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Environmental remediation using nanomaterial as adsorbents for emerging micropollutants

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ABSTRACT

Water shortage and scarcity are issues of global concern. Water pollution caused by organic micropollutants further aggravates the problem, by rendering an already scarce resource unfit for human consumption. The existing conventional wastewater treatment methods and infrastructure were not designed to eliminate micropollutants. Therefore, their inefficiencies call for modern methods for removing emerging micropollutant residues such as Active Pharmaceutical Ingredients (APIs), Endocrine Disrupting Compounds (EDCs), personal care products and pesticides. The use of nanomaterials, for the abatement of micropollutants in water is gaining traction in recent years, due to the abundance of sustainable, cost-effective raw materials, especially plant extracts. Synthesis of nanoparticles and their application in removal of micropollutants in wastewater streams is addressed through this review.

1. Introduction

Diverse regions around the globe face water scarcity (Ngumba et al., 2020; Madivoli et al., 2016). Aquatic pollution is increasingly making water unfit for human consumption (Basheer, 2018). Active pharmaceutical ingredients (APIs), and endocrine disrupting compounds (EDCs) are common emerging pollutants finding their way into water bodies, hence compromising water quality (González et al., 2020; Gonsioroski et al., 2020; Kairigo et al., 2020; Ngumba et al., 2020; Muriuki et al., 2020). Pharmaceuticals such as antibiotics, steroids, and antiretroviral agents pose a serious threat to the environment and human health (Ngumba et al., 2016; Wanakai et al., 2022; Madivoli et al., 2020a). These emerging micropollutants, especially antibiotics, propagate the evolution of antimicrobial resistance among environmental microorganisms (Kairigo et al., 2020; Wanakai et al., 2022). Research reveals that conventional methods used to treat wastewater do not provide complete removal of these pharmaceuticals (Kamaz et al., 2019; Nam et al., 2017; Rogowska et al., 2020). Hence the need to explore new strategies that can effectively and efficiently remove these pollutants from surface waters as they pose an existential threat to human civilizations around the globe.

Previous studies have reported growing interest in use of nanomaterials for degradation and removal of aquatic contaminants (Anjum et al., 2019; Kokkinos et al., 2020a; Mukhopadhyay et al., 2021; Yunus et al., 2013). Popular nanomaterials of interest include metallic nanoparticles, biopolymers such as cellulose, chitin, chitosan among others; which extend to one-hundred nanometric dimensions (Kumari et al., 2019; Madivoli et al., 2022). The nanomaterials possess unique properties compared to their bulk counterparts. For instance, they exhibit improved surface area to volume ratio, enhanced adsorption capacity of micropollutants, ease of regeneration and higher selectivity in removal of pollutants from various environmental matrices such as water, soil and air (Roy et al., 2021; Madivoli et al., 2016). The increasing environmental pollution from textile, heavy metals, pharmaceutical and chemical industries drive the need for use of nanoparticles to remove these pollutants from different matrices (Handojo et al., 2020). Continued water pollution makes metallic nanoparticles appropriate candidates for pollution remediation, which is not possible with conventional wastewater treatment methodologies widely practiced (Kumari et al., 2019). A critical discussion of various synthesis methods for metallic nanoparticles and their application in the removal of micropollutants in wastewater have been addressed in this review.

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Special emphasis has been given to green synthesis of metallic nanoparticles using plants extracts due to their capping and stability potential which prevents agglomeration (see Table 1).

2. Synthesis of Metal Nanoparticles

Metallic nanoparticles can be obtained using various approaches, which include either physical, chemical, biological methods or a combination of these (Fig. 1; Ijaz et al., 2020; Iravani et al., 2014; Tulinski & Jurczyk, 2017).

These methods are classified either under top-down or bottom-up approach but both are employed to exploit the novel properties of matter at the atomic and molecular levels. In principle, the top-down approach creates materials at the nanoscale by use of large microscopic devices that are externally controlled while the bottom-up approach utilizes molecular components that build complex structures by means of chemical reactions among the atoms/ions/molecules (De Oliveira et al., 2020). These strategies which employing the use of either physical and chemical techniques comprise of solvothermal synthesis, sol–gel methods, laser ablation, chemical reduction, ball milling, ion sputtering, and biological reduction methods (De Oliveira et al., 2020). However, these techniques often involve complex processes, form precipitates that are mostly amorphous, have high energy requirements with difficulties in controlling the growth rate of the metal nanoparticles and often pose environmental risks. It's also worth noting, that these approaches often give rise to multi-shaped nanoparticles that require purification steps which leads to low yields. Therefore, the development of sustainable experimental protocols to produce nanomaterials using ingenuine techniques such as biological entities is a worthwhile venture as they mitigate against all this cons. Hence the current drive in utilization of biological methods which employ the use of microorganisms such as fungi, bacteria such as *Geobacter sulfurreducens* (Chabert et al., 2020; Khan et al., 2020; Vasylevskyi et al., 2017), *Escherichia coli* and secondary metabolites from various plant species are increasingly attracting attention due to their safety, simplicity and ease of nanoparticles production (Gavamukulya et al., 2020; Madivoli et al., 2020b; Nyabola et al., 2020). In the preceding sections, a detailed explanation of physical, chemical and biological methods will be discussed in more detail outlining the pros and cons of each technique.

2.1. Chemical methods

In this approach, chemical reducing agents are used to reduce metal ions into their corresponding metallic nanoparticles. Some chemical methods of nanoparticle synthesis utilize chemical generated from organic matter while others use inorganic precursors (Iravani et al., 2014; Schütte et al., 2017). For instance, titanium oxide nanoparticles were synthesized by the sol–gel method by the dissolution of titanium chloride using urea in an ice bath (Madivoli et al., 2020a). In this study, the authors obtained crystalline TiO_2 NPs with diameters ranging between 200 - 1000 nm in size. The nanoparticles had TiO_2NPs crystalline peaks at 101, 004, 200, 105 and 204 planes as observed from XRD diffractograms with TiO_2NPs vibrational peaks observed at 3406 cm^{-1} and 3107 cm^{-1} in the IR spectra. Similarly, Ahmad et al. (2021) synthesized TiONPs with an average size of 18.3 nm using titanium tetra isopropoxide, glacial acetic acid and double distilled water. The obtained TiONPs nanoparticles exhibited XRD peaks at 2theta values of 101, 103, 004,200, 105, 211, 204, 116 and 220 planes. In another study, (Mushtaq et al., 2020) obtained TiO_2NPs with sizes ranging between using a simple sol–gel method.

Production of silver nanoparticles was achieved using chemical reduction of silver ions employing reducing agents such as sodium borohydride (Diantoro et al., 2015) where the researchers obtained silver nanoparticles of 24.3 diameter size. In that study, the 2theta values were 111, 200, 220, 311, and 222 planes which are unique for metallic silver nanoparticle. In another study, synthesis of silver nanoparticles from silver nitrate salt using combination of sodium citrate and tannic acid of average size of 30 nm were obtained (Ranoszek-Soliwoda et al., 2017). Additionally, synthesis of copper nanoparticles was achieved using wet chemical reduction of copper sulfate solution and hydrazine (Sierra-Ávila et al., 2015). In that study, a mixture of allyamine and polyallylamine was used as stabilizing agents to obtain copper nanoparticles of about 31 nm in size. Khan et al. (2015) reports synthesizing copper nanoparticles by reduction of copper (II) sulfate pentahydrate salt precursor and capping agent as starch to obtain nanoparticles with an average size of 28.73 nm. In another study,

Table 1
A summary of removal efficiencies of organic pollutants using Nanoparticles.

Pollutants	Specific pollutants	Type of nanomaterial	Removal Efficiencies	References
Antibiotics	tetracycline, Piperacillin, Tazobactam, Ethromycin	magnetite nanoparticles (Fe_3O_4)	Exhibited more 90 % removal	(Stan et al., 2017)
	Ampicillin, Amoxicillin, Penicillin	Functional bentonite-support nanoparticles Fe/Ni (B-Fe/Ni)	80.6 %, 94.6 %, 53.7 % Respectively	(Weng et al., 2018)
	Ceftriaxone, Cefadroxil	Zero-valent copper nanoparticle	Greater than 85 % for 20 min	(Oliveira et al., 2018b)
	Sulfamethoxazole, rifampicin	(Fe_3O_4)	90 %	(Stan et al., 2017; Wanakai et al., 2022)
	Mitoxantrone	Manganese nanoparticles	77.3 % (real samples) and 97.4 % (lab samples).	(He et al., 2021b)
	Levofloxacin	Combination of ZnO and Graphene oxide nanoparticles	99.2 % removal at 50 umL^{-1} and 99.6 % at 400umL^{-1} concentrations	(El-Maraghy et al., 2020b)
Steroids	Estrone, 17-alpha ethinylestradiol	Biogenic manganese oxide nanoparticles	100 % removal for 5 h	(Furgal et al., 2014)
	17β-estradiol and 17α-ethynyl estradiol	graphene nanomaterials		(Jiang et al., 2017b)
	Progesterone and testosterone Estradiol and Estrone	Titanium oxide nanoparticles	44 % and 33 % respectively 80 %	(Lotfi et al., 2022b)
Pesticides	Deltamenthrin, Cyhalothrin, Bifenthrin	magnetite nanoparticles (Fe_3O_4)	80.2 %	(Fan et al., 2017)
	Cypermethrin, chlorpyrifos	CNTs	70 %	(Hou et al., 2014)
Heavy Metal ions	Pb^{2+}, Cu^{2+}, Cd^{2+}, Ni^{2+}	Mesoporous magnetite NPs	98 %, 90 %, 87 %, 78 % respectively	(Fato et al., 2019)
	Pb	Magnetite nanocomposite/aluminium metal organic framework	492 $mg.g^{-1}$	(Ricco et al., 2015b)
	Zn^{2+},Cd^{2+}, Co^{2+} Pb^{2+}, Hg^{2+}, Cd^{2+}	Graphene oxide NPs	246 $mg.g^{-1}$, 106.3 $mg.g^{-1}$, 68.2 $mg.g^{-1}$, 602 $mg.g^{-1}$, 374 $mg.g^{-1}$, 181 $mg.g^{-1}$ respectively	(Yang et al., 2019)
	Cr^{4+}, Pb^{2+}, Cd^{2+}	Magnetic Nickel-Ferrite Nanoparticles	85.21 % after 90 min, 77.41 % after 120 min, 84.45 % after 90 min respectively	(Khoso et al., 2021)
	Cu(II)	Silica-coated magnetic nanoparticles	143 $mg.g^{-1}$	(Plohl et al., 2019)

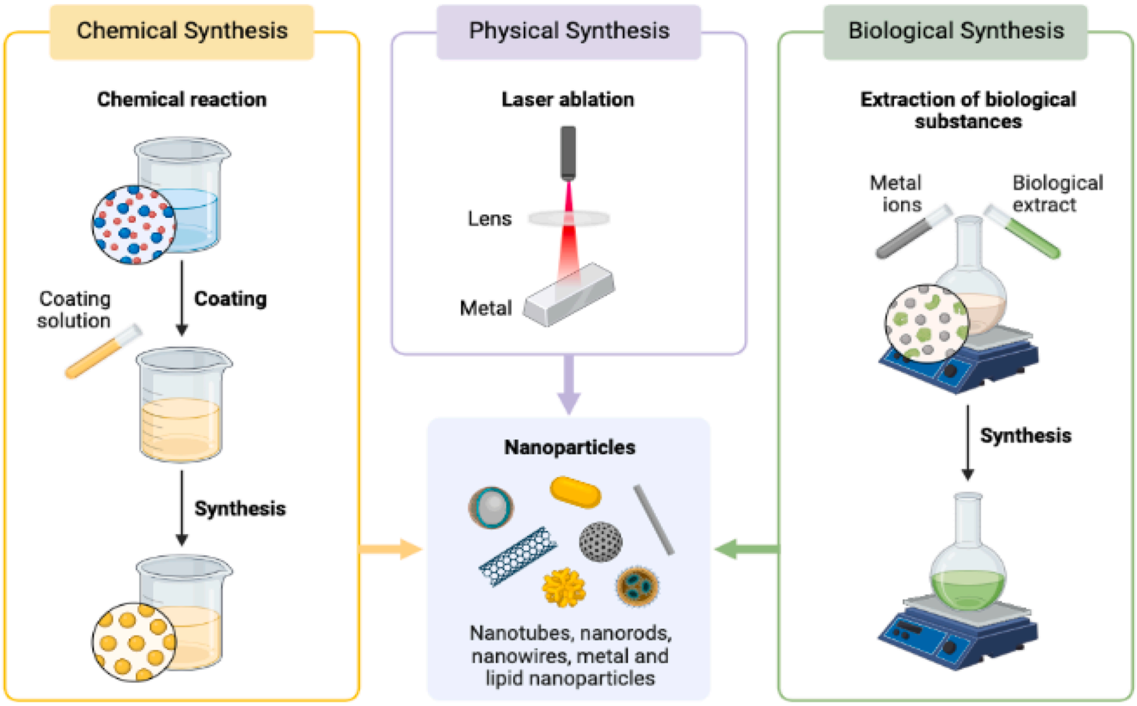

Fig. 1. Techniques used during synthesis of nanoparticles. Image created in biorender.com.

platinum nanoparticles of about 10 nm were obtained by reduction of platinum ions using sodium borohydride and polyethyleneimine as reducing and protective reagents respectively (Nagao et al., 2017). Hussain et al. (2020) reported synthesizing gold nanoparticles using L-ascorbic acid and polyvinylpyrrolidone as reducing and stabilizing agents respectively in different solvent system to achieve nanoparticles in the size ranging from 22 to 219 nm. Both smaller (spherical nanoparticles) and bigger (varying shapes) nanoparticles were produced in this study depending on the polarity index of the reaction medium.

While chemical reduction is appropriate strategy that can be employed to obtain metallic nanoparticles, it has a host of drawbacks. It results in the generation of toxic byproducts, which were reported to be more toxic than the intended target for removal hence a threat to the ecosystem (Rahimi and Doostmohammadi, 2019). The transfer of pollutants between the phases has also been evident in the chemical methods for synthesizing nanoparticles (Ngumba et al., 2020; Gudikandula & Charya Maringanti, 2016). These drawbacks make the method expensive to operate as they lead to generation of other environmental pollutants that have unknown or adverse impact to the environment.

2.2. Physical methods

Several physical methods for the synthesis of metallic nanoparticles exist which include laser ablation, ultrasonication, ball milling, pyrolysis, lithography and sputtering (Fig. 2).

Due to its fast-processing times which provides better control over the size and shape of the nanoparticle's particles, high yields and long-term stability of the generated nanoparticles, laser ablation is often considered an alternative to chemical synthesis methods. In this case, a solid surface is irradiated with a laser beam leading to a low flux plume which is evaporated or sublimated to form nanoparticles. For instance, copper nanoparticles with an average size of 51 nm with a quasi-spherical shape as evident from the SEM images have been obtained (Mohammed et al., 2019). In another study, zinc oxide nanoparticles were synthesized using spray laser pyrolysis in the range of 10 to 25 nm and with a hexagonal wurtzite structure observed from the TEM images (Reza et al., 2011). Evaporation-condensation method was employed in synthesis of zinc oxide nanoparticles (Vodop'yanov et al., 2017). Copper oxide nanoparticles of the size ranging from 3 to 40 nm have also been synthesized using induced laser ablation where the TEM images revealed the particles were nearly spherical in shape (Khashan et al.,

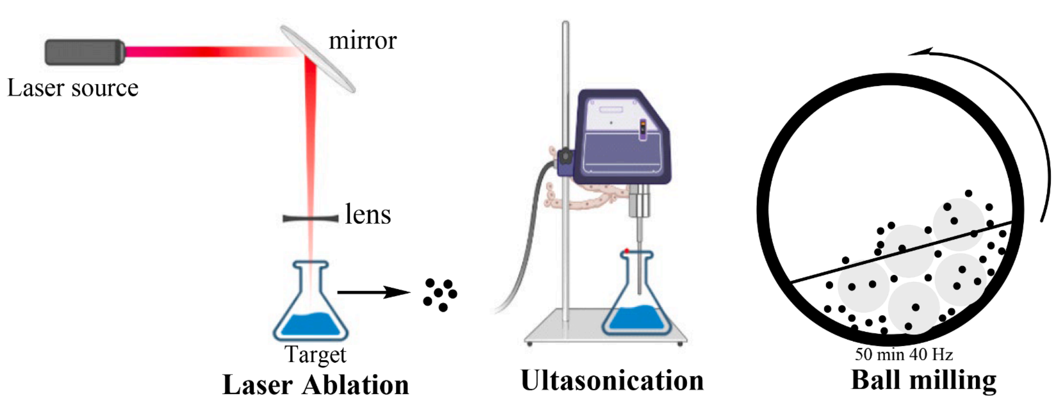

Fig. 2. Physical methods for synthesis of metal nanoparticles (image created in biorender.com).

2015a). Induced laser ablation method has also been employed in the synthesis of copper oxide colloidal nanoparticles and silver nanoparticles (Iravani et al., 2014; Khashan et al., 2015b) Sputtering on the other hand involves the deposition of a thin film of nanoparticles generated by the collision of ions over a substrate followed by annealing. It is commonly referred to as physical vapor deposition and its efficiency is dependent on substrate type, duration of annealing, temperature used during deposition which all directly affect the size and shape of the nanoparticles (Khashan et al., 2015a). It has been used to synthesis platinum nanoparticles on a glycerol matrix at varying argon pressure (Caillard et al., 2021). In that study, platinum nanoparticles in the size range of 1.8 to 3.2 nm were obtained as pressure increased from 1.0 to 9.0 Pa. In ball milling, the kinetic energy of the balls is transferred to the bulk material, which results in the reduction in grain size. In that case, parameters such as the type of mill, milling atmosphere, milling media, intensity, time and temperature were judicially selected because they play a major part in controlling the shape and size of the NPs. This technique has been used to obtain silver nanoparticles with an average crystal size of 28 nm by use of a high energy planetary ball mill (Khayati and Janghorban, 2012). Although the physical route for synthesis of metallic and metal oxide nanoparticles with uniformly-sized particles is employed, it is expensive because it involves energy intensive processes which make the whole process very costly (Almatroudi, 2020; Wu et al., 2019).

2.3. Biological methods

Use of biological agents for synthesis of nanoparticles in cost-effective manner while ensuring minimal production of toxic byproducts was reported (Keat et al., 2015; X. Li et al., 2011). This approach utilizes reducing agents present in extracts from plants, intracellular and extracellular matrices of microorganisms such as fungi and bacteria (Chabert et al., 2020; Gavamukulya et al., 2020; Madivoli et al., 2020b, 2022; Nyabola et al., 2020; Vasylevskyi et al., 2017) (Figs. 3-4).

Microorganisms such as bacteria and fungi were used as reducing agents for metal ions in the biosynthesis of metal oxide nanoparticles (Singh et al., 2016). Silver nanoparticles were reportedly synthesized using THG-LS1.4, a *Pseudomonas* Sp. resulting to nanoparticles of irregular shape in the size ranging from 10 to 40 nm from the FE-TEM results (Singh et al., 2018a). In another study, silver nanoparticles were synthesized using BS-161R strain of *Pseudomonas aeruginosa* in which spherical nanoparticles were obtained with an average size of 13 nm (Kumar and Mamidyala, 2011). *Pseudomonas aeruginosa* strain of ATCC 90271 were also utilized in the biosynthesis of gold nanoparticles which achieved nanoparticles ranging from 15 to 30 nm (Husseiny et al., 2006). Another study utilized *Bacillus niabensis* 45 to synthesize spherical gold nanoparticles ranging from 10 to 20 nm (Y. Li et al., 2016). Other microorganisms such as *Acinetobacter baumannii* were employed in synthesis of silver nanoparticles which were spherical in shape with size ranging from 37 to 168 nm (Shaker and Shaaban, 2017). In another study, *Geobacter sulfurreducens* were utilized in the synthesis of gold nanoparticles of an average size of 20 nm (Sultana et al., 2016). Despite their contribution in synthesis of metallic nanoparticles, use of microorganisms has limitations due to toxic nature of some bacteria and also the requirement of highly aseptic conditions in synthesis (Grasso et al., 2020). Recently, focus has been redirected to a more cost-effective and environmentally friendly method for biosynthesizing metal and metal oxide nanoparticles using plant extracts as reducing and stabilizing agents (Bao et al., 2021) (see Fig. 5).

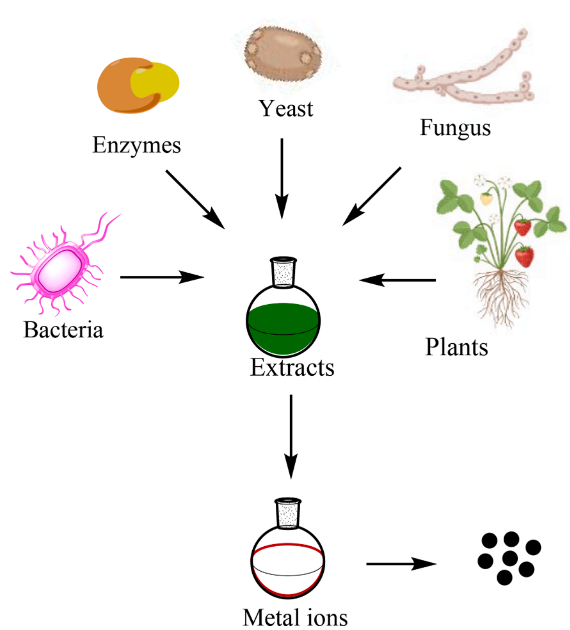

Fig. 3. Biological methods used to synthesize metal/metal oxide nanoparticle.

The biomolecules contained in plant extracts such as phenols, tannins, proteins, flavonoids and terpenoids were reported to be excellent reducing and stabilizing agents in the synthesis of metallic and metal oxide nanoparticles (Singh et al., 2018b). Copper oxide nanoparticles were synthesized using aqueous leaf extracts of *Calotropis gigantea* plant which were spherical in shape with an average size of about 20 nm (Sharma et al., 2015). Elsewhere, green synthesis of copper oxide nanoparticles was obtained using leaf extracts of *Psidium guajava* which resulted to mono-dispersed and spherical nanoparticles of average size of 6 nm (J. Singh et al., 2019). Green magnetite nanoparticles were synthesized using aqueous extracts of *Cucumis sativus, Vitis vinifera,* and *Citrus limon* for the removal of antibiotics from wastewater (Stan et al., 2017). In this study, the crystalline size of magnetite nanoparticles using the *Cucumis sativus, Vitis vinifera,* and *Citrus limon* were 11 nm, 12 nm and 8 nm respectively with different shapes. In addition, tea extracts achieved the green synthesis of manganese nanoparticles for removal of mitoxantrone from wastewaters (He et al., 2021a) with the size of the synthesized nanoparticles ranging from 40 to 60 nm. In another study, (Ndikau et al., 2017) used *Citrullus lanatus* (watermelon) fruit extract to synthesize silver nanoparticles. In that study, the size of silver nanoparticles was reported to have an average diameter of about 17.96 nm which were spherical in shape. Similarly, (Wu et al., 2020) obtained copper nanoparticles using *Cissus vitiginea* extracts as antioxidant and antibacterial agents for urinary tract infection pathogens. Synthesis of nanoparticles using biological approaches is gaining popularity compared to physical and chemical methods (Bhardwaj et al., 2020; Pattanayak et al., 2021). The plant extracts contain biomolecules with functional groups capable of reducing metal ions into their nanoparticles sizes (Sharma et al., 2015). Furthermore it is economically viable, and eliminates the use of additional reagents because the extracts both reduce and stabilize the nanoparticles through capping (Wanakai et al., 2022; Singh et al., 2018b). This method offers an eco-friendly way of synthesizing the nanoparticles (Jeevanandam et al., 2022).

2.4. Mechanism of green synthesis of metallic nanoparticles using plant extract

Phytochemicals in plant extracts such as terpenoids, flavonoids, phenolic compounds and alkaloids are characteristic reducing agents in the reduction of metal ions into metallic nanoparticles and metallic oxide nanoparticles (Jayachandran et al., 2021a). The rate of formation of metallic nanoparticles using plant extracts depends on extracts concentration, pH of the medium, temperature, and reaction or contact time between the metal ion solution and the plant extract. Studies have proposed the mechanism of synthesis of metallic nanoparticles using plants extracts (Qamar and Ahmad, 2021; Singh et al., 2018b). The common adopted mechanism involves three step process, an activation step where the metal ions are reduced triggering nucleus formation, a

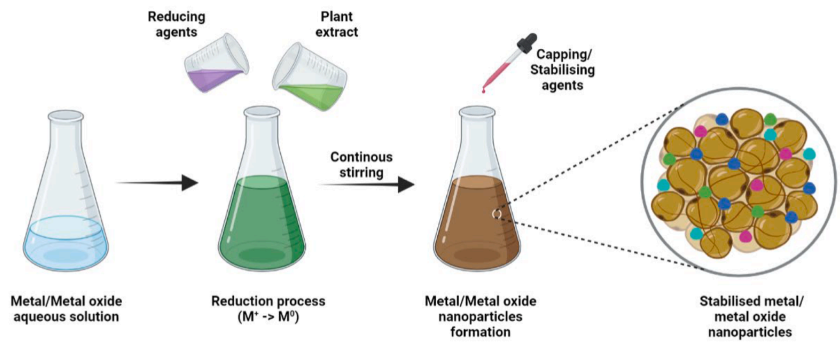

Fig. 4. An illustration of the synthesis of metal/metal oxide nanoparticles by reduction of metal/metal oxide ions (image created in BioRender.com).

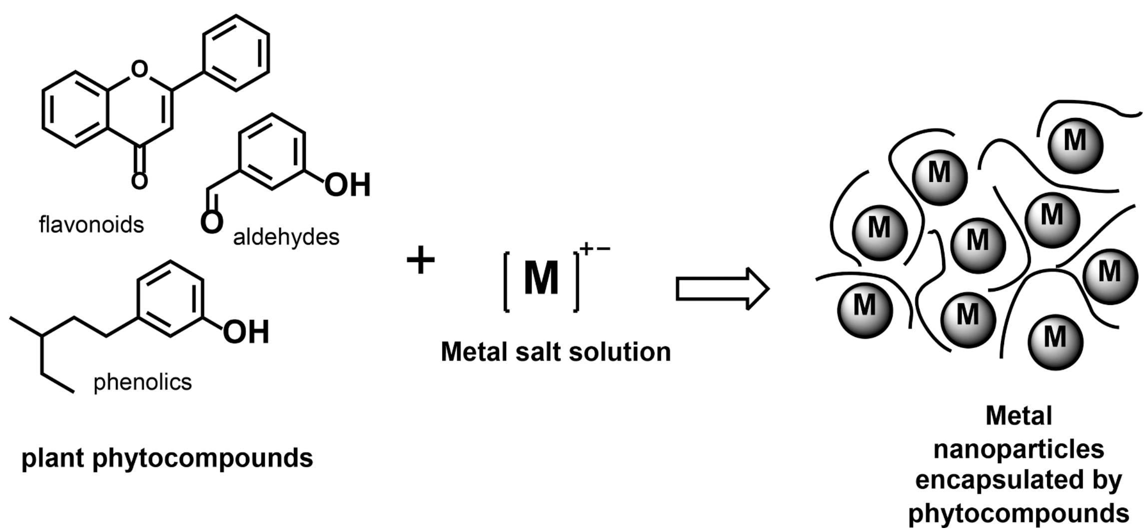

Fig. 5. Mechanism of nanoparticles synthesis using plant extracts and metal salt, image modified from (Jayachandran et al., 2021b).

growth process where nanoparticle formation becomes stabilized, and a termination step which dictates the shape of the resultant nanoparticles (Jayachandran et al., 2021b).

3. Application of nanoparticles in environmental remediation

Utilization of metallic nanoparticles in the removal of antibiotics, steroids, heavy metals and pesticides from wastewater were reported in literature. Removal by adsorption is favored because of the sustainability nature and diversity of the adsorbents.

3.1. Removal of antibiotics

The use of metallic nanoparticles in the removal of antibiotics in aqueous reservoirs was much more promising than the conventional methods used for wastewater treatment. The use of nanoparticles in antibiotic removal eliminates the drawbacks linked with wastewater treatment methodologies due to antimicrobial resistance (Ngumba et al., 2016; Ngumba et al., 2020; Stan et al., 2017). The occurrence of residual antibiotics in the environmental compartments, especially below therapeutic concentrations is a cause for concern due to their ability to fuel the development and propagation of antibiotic resistance among the environmental microorganisms (Bengtsson-Palme and Larsson, 2016; Kairigo et al., 2020; Tran et al., 2018). Antibiotic resistance is a global threat to public health (Lomazzi et al., 2019; Minarini et al., 2020) World Health Organization, 2021; (Zhang et al., 2022).

Removal of trace-level antibiotic has been achieved using nanomaterial adsorbents (Malakootian et al., 2019). Magnetite nanoparticles (Fe_3O_4) were reported to be effective adsorbents for the removal of tetracycline, rifampicin, ampicillin, tazobactam, piperacillin, sulfamethoxazole, ethromycin and trimethoprim antibiotics with a removal efficiency of more than 90 % (Stan et al., 2017; Wanakai et al., 2022). Antibiotics such as mitoxantrone (MTX) were successfully removed from wastewater using green synthesized manganese nanoparticles from synthetic and real water with a percentage removal efficiency of 97.4 % and 77.3 % respectively (He et al., 2021b). The same study reported that the method was cost-effective with increased adsorptive capacity. Levofloxacin was removed using a combination of zinc oxide nanoparticles and graphene oxide nanoparticles with a removal efficiency of 99.2 % and 99.6 % for 50 and 400 μg/ml concentrations respectively (El-Maraghy et al., 2020a). Another study reported above 85 % removal efficiency of β-lactam antibiotics, Cefadroxil and ceftriaxone using zero-valent copper nanoparticles (Oliveira et al., 2018a). Photodegradation of trimethoprim was achieved using Ni/TiO_2-P25, Cu/TiO_2-P25, Ag/ TiO_2-P25, Au/ TiO_2-P25 nanoparticles with 80 % degradation of the initial concentration (Oros-Ruiz et al., 2013).

3.2. Removal of steroids

Steroid hormones are micropollutants of concern, which affect early development and reproduction in aquatic and terrestrial organisms (González et al., 2020; Ojoghoro et al., 2021; Thrupp et al., 2018). The application of carbon-based nanoparticles has been employed for the removal of steroids in wastewaters (Nguyen et al., 2021). In the study faster adsorption of estradiol was observed in less than an hour on carbon nanoparticles. Under situ conditions, complete removal of estrone and 17-alpha-ethinylestradiol were achieved using biogenic manganese oxide nanoparticles after 5 h (Furgal et al., 2014). Use of graphene nanomaterials demonstrated improved adsorption of 17β-estradiol and 17α-ethynyl estradiol (Jiang et al., 2017a). Moreover, the removal of oestradiol and oestrone (80 %) were achieved using titanium dioxide nanoparticles of sizes between 10 and 30 nm embedded in a polyethersulfone membrane (Lotfi et al., 2022a). In the same study, removal of progesterone, testosterone (44 % and 33 %) respectively was achieved.

3.3. Removal of pesticides

Application of nanomaterials in removal of pesticides in wastewater, agricultural effluents and drinking water was previously investigated. Graphene a carbon-based nanoparticle, was used in pesticide removal in water purification with a reported adsorption capacity range of 600 to 200 mg/g of pesticides (Hesni, 2020; Moradi Dehaghi et al., 2014). Elsewhere, graphene modified with silica reported improved adsorption of organophosphorus pesticides in water (X. Liu et al., 2013).

Metal nanocrystalline oxides such as titanium oxides, cerium oxides and magnesium oxides were employed for pesticide removal because of their high adsorption capacity. Degradation of residual organophosphate parathion methyl pesticide to less toxic products under conducive temperature ranges was achieved using nanocrystalline cerium (IV) oxide (Tolasz et al., 2020). The application of nanocrystalline metal oxides for the removal and destruction of organophosphorus pesticides is limited because of its cost implications (Saleh et al., 2020). Development of other types of nanomaterials for environmental management of pesticide pollution in water is therefore necessary.

3.4. Removal of heavy metals

Nanomaterials are promising technology for the removal of heavy metal ions in water (L. Liu et al., 2019; Yang et al., 2019). Nanomaterials used for heavy metal removal in wastewater include metal oxide-based nanoparticles, zero-valent metal, nanocomposites and carbon-based nanomaterials (Yang et al., 2019). Synthesis and application of magnetic nanocomposite on aluminium metal–organic framework (MOF) achieved removal efficiency of 492.4 $mg.g^{-1}$ of lead (II) ions (Ricco et al., 2015a). Among the carbon-based nanomaterials, carbon nanotubes (CNTs) and graphene-based materials have been employed in heavy metal removal in water. The CNTs achieve heavy metal removal by chemical interactions of the metal ions and functional groups such as carboxylic and hydroxyl groups on the surface of the CNTs (Gupta et al., 2016). Although the use of CNTs in the removal of heavy metals proves effective, it is limited due to its cost implication in a commercial application. In addition, CNTs form byproducts, which can be toxic, and their removal accrues additional costs.

Graphene nanomaterials have also achieved heavy metal ions removal from wastewater. Lead (II), Mercury (II), Cadmium (II) have been removed using graphene oxide with an efficiency of 602, 374 and 181 $mg.g^{-1}$ respectively (Yang et al., 2019). Studies show that silica-based nanomaterials achieve the removal of heavy metals. Functionalized silica nanospheres were reported to remove copper (II) ions from an aqueous water solution (Kong et al., 2014).

4. Drawbacks in the use of nano adsorbents for water purification

The environmental and health impact of both natural and engineered metal-based nanomaterials have not been extensively reported though their negative impact is associated with their small sizes or chemical properties especially for the mobile particles and not those incorporated into a material (Aragaw et al., 2021). None the less, their utilization in wastewater treatment will result in a significant increase in their concentrations in the aquatic environment where they will find their way into living organism causing health problems (Aragaw et al., 2021; Cervantes-Avilés and Keller, 2021). For instance, various nanoparticles have been found in influent, post-primary treatment, effluent of the activated sludge process and in the reclaimed water of a full-scale wastewater treatment plant (WWTP). In this case, the concentration of metal-based NPs in influent wastewater were found to range between 1,600 – 10700 ng/L, while in reclaimed water they ranged between 0.6 and 721 ng/L. It is worth noting while this study reported on what is found in the water cycle before and after passing a waste water treatment plant they did not report on the impact of using various metal nanoparticles as the primary treatment method hence their contribution to these amounts as a result of leaching wasn't reported (Cervantes-Avilés and Keller, 2021). However, they observed that the activated sludge process and reclaimed water system can be able to remove between 84 and 99 % of metal nanoparticles for most NPs under study though the removal of Mg, Ni, and Cd ranged between 70 and 78 %. Moreover, they also noted that the concentration of NPs was significantly higher in the waste activated sludge samples than in the anaerobic sludge or waste water as the secondary treatment resulted in their precipitation hence this can be employed as a strategy to remove NPs (Cervantes-Avilés and Keller, 2021).

Other drawbacks associated with use of nano adsorbents for removal of contaminants includes inability to recover and reuse them after treatment and their agglomeration in aqueous media brought about by strong van der Waals forces(Kokkinos et al., 2020b). Due to this, their water treatment efficiency is drastically reduced resulting in a flurry of strategies to stabilize them through surface coating using materials such as polymers, secondary metabolites, carbon, inorganic materials. Agglomeration control and recoverability is also enhanced if the nanoparticles are entrapped, anchored, or embedded in a polymetric matrix such as cellulose, chitosan, polyvinyl pyrrolidine among other polymers to obtain stable nanocomposites which makes their reusability and regenerability easier(Moreira et al., 2022).

5. Recovery and regeneration of nano adsorbents.

Recovery of nanoardsobents from water after the adsorption of micropollutants is paramount because it prevents downstream toxic effects in the natural environment. Similarly, regeneration of the recovered nano adsorbents makes it possible for them to be reused in new processes, thereby enhancing their sustainability. Nano adsorbent recovery techniques need designs that are efficient, simple to use, fast and sustainable in terms of cost and energy consumption. The most common methods for removal nanoparticles include application of a magnetic field for removal magnetic nanoparticles. Besides the magnetic methods, filtration and centrifugation are paramount in recovery of nano adsorbents(Moreira et al., 2022).

Various technologies or combination of technologies have been used, as discussed above, to produce nano adsorbents with high adsorption capacity and selectivity for selected micropollutants of emerging concern.

Regeneration methods are determined by the type of adsorbent and adsorbate, their stability and level of toxicity. Based on that, thermal, chemical and electrochemical methods have been used for regeneration of nano adsorbents from media (Khan et al., 2022; Moreira et al., 2022).

6. Conclusion and recommendations

This review highlights the increasing attention that nanotechnology is getting in regard to the environmental removal of aquatic contaminants. The efficiency that nanomaterials bring in their applications is crucial in addressing persistent water pollution. Different metallic nanoparticles have shown positive response in the removal and degradation of water pollutants including, antibiotics, steroids, heavy metals and pesticides. This review also indicates that green synthesized nanoparticles, due to their cost-effectiveness, environmental friendliness and easy-to-make procedures have also been highly considered for environmental remediation of water pollution. However, the exploration of different plant extracts for the green synthesis of metal nanoparticles for pollutant removal from water need to be strengthened by continuous research in this area of the application of nanotechnology in environmental remediation. This will advance the application of nanomaterials to curb environmental pollution caused by effluents from pharmaceutical, textile and other chemical industries.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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