



# Recent advances in greenly synthesized nanoengineered materials for water/wastewater remediation: an overview

Ahmed M. Elgarahy<sup>1,3</sup> · Khalid Z. Elwakeel<sup>2,3</sup> · Abdullah Akhdhar<sup>2</sup> · Mohammed F. Hamza<sup>4,5</sup>

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## Abstract

With the growth in the global human population, resource availability has become minimal. The creation of technology that is free of toxins for the remediation of the water/wastewater treatment for the sustainable development of global civilization is a matter of urgency. The development of cleaner and greener technologies with significant health and environmental benefits would be greatly influenced by nanotechnology. Nanotechnology technologies are being investigated for their potential to offer ways to remove water pollutants, as well as to increase the efficacy of conventional technologies used in environmental cleanup. Green nanotechnology is a nanotechnology area that envisions sustainability across a number of applications. This paper addresses issues relevant to green nanotechnology for sustainable development. Nanomaterials synthesis and applications have been used to solve water pollution by reducing the cumulative energy consumption during the synthesis or production process, the ability to recycle and manufacture new products and the use of environmentally friendly nanomaterials in water/wastewater remediation have been reviewed in the current study. Green nanotechnology offers choices to develop the next generation of water treatment systems.

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✉ Khalid Z. Elwakeel  
kelwkeel@uj.edu.sa

Ahmed M. Elgarahy  
ahmedgarahy88@yahoo.com

Abdullah Akhdhar  
aakhdhar@uj.edu.sa

Mohammed F. Hamza  
m\_fouda21@hotmail.com

<sup>1</sup> Egyptian Propylene and Polypropylene Company (EPPC), Port Said, Egypt

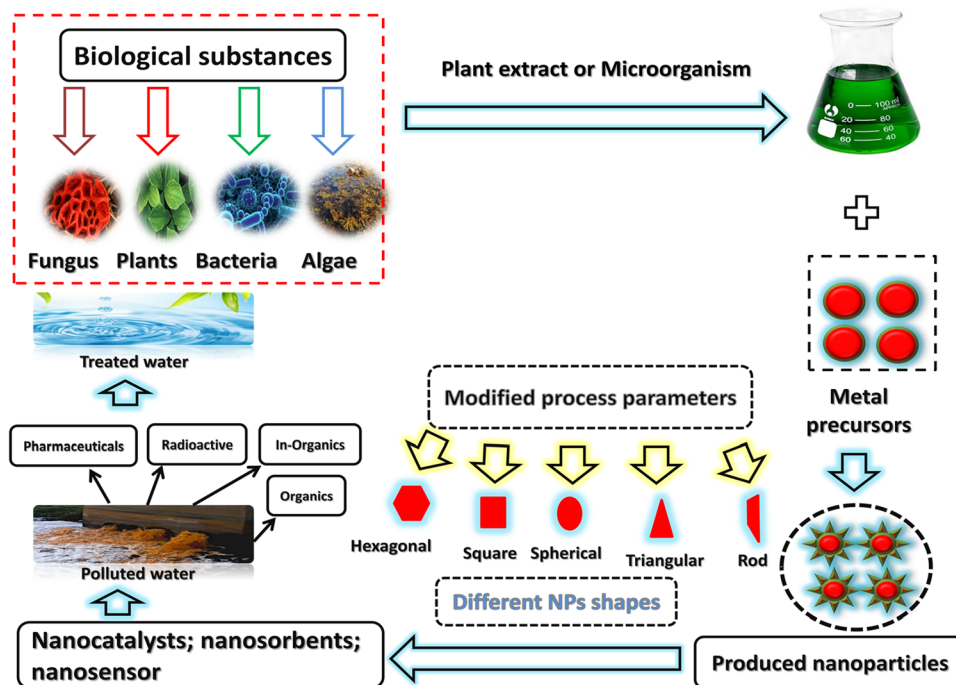
<sup>2</sup> College of Science, Department of Chemistry, University of Jeddah, Jeddah, Saudi Arabia

<sup>3</sup> Environmental Science Department, Faculty of Science, Port Said University, Port Said, Egypt

<sup>4</sup> Guangxi Key Laboratory of Processing for Non-Ferrous Metals and Featured Materials, School of Resources, Environment and Materials, Guangxi University, Nanning 530004, People's Republic of China

<sup>5</sup> Nuclear Materials Authority, El-Maadi, POB 530, Cairo, Egypt

## Graphic abstract



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## Introduction

Around 70% of the atmosphere of the earth is occupied by water. Sea and ocean water ~97% of the water body of the world is saline and not suitable for drinking, industrial or agricultural utilization [1], whereas freshwater is 3% of the earth's water. At a closer look, about 30% and 69% of the freshwater are underground and trapped water in glaciers and ice caps, respectively, which are difficult to use. The only available fresh supply of water for usage is <1%, found in rivers, ponds, lakes, etc. [2]. Undoubtedly, water is one of the main and valuable resources on earth and a vital weapon for human development, being necessary for the survival of numerous biota on our planet. It is widely used for many purposes including, but not limited to, agriculture, drinking, industrial purposes, mining, cleaning, etc. The global population increase rate is nearly about 80 million people/year resulting in an enhancement in the freshwater consumption of 64 billion m<sup>3</sup>/year [2]. Water quality is deteriorated attributing to numerous human activities (i.e., agricultural, mining, and deforestation) as well as the increased demand for clean and safer water. Various industrial sectors such as paper, pulp, food, textile, and pharmaceutical industries are known to be significant contributors to water contamination [3–7]. Wastewater discharges (effluents) from the different

industrial sectors are discharged directly or indirectly into the aquatic environments. Annually, about 300–400 million tonnes of water pollutants (i.e., heavy metals, dyes, sludge, and other toxic chemicals) is released into the water bodies [8]. Seepage of these non-biodegradable pollutants in water assets for prolonged periods (above statutory limits) is undesirable because of their bioaccumulation behaviors through the food chain, harming different living organisms considering their mutagenic, immunogenic, carcinogenic, and teratogenic properties and consequently provokes ecological and human issues in our biosphere [9, 10]. Besides, the urgent necessity for improving water quality cannot be ignored. It has been articulated that by the year 2030, above 3.9 billion people are facing water shortages, globally. From all the above mentioned, it becomes clear that water/wastewater treatment has become an indispensable necessity [11].

The provision of safe and balanced drinking water is a global problem. Water and wastewater disposal schemes are chemically complex, inefficient and to a degree toxic to the environment [12]. There are numerous water pollutants such as heavy metals (i.e., arsenic, aluminum, cadmium, chromium, cobalt, copper, manganese, magnesium, mercury, molybdenum, lead, iron, nickel, uranium, and zinc) [13], dyes (i.e., (a) cationic, (b) anionic and (c) nonionic) [14], pharmaceutical pollutants (i.e., paracetamol, tramadol, and

ciprofloxacin) [15], herbicides/pesticides, and phenols [16, 17]. A tolerance limit specified by each pollutant has been set by the World Health Organization (WHO), and different therapeutic approaches have been applied to meet these limits. Currently, numerous operating scenarios are operated for water/wastewater treatment which is categorized into (1) mechanical, (2) thermal, (3) chemical, (4) physical, and (5) biological [18]. Mechanical methods include screening, sedimentation, floatation, filtration, reverse osmosis, and forward osmosis. Thermal methods include evaporation, distillation, and steam stripping. Physical methods include adsorption, extraction, and flocculation/coagulation. Chemical methods include precipitation, wet oxidation, Fenton, ozonolysis, and ion exchange. Besides, the electrocoagulation process is an attractive method for the treatment of wastewater because it is considered a rapid and well-controlled process that requires fewer chemicals, provides good reduction, yields, and produces less sludge [19–23]. Biological methods include phytoremediation, biotransformation, biomineralization, and bioaccumulation. Nakshatra et al. have reviewed and discussed the remediation of water by using nanomaterials synthesized by the green method [24]. However, the current review article gives more focus on the different methods of green preparation of nanoparticles and different applications such as nanoadsorbents, nanocatalysts, water nanofiltration, and nanomaterial-based sensors. This paper aims to summarize the recent advances in the elimination and detection of aqueous pollutants and harmful contaminants using a variety of green synthesized nanomaterials.

## Nanotechnology

One of the current situation's major problems is to achieve sustainable growth for future generations by using green chemistry principles to include green materials such as green nanoproducts without toxic end products. Nanoscience and nanotechnology are branches of engineering and science concerned with the treatment of materials or emphasizing the importance of nanometer-scale matter (1–100 nm). Therefore, the nanometer is referred to as one billionth of a meter ( $1 \times 10^{-9}$  m) [25]. Nanoscience is the approach of microscopic, molecular-, and macromolecular-scale analysis of the nature and monitoring of resources, where the properties of the synthesized composite vary considerably from those of a larger scale. The combination of material science, physics, chemistry, and biology, which deals with the regulation of matter on larger scales between molecular and micron size, is also concerned. Nanotechnology can be defined as the division of technology that covers the dimensions 1–100, in particular the handling of individual atoms and molecules. Therefore, nanotechnology synthesizes, characterizes,

produces, and introduces devices, structures, and processes by adjusting the size and form of the nanometer scale [26].

## Manufacturing of nanomaterials

The implementation of the principles of green chemistry in the nanomaterial synthesis method is an emerging field of sustainable development. All nanoproducts must be manufactured at different stages of development to create nanoscale particles, materials, and devices. Techno-economic analysis in terms of life cycle assessment (the economic feasibility of the synthesis process, manufacture of nanomaterials, and their fate after emitted into the environment until its end of life [27]) should be considered during nanomaterials development. It is expected that newly green developed materials (a) have high surface functionality, (b) exhibit size-dependent properties, and (c) contain a large range of materials and elemental compositions that is compatible with green chemistry principles (Table S1; see supplementary) [28]. The assessment of these products, before being accepted on a commercial basis, offers an opportunity to reduce the negative impact of the content, which is a must. Remarkable merits of green nanomanufacturing can be mentioned as follows [29]:

- (1) Creates relatively safe, clean, and more efficient nanoproducts.
- (2) Eliminates the need for productive toxic chemicals and solvents.
- (3) It is comparably cheaper and eco-friendly.
- (4) No toxic end product.
- (5) Needs fewer regulations concerning manufacturing and safety.

Two major approaches are adopted for nanomaterial manufacturing: bottom-up and top-down techniques [30, 31]:

*Bottom-up approach* Synthesize nanostructures by starting from the atom to the nanoscale by self-assembling of organic/inorganic materials.

*Top-down approach* Diminish the substance to the nanoscale from bulk. Nanomaterials are preferable to be templated in synthesis.

The top-down process includes nanomaterial synthesis by physical methods, for example, lithography, frying, and etching [32]. The top-down approaches begin with microsystems and reduce them to the nanoscale, cutting the larger material by molding it down to meet the dimensions of the nanoscale. Contrarily, bottom-up methods use a precursor to assemble the substance on an atomic scale via growth and nucleation via chemical reactions such as sol–gel and self-assembly [33].

Top-down techniques are widespread because of the ease and simplicity of use than bottom-up approaches to nanomaterial synthesis. By comparing both mentioned methods, it is often believed that top-down methods produce more waste than bottom-up technology. The bottom-up techniques are therefore the ultimate tools for sustainable processing that include tailor-made reaction design, methodology, and size-controlled synthesis by unintentional waste minimization. Commonly, the manufactured engineered nanoparticles (ENPs) can be classified into zero-dimensional, one-dimensional, two-dimensional, and three-dimensional [34]. Several of the nanofabrication processes have low product yields, which contribute to low material production and a disproportionate production of waste. Besides, some synthesis methods are potentially triggered by the unintended release of nanomaterial in the atmosphere to have unintentional effects on human health (acute and chronic). The design and use of these ENPs offer clear reasons for the use of green chemistry principles to generate and apply new nanomaterials. Each nanoproduct's production consists of high energy usage, hazardous chemicals, low material processing, inefficient, repetitive purification, and many other ways of setting up greener nanomaterial synthesis processes. Greener synthesis of nanomaterials draws worldwide attention. There are some advantages over chemical-based synthesis to the green synthesis of nanomaterials [35]. Green synthesis can be used to produce a higher number of particles in less time under low reaction conditions, highly efficient, multifunctional, and less risky nanomaterials. Nasrollahzadeh et al. [36] reviewed the trends and prospects exploiting the sustainable applications of green synthesized nanomaterials for the removal of contaminants and metal ions from aqueous solutions. Recent trends and challenges concerning these nanomaterials have been highlighted, including challenges with toxicity and biosafety and its future applications for water treatment and water purification. To extract toxic materials and toxins from water, it was concluded that green-synthesized and biogenic nanocatalysts and nanomaterials can efficiently and cost-effectively remove inorganic, renewable, chemical, and heavy metal pollutants from aqueous systems [36].

### Carbon-based nanomaterials

Carbon-based materials including carbon dots, fullerenes, nanodiamonds, and nanofoams are a much investigated class of nanomaterials. Carbon nanotubes are only layers of graphite formed into a tube shape that may be single- or multiwalled based on the number of layers. Using a one-step hydrothermal technique, a functional group-rich magnetic nanocomposite (MNC) was prepared using the amino derivative of carbon nanotubes and 1-formylimidazole-modified graphene oxide as functional reagents [37]. Characterization results suggested that the nanocomposite obtained showed satisfactory saturation magnetism and could be used to rapidly extract

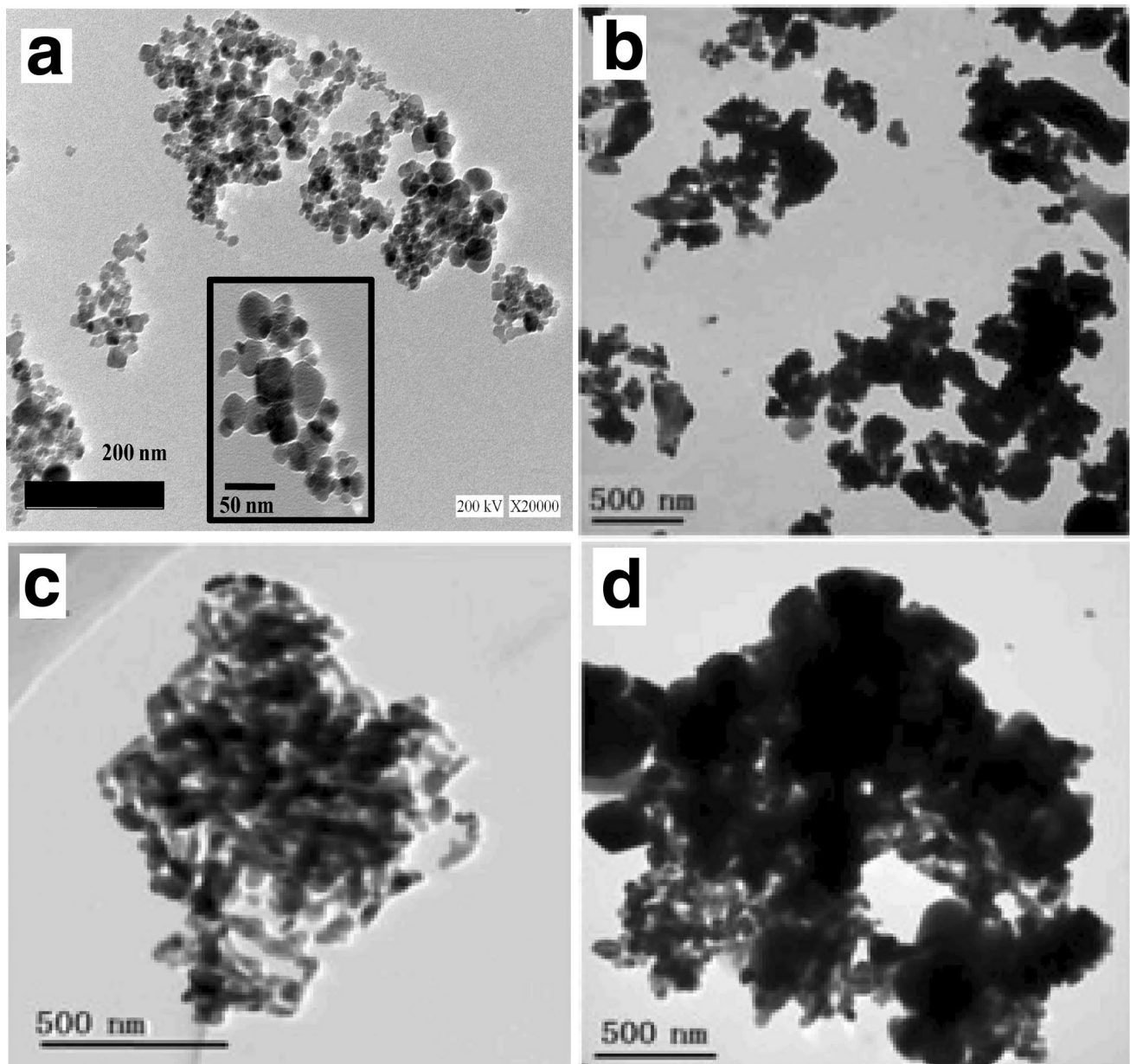
glucocorticoids using the magnetic solid-phase extraction (MSPE) method. Low detection limits (0.0075–0.16 ng/L), broad linearity (0.05–1000 ng/L), and outstanding precision (RSD < 10%) were obtained. Magnetic carbon nanotubes (M-CNTs) were tested to extract microplastics (MPs) [38]. The observed successful removal of MPs from solutions and wastewater samples highlights M-CNTs as promising pollution control material for MPs [38]. Due to their appealing physicochemical, mechanical, thermal, and electrical properties, carbon nanotube membranes have been shown to provide tremendous potential for separation applications. The key problem is how CNTs with their unique properties can be incorporated into a stable membrane structure with excellent separation efficiency. Rashed et al. discussed in detail the developments in the manufacturing of CNT membranes and their drawbacks, followed by a detailed review on the use of these CNT membranes in water treatment [39]. A new method was developed to load two MOFs (ZIF-8 or UiO66-NH<sub>2</sub>) on carbon nanotube aerogels (CNT) by in situ nucleation and development of nanoparticles of MOFs on carbon nanotubes. In addition, MOF@CNT's hydrophilia, mechanical properties, and thermostability have been investigated [40]. The findings showed strong hydrophilia, compression resilience, and thermostability for MOF@CNT. The adsorption capabilities of MOF@CNT were higher than single MOF nanoparticles with an analysis of the adsorbability of herbicides (chipton and alachlor); moreover, the study showed a synergetic influence among MOF and CNT. The preparation of spongy carbon nanostructures using nanoporous graphene (NPG) was achieved to absorb oil spills from the surface of water [41]. Having altered the powder form to sponge, an increase of 11–14% was recorded in adsorption capacity of nanoporous graphene in sponge in comparison with powdery form [41]. In addition, the nanoporous graphene sponge (NPGS) has been shown to be completely recyclable and versatile, recycled by heat treatment, solvent extraction, and mild suction filtration with sufficient recovery percent. Remarkably, the adsorption percent of the NPGS reached up to 98% even after it had been used 10 times. Based on the proper efficiency of the NPGS, it can be a perfect candidate for oil spill cleaning [41].

Graphene is also a carbon-based, single-layer construction similar to natural graphite formed from one carbon atom. Magnetic graphene oxide-functionalized lauryl sulfate (MGOLS) was utilized for the fast removal of methylene blue (MB) using batch sorption experiments. The maximum Langmuir loading capacity reached 624.42 mg/g [42].

### Metal nanoparticles

Popular examples of recently prepared nanoparticles include nanogold, nanosilver, and metal oxides such as titanium dioxide and iron oxide. Many metallic nanoparticles form solid





**Fig. 1** TEM images of **a**  $\text{Fe}_4\text{O}_4$  [43], **b**  $\text{CuO}$ , **c**  $\text{Co}_3\text{O}_4$ , and **d**  $\text{Mix-CuO/Co}_3\text{O}_4$  [44]

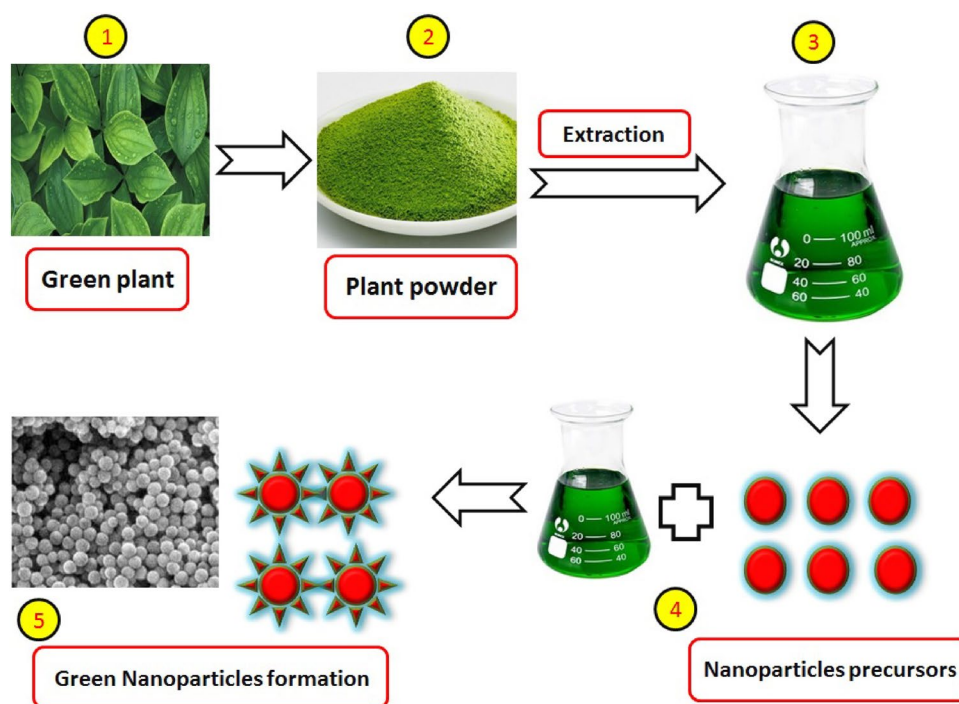
colloidal solutions. Also, surface modifying is important to accomplish objectives when they have a high volume-to-surface ratio. They can be synthesized in many ways, such as a rod, dot, or cubes, and also have special optical properties such as fluorescence or increased resonance on the surface, facilitating faster identification and thus their imaging applications at low concentrations. Recently, iron oxide has been extensively used in the preparation of magnetic adsorbents for water detoxification. TEM images of  $\text{Fe}_3\text{O}_4$  nanoparticles are given in Fig. 1a [43], while Fig. 1b–d shows the TEM images of  $\text{CuO}$  (b),  $\text{Co}_3\text{O}_4$  (c), and  $\text{Mix-CuO/Co}_3\text{O}_4$  (e) [44].

## Nanomaterials green synthesis

Green synthesis is a modern tool for the design of new nanomaterials that are harmless to human and environmental health and can revolutionize large-scale, pro-stop nanomanufacturing processes based on the principles of green chemistry [45]. Different definitions should be considered including:

*Green chemistry* It is the nature of chemical products and processes that minimize and eliminate toxic materials uti-

**Fig. 2** Green synthesis of nano-materials using plant extract [55]



lization. It is used during a chemical product's life cycle (manufacture, usage, and final disposal).

*Sustainability* Development meets the needs of the present without sacrificing future generations' potential.

*Green nanotechnology* Technology used to develop sustainable health and avoid possible hazards related to technologies. It requires the use and processing of nano-products.

Green nanotechnology has two objectives: synthesis method products, where the as-prepared innovative nano-materials can be further performed in different applications such as nanosensors, semiconductor photocatalysis, and novel membrane for pollution monitoring, environmental remediation, and wastewater purification, respectively [46, 47]. Arguably, green nanotechnology is the most important branch of nanoscience, using 12 green chemicals principles for various potential uses [48]. Table S1 (see Supplementary Material) provides the main principles of green chemistry. These greener nanomaterials have wide potential as novel drug carriers in the field of nanomedicine [49]. Greener nanomaterial synthesis sets a benchmark for making nano-products and nanomaterials cleaner stable, safe, and more sustainable [50]. Green chemistry's fundamental principles are the use of non-toxic, biodegradable, economic, and energy-efficient materials and reactions. Nanomaterial synthesized with plants, bacteria, and other natural resources is commonly called green nanomaterials. Certain chemistry methods also qualify for methods of green chemistry synthesis; however, the use of all-natural materials in the field

of nanoproduction has been widely used [51]. Nanomaterials synthesized using green synthesis methods are similar to their chemical counterparts and of similar effectiveness in various works of literature. Green syntheses of nanoparticles in contrast to chemical or microbial synthesis are easier, cheaper, more effective, and environmentally friendly. To use toxic solvents, high-pressure, high-energy, and high-temperature conversion is needed in the chemical synthesis method. On the other hand, microbe synthesis is not possible on a large scale because of its laboratory maintenance. The properties of nanomaterials can also be altered by controlling reaction conditions such as temperature and pH concentration [52]. Nanosensing, nanomedicine, nanotherapeutics, energy storage, and so on are major uses of these greener nanomaterials. Greener processes, in particular, have paved the way for safe and sustainable nanotechnology [53]. Many challenges and issues relate to green nanotechnology, but the goal of a green and sustainable solution is not diminished. Two problems that have hindered progress have been the poor awareness of the new risks presented by nanotechnology and the lack of adequate policies to handle any new risks. Nevertheless, scientists, engineers, and entrepreneurs continue to move forward, tackling problems ranging from technological to regulatory and anywhere in between. Just as new perspectives from scientists have been demanded by the concepts of nanoscale innovation, they also demand new approaches to handling, manufacturing, financing, and deploying novel technologies in the larger chemical sector [54]. Figure 2 shows the overall green nanomaterials synthesis methodology [55]. Various multifunctional

green-based nanomaterials have been synthesized using different methods and their potential applications with a specific structure, scale, morphology, and crystallinity have been investigated. Green synthesis of plant nanomaterials is a bottom-up approach involving oxidation and reduction [56]. A variety of primary and secondary metabolites (i.e., alkaloids, flavonoids, phenolic acid, terpenoids) are found in the plant extract. These are the compounds that reduce/convert soluble atoms in solutions into nanoparticles [57]. These are the major triggers of redox reactions by the synthesis of green, environmentally friendly nanomaterials. The literature review shows that the synthesis process is the key contributor to non-material's life cycle impacts, as toxic waste is more likely at this stage to be produced.

### Green preparation methods

Nanoparticles may be synthesized using reducing agents from natural sources such as polysaccharides and plants or biological microorganisms such as bacteria and fungi.

### Biological synthesis

Biological synthesis of metallic nanoparticles is a green and eco-friendly process, and microorganisms such as bacteria, actinomycetes, fungi, and algae can be used as reducing agents for metal ions. The reduction process of the metal can be performed internally to the cell or an external reaction [58].

### Plant extract mediated synthesis

In the synthesizing of metal nanoparticles, extracts were used of different plant species; alternately, live plants were also used [59, 60]. The mode of use of plant extracts for the production of nanoparticles is simple, in that the extract is mixed with a metal salt solution at different temperatures and kept under constant stirring (Fig. 2), sometimes under ultrasonic or microwave irradiation, for a specific duration of time. The single-step biogenic reduction of metal ion to base metal is rapid, can be performed at room temperature and atmospheric pressure, making it easy to scale up the process. The identified reducing agents are plant secondary metabolites, chemically classified as alkaloids, tannins, terpenoids, and co-enzymes [61].

### Chemical synthesis

Nanoparticles are formed using polyelectrolyte, enzymatic treatment, ultrasonic, acid hydrolysis, chemo-mechanical treatment, and nanoprecipitation by various techniques such as ionotropic gelation and microemulsion method.

**Polyelectrolyte complexation** Polyelectrolyte complexes (PEC) form by the interaction of polyions with opposing charges or their salts. The electrostatic interaction between the polyelectrolyte ionic groups is responsible for PEC formation. Additional interactions, including hydrophobic and hydrogen bonds, lead also to complex development. An example of this type of nanosynthesis is the synthesis of chitosan/streptokinase and polyethylene glycol (PEG)-grafted chitosan/streptokinase nanoparticles (NPs) by PEC method [62].

**Enzymatic treatment** In the presence of pullulanase enzymes, the extremely ramified amylopectin is debranched. The amylopectin's decomposition relies highly on its crystalline form. In the gelatinized suspension of maize starch, pullulanase hydrolytic studies have shown that nanoparticles in starch have unequal forms and a range of dimensions of 15–45 nm [63].

**Ultrasonic** Piezoelectric conversion, which functions in high voltage energies of frequencies of 20 kHz, is used for ultrasonic nanoparticle synthesis. It induces swift movements in liquid samples, leading to a violent collapsing of bubbles known as cavitation. The lack of chemical extraction is its main advantage over other approaches like acid hydrolysis. Therefore, several investigations have studied the effect of ultrasound therapy on the physical properties of suspensions. The effect of ultrasound pretreatment on starch properties, water status, pore characteristics, and the oil absorption of potato slices was evaluated [64]. The findings indicated that ultrasound pretreatment contributed to the surface degradation of starch granules and increased power disorganized the structure of starch. In addition, after ultrasound pretreatment, the proportion of bound water and immobilized water was modified.

**Acid hydrolysis** For semi-crystalline preparation, acid hydrolysis is the simplest process. The amorphous regions erode when they are treated with moderate concentrations of strong acids like sulfuric acid or hydrochloric acid and aid the isolation of resistant crystalline moieties. Suman et al. [65] have stated that acid hydrolysis can prepare starch nanoparticles/nanocrystals.

**Chemo-mechanical treatment** The chemo-mechanical process utilizes a mixture of 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO) oxidation and microfluidizer for the preparation of nanofibers. For example, TEMPO-oxidized cellulose nanofiber (TEMPO-CNF) made from bagasse was characterized and used as a sustainable material for the preparation of new nanocomposites. The as-prepared nanofiber was used for Brilliant Blue dye removal from water.

**Nanoprecipitation** Nanoprecipitation is the easiest and most readily reproducible single-step process used to manufacture nanomaterial-based synthetic polymer nanoparticles. For example, starch nanoparticles were prepared based on the precipitation of amorphous starch in ethanol [66]. Zhang et al. [67] synthesized photocrossing cinnamic acid-modified starch nanoparticles by an esterification reaction using 4-dimethylaminopyridine and 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide as catalysts. The co-precipitation process is known as an easy and convenient route for the preparation of  $\text{Al}_x\text{MgFe}_{2-x}\text{O}_4$  nanoparticles from an aqueous solution containing  $\text{Al}^{3+}/\text{Mg}^{2+}/\text{Fe}^{3+}$  salts by adding an alkaline solution at room temperature under an inert atmosphere [68].

#### i) **Iontropic gelation**

This technique is quick and easy to prepare in the aquatic environment. The mechanism involves the electrostatic interaction of charged functional groups with an oppositely charged molecule. For example, chitosan is dissolved in acetic acid, and then under a constant mechanical ring, polyanion or anionic polymers were added dropwise. The mechanism involves the electrostatic interaction of the chitosan amine group with the negative charge of polyanion. Besides, the solution may also contain stabilizing agents such as poloxamer before or after adding polyanion. Another example is the addition of calcium for the ionotropic gelation of alginate. This gelation mechanism allows structuring the sorbent as beads before chemical modification [69].

#### ii) **Microemulsion method**

Here, the formation of nanoparticles takes place in the aqueous core of the reverse micellar droplets and is thus linked by a cross-linking agent. Surfactant is dissolved in the right solvent for stabilization and added to the solution [70]. Organic solvents are removed through evaporation under low pressure, while excess surfactants contained in the prepared nanoparticles may be removed by precipitation with calcium chloride. This technique will make the size distribution of the nanoparticles collected by this process smaller than 100 nm [71]. By adjusting the volume of the cross-linking agent, the size of the nanoparticle can be further regulated. It has many drawbacks, though, since it takes time, uses organic solvents, and requires complicated washing steps [72].

## **Nanoadsorbents**

This needs an alternative wastewater treatment technology that is greener and more sustainable. The solution to the present challenge is nanotechnology [73]. Generally, sorption can be divided into adsorption and absorption. The

concept of adsorption is interpreted as the emerging adhesion between atoms, ions, or molecules whether in a liquid or gaseous or solid states and the surface. The ions, atoms, or particles that adhere to create a film on the substance's surface in which they are bound and termed as adsorbate, while the substance on which they are appended are named as adsorbent [74]. Adsorption is diverse from absorption because in absorption, the absorbate (fluids) is dissolved via an absorbent whether solid or liquid. Adsorption forms on the outside surface, while absorption entails the whole material volume. Sorption is correlated to the couple manners, while desorption is considered as counter-reaction or reversed the adsorption process. Due to their higher surface-to-volume relationship, nanomaterials have been commonly considered for environmental cleaning and remediation [75]. An additional benefit is also provided by other unique changes in its physical, chemical, and ecological characteristics. The development of new nanomaterials with improved performance, selectivity, and the ability to handle wastes are underway [76]. Water purification nanotechnology plays a major role in maintaining global water quality and safety. In the following points, the use of nanotechnologies to treat wastewater is summed up:

- (1) Using nanoscale filters such as membranes for nanofiltration.
- (2) Via nanoadsorbent compounds, including nanomagnetite or metal oxides, nanoclays, nanometals.
- (3) Nanophotocatalysis for environmental remediation using nanosized semiconductor materials.
- (4) Nanocomposites, such as nanomagnetite incorporated sorbents for various applications.
- (5) Heavy metal remediation nanomaterials.
- (6) Metal and metal oxides for the elimination of pathogenic microbes from water.

Several research studies have demonstrated that nanobased remediation technologies have proved more safe, affordable, and successful than conventional remediation technologies [77, 78]. Nanomaterials were used for pollutant detection and management, remediation, and pollution prevention [79]. Nanomaterials were also used to boost membrane separation processes, which contribute to greater selectivity and lower costs [80]. Nanomaterials have various progressive measures, such as special, quantum confinement-driven properties [81]. For water purification and processing, novel photocatalytic membranes are prepared using semi-conductive nanomaterials against conventional membranes [82]. Besides, different techniques are employed to address wastewater treatment issues such as photocatalysis, nanofiltration, and adsorption, using titanium dioxide, zinc oxide (ZnO), polymer membranes, ceramic membranes, carbohydrate nanostructures, nanomagnetic membranes, and magnetic nanoparticles



**Table 1** Sorption capacities of different nanomaterial-based sorbents toward different water pollutants

Sorbent-based nanomaterial	Water pollutant	Sorption capacities (mg g <sup>-1</sup> )	References
Hierarchical MgO nanostructure	Malachite green	1205.23	[125]
Hierarchical MgO nanostructure	Congo red	1050.81	[125]
Fe <sub>3</sub> O <sub>4</sub> /HA nanosorbents	Malachite green	199.98	[126]
Magnetic nanocrystalline ZnFe <sub>2</sub> O <sub>4</sub>	Evans Blue	46	[127]
Graphite oxide nanomaterial	Methylene blue	288	[128]
Graphite oxide nanomaterial	Acid orange 7	232	[128]
Copper nanoparticles	Methylene blue	64	[129]
MIL-Ti metal–organic frameworks (MOFs) nanomaterials	Basic blue 41	1257	[130]
MIL-Ti metal–organic frameworks (MOFs) nanomaterials	Basic red 46	1296	[130]
MIL-Ti metal–organic frameworks (MOFs) nanomaterials	Methylene blue	862	[130]
Polyphenol stabilized gold nanoparticles (AuNPs)	Methylene blue	595.23	[131]
Polymer–bixin nanofibers	Brilliant green	254	[132]
Polymer–bixin nanofibers	Methylene blue	79	[132]
Uncalcined MgAlNi-Ba-Fe	Methyl orange	763.35	[133]
Calcined MgAlNi-Ba-Fe	Methyl orange	756.42	[133]
MCM-41 NPs	Oil	100	[134]
MCNCs/starch-g-(AMPS-co-AA) hydrogel nanocomposite	Crystal violet	2500.0	[135]
MCNCs/starch-g-(AMPS-co-AA) hydrogel nanocomposite	Methylene blue	1428.6	[135]
Hybrid multiwalled carbon nanotube (CNT)-coated biochars	Methylene blue	6.2	[136]
Cellulose capped Fe <sub>3</sub> O <sub>4</sub> nanofluids	Methylene blue	13.54	[137]
xGnP® graphite nanoplatelets (GNP)	Drimaren Dark Blue CL-R	22.14	[138]
xGnP® graphite nanoplatelets (GNP)	Direct Red 80	38.36	[138]
xGnP® graphite nanoplatelets (GNP)	Chrysophenine	28.68	[138]
xGnP® graphite nanoplatelets (GNP)	Eosin Yellowish	156.77	[138]
Fe <sub>3</sub> O <sub>4</sub> -thiourea-formaldehyde	Titan yellow	650.50	[139]
Fe <sub>3</sub> O <sub>4</sub> -thiourea-formaldehyde	Rose bengal	869.51	[139]
Chitosan-alginate nanoparticles (CANPs)	Hg (II)	217.39	[140]
Fe <sub>3</sub> O <sub>4</sub> -thiourea-formaldehyde	As(V)	147.59	[141]
Chitosan-CuO	As(V)	28.1	[142]
TiO <sub>2</sub> nanoparticles coated chitosan	Cu (II)	526.50	[143]
TiO <sub>2</sub> nanoparticles coated chitosan	Pb (II)	475.50	[143]
2-Mercaptobenzimidazole derivative of chitosan	Ag(I)	323.6	[43]
TiO <sub>2</sub> nanoparticles entrapped chitosan	Cu (II)	715.70	[143]
TiO <sub>2</sub> nanoparticles entrapped chitosan	Pb (II)	579.10	[143]
Magnetic nanocomposite particles (MNCs)	Pb(II)	53.33	[144]
Magnetic nanocomposite particles (MNCs)	Cd(II)	48.53	[144]
Zinc oxide nanoparticles	Cr(III)	88.547	[145]
Silica-supported hydrophilic carbonaceous nanoparticles (SHNPs)	Cd(II)	0.54	[146]
Silica-supported hydrophilic carbonaceous nanoparticles (SHNPs)	Ni(II)	13.48	[146]
Silica-supported hydrophilic carbonaceous nanoparticles (SHNPs)	Pb(II)	8.87	[146]
Lignin-based hybrid magnetic nanoparticles	Pb(II)	150.33	[147]
Lignin-based hybrid magnetic nanoparticles	Cu (II)	70.69	[147]
K <sub>2</sub> Mn <sub>4</sub> O <sub>9</sub> nanomaterial	Cr(III)	41.8	[148]
K <sub>2</sub> Mn <sub>4</sub> O <sub>9</sub> nanomaterial	Cr(VI)	3.25	[148]
Fe <sub>3</sub> O <sub>4</sub> -thiourea-formaldehyde	Cr(VI)	222.51	[141]
CuO-Chitosan	Cr(VI)	136.21	[149]
Graphene quantum dots nanomaterials	Carbamate pesticide oxamyl	125	[150]
Single-walled carbon nanotubes (SWCNT)	Ciprofloxacin	724	[151]
Single-walled carbon nanotubes (SWCNT)	Oxytetracycline	554	[151]

**Table 1** (continued)

Sorbent-based nanomaterial	Water pollutant	Sorption capacities (mg g <sup>-1</sup> )	References
Multiwalled carbon nanotubes	Tetracycline	269.54	[152]
Granular carbon nanotubes (CNTs)	Diclofenac sodium	64.61	[153]
Granular carbon nanotubes (CNTs)	Carbamazepine	87.30	[153]
H <sub>2</sub> O <sub>2</sub> treated MWCNT	Fulvic acids	321.9	[154]
Carboxyl-modified multiwalled carbon nanotubes	Linear alkylbenzene sulfonates	189	[155]
Polyvinyl alcohol/silica-based nanofiber	Bisphenol A	682.35	[156]
Amorphous carbon nanotubes	Resorcinol	800	[157]
Multiwalled carbon nanotubes (CNTs)/CoFe <sub>2</sub> O <sub>4</sub>	Sulfamethoxazole	6.98	[158]
Magnetic CNTs–C@Fe–chitosan composite	Tetracycline	104	[159]

(nZVI) [83]. For the detection and elimination of chemical and biological pollutants, including heavy metals, pharmaceutical waste, pesticides, and their intermediates, cyanides, algae, viruses, microbes, parasites, organics, and antibiotics from wastewater, novel metal/metal oxide nanoparticles, nanomembranes, and other nanomaterials are used [84, 85]. Membrane processes, nanobased materials, and the combination of them offer a wide range of possibilities for water treatment by filtration and photocatalysis at the same time. About sustainability concerns, the emphasis has been moved toward the use of greener wastewater treatment systems for environmental applications. This will reduce the risk of hazardous waste production and mitigate the risk of harmful end products by nanomaterials synthesized using green chemistry techniques to purify the environment. Sorption capacities of different nanomaterial-based sorbents toward different water pollutants are summarized in Table 1.

## Nanocatalysts

Research into advanced oxidation processes (AOPs) including nanobased wastewater treatment technology was motivated by conventional technical deficiencies to promote environmental sustainability [86]. The main aim of such AOPs is the production of highly reactive (in situ) or free radical particulates to rapidly dissolve and mineralize unmanageable organic compounds and toxins, water contaminants, toxicants, pesticides, and disinfection by-products [87]. Nanobased photocatalysis has become a promising green chemical remediation technique in recent years. Nanophotocatalysis has emerged among many green earth proposals as the most exciting therapy technology; it utilizes the plentiful natural sunlight or artificial light energy [88]. Photocatalytic techniques have been successfully used in recent years to remove these toxins from wastewater. The ability to degrade various compounds such as dyes, pharmaceuticals, endoscopic chemicals, phenols, or toxins from

wastewater has been proved by photocatalytic oxidation [89]. The photocatalytic processes have proved to be effective in the degradation of organic bio-recalcitrant compounds. The increasing fears of the public regarding many chemicals in the atmosphere have contributed to the need to implement innovative treatment solutions that concentrate on advanced oxidation, i.e., the photocatalysts. The main advantage of the photocatalytic process over conventional technology is that no extra treatment is required and that secondary disposal approaches are avoided [90]. There is no need for costly oxidizing agents relative to other advanced oxidation methods, especially those involving the use of oxidants such as hydrogen peroxide and ozone, since the atmospheric oxygen gene functions as an oxidant, this is the additional value of nanophotocatalysts. However, many drawbacks exist such as the recombination of electron–hole pairs and the difficulty of regeneration (separation of the powder after reaction) [91, 92]. Since nanocatalysts rely on the shape, dimension, and structure of their synthesis and efficacy, they must be synthesized to meet the objective of green nanotechnology. Nanocatalyst architecture and production is the basis for the total degradation of toxins into eco-friendly products [93].

This is one of the ways in which green chemistry can contribute to a safe way to green nanotechnology. Heterogeneous photocatalysts can quickly degrade both organic and inorganic pollutants [94]. Pollutant degradation was performed by speeding the chemical reaction rate in the presence of a semiconductor catalyst. This method relies mainly on the formation of hydroxyl radicals (OH) able to turn various toxicants/non-biodegradable pollutants into non-toxic end products, such as CO<sub>2</sub> and H<sub>2</sub>O [95]. A wide range of environmental pollutants has been treated with many types of nanocatalysts, such as metal nanoparticles, doped nanocomposites, nanotubes, and bimetallic nanoparticles [96]. Despite comprehensive field studies, the development of effective semi-conductive photocatalysts capable of working in solar, visible, and UV light poses a challenge.

Sherin et al. used the novel *Terminalia bellerica* kernel extract for the synthesis of biogenic silver nanoparticles [97]. The optimum synthesis of silver nanoparticles was achieved under environmental conditions at concentrations of 0.016 mg/mL kernel extract and 2.0 mM silver nitrate. In that study, silver nanoparticles were characterized by ultraviolet–visible absorption spectroscopy, transmission electron and scanning electron microscopy, energy-dispersive X-ray analysis, X-ray diffraction, and Fourier transform infrared spectroscopy. The synthesized silver nanoparticles displayed an innate catalytic reduction of organic pollutants such as 4-nitrophenol, methylene blue, eosin yellow, and methyl orange. An artificial neural network (ANN) model based on experimental data was developed to predict the catalytic performance of nanosilver. A good correlation between ANN model-based results and experimental data indicated that it could be used to forecast the catalytic performance and hence the extent of pollutant reduction at various catalyst concentrations [97].

Photoelectrocatalytic (PEC) water treatment is a promising technology for organic pollution abatement [98]. Much of the research focused on material discovery and optimization. However, challenges exist in scaling up PEC processes and are associated with designing reactors with effective light irradiation on electrode surfaces and, simultaneously, efficient electrode configurations. Montenegro-Ayo et al. designed and demonstrated key reactor design principles, which influence reaction mechanisms, for a reactor using a TiO<sub>2</sub> nanotube-coated disk flow reactor [98]. Degradation of organochlorinated 2,4-dichlorophenol was studied as a representative carcinogenic micropollutant. The synergistic photoelectrocatalytic process showed fivefold faster degradation kinetics than solely electrocatalytic treatment or a greater than twofold enhancement over photocatalysis alone. Applicability of photoelectrocatalytic treatment was demonstrated over a wide range of micropollutant concentrations with almost complete abatement even at concentrations up to 25 mg L<sup>-1</sup> of 2,4-dichlorophenol [98]. Mechanistically, the increase in applied current density efficiency for degradation of 2,4-dichlorophenol was due to stabilization of charge carriers and higher oxidants production rates in the PEC system. Carboxylic acids were identified as the main by-products formed from the cleavage of the phenolic ring moieties in 2,4-dichlorophenol. However, very importantly they achieved dehalogenation photoelectrocatalysis with evidence of chlorine heteroatoms released as innocuous chloride anions. Overall, the research of Renato et al. demonstrated the importance of PEC reactor design and how properly orientated TiO<sub>2</sub> nanotube-coated disk flow reactors leverage both novel material designs and reactor architectures to achieve pollutant degradation.

Photoelectrocatalysis provides an excellent frame for the application of photocatalytic nanostructured materials on

easily recoverable supports. The study of Cerrón-Calle et al. reported a two-step synthesis of hierarchically nanostructured ZnO/Ag composite photoelectrodes [99]. Wurtzite ZnO was selectively electron created as spheroidal seeds on fluor doped tin oxide substrates and nanodecorated with Ag nanoclusters under electrochemical control. Hierarchically organized nanorods were selectively chemically grown on the plane (002) perpendicular to the substrate from ZnO/Ag seeds. Solutions emulating dye effluents with the usual contents of 0.1 M of NaCl and a model azo dye (Methyl Orange) were decolorized using ZnO/Ag nanorods in different treatments. Photocatalysis attained discrete decolorizations of 8%, whereas photoelectrocatalysis completely decolorized solutions after 60 min [99]. The influence of the metal/semiconductor interface (ZnO/Ag) as introduced Schottky barrier was studied demonstrating a fourfold enhancement on decolorization kinetics with respect bare ZnO nanorods. The influence of the seed growth control on the final photoelectrocatalytic response is reported to control the hierarchical organization of nanorods. This resulted in different decolorization kinetics as a result of the differences in the efficient use of the delivered photons conditioned by the photoelectrode structure [99].

## Electrochemical advanced oxidation process (EAOP)

In practice, it consists of two types of chemical reactions: oxidation and reduction reactions occur at the anode and cathode surfaces, respectively. The generated redox reactions throughout the electrolytic cell can eliminate a variety of water pollutants (i.e., heavy metals and organic pollutants) [100]. Generally, EAOP can be categorized into (i) electrochemical direct (anodic oxidation) and indirect oxidation. Instantly, the first scenario (direct EO) occurs at the anode and includes direct charge transfer reactions between the anode surface and contained water pollutants that result in electrons mediation which can oxidize organic water pollutants [101], whereas the second scenario (indirect EO) are operated by the in situ electrogeneration of powerful reactive oxidant species (ROS), mediators, such as oxygen and chlorine active species at the electrode surface [102]. Economically, EAOP has numerous merits: (i) low cost capital and operational costs, (ii) moderate operational parameters at ambient pressure and temperature, (iii) no additional requirement of chemicals, (iv) no secondary wastes generation, and (v) flexibility to combine with other traditional water treatment techniques. Recently, tunable nanobased materials have offered unprecedented advantages for electrochemical water treatment. For example, and not as a limitation, they characterize by (i) unique physicochemical and geometries characters of morphology, crystallinity and porosity, (ii) high

**Table 2** Removal efficiencies of carbon nanomaterials (CNT)-based electrochemical toward a variety of water contaminants through treatment systems and adsorption systems

Contaminants	Cathode	Anode	Removal efficiency (R %)	System configuration	References
Formate	Ti	BTO-CNT	25%	Filtration	[160]
Formaldehyde	Ti	BTO-CNT	33.5%	Filtration	[160]
<i>E. coli</i>	Stainless steel	CNT	75%	Filtration	[161]
m-Cresol	CNT	Ti/SnO <sub>2</sub> -Sb <sub>2</sub> O <sub>5</sub> -IrO <sub>2</sub>	82%	Batch	[162]
Ethanol	Ti	BTO-CNT	85.7%	Filtration	[160]
Oxalate	Ti	Graphene-CNT	87%	Filtration	[163]
Phenol	CNT	CNT	87%	Filtration	[164]
Geosmin	CNT	CNT	87.2%	Filtration	[164]
Tetracycline	Ti	Graphene-CNT	88%	Filtration	[163]
Methanol	Ti	BTO-CNT	88.7%	Filtration	[160]
Phenol	Stainless steel	SnO <sub>2</sub> -Sb <sub>2</sub> O <sub>4</sub> -CNT	90%	Batch	[165]
Ferrocyanide	Ti	CNT	> 90%	Filtration	[166]
Tetracycline	CNT	CNT	90.3%	Filtration	[164]
Phenol	Ti	Graphene-CNT	93%	Filtration	[163]
C.I. basic blue 3	CNT-PTFE	Pt	94%	Batch	[167]
C.I. direct red 23	CNT-PTFE	Pt	94%	Batch	[168]
Methyl orange	Stainless steel	Sb-doped-SnO <sub>2</sub> CNT	95%	Filtration	[169]
C.I. basic yellow 2	CNT-PTFE	Fe	96%	Batch	[170]
Methyl orange	CNT	CNT	96%	Filtration	[164]
Chromium	CNT	Carbon paper	96%	Batch	[171]
Oxalate	Ti	BTO-CNT	98%	Filtration	[160]
Methylene blue	CNT	CNT	98%	Filtration	[172]
p-Nitrophenol	Stainless steel	CNT-Ce-PbO <sub>2</sub>	98.2%	Batch	[173]
Tetracycline	CNT	CNT	99%	Filtration	[174]
4-Chlorophenol	Stainless steel	LAS-CNT-PbO <sub>2</sub>	99.5%	Batch	[175]
MS2 virus	Stainless steel	CNT	99.6%	Filtration	[161]
MS2 virus	Stainless steel	CNT	> 99.9%	Filtration	[176]

CNT, Carbon nanotubes; BTO, bismuth-doped tin oxide

selectivity toward target pollutants, (iii) elevated production rate of mediators, further degrading water pollutants, (iv) an enhancement of mass transfer rate from bulk solutions to electrodes surfaces, (v) maximizing electrodes surface areas to adsorb more charged ions, and (vi) reduction in the dependence on the noble and non-earth abundant metals [103]. Table 2 presents the removal efficiencies of different nanoengineeringbased materials (carbon nanomaterials) against a variety of water contaminants through electrochemical and adsorption systems.

## Water nanofiltration

Membrane filtration is a widely recognized and superior wastewater disposal technology used for providing a physical barrier to the efficient removal of undesirable

molecules. Membrane manufacturing is used worldwide for more than three decades to effectively separate a vast range of water and wastewater toxins [104]. The membrane is a thin film of semipermeable substances that separates pollutants when motor pressure is exerted by the membrane. Membranes create a physical barrier that only allows specific materials to migrate because of their chemical and physical properties. Among the other conventional water treatment technologies, membrane filtration is most efficient since it is very easy and highly reliable, needs no use of chemicals and additives, and is easy to scale, rapid, and flexible. Besides it combines with other advanced treatment technologies [105]. The low-pressure (microfiltration and ultrafiltration) and high-pressure (nanofiltration and reverse osmosis) filtration technology is categorized based on the respective membranes molecular weight cutoff values and transmembrane pressure. These four membrane processes are



best defined for the particle size that can be removed from the raw water. Among these, nanofiltration is a sustainable alternative for certain contaminants removal. High-pressure nanofiltration (NF) is a technique that removes organic toxins, bacteria, viruses, milk, biological matter, and salts. Besides, NF can be used for water hardness removal. The NF membrane has a pore size ranged between 1 and 100 nm. Up to 99.9% of molecular removal within the 1–100 nm range is achieved for different pesticides using NF membranes [106]. NF is ideal for removing low-weight molecular compounds as low as 100–200 Da and is therefore chosen for pesticide removal. Higher energy than MF and UF is needed for NF. NF is higher than UF and lower than RO. Until now, NF is the only known filtration system that separates organic pollutants and pesticides [107]. For example, loose nanofiltration (NF) polyvinylidene fluoride (PVDF) hollow fiber membranes with a multilayer structure have been successfully prepared based on a solvent-free process [108]. Graphene oxide (GO) was used through vacuum filtration to cover the interface pores of pristine PVDF membranes, and polypyrrole (PPy) was polymerized on the surface to further decorate the structure of the membrane. Interestingly, due to the synergistic effect of GO and PPy, the altered membranes showed a multilayer structure. The structure and property of PVDF loose NF membranes were investigated. After modifying by GO and PPy, the hydrophilicity improved obviously. Also, the Molecular Weight Cut Off (MWCO) was around 3580 Da, and the skin layer's smallest pore size decreased to 2.5–4 nm. Besides, for negative dyes, the PVDF loose NF hollow fiber membranes presented a strong dye rejection (about 98.5 percent), while a low salt rejection for NaCl (about 4 percent) demonstrated a great potential for accurately separating dye/salt. Specifically, no solvent was used in all the preparation procedures. This work provided a novel green preparation strategy for loose NF membranes [108].

## Nanomaterial-based sensors

Pollution potential requires the development of fast, simple detection methods for monitoring organic, inorganic, and pathogenic pollutants. The recognition of contaminants is crucial in certain emerging circumstances. Therefore, the need for devices with superior sensing capabilities and improved position increases. Devices like nanosensors have emerged as an alternative to traditional research methods to track and detect traces of pollutants in specific settings because they are extensive and potentially cost-effective. A nanosensor consists of a nanomaterial, an ingredient for detection, and a signal translation mechanism. Interest analysis (contaminants) interacts with the identifier variable and

produces a detectable signal. The device can be optical, electrochemical, electronic, or vibrational. The high sensitivity, selectivity, and low limit detection values indicate that the nanosensors are suitable for the detection of pollutants in water, as a promising tool for drinking and consumer water quality control [109].

Chowdhury et al. investigated the possibility of using COOH-functionalized cadmium telluride (CdTe) quantum dots (QDs) as fluorescent nanosensors for the detection of some environmentally hazardous metal ions such as ( $\text{Cr}^{3+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Co}^{2+}$ ) in an aqueous phase. In real samples like paint, water from the river, rainwater, etc. the optical techniques and principal component sensor analysis have successfully applied to the testing of dissolved metal ions as a useful, successful optical sensor of water-dissolved metal ions that are responsible for water pollution. They found that the CdTe nanosensor's optical response was time and temperature-dependent. A strong "turn-off" fluorescence response of CdTe is observed in presence of all metal ions [110].

Mekuria et al. detected the heavy metals in tiny amounts from the contaminated water source using carbon and cobalt ferrite nanocomposite [111]. Heavy metals in the environment, particularly in drinking water, become a primary environmental concern. Chromium is one of the heavy metals that contaminate water. Mekuria et al. have used CNTs which intercalated with magnetic nanoparticles of cobalt ferrite ( $\text{CoFe}_2\text{O}_4$ , CFO) and used for the detection, identification, and quantitation of chromium by observing changes in the magnetic properties of the composite [111]. The magnetical properties of CFO nanoparticles and CNT composites are calculated to quantify magnetization changes when treated with a low chromium level of 0.3% by mass. They used 0.097 mg of  $\text{K}_2\text{Cr}_2\text{O}_7$  on 31.2 mg of CNT-CFO composite which enhanced the saturation magnetization significantly by 71%. The CNT-CFO reacted to chromium differently and substantially than the other heavy metals to chromium hexavalent. Moreover, they explained the CNT-CFO nanocomposite as the best potential magnetic nanosensor for chromium. These techniques were used to develop, describe and utilize CNT and CFO nanoparticles as nanosensors for the identification, detection, and quantitation of chromium in drinking water sources such as rivers, ponds, pools, groundwater, lakes, and seawater.[111].

M. Rabbani et al. [112] studied nanotechnological biosensors, their types, and performance parameters. One of the most important developments of science is sensor technology, which senses an event and generates a signal consistent with the event. Sensing technologies have been developed and applied in many areas over time. Among them are popular biomedical applications. Biomedical sensing and the identification of different biomedical phenomena are at the core of many diagnostic processes in the world today. They

also play an essential role in improving the quality of life. The efficiency of biosensors has significantly improved with the inclusion of nanomaterials such as nanoparticles, nanowires, carbon nanotubes, and graphene. Miniature or flexible sensors with stable and multidimensional properties have grown. Ongoing research has developed excellent applications of nanotechnological biosensors for improved quality of life, from diagnostics and nanomedicine to environmental monitoring [112].

Fluorescent nanosensors are recognized as valuable research tools due to their unexpected features (e.g., high sensitivity/selectivity, enhanced capability for detection, low cost, portability, and quick on-site detection). Singh et al. wrote about the recent developments in fluorescent nanosensing technology for the detection of lead ions ( $\text{Pb}^{2+}$ ). For such applications, various types of nanomaterials explored have been categorized and performance assessed, particularly in terms of sensitivity. They published a review article that lets researchers gain insights into the status and significance of optical nanosensors in curbing lead pollution and related diseases. Moreover, they explained the technical challenges and prospects in the development of nanosensing systems for  $\text{Pb}^{2+}$  are also discussed [113].

Cheng et al. used a fluorescent nanosensor based on porphyrinic metal–organic framework nanoparticles (MOF-525 NPS) for sensitive and selective monitoring of  $\text{Cu}^{2+}$  in aqueous solution and living cells. The MOF-525 NPs with attractive properties, including ultrasmall size, good water dispersity, and intense red fluorescence, are prepared via a facile and environment-friendly hydrothermal route. Due to the strong affinity of  $\text{Cu}^{2+}$  to the porphyrin ligand in MOF-525 NPs, the fluorescence signal of MOF-525 NPs could be saturated statically by  $\text{Cu}^{2+}$  with high selectivity. With a low detection limit of 220 pM, the proposed fluorescent nanosensor has a linear response in the range of 1.0–250 nM. They successfully employed the detection of  $\text{Cu}^{2+}$  in water samples and the intracellular imaging of  $\text{Cu}^{2+}$  in living cells, demonstrating its great potential in the sensing and biological fields [114].

Materials based on silver nanoparticles are ideal as optical sensors for water pollutants, given the consequences for human health and the environment due to water pollution. The spontaneity of life-related processes, such as the synthesis of cellular constituents and the transfer of nutrients into cells, is disrupted by the contaminants found in the water, and this induces long/short-term diseases [115]. Proposito et al. studied the synthesis of silver nanoparticles, paying attention to the stabilizers and mostly used ligands, to the characterizations, to the properties and applications as colorimetric sensors for water pollutants [115]. Since water pollutants our attention they focused in their study on several heavy metals ions, such as Hg(II), Ni(II), Cu(II), Fe(III), Mn(II), Cr(III/V) Co(II) Cd(II), Pb(II), due to their

dangerous effects on human health. Besides, several systems based on silver nanoparticles are employed as pesticide colorimetric sensors in water [115].

Ghasemi et al. used thiazolylazopyrimidine-functionalized  $\text{TiO}_2$  nanosensor ( $\text{TiO}_2$ -TAP) for developing sensitive and selective colorimetric detection of  $\text{Cu}^{2+}$  in water samples. Characterization of  $\text{TiO}_2$ -TAP NPs using Fourier transmission infrared (FT-IR), field emission scanning electron microscopy (FESEM), energy-dispersive X-ray spectroscopy (EDX), and X-ray diffraction (XRD) analysis revealed that the  $\text{TiO}_2$  NPs were effectively modified with the synthesized epoxy-activated thiazolylazopyrimidine.  $\text{TiO}_2$ -TAP has demonstrated high copper ion affinity, sensitivity, and selectivity in aqueous media over other competing metal ions. The results of that work showed that the  $\text{Cu}^{2+}$  ions at optimal pH 5.0 were sensed and adsorbed by the  $\text{TiO}_2$ -TAP. The proposed method was successfully applied for the sensitive and selective detection of  $\text{Cu}^{2+}$  in tap water, seawater, and well water. Therefore in any physical and biological conditions, the established nanosensor with great features such as cost-effective, excellent sensitive and selective, short response times, and high adsorption efficiency for  $\text{Cu}^{2+}$  can be used [116].

Schiesaro et al. investigated the electronic and molecular structure and morphology of innovative nanostructured materials whose optical properties react to heavy metals in water samples. They addressed the presence of mercury ions at the ppm levels with silver nanoparticles (NPs), stabilized with a hydrophilic ligand sodium 3-mercaptopropionate (3MPS). TEM morphological analysis sheds light on the structure of the AgNP-3MPS/Hg aggregates, revealing the formation of Ag/Hg alloy nanoparticles [117].

Molybdenum disulfide ( $\text{MoS}_2$ ), an inorganic analog of graphene with a distinctive structure, is being envisioned as the next-generation 2D layered transition metal dichalcogenide (TMD) nanomaterial toward greatly diversified sensing applications and nanoelectronics.  $\text{MoS}_2$  and its composites have unlocked a new period in the fabrication of nanosensors because of their exciting electrical, physicochemical, catalytic features and biocompatibility including an adjustable bandgap ranging from 0 (semimetal) to 2 eV (semiconducting), huge specific surface area, greatly exposed active sites on the plane edges, greater ionic conductivity as compared to the oxides, decent carrier mobility, etc. [118]. Sha et al. covered the characteristics, the functionalization of  $\text{MoS}_2$ , and its applications in biomedical and environmental monitoring nanosensors [118]. They explained the modern developments of  $\text{MoS}_2$  and its nanocomposite-based sensors in major applications of biomedical and environmental monitoring, emphasizing the sensing performances which comprise of sensitivity, selectivity, durability,

**Table 3** List of nanomaterial-based electrochemical sensor and biosensor for environmental applications

Nanomaterial-based sensor	Pollutant	Detection limit	Linear range	References
Ag NPs	E. coli	0.4 pM	0.4–1.3 pM	[177]
Ag NPIs	Pb <sup>2+</sup> , Cd <sup>2+</sup> , and Cu <sup>2+</sup>	0.5 ng mL <sup>-1</sup>	0.5–70 ng mL <sup>-1</sup>	[178]
Ag NPs-ssDNA	Hg <sup>2+</sup>	3 pM	0.01–100 nM	[179]
Ag-Si core-shell NPs	NB	1.68 μM	10–600 μM	[180]
Ag-Si core-shell NPs	NAC	2.5 nM	2.5 nM–10 μM	[181]
Ag NPs-GR	AIV H7	1.6 pg/mL	1.6 mg–16 ng/mL	[182]
Au NPs	Hg	1 μM L <sup>-1</sup>	–	[183]
Au-Se NPs	Hg <sup>2+</sup>	1.0 ppb	14–3500 ppb	[184]
Au-Se NPs	NO <sub>3</sub> <sup>-</sup>	8.6 μM	16 μM–5 mM	
Au NPs	As <sup>3+</sup>	32.5 pM	1.3–200 nM	[185]
Au-TiO <sub>2</sub> NTAs	BPA	6.2 nM	0.1 μM–38.9 μM	[186]
Au-Graphene	Hg <sup>2+</sup>	0.001 aM	1.0 aM–100 nM	[187]
Au NPs-BSA-rGO	Hg <sup>2+</sup>	0.05 nM	0.1–130 nM	[188]
MWCNTs@GONRs	1-aminopyrene	1.5 nM	8–500 nM	[189]
Pd NCs-PPy	NO <sub>3</sub> <sup>-</sup>	0.45 μM	100–1400 μM	[190]
PtPd-rGO NRs	TNT	0.8 ppb	0.01–3 ppm	[191]
Pt NPs	H <sub>2</sub> O <sub>2</sub>	100 nM	0.05–20 mM	[192]
CNT-PSS/Bi	Cd(II)	0.18 nM	4.4–241 nM	[193]
CNT-PSS/Bi	Pb(II)	0.2 nM	2.4–434 nM	
Pd NPs-PVP	H <sub>2</sub> O <sub>2</sub>	8 nM	0.01 μM–1 μM	[194]
SWCNT	catechol	2.3 nM	0.1–2 μM	[195]
PAL/MWCNTs	Capsaicin	0.03 nM	–	[196]
GQD-AuNPs	Cu(II)	0.05 nM	–	[197]
GQD-AuNPs	Hg(II)	0.02 nM	–	
rGO-AgPd NPs	SAL	1.44 mL <sup>-1</sup>	0.01–100 ng mL <sup>-1</sup>	[198]
rGO-AgPd NPs	RAC	1.52 pg mL <sup>-1</sup>	0.01–100 ng mL <sup>-1</sup>	
rGO-AgPd NPs	CLB	1.38 mL <sup>-1</sup>	0.01–100 ng mL <sup>-1</sup>	
SPIMs-WGA	E. coli	–	10 <sup>2</sup> –10 <sup>7</sup> cfu MI <sup>-1</sup>	[199]
Pt/PPy NSs	Hg <sup>2+</sup>	0.27 nM	5–500 nM	[200]
b-CD-PtNPs/GNs	α-NAP	0.23 nM	0.8–220 nM	[201]
b-CD-PtNPs/GNs	β-NAP	0.37 nM	3–300 nM	
GONRs	TNT	4 μM	4–83 μM	[202]
PAMAM-SWCNHs-Pt	PCT	0.18 mg mL <sup>-1</sup>	10 pg <sup>-20</sup> ng mL <sup>-1</sup>	[203]
PAMAM-Au	Catechol	1.74 pg mL <sup>-1</sup>	50 nM <sup>-10</sup> mM	
PANI-NF	VOCs	3 ppm	3.0–300 ppm	[204]
Pd WLNCs/g-C3N4	hupA	1.30 nM	3.9 nM–20.8 μM	[205]
Pd WLNCs/g-C3N4	Ops	0.33 nM	1.0 nM–14.9 μM	

NPs, Nanoparticles; NPIs, nanoparticles; TdT, Ag nanoparticles on terminal deoxynucleotidyltransferase; Ag NPs-ssDNA, extended ssDNA; NB, nitrobenzene; NAC, nitroaromatic compounds; GR, graphene; AIV H7, avian influenza virus H7; NTAs, nanotube arrays; BPA, bisphenol A; BSA, bovine serum albumin; rGO, reduced graphene oxide; MWCNTs, multiwalled carbon nanotubes; GONRs, graphene oxide nanoribbons; NCs, nanoclusters; PPy, polypyrrole; NRS, nanoribbons; TNT, trinitrotoluene; CNT, carbon nanotubes; PVP, polyvinylpyrrolidone; SWCNT, single-walled carbon nanotubes; PAL, phenylalanine ammonia-lyase; MWCNTs, multiwalled carbon nanotubes; GQD, graphene quantum dots; SAL, salbutamol; RAC, ractopamine; CLB, clenbuterol; SPIMs, surface of the printed interdigitated microelectrodes; PPy NSs, nanospherical polypyrrole; b-CD, b-cyclodextrin; GNs, graphene nanosheets; PAMAM, poly(amidoamine); SWCNHs, single-walled carbon nanohorns; PCT, prolactin; PANI-NF, polyaniline nanofibers; VOCs, volatile organic compounds; WLNCs/g-C3N4, wormlike nanochains/graphitic carbon nitride; hupA, huperzine; Ops, organophosphorus pesticides

reproducibility, detection limit, and their viability in the real environment [118].

A hydrothermal synthesis in a step-by-step process and subsequent annealing, as well as a Co-Zn ratio was successfully used for small-scale (under-40 nm) nanocomposite ( $\text{Co}_3\text{O}_4/\text{ZnO}$ ) preparation, which is dense in oxygen vacancies. Also, a loosely structured framework of the nanocomposite can effectively increase visibility on the surface and improve mass transfer at active sites. As a result, for electroanalysis of Hg(II) by square wave anodic stripping voltammetry (SWASV), the as-obtained  $\text{Co}_3\text{O}_4/\text{ZnO}$  sensor has an impressive sensitivity efficiency of  $504.74 \mu\text{A} \mu\text{M}^{-1} \text{cm}^{-2}$ . Otherwise, the diverse detection efficiency of the sensor with different molar ratios of Co to Zn is investigated, demonstrating the effectiveness of the  $\text{Co}_3\text{O}_4/\text{ZnO}$  sensor with a molar ratio of 2 Co to 1 Zn [119]. Besides, metal oxide-based nanocomposites have superior benefits to fabricate sensing interfaces for electroanalysis of heavy metal ions due to the introduction of various advantages (i.e., environmentally friendly, low-cost, and high activity) into one material [119].

## Electrochemical Sensors

In general, the electrochemically driven process can be classified into three main subclasses: (i) reductive faradaic scenarios (i.e., electrogeneration of peroxide, electrochemical reduction of metals, electrochemical reduction of oxyanions, and electrochemical dehalogenation), (ii) oxidative faradaic scenarios (i.e., electrochemical oxidation, electrogeneration of chlorine, electrocoagulation and photoassisted process), and (iii) non-faradaic electroseparation (i.e., electrosorption, capacitive deionization, selective deionization, electrodesialysis, and electrodesialysis reversal) [120]. For a more accurate scientific view, electrochemical pathways have been considered as one of the most effective, eco-friendly, versatile, and scalable strategies for the detection and remediation of different water pollutants from aquatic systems [121, 122].

In the last decades, electrochemical detection (sensing) based on electrochemical sensors has become a promising approach to monitor water pollutants by transforming changes into electrical signals. Majorly, several different analytical techniques such as potential analysis, conductometry, and coulometry are great examples of different electrochemical detection methods and characterize by numerous advantages such as quick response, miniaturization, sensitivity and selectivity, low cost, and facile operation [123]. An integration of nanostructured materials with electrochemical sensors and biosensors has been introduced as powerful analytical methods by captivating the benefit of easy to handle, cost-effective, highly sensitive and selective, rapid response, facile to fabricate, and portable. Increased heavy metal ion detection and the use of electrochemical-based detection

technologies combined with engineered nanomaterials are a promising and revolutionary primary strategy to potentially restrict heavy metal poisoning. It is also important to interpret the parameters at the nanobiointerface level that merely affect cross-interactions between nanomaterials and heavy metal ions. Table 3 displays a list of nanomaterial-based electrochemical sensors and biosensors for environmental applications.

## The advantages and disadvantages of green nanomaterials

Because of improved adsorption and/or catalytic activity and substance specificity, many nanomaterials eventually offer a potent alternative to traditional treatment methods. However, due to technical difficulties (e.g., scaling up, device set up), environmental considerations, and cost-effectiveness, most applications are not yet ready for the market, and thus, only a few nanosized commercial products are available on the market [103]. In addition, there are some other disadvantages associated with the use of nanomaterials that need to be discussed. The mass production of nanomaterials for their practical use may sometimes be a difficult problem. Furthermore, a serious boundary can be found for industrial uses when huge amounts of nanomaterial are required at economical prices for water treatment purposes [124]. The prevention of the release of nanomaterials to the environment where they can accumulate for long periods is another significant problem. Besides, Gehrke and Geiser have pointed out that there are no online monitoring systems to date that could provide accurate real-time measurement data on the quality and quantity of nanoparticles present only in trace quantities in water, thus providing a high potential for innovation [80]. Nevertheless, in the coming decades, green synthesized nanomaterials may offer great potential in water treatment and environmental remediation, in particular in the design of point-of-use systems and the complete degradation of emerging water and wastewater contaminants.

## Conclusion

Nanotechnology provides an opportunity to address global issues that have a huge impact on humanity. The development and applications of advanced green nanomaterials seem extremely promising for water remediation and pollutants nanosensors, as demonstrated by the several studies presented in this review. The novel, rational, feasible, and eco-friendly nanomaterials of different compositions can be formed by simple biological methods, such as plant extract. The special emphasis in the review has been given on nanomaterials green synthesis, nanoadsorbents, nanocatalysts,



electrochemical advanced oxidation process, water nanofiltration, and nanomaterial-based sensors. Research has shown that, even after numerous benefits, certain drawbacks and challenges have to be tackled. As evident from the reviewed literature, a wide range of nanomaterials have been tested for the removal of inorganic and/or organic pollutants. Green nanotechnology has a major potential to contribute to resolving the green problem along with sustainable growth. Sustainable nanotechnology production will include adopting a life cycle designed to determine the environmental effect of nanoproducts. Besides, some factors such as the potential life cycle assessment of newly synthesized nanoproducts should be taken seriously when accessing contribution to green growth. The use of green chemistry principles in the field of nanotechnology allows for understanding improved materials and processes; however, improvements can still be made. Nevertheless, the advancement of large-scale production and cost-effective sustainable engineered nanomaterials through greener chemistry, as well as their possible toxicity to the environment and human health after exposure, needs further studies. As the hybrid nanostructures required for catalysis can lead to complexities and increasing costs, increasing demand for the design and manufacture of these nanomaterials with multiple integrated features and optimized synthetic routes are required. Therefore, should be further investigated before their safe introduction into the natural environment.

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## Compliance with ethical standards

**Conflict of interest** The authors confirm that the study reported in this paper has no established conflicting financial interests or personal partnerships that may have affected them.

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