechanism of treatment	References
<i>Juncus inflexus</i>	MB	FeO	–	83–80–96%	6	UV–Vis spectroscopy, TEM, DLS, XRD and FTIR	(Swetaleena Mishra et al. 2022)
<i>Xanthan gum (XG)</i>	Malachite green (MG)	ZnO	46 min	99.45%	8	photocatalytic	(Bassi et al. 2022)
<i>Azadirachta indica</i>	MG, MB, MO, and industrial contaminant	MgO	60 min	97%	4	bio-adsorbent	(Sahoo et al. 2022)
<i>Piper longum</i>	amoxicillin and pharmaceutical effluent	ZnO	320–250–220 min	96,69,48%(respectively)	–	photocatalytic	(Asha et al. 2022)
<i>Mimusops elengi</i>	Congo red dye	SnO ₂	80 min	92.1%	7.5	photocatalytic	(Nivetha et al. 2022)
<i>Aqueous quince</i>	Phenol	Co ₀ -4Zn ₀ -6Fe ₂ O ₄	120 min	92.1%	–	adsorption and catalytic applications	(Tatarchuk et al. 2022)
coffee waste (CWE)	2,4 DNA	Ag	42–30 min	94.6–97.7%	–	photocatalytic flow-rate performance, antibacterial activity, and electrochemical investigation	(El-Desouky et al. 2022)

Synthesis techniques

In recent years, much research has been done to synthesize NPs in several ways (Gahlawat and Choudhury 2019; Thakkar et al. 2010). The type of NPs structure depends on the type and method of its production and synthesis. These methods of producing NPs are divided into two general categories, and again, each of these methods ends in more detailed categories (Fig. 3); these two methods are called top-down and bottom-up (Salem and Fouda 2021; Abid et al. 2021). In the first view, as the name implies, “bottom-up” NPs go through a process in which they first assemble the smallest components of an atom and then become nuclei and then NPs, which includes chemical and biological methods. On the other hand, at “top-down” view, NPs are formed by breaking down larger components into smaller ones, which involves the disintegration of the bulk material into smaller components (Shedbalkar et al. 2014; Kharisov et al. 2016; Gahlawat and Choudhury 2019). In the second view, a biological substance is produced by shrinking a complex organism into its constituent parts, such as creating tiny crystals by splitting its hard mineral mass tissue. In contrast, the “bottom-up” view collects material at the molecule and atom scale for more complex structures, which can be called molecular self-assembly (Zhang 2003; Liu et al. 2011).

Top-down synthesis

Top-down synthesis is a physical method in which the larger molecule is broken down into smaller molecules and then, these smaller molecules are converted into NPS (Ijaz et al. 2020). These physical methods are less applicable than chemical methods since they are not economical and have high energy consumption and quantity in production (Sasson et al. 2007). The sputter deposition method is one of the physical methods used to produce NPs. In the sputtering method, atoms are driven from the surface of matter by kinetic energy, which is introduced by energetic particle flux (usually ions) (Willmott 2004; Betz and Wehner 1983). Laser ablation is another method of examination in which the process is complex, but it is a cheap and economical method. In this method, a layer of solids is generally separated by laser radiation (Yang et al. 2006; Ling et al. 2014). Other technical methods include mechanical milling, etching, and grinding (Ijaz et al. 2020).

Bottom-up synthesis

Another alternative method that can produce significantly less waste and simultaneously be economical is the bottom-up approach. This approach is inspired by biological systems

Table 3 A brief summary of polysaccharide-based synthesis of NPs characterization, treatment techniques, and pollutant(s) removed

Scientific name	Pollutant	Time	Efficiency	pH	Mechanism of treatment	References
MIL101(Fe)/ZnO chitosan composites beads	tetracycline	240 min	99.18%	2–6.5	adsorption and photocatalytic degradation	(Patel and Yadav 2022)
carboxymethyl chitosan-activated carbon (CMCH-AC)	Pb2+, Cu2+	6 h	95.8%–95.9%	7–10	Adsorption	(Abdel Hafez et al. 2022)
CNC/CHT	Erichrome black-T (EBT) dye	30 min	99.90%	2.1	absorption and coagulation-flocculation	(Oyewo et al. 2022)
Chitosan/Fe 2 O 3 Nanocomposite	MO	5 h	75.04%	2	photocatalytic	(Jadon et al. 2022)
CS (chitosan)/Ag-NPs	S. aureus and P. aeruginosa	2 h	90%	–	Membranes	(Cortes et al. 2022)
PS-CSNC	RhB and MG	100 min	96.04–98.15%	6.2	photocatalytic adsorptions	(Sakthivel et al. 2022)
Fly-ash Cenosphere-Chitosan (FCC) composite	COD-solid	40 min	63.6–90%	5	Adsorption	(Priya, Jeyanthi, and Thiruvenkatamani 2022)
AF-NCh-AFNCh-EPH	Congo red (CR)	24 h	92.5–96.8%	5.5	Adsorbent	(Selim et al. 2022)
Starch-FeS@PSB and Chitosan-FeS@PSB	Pb(II) and nitrogen(NO3-N and NH4-N)	100 min	above 70%	5–3-6	complexation, electrostatic attraction, REDOX and physical adsorption	(H. Wang et al. 2022)
Ionic Liquid-Thiourea Chitosan (ILTC)	Cd(II) and Hg(II)	60 min	99.0±0.3%	3	Adsorption	(Shekhawat et al. 2022)
nano-porous chitosan (NC)	RhB	180 min	86.84%	9	Adsorption	(Pompeu et al. 2022)
EGDE	Acid Orange 7 (AO7, monovalent), Acid Red 13 (AR13, divalent), and Acid Red 27 (AR27, trivalent) dyes	30 min	97%	5	Adsorption	(Kalidason and Kuroiwa 2022)
chitosan/Fe2O3/NiFe2O4	MG	60 min	96.51%	8	Adsorption	(Ansari et al. 2022)
CS-PAR	Cu(II)	250 min	92.91%	5	complexation between the N-containing functional groups and Cu(II)	(F. Wang, Gao, et al. 2022)
Fe3O4/CS/GA NPs	dye-COD-TOC	90 min	94.83–74.19–61.53%	6.8	Adsorption	(TaheriAshtiani and Ayati 2022)
ZnO@Fe3O4 chitosan–alginate nanocomposite	acid violet 7 (AV7) dye	120 min	94.21±1.02%	6	adsorption and photocatalytic degradation	(Namrata Roy et al. 2022)
Chi-30PEI	Phenol red	30 min	94%	6	Adsorption	(Lau et al. 2022)
CS/Ag	MB, <i>Bacillus subtilis</i> and <i>Escherichia coli</i>	220 min	88%	–	antibacterial and photocatalytic	(Nandana, Christeena, and Bharathi 2022)
chitosan-based adsorbent was grafted with a mixture of IA/MAM/bentonite	Pb2+	60 min	98%	4	Adsorption	(Azizinezhad 2022)
Chitosan-FeS@WNS	Pb(II)	210 min	78.90%	5	physical adsorption, ion exchange, electrostatic attraction	(R. Liu et al. 2022)
CS-Fe ³⁺ O ⁴ -Ag-NPs	amoxicillin (AMX)	40 min	89.17%	4	Adsorption	(Mahmodi Sheikh Sarmast et al. 2022)

Table 3 (continued)

Scientific name	Pollutant	Time	Efficiency	pH	Mechanism of treatment	References
CC-GP-D	Cu ²⁺ , Pb ²⁺ , Cd ²⁺ , Co ²⁺ and Ni ²⁺	50 min	Cu: 96.64% Pb: 95.55% Cd: 99.4% Co: 92.34% Ni: 89.79%	7	Adsorption	(Zheng et al. 2022)
AC-NB-C	MP and acenaphthene (ACE) and naphthalene (NAP)	–	mp: 99.32% ACE: 98.72% NAP: 99.02%	6	Membranes	(Barman et al. 2022)
Hal-NH2/CS/PVA	Cd(II) and Pb(II)	120 min	Cd: %84 Pb: 78%	5.5	monolayer adsorption	(HMThShirazi, Mohammadi, and Asadi 2022)
PGS-CS-GO	methylene blue	300 min	99%	7	electrostatic interaction, formation of hydrogen bonds, π - π stacking	(Rostamian et al. 2022)
(Chitosan-[BMIM][OAc])	Cr(VI)	60 min	87%	3	hydrogen bonds, electrostatic interaction	(Sheth et al. 2022)
AIC@MC	Cr(VI), Staphylococcus aureus, Bacillus subtilis, Pseudomonas aeruginosa, Escherichia coli and Candida albicans	25 min	99%	2	attraction/ion exchange, chelation	(Hamza et al. 2022)
ATA@MC	Cr(IV), Cd(II), Pb(II), Co(II), and Ni(II)	25 min	Cr: 99.4% Cd: 63.9% Pb: 57.5% Co: 60.9% Ni: 44.5%	5	attraction/ion exchange, chelation	(Hamza et al. 2022)
CS-CTAB-AL	Tartrazine	45 min	90%	10	electrostatic interaction or van der Waals forces	(Ranjbari et al. 2022)
chitosan/Fe ₃ O ₄ /graphene oxide hydrogel	Eriochrome black-T and MB	140 min	98%	2mb, 8ebt	Adsorption	(Al-Wasidi et al. 2022)
MCB	amaranth dye	1500 min	98.60%	3	Adsorption	(F. Wang, Li, et al. 2022)
CS-Fe@Cu-BTC	Paraquat	40 min	91%	6	photocatalysis, light irradiation in the presence of H ₂ O ₂	(Vigneshwaran et al. 2022)
CS@S-nZVI/TB	Pb ²⁺	20 min	87%	4	oxidation, reduction, and complexation reactions	(Xu et al. 2022)
Chitosan/magnesium oxide/poly-ethylimine composite	Congo red dye	140 min	94.17%	2	ion exchange	(Almehizia et al. 2022)
Chi-WPI-MNPs	MB	4 h	76%	12	hydrogen bond and ionic exchange	(Chamchoy et al. 2022)
XMPC-Xanthate-Modified Magnetic Fe ₃ O ₄ @SiO ₂ -based polyvinyl alcohol/chitosan	Pd(II), Cu(II), and Cd(II) ions	120 min	80%	5.5	hydrogen and chemical bond	Wang et al. (2022)
PVDF/g-C ₃ N ₄ /chitosan (PCC) membrane	RhB	–	72.74%	3	adsorption	(Gharbani and Mehrizad 2022)

Table 3 (continued)

Scientific name	Pollutant	Time	Efficiency	pH	Mechanism of treatment	References
Fe ₃ O ₄ -GO/Ch bead	Pb(II)	125 min	98–99%	6	adsorption	(Shraddha Mishra and Tripathi 2022)
FO@SD@CS	Ag(I)	200 min	80%	6	ion exchange and hydrogen bonding	(Huang et al. 2022)
Zn-PB/CS	MO	300 min	86.10%	4	photocatalytic degradation	(Aadnan et al. 2021)
PEI-CMC-IIS	Gd(III)	100 min	90%	7	chelation adsorption	(E. Liu et al. 2022)

in which nature has harnessed the available chemicals to build all the required structures. With the hope of replacing and imitating nature to create self-assembling clusters to build elaborate and larger structures, researchers are trying to use this approach more and improve it, atom by atom and molecule by molecule. Of course, several methods of this approach are under development or are at the beginning to be used in the synthesis of NPs. This approach is generally divided into two methods, chemical and biological methods.

Chemical methods

The most common chemical method used to produce NPs is sol-gel. This method, however, is harmful to the environment since the materials used for hydrolysis during the sol-gel process are destructive (Joshi and Adhikari 2019; Tobiszewski et al. 2017). Another chemical method is chemical vapor deposition (CVD). CVD is one of the main methods used to produce carbon nanotubes (Choy 2002). The disadvantages of the CVD method are the need for special equipment and the formation of toxic gases. Laser pyrolysis is another method that is used in the fields of chemistry, electrochemical electronics, and chemicals (Ijaz et al. 2020; Spreafico et al. 2021). These methods often require multiple steps, controlled synthesis conditions such as pressure, pH, and temperature, expensive equipment, and toxic chemicals. In addition, these methods create biological hazards for the environment by producing dangerous and toxic byproducts. Therefore, methods based on biogenic synthesis were found to solve the above challenges.

Biological methods

“Why are biologically produced NPs so intriguing and increasingly important nowadays?” is the first question about the green synthesis of NPs. The answer is the expansion of green chemistry; Green chemistry is the concept of developing chemical products and processes that reduce the use and production of hazardous substances and waste. Green chemistry is made up of 12 principles (Fig. 2) with which green synthesis is closely related (Anastas and Warner 1998). NPs made by biological methods are favored over those made by physicochemical procedures because of their unique characteristics (Hussain et al. 2016). For the production of metal or metal oxide NPs, green synthesis is analogous to chemical-reduction chemical reduction. An expensive chemical reducing agent is replaced by extracting a natural product, which is a safe and environmentally friendly method and prevents the production of harmful and toxic substances (Sabouri, et al. 2020a, b; Singh et al. 2015a, b). In general, green synthesis methods are divided into three main categories: Microorganism-based, plant-based, and polysaccharide-based synthesis of NPs, which are discussed in detail in the

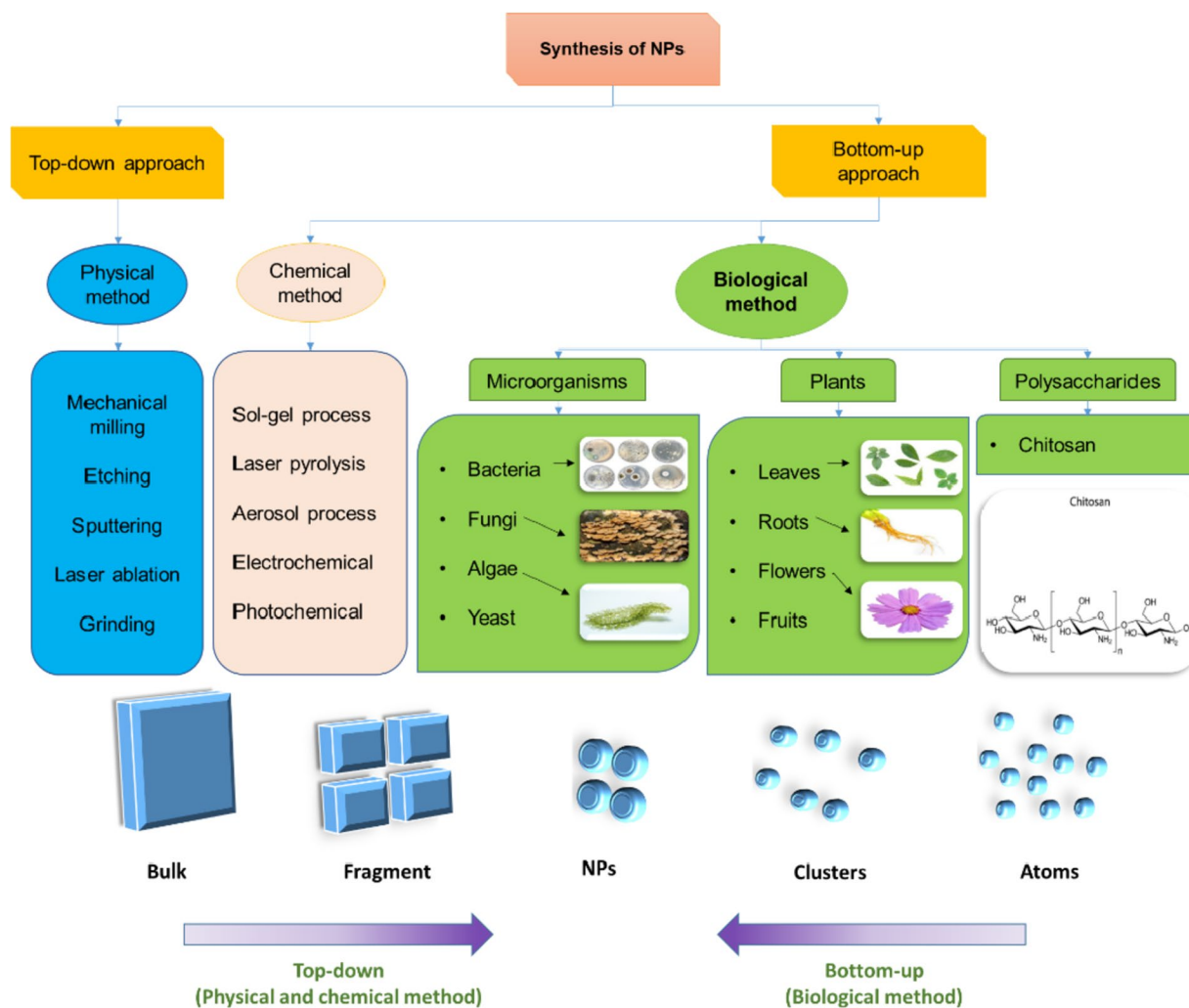


Fig. 3 Schematic of “top-down” and “bottom-up” approaches and their types in the synthesis of NPs

following on various aspects and factors affecting the process of each of them.

Microorganism-based synthesis of NPs

Microorganisms have a high capacity to synthesize NPs that are cost-effective, environmentally friendly, avoid toxic harmful chemicals, and require less energy than physicochemical methods. Figure 4 shows the green synthesis process for the production of NPs, in which NPs need biocompatible stabilizing agents as stabilization and surface functionalization to produce stable flower-shaped, spherical, and rod-shaped NPs (Ito et al. 2016; Jadoun et al. 2022). Microorganisms have advantages over traditional non-green sources for the synthesis of NPs, including high biocompatibility, renewable, availability, and non-production of

byproducts harmful to human health and the environment (Fariq et al. 2017; Park et al. 2016; Salem and Fouda 2021).

A branch of microorganisms that has attracted the attention of scientists is bacteria, which has advantages such as cost-effectiveness and production of toxic substances less than other microorganisms. Bacteria can be artificially grown and cultured at a high speed and under suitable conditions. Therefore, these materials are widely used in antimicrobial water and wastewater treatment. Although they grow faster than other microorganisms, they are slower than other physical and chemical methods (Velusamy et al. 2016; Pantidos and Horsfall 2014; Fariq et al. 2017).

Several factors affect the synthesis of NPs using microorganisms, which can affect the efficiency and rate of synthesis, among which reaction time, size, pH, nanocatalyst, and temperature play a more important role. However, the synthesis in which the extracts of microorganisms are used is less than that of plants. The microorganisms mentioned in

this review are fungus, bacteria sludge fungus, and microalgal (Swain et al. 2022; Hammad et al. 2021; Qiao et al. 2022; Koçer and Özçimen 2022; Ri et al. 2022; Zhang et al. 2022; Zhou and Li 2022; Abu Elella et al. 2022), in which Fe, Al, Si, Pd(II), ZnO, CuO, and Ag are generally used as NPs. Table 1 shows the list of microorganisms used in wastewater treatment and their synthesis characteristics.

Effect of time

The production of NPs through microorganism-based synthesis is a process that heavily relies on time and can be subject to various factors that may affect the outcome. These factors may include the growth phase of the microorganisms, the concentration of metal ions utilized, and the length of the synthesis process. The duration of the synthesis process, in particular, can significantly impact the size, shape, and stability of the final NPs. When discussing the removal of dye contaminants or metal ions from a solution using an adsorbent, the term “contact time” is often used to describe the duration for which the adsorbent is in contact with the solution. This duration is crucial as it allows the adsorbent to rapidly absorb the pollutant ions from the solution (Singh et al. 2015a, b). The rate of the reduction process can vary depending on multiple factors such as the growth phase of the microorganisms and the concentration of metal ions. Specifically, during the exponential phase of bacterial growth, where microorganisms are actively dividing and producing biomolecules that can act as reducing agents for the metal ions, the reduction in metal ions can occur at a faster pace (Durán et al. 2005). Typically, longer synthesis times can result in the production of larger NPs, while shorter synthesis times can lead to the creation of smaller NPs (Kato and Suzuki 2020). The reason why the duration of the synthesis process affects the size and shape of the resulting NPs is that the reduction in metal ions to their metallic forms is a nucleation-dependent process. In other words, the formation of nuclei is the initial stage of NPs

creation. Furthermore, the stability of the resulting NPs can also be influenced by the duration of the synthesis process. In general, longer synthesis times can result in the production of more stable NPs. This is because the biomolecules produced by the microorganisms can act as stabilizers for the NPs (Jha et al. 2009).

Effect of size

Extensive research has delved into the influence of size on the microorganism-assisted production of NPs. Studies indicate that the size of the resultant NPs can significantly impact their stability, reactivity, and toxicity. Moreover, the size of the synthesized NPs can also influence their toxicity, where smaller NPs are generally more toxic compared to larger ones. This is because smaller NPs can easily infiltrate biological barriers and interact with cellular components, making them more potent for biomedical applications such as drug delivery and imaging. Additionally, smaller NPs exhibit higher reactivity in comparison with larger (Singh et al. 2016). The superior catalytic and sensing capabilities of smaller NPs make them highly desirable in various applications. Nonetheless, it is worth noting that smaller NPs are susceptible to aggregation and oxidation, which can potentially impact their stability and performance (Fariq et al. 2017). Determining the ideal size for NPs is contingent on various factors, such as the microorganism species, the concentration of metal ions, and the desired characteristics of the NPs. In a study conducted by Kumar et al., Ag-NPs with a size range of 10–25 nm were synthesized in vitro. The NPs were stabilized through the use of a capping peptide and the presence of the reduced cofactor nicotinamide adenine dinucleotide phosphate (NADPH). To synthesize the Ag-NPs, Kumar et al. utilized the nitrate reductase enzyme obtained from *Fusarium oxysporum*, as well as *phytochelatin*s and *4-hydroxyquinoline*. The resulting NPs had a size range of 10–25 nm and were stabilized with the help of a capping

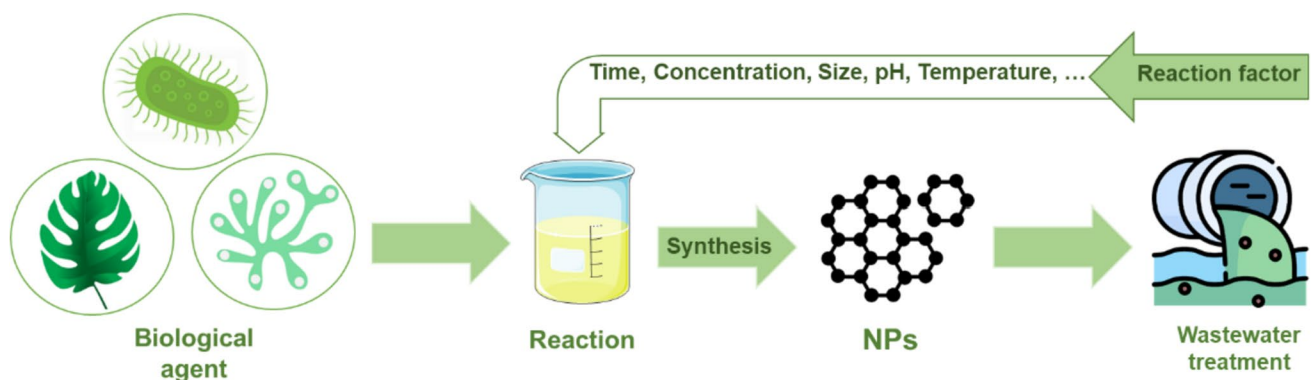


Fig. 4 Green synthesis process to produce NPs for wastewater treatment

peptide in the presence of the reduced cofactor NADPH (Kumar et al. 2007).

Effect of pH

The level of acidity or alkalinity in the growth medium has a significant impact on the functioning of biomolecules and the durability of the produced NPs. When utilizing microorganisms for the synthesis of NPs, the process is most effective at neutral pH level. This is due to the heightened activity. Nevertheless, it is important to note that the ideal pH can vary depending on the microorganism species utilized and the concentration of metal ions present. In general, NPs produced at higher pH levels have a greater degree of stability compared to those synthesized at lower pH levels. This can be attributed to the enhanced resilience of the biomolecules responsible for the reduction process at higher pH values (Fariq et al. 2017). *Shewanella oneidensis* was the subject of a distinct study investigating the impact of pH levels on the synthesis process, where NPs were synthesized through both passive and active methods. The active approach involved using ferrihydrite as an electron acceptor to produce Fe^{2+} in a high pH environment, followed by converting Fe^{2+} and Fe^{3+} close to negatively charged cell walls (Li et al. 2011).

Effect of temperature

Numerous investigations have delved into the influence of temperature on the biosynthesis of NPs derived from microorganisms. As an illustration, Singh et al. conducted a study exploring the impact of temperature variations on the fabrication of Ag-NPs utilizing *Bacillus subtilis*. The investigators observed that the prime temperature for achieving the highest yield of Cu-NPs was 30 °C, as any temperature deviations beyond this range led to a notable decline in NPs production (Wang et al. 2015). This was discovered in a study conducted by Khatami et al. where they scrutinized the impact of temperature fluctuations on the biosynthesis of Cu-NPs utilizing *Pseudomonas aeruginosa*. Results showed that the most favorable temperature for achieving maximum NPs synthesis was 30 °C. Any temperature above this range was observed to cause a decline in NPs yield (Ali et al. 2022). Moreover, temperature affects the shape and size of produced NPs. The results of a study show that when the temperature was lowered to 20 °C, only spherical Ag-NPs ranging in size from 2 to 5 nm were produced. Further reduction in temperature, from 20 to 15 °C, resulted in a combination of both spherical NPs and nanoplates. When the temperature was lowered even further to 4 °C, only a few larger spherical NPs ranging in size from 70 to 100 nm were formed. These findings clearly demonstrate that the incubation temperature has a noteworthy effect on both the size and shape of the NPs produced. Thus, it becomes critical

to standardize the reaction conditions in order to obtain the desired size and shape of NPs (Ramanathan et al. 2011; Devi et al. 2021).

Plant-based synthesis of NPs

Various parts of plants, including roots, stems, seeds, leaves, and fruits, due to their unique physicochemical properties, have led to use in the synthesis of NPs (Gomathi et al. 2017). Plants can independently stabilize NPs, so researchers use them as a reducing agent in the green synthesis of NPs, eliminating the need for stabilizing agents (Shrikhande et al. 2015; Pantidos and Horsfall 2014). During their research and experiments, to have the best efficiency in NPs synthesis, researchers should consider choosing plant extracts with more bioactive components to lead to their proper application in various fields (Mondal et al. 2020). Plant extracts are often used to produce metal NPs and their oxides (Malik et al. 2014). The presence of biologically active molecules and secondary metabolites in plant extracts has caused metal ions to be reduced to nanostructures in a rapid single-step process. Numerous metabolic compounds, including phenols, alkaloids, carbohydrates, and bio enzymes found in various plant species, are effectively used to synthesize various NPs (Kudr et al. 2017; Bilal et al. 2019). A wide range of Ag-NPs using different plant extracts has been synthesized in different shapes and sizes. The morphology of the NPs produced depends on the combined amount of metal salt and the amount of plant extract used (Safaepour et al. 2009; Chandran et al. 2006). Also, the synthesis of various NPs of copper, iron, iron oxide, zinc oxide, and palladium has been used successfully. One of the most crucial disadvantages of using microorganisms to synthesize NPs is their limitations in manufacturing conditions and high cost, so they are not practical on an industrial and large scale. Considering the benefits of plant extracts as a cost-effective and environmentally friendly method, Table 2 shows the list of plant extracts used in wastewater treatment.

The green synthesis of NPs by plant extracts consists of consecutive steps (Fig. 5) that are affected by several factors. Changes in these factors can lead to the optimization of NPs synthesis reaction conditions. These factors include temperature, pH, incubation period, aeration, salt concentration, redox conditions, mixing ratio, and irradiation. Also, the shape and size of NPs affect the synthesis, which depends on chemical and physical factors (Salem and Fouda 2021). Therefore, factors such as temperature, pH, concentration, and reaction time play a vital role in the synthesis of NPs and affect the rate of intracellular NPs and their size, which will be described in the following.

Effect of temperature

Using UV–Vis, FTIR, SEM, TEM, and XRD, researchers can study and monitor the effect of temperature on NPs synthesis (Fagier 2021). The temperature naturally affects NPs synthesis using plant extracts (Kamran et al. 2019). For instance, the synthesis of ZnO/TiO₂-NPs using *Calopogonium mucunoides* leaf extract as a reducing and stabilizing agent for different calcination temperatures of 500 °C, 600 °C, 700 °C, and 800 °C performed to reveal the effect of temperature on the NPs synthesis process. From the UV–Vis spectra analysis, the highest photocatalytic efficiency of ZnO/TiO₂ synthesis is 98.26%, which is obtained with a calcination temperature of 800 °C. On the other hand, the crystallite size of the composites is affected by calcination temperature during synthesis. The results showed that the average crystal sizes of ZnO/TiO₂ composites at 500 °C, 600 °C, 700 °C, and 800 °C were 19.99 nm, 11.87 nm, 7.62 nm, and 7.61 nm, respectively. In addition, the crystal sizes of ZnO/TiO₂ composites at 500 °C, 600 °C, 700 °C, and 800 °C were 15.73 nm, 15.21 nm, 8.86 nm, and 8.94 nm, respectively, which shows the effect of temperature on the crystal size of composites (Rusman et al. 2022). Another study investigated the green synthesis of ZnO-NPs using *Syzygium cumini* leaf extract for seed germination and wastewater purification. This study analyzed the effect of temperature on the degradation of RhB dye with ZnO-NPs in the temperature range of 25–80 °C. The result showed that increasing the temperature leads to increased degradation and reaction speed. Increasing the temperature increases the electron–hole recombination, which helps to complete the reaction and degradation. This study obtained the maximum degradation at 80 °C, which has 98% efficiency (Rafique et al. 2022).

Effect of pH

The reaction pH plays an essential role in the fabrication of NPs and is one of the practical factors in forming NPs and their properties. As a result, changes in the pH of the reaction affect the morphology of the NPs produced. On the

other hand, many biological resources used in the synthesis process cannot be activated in an acidic or alkaline environment, indicating pH's importance in the synthesis process (Kamran et al. 2019). The most critical parameter in the adsorption process is pH. In a study for furfural adsorption using the green synthesis of zero-valent iron (nZVI) NPs, the effect of pH was evaluated. In this study, increasing the pH from 2 to 12 increased the furfural uptake at the AC/nZVI nanocomposite level. The maximum absorption was obtained with a reaction time of one hour and a concentration of 250 mg/l at pH = 3, 5, 7, 9, and 11. On the other hand, the removal efficiency at neutral pH is slightly higher than the alkaline and acidic states, and therefore, pH = 7 was chosen as the optimal state. The AC/nZVI also has a positive charge at pH above pHPzc (pH point of zero charge) and a negative charge at pH below pHPzc. As a result, in solutions with pH < 6.76, the nanocomposite is positively charged, and due to the negative charge of the furfural dye molecules, the electrostatic attraction between the H⁺ ion and the dye increases. Therefore, lowering the pH due to the increase in H⁺ ions in the solution ultimately increases the adsorption rate (Rashtbari et al. 2022a, b). In another research, the green synthesis of ZnO-NPs on activated carbon prepared from *walnut bark* extract and its efficiency in removing eosin Y (Eo-Y) and erythrosine B (Er-) were investigated. The results obtained by analyzing the effect of pH on the adsorption efficiency of Eo-Y and Er-B on nano-180 composites show that by increasing the pH from 3 to 9, the adsorption of Eo-Y and Er-B on the surface of nanocomposites decreases and the maximum speed removal of Eo-Y and Er-B in nanocomposites occurs at pH 3. At pH above pHPz, AC-ZnO has a negative charge, and at pH below pHPzc, AC-ZnO has a positive charge. As a result, for solutions with a pH less than 6.76, the nanocomposite has a positive charge at its surface, and the Er-B and Eo-Y dye molecules have a negative charge. As the pH decreases, the H⁺ ion in the solution increases and creates an electrostatic attraction between the H ion and the dye, which increases the absorption rate. In contrast, for solutions with a pH greater than 6.76, the dye and adsorbent have a negative charge and repel each other, and adsorption does not

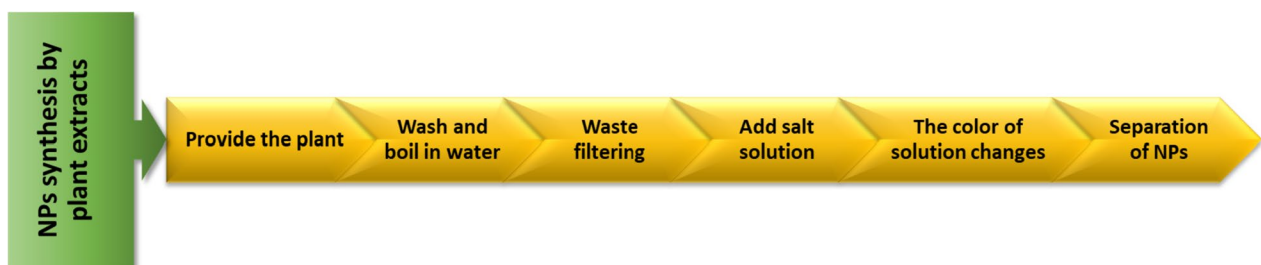


Fig. 5 Steps of green synthesis of NPs by plant extracts

occur (Rashtbari et al. 2022a, b). In another study, the fruit extract of *Syzygium malaccense* (*S. malaccense*) was used as a biological reducing agent to make Ag-NPs, and the effect of pH was evaluated. By examining the effect of pH on the degradation of MB, it can be concluded that pH determines the surface charge characteristics of the photocatalyst and the size of the aggregates produced; therefore, is an effective parameter in photocatalytic reactions. At pH = 6, due to the high electrostatic adsorption of silver (positively charged) with the dye, dye adsorption occurs faster. But at high pH, the hydroxyl radicals are quickly removed and have no time to react with the dyes, reducing the reaction efficiency (Herbin et al. 2022). In a study on the green synthesis of ZnO-NPs using *S. cumini* leaf extract, the effect of pH with a range of 1–11 changes on optical degradation was studied. As a result, the maximum optical degradation of RhB dye in an alkaline medium is obtained due to the production of hydroxide ions (OH⁻). Hydroxide ions increase degradation by producing radicals (OH[·]). In contrast, optical degradation of RhB is reduced at lower pH since hydroxyl radicals tend to combine with hydroxyl anions. Thus, fewer free hydroxyl ions form much fewer hydroxyl radicals, which reduces the decomposition of light at lower pH. Maximum optical degradation of RhB occurs at pH 9, and with increasing pH, the optical degradation of dye decreases. Therefore, pH affects the surface charge properties of the catalyst and the chemical structure of RhB dye in the presence of ZnO-NPs by visible light irradiation. Therefore, the light degradation reaction depends on the pH of the solution (Rafique et al. 2022). In another study, the removal of RhB using novel CQD from *muskmelon peel* under sunlight and ultrasonication was investigated, which evaluated the effect of pH on the efficiency and rate of dye degradation. It was concluded that the rate of RhB degradation is strongly dependent on the pH of the solution. According to the effect of photocatalytic degradation that changes the pH of CQD catalyst and RhB dye concentration, five different pH (initially 3, 5, 7, 9, and 11) were selected as catalysts to evaluate the effect of pH. Among selected pH, pH = 5 increased the RhB removal efficiency from 18.59 to 95.65%, while the irradiation time increased from 5 to 35 min. Also, pH = 5 has the maximum degradation of RhB compared to other pH conditions. At pH higher than 5, repulsive forces between CQD catalysts and RhB molecules reduce the dye degradation efficiency (Preethi, Viswanathan, and Ponpandian 2022). In a study on the synthesis of S-ZrON-NPs from the *pericarp* extract of *S. mukorossi*, the pH changed from 2 to 12 for about 3 h. The results show that the removal percentage of S-ZrON at pH = 10 is significant because of the hydration and dehydrogenation effect (Alagarsamy et al. 2022). In another survey, *Crataegus pontica* *C. Koch* leaf extract was used as a green reducing and stabilizing agent to synthesize calcium oxide nanosheets for photodegradation of MB dye.

Examining the effect of different pH (range 5–11) shows that cationic dyes (such as MB) at pH > 7 show better performance due to electrostatic interactions between the dye and the negatively charged catalyst. Therefore, the photocatalytic efficiency increases with increasing solution pH. This rate reaches 98.99% for pH = 9, and therefore, pH = 9 was chosen as the optimal pH (Meshkatalasadat et al. 2022). Therefore, as these studies and the pH column in Table 2 show, pH range affects the green synthesis of NPs.

Effect of reaction time

Reaction time is the time required to complete the reaction since factors such as temperature and pH can change the reaction time (Fagier 2021). In the study related to furfural adsorption using the green synthesis of nZVI-NPs, reaction time with adsorbent on furfural adsorption was also investigated. In the first 60 min, the adsorbent removal process was performed at high speed and, after 60 min, increased with a gentle slope to finally reach equilibrium in 120 min. Therefore, the optimal adsorbent contact time for furfural adsorption was 60 min. The change in the adsorption rate is due to the reduction in the levels available for the adsorption of pollutants through time (Rashtbari et al. 2022a, b). In the study of green synthesis of ZnO-NPs using *S. cumini* leaf extract, irradiation time and photocatalytic activity of ZnO-NPs synthesized for regular light irradiation intervals are investigated. As a result, with increasing the time of visible light irradiation at a constant pH = 9, the absorption intensity decreased significantly, which indicates a decrease in dye concentration (Rafique et al. 2022). In another study on the synthesis of ZnO-NPs on activated carbon prepared from *walnut bark* extract and estimating its efficiency in removing eosin Y (Eo-Y) and erythrosine B (Er-), time contact on reaction adsorption rate was also investigated. The results show that the removal of Er-B and (E) Eo-Y as a function of contact time decreased over time. At the beginning of the test, the absorption rate is fast, but the adsorption rate decreases over time until it finally reaches saturation in 15 min (Rashtbari et al. 2022a, b). In another study, the synthesis of S-ZrON-NPs from the *pericarp* extract of *S. mukorossi* was investigated for adsorptive removal of MB dye. In this study, to evaluate the effect of contact time, 20 mg/l as an initial MB concentration at pH = 10 was contacted with 0.3 g of S-ZrON under different time intervals (0–300 min). As a result, it was observed that the removal efficiency increased over time until it finally reached an equilibrium point (Alagarsamy et al. 2022).

Effect of concentration

The concentration, like other factors, affects the morphology of the synthesized NPs and other reaction properties

(Kamran et al. 2019). In a study on furfural adsorption using the green synthesis of nZVI-NPs, the effect of adsorbent concentration on furfural adsorption was also investigated. The results show that increasing the adsorbent concentration from 0.5 to 6 g/l increased the furfural uptake from 28.22 to 83.32%. Investigating the effect of increasing adsorbent concentration on furfural yield was concluded that after 4 g/l, the removal efficiency was slow and almost constant (Rashtbari et al. 2022a, b). In another paper, nZVI-NPs were synthesized using *Cleistocalyx operculatus* leaf extract. In this study, by gradually adding leaf extract to FeCl₃ for 4 s per drop, the effect of concentration on the removal of RhB organic dyes was evaluated. Results show that by increasing the concentration of the extract and increasing the percentage of RhB removal, the Fe(III)/CE ratio increased to 100%, which indicates the effect of concentration on the reaction. However, by increasing the concentration of leaf extract to a desirable level, the RhB removal efficiency decreased. Also, by increasing the concentration of the extract, the reaction of nZVI with other organic compounds in the extract can reduce the removal efficiency of RhB (Le et al. 2022). In a study on the green synthesis of ZnO-NPs using *walnut bark* extract and its effect on the removal of eosin Y (Eo-Y) and erythrosine B (Er-), the effect of concentration nanocomposite particles was also investigated on the adsorption rate. According to the experimental results, with increasing the concentration of nanocomposite particles, the amount of Eo-Y and Er-B in the solution decreased. With the increase in adsorbent particles, the level of adsorption decreases and ultimately will decrease the adsorption rate (Rashtbari et al. 2022a, b). In the study on the removal of RhB using CQDs from *muskmelon* peel, the effect of CQDs and RhB concentration on the rate of color degradation was also investigated. The results show that the concentration of catalyst and dye significantly affects the overall dye degradation rate. Therefore, CQD catalysts with a concentration of 0.75 mg/ml and RhB dye with a concentration of 8 µM/ml were selected as the most optimal conditions for RhB decomposition (Preethi et al. 2022). In a study on the synthesis of S-ZrON-NPs from the *pericarp* extract of *S. mukorossi*, the removal of MB as a function of adsorbent was evaluated. As a result, MB removal increases steadily, peaks, and gradually decreases. The initial concentration of adsorbent always plays a significant role in the adsorption removal efficiency. Also, in this study, 100–1000 mg/l of MB with 0.3 g of adsorbent was tested at room temperature. The results showed that adsorption efficiency decreases with an increase in the adsorbate concentration (Alagarsamy et al. 2022). In a study on the use of *Crataegus pontica* *C. Koch* leaf extract to synthesize photodegradation of MB dye calcium oxide nanosheets, the effect of MB dye concentration on dye degradation was investigated. In this study, MB with three concentrations of 10 ppm, 20 ppm, and 30 ppm was used, and it was found

that by increasing the concentration from 10 to 30 ppm, the degradation rate decreased from 99.8 to 80.2%. Therefore, increasing the dye concentration can affect the formation of active species on the catalyst's surface and the penetration of light into the solution (Meshkatsadat et al. 2022).

Polysaccharide-based synthesis of NPs

The green synthesis of NPs, as mentioned, seeks to replace new materials with chemicals that must be environmentally friendly and free of adverse effects. In addition to plants and microorganisms, another group of materials that are abundant in nature is polysaccharides. Polysaccharides, which have received much attention in recent years, have all the necessary properties to be used as reducing agents in NPs synthesis. Many studies have been done on the use of polysaccharides and the discovery of their various applications, especially in water and wastewater treatment (Table 3). Polysaccharides facilitate the bonding of metals to the surface due to several bonding sites. Another unique feature is their ability to stabilize and control the size of NPs during synthesis. Chitin, Chitosan, and their derivatives are among the most abundant branches of polysaccharides that have attracted many researchers' attention in recent years due to their distinctive properties. Chitosan is a partially deacetylated and modified natural linear polysaccharide of chitin in which β-linked D-glucosamine and N-acetyl-D-glucosamine agents are randomly selected and arranged in different states (Renault et al. 2009). Chitosan has many applications in various fields, but nowadays primary application of chitosan is in water and wastewater treatment (Peniston and Johnson 1970). Studies show that as a chelating polymer, chitosan can absorb harmful ions of heavy metals such as mercury, lead, and copper from wastewater (Masri and Randall 1978). The following is a review of recent studies and the factors affecting the synthesis process (Table 3).

Effect of dose of adsorbent

In a study, researchers found that TC, an antibiotic widely used in human and veterinary medicine, was resistant to degradation. This study succeeded in synthesizing green chitosan MIL101 Fe/ZnO composite beads, which showed that with increasing the adsorbent dose due to the creation of more active sites for the reaction, the desired contaminant's removal efficiency increased rapidly at the adsorbent dose of 1 g/l, which increased efficiency. However, by operating this action, the absorber capacity was interestingly reduced; this was related to the excessive community of active places. The reaction was equilibrated by increasing the adsorbent dose by 2 g/l of solution. The efficiency obtained in these experiments for the adsorbent was 98.56% with a contact

time of 120 min while continuing the reaction for 240 min saw 99.18% efficiency, which is unique (Patel and Yadav 2022). In another paper, anionic surfactants and ionic liquid have been used (Aliquat-336), which successfully synthesized CS-CTAB-AL green beads. The purpose of synthesizing this adsorbent was to absorb Tartrazine (TZ) dye from water sources optimally. For this purpose, to find the optimal amount of adsorbent, the dose was increased from 0.17 to 3.0 mg/l. The results showed that the adsorption efficiency increased from 12.0 to 90.36% at the 2.0 mg/l concentration. However, this amount of protection did not cause a significant change in the amount of efficiency. It was stated that increasing the adsorbent dose to the optimal value increases the number of active and free sites, which was also expected (Ranjbari et al. 2022).

Effect of pH

Another influential parameter for the adsorption process is the acidity of the reaction solution. In reactions, the point of zero charges of the solution must be identified, which can be obtained by performing a series of tests. This pH indicates that at values greater or less than this value, the surface charge of the adsorbent grains is positive or negative. Some materials in acidic environments can remove contaminants better than others in alkaline environments, so pH studies are critical and vital (Tian and Zhao 2021). In a study aimed at removing congo red dye using AF-NCh-EPH nanocomposite adsorbent, which succeeded in adsorbing the contaminant at 230 mg/g, the results showed that the acidic environment was due to the presence of amino functional groups, which become protonated and eventually increase the absorption of anionic colors such as congo red. Also, in this experiment, by increasing the pH value to 8, a sharp decrease has been witnessed in dye absorption, which is in line with previous studies due to the negative charge of OH⁻ functional groups that repel the anionic structure of the dye. Experiments with lowering the pH also showed that the congo red dye structure is sensitive to pHs below 5 and changes color to blue in that medium, also precipitating due to the hydrophobic properties present between the dye molecules (Selim et al. 2022). The results show the importance of the acidity of the reaction solution. This amount is identified and reported in studies to determine the best conditions for the interaction between the adsorbent and the contaminant.

Effect of contact time

Another critical parameter to be studied is the contact time of the contaminant with the adsorbent. Contact time means the time it takes for the adsorbent to be immersed in a solution of dye contaminants or metal ions. In the meantime, the adsorbent first absorbs the ions of the pollutants rapidly.

Then, after a certain period, the adsorption process reaches equilibrium, called the equilibrium absorption period. In a study to adsorb copper and lead ions, a new adsorbent, carboxymethyl chitosan-activated carbon derivatives, was synthesized, which showed a high ability to adsorb heavy metal ions. Then, by performing experiments and changing the amount of carbon in the adsorbent in different ratios, they found that after 120 min, the amount of adsorbed ions did not change much, which showed the equilibrium time (Abdel Hafez et al. 2022). In another study that used hydrogels, the researcher synthesized chitosan/Fe₃O₄/graphene oxide hydrogel, which could absorb dyes. The results showed that this adsorbent could remove eriochrome black-T and MB dyes from the aqueous medium. One experiment was performed to find the optimal adsorption time. The results showed that there was an 86% absorption rate of Eriochrome Black-T after reaching 140 minutes and 73.33% absorption of Methylene Blue after the same duration. However, no significant change was observed beyond 140 minutes. As shown in the mentioned studies, they showed that they all followed a specific model. This model states that the number of pollutants absorbed increases until the optimal absorption time is reached. Then, due to the saturation of active sites, this amount does not increase much and reaches equilibrium (Al-Wasidi et al. 2022).

Effect of isotherm and kinetic study

Another critical factor that should be studied in chemical reaction mechanisms is the kinetics of chemical reactions. This factor shows the reaction rate in qualitative or quantitative ways, which provides an essential insight into the dependence of the reaction rate on other factors such as temperature, concentration, and pressure. A proper understanding of the relationship between variables and interactions is critical to controlling the reaction and achieving the desired result. In a study with AF-NCh-EPH nanocomposite adsorbent, after removing dye from aqueous media, first-order Pseudo and second-order Pseudo models were performed to study the interaction between chitosan nanocomposite and congo red anion dye. After comparing the results of the two methods, the researchers considered the second-order Pseudo mechanism suitable for the intended reaction. Another critical parameter of the isotherm is the chemical reaction, which is an equation that shows the transfer of matter from the soluble phase to the adsorbent phase and follows various models, the most famous of which are Langmuir, Freundlich, and Tamkin. In this study, Langmuir, Freundlich, and Tamkin, and the linear adsorption isotherms models evaluated the absorption. After experiments and comparing the results, they found the Langmuir isotherm model more appropriate. According to the Langmuir isotherm, it can be understood that the adsorbent nanocomposite has a

homogeneous surface nature, and the anionic dye is completely adsorbed to the active sites synthesized through the single layer formation mechanism (Selim et al. 2022). Different models were used the same way in other studies, and the best model was identified.

Effect of reusability

During the economic evaluation of synthesized adsorbents and to evaluate their use, the issue of their reuse is of great importance. An adsorbent is known to be suitable when it can still show a high-adsorption capacity after repeated use and recovery. One of the pollutants that have spread in water and wastewater sources today is polyaromatic hydrocarbons (PAH), where high-adsorption nanocomposites should be used to remove them. Researchers succeeded in green synthesizing chitosan-based nanocomposites using activated carbon nano-bentonite (AC-NB-C), which can remove the desired contaminant and naphthalene (NAP) from water sources. Due to its economic importance, the adsorbent should be suitable for multiple uses. The experiments showed that the adsorbent did not significantly reduce adsorption efficiency after seven complete cycles, but after the eighth cycle, the efficiency decreased to 73%. Due to its cheap and environmentally friendly nature, the adsorbent can be used stably in wastewater treatment (Barman et al. 2022). In another study, researchers identified heavy metal ions in water, including Pd (II), Cu (II), and Cd (II), a chitosan-based nanocomposite called magnetic xanthate-modified polyvinyl alcohol and chitosan composite XMPC developed the test and concluded that it has a high ability to remove significant amounts of pollutant ions. To measure the reusability of this adsorbent, they continued up to four complete cycles. After the fourth cycle, the adsorption capacity decreased significantly, but it still showed an adsorption capacity above 50% (S. Wang et al. 2022). As shown in the mentioned studies, the adsorption capacity decreases after successive adsorption and desorption cycles. This amount varies in different adsorbents depending on the unique characteristics of the adsorbent.

Future challenges and prospective

Achieving economic well-being, environmental protection and just social progress requires sustainable development in all aspects. One of the dimensions of sustainable development is wastewater treatment so that the use of natural resources does not lead to a decrease in the quality of life, unfavorable socio-economic conditions and risks to human health and the environment (Muga and Mihelcic 2008). Among the wastewater treatment methods, the use of green

agents and biogenically synthesized NPs can be a sustainable solution that faces challenges and limitations.

Green synthesized NPs have a high-adsorption capacity than conventional nanomaterials, and their synthesis methods are stable, simple, and inexpensive. However, challenges related to green synthesis processes, such as efficiency, and green materials' structural and thermal properties, will be crucial problems. Perspectives for future studies of green nanotechnology include the study of the recycling and reuse of green nano adsorbents and their application in dynamic fixed-bed systems, the use of large-scale and industrial adsorbents, and the assessment of their environmental impact (Queiroz et al. 2022). Other advantages of green synthesis processes over conventional synthesis processes include higher resistance to corrosion, stability in oxidative environments, antifungal, antiviral, and antimicrobial behavior, and optoelectronic, magnetic, and catalytic properties. Therefore, due to the superiority of the green synthesis process, it is necessary to solve the challenges of controlling the toxicity of metal NPs and controlling their size and shape (Kurahde et al. 2021).

The most critical factor in nanochemistry is the particle size; by using different plants, due to the difference in the reduction in metal ions, particles with different sizes of metal can be obtained (Zahoor et al. 2021). To control the size and shape of nanomaterials, it is necessary to conduct studies to reduce the reaction time and optimize the reactions and process parameters such as temperature and pH. In this way, it is necessary to evaluate the effect of the metabolite of plant extract and cellular components of microorganisms during the process. Studies are also needed to separate and increase the purity of NPs from the reaction mixture (Kumar 2021). Antibacterial properties and their activity are applications of biosynthesis of nanomaterials using plant extracts, which requires studies to optimize reaction conditions. Also, due to the emergence of new viruses such as COVID-19, it is necessary to study the antiviral properties of these nanomaterials, especially nanomaterials derived from plant extracts in the future (Bhavyasree and Xavier 2022).

On the other hand, the synthesis of NPs using plants is simpler and more accessible than artificial green methods such as bacteria and fungi, which are accompanied by dimensional and morphological control. It is necessary to study the interaction of nanomaterials with biological systems to assess the risks posed by them to human health (González-Poggini et al. 2021). One of the challenges of wastewater treatment is to improve the removal efficiency of resistant pollutants. In this regard, improving hydrophilicity, the efficiency of template elution, stability of site recognition, and rapid establishment of the optimized imprinting system will be among the plans and goals (Li et al. 2021). In addition to studies on the control of NPs from pathogens, it is necessary to evaluate their effects on

specific species of microbes and even pathogens during bioinspiration processes. In this way, green chemistry can be used by reducing the use of hazardous substances in chemical processes to finally achieve better results in the biosynthesis of NPs by using plant extracts and biologically active biomolecules (Naikoo et al. 2021).

Plant extracts have different chemical compositions. Therefore, determining the effective phytochemicals in the synthesis process of nanomaterials with controlled properties are complex and challenging. However, by changing the condition, the levels of these phytochemicals can be changed. Some of these plant extracts have detoxifying properties suitable for metals. Extracellular synthesis of metal and metal oxide of NPs using different plant extracts is an important topic that needs to be studied (Aslam et al. 2021). Water contains other impurities such as acids, alkanes, and salts, and it is necessary to use multi-purpose adsorbents to purify all water impurities. Minor damage and bio-deposition due to toxicity and bacteria in the water reduce the efficiency of adsorbents, which is one of the challenges of this process (Baig et al. 2021). Microalgal nanotechnology is used to synthesize various metals, metal oxides, and other NPs. Different factors affect the quality and quantity of synthesis and production rate of NPs. However, suitable conditions and microalgae for synthesizing different NPs have not yet been identified. On the other hand, due to the high potential of microalgae nanotechnology, most studies have been done on the synthesis of metal NPs, which requires studies on other NPs (Taghizadeh et al. 2021).

In contrast, due to the risk of food security threats from plant products in green synthesis, it is necessary to pay special attention to biological waste. The presence of different microorganisms such as bacteria, fungi, and yeast has caused differences in the reaction mechanism for NPs biosynthesis. Understanding this mechanism requires control of the morphology and other properties of synthesized NPs that must be examined. Research on better control of stabilization in nanomaterials, coupled with effective management of waste from nanomaterial synthesis, is very important due to the risk of toxicity to soil and water. Bimetallic NPs are effective in improving the properties of iron NPs by improving their catalytic properties, adsorption level, and chemical properties, which need to be evaluated in the future (Mondal et al. 2020). In general, due to the superiority of the green synthesis method in terms of environmental friendliness, low cost, simple process, and lower energy requirements, NPs obtained from green synthesis can be used in various industries, including medicine, agriculture, medicine and food on an industrial and large scale. Achieving this goal requires less time-consuming, reproducible, more reliable, and stable processes and the ability to recover waste to ultimately

help treat wastewater by removing contaminants, including heavy metals (Frattini et al. 2021; Soltys et al. 2021; Zahoor et al. 2021).

Conclusion

In this review, the previous research on the use of biogenically synthesized NPs in wastewater treatment was reviewed. Green synthesized NPs are used in the removal of various pollutants, including organic and inorganic pollutants such as dyes and heavy metal ions from wastewater. In the articles reviewed, the first group of studies dealt with microorganism-based synthesis of NPs. In this group, several microorganisms such as fungus, bacteria, microalgal, and fungal have been used to eliminate contaminants such as dye (MB, MO), azo nitrate, and Cr(v), using mechanisms such as hydrolysis, catalytic, and membrane bioreactor (MBR) filtration. The second group of studies has investigated the plant-based synthesis of NPs, where different parts of the plant have been used as reducing and stabilizing agents. Different plant extracts have their unique physicochemical properties and can be used in a wide range of wastewater treatments. Applications of plant extracts include the removal of RhB dye, MB dye, nitrate, organic dyes, nitrophenol, and heavy metals using mechanisms such as filtration, adsorption, photocatalyst, etc. The third group of studies has used polysaccharide-based synthesis of NPs, especially chitosan. More than half of the polysaccharide studies were on the removal of acidic dye contaminants, and the rest were on the removal of various types of heavy metal ions and unusual contaminants such as pharmaceuticals and bacterial contaminants. Finally, due to their high stability, low cost and energy, and environmental friendliness, biogenically synthesized NPs have a high potential for industrial and large-scale wastewater treatment in the future. Achieving this goal requires further studies to reduce reaction time and increase the stability and reliability of this process.

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