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Recent advances in the use of biogenic nanomaterials and photocatalysts for wastewater treatment: challenges and future prospects

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In many parts of the world, the availability of clean water is almost an impossible task owing to the intrusion of contaminants in flowing or stagnant streams which renders them unsafe for use by man. Water pollution is a serious environmental problem that poses serious dangers to humans, the environment and aquatic life. Also, the recent rise in the spate of emerging contaminants as well as bacteria in waters recovered from process streams, manufacturing and other production activities, have resulted in unforeseen consequences including environmental pollution, health related sicknesses (diarrhoea, dysentery, cholera, skin irritations, lung infection, etc.) as well as loss and extinction of aquatic lives, hence, the need to consider viable methods of treating waste waters so as to render them safe for use by these organisms. This will in turn preserve life below water- SDG 14 as well as promote the use of clean water and a healthy environment- SDG 6. Among the several existing nanotechnologies tailored towards the treatment of wastewater, a couple of inorganic toxic nanomaterials/nanosubstances have been adopted which render such treated waters as potential risks to humans and aquatic lives. However, green nanoparticles are considered potent and viable means of treating these waters, especially when literature has it that some nanomaterials are toxic in nature. Furthermore, the paper also reports on some unpopular but very potent emerging green nanomaterials, alongside recent advances, applications, related challenges and ways to address them. Information on future prospects of green nanoparticles as potential long-term sustainable water purification and wastewater treatment technologies are also included; therefore, this study is focused on addressing issues related to SDGs 3 (ensure healthy lives and promote wellbeing), 6 (clean water and sanitation), 12 (responsible consumption and production) and 14 (life below water).

KEYWORDS

contaminants, green nanomaterials, wastewater, wastewater treatment, water pollution

1 Introduction

In several parts of the world, the availability of water is bedeviled by the degree of wastewater contamination which renders water unsafe for consumption. Human and natural causes both contribute to water pollution (Rosbero and Camacho, 2017). Industries such as the ceramics, super-phosphate, steel, zinc, coal, aluminum, brick, uranium, oil and gas, and zinc usually discharge toxic chemicals in wastewater (Liao et al., 2008; Konishi et al., 2007). However, numerous mechanical and physico-chemical approaches have been adopted as means of overcoming these challenges. Researchers are also exploring other technologies including nanomaterials as possible means of improving low-cost water purification (Jiang et al., 2014; Sanni et al., 2022a). As a result of low cost, high efficiency and reusability, nanotechnology has been proposed as one of the most viable means of purifying water (Mukherjee et al., 2016).

Nano-adsorbents, nano-membranes, nano-metals and photocatalysts are all viable examples of nano-modified materials that hold great prospects as novel alternatives over conventional water treatment technologies with the potential of meeting specific needs of the end-users (Gurushantha et al., 2017; Chowdhury et al., 2016; Karthik et al., 2020; Sanni et al., 2022b).

Recently, nanoscience and nanotechnology have emerged as promising wastewater treatment techniques (O'Carroll et al., 2013). Nanostructured materials have become widely known for use in the removal, conversion and breakdown of dangerous organic (Kalpana and Rajeswari, 2018; Kalpana et al., 2016) and emerging inorganic contaminants due to their unique physicochemical features (Lapworth et al., 2012). These include their high chemical reactivity, thermal stability, strong electron transfer ability, catalytic activity and large specific surface area (Prasad et al., 2014; Kaviya and Prasad, 2015; Nasrollahzadeh et al., 2018a; Nasrollahzadeh et al., 2018b; Yi et al., 2018; Peng et al., 2019; Yi et al., 2019). Biogenic synthetic methods for NPs involve the reduction of metal ions by biological entities to form nanoparticles (Wang, 2000; Lee et al., 2004). For example, *Pseudomonas aeruginosa* has been used to synthesize silver nanoparticles (AgNPs), with strong antibacterial properties, making them suitable for the disinfection of wastewater (Saxena and Bharagava, 2020; Saud et al., 2024). Similarly, plant extracts, such as those of *Azadirachta indica* (neem), have been utilized to produce gold (Au) and AgNPs, which exhibit catalytic activities that are useful for degrading organic pollutants in wastewater (Kumar et al., 2019; Li et al., 2024). Biogenic nanomaterials have been applied in the removal of heavy metals (Iwohari et al., 2014), dyes, and organic pollutants from wastewater (Atarod et al., 2015; Ehrampoush et al., 2015; Eskandarloo et al., 2017). For instance, iron oxide nanoparticles synthesized using *Magnolia kobus* leaf extract have shown high efficiency in removing arsenic from contaminated water (Lunge et al., 2014; Banihashem, et al., 2024). Additionally, biosynthesized zinc oxide nanoparticles (ZnONPs) (Naseem, et al., 2024), Ag-ZnONPs (Patil et al., 2016) and CuNPs have demonstrated the ability to degrade organic dyes under visible light (Mehr et al., 2018).

Photocatalysis is a process where a material, upon absorbing light, generates reactive species capable of breaking down pollutants (Jaafar et al., 2019; Jaafara et al., 2019). Titanium dioxide (TiO_2) is the most extensively studied photocatalyst, but research has

expanded to include other materials that can operate under visible light which enhances their performances. TiO_2 is renowned for its photocatalytic activity, especially under UV light. However, its application is limited by the fact that ultraviolet (UV) light constitutes only a small fraction of sunlight (Sah et al., 2024). To overcome this limitation, researchers have explored doping TiO_2 with metals such as Au and Ag or non-metals like nitrogen, to extend its photon characteristics into the visible region, thus enhancing its photocatalytic efficiency for degrading a wide range of organic pollutants in wastewater (Chen et al., 2008). Beyond TiO_2 , ZnO, graphitic carbon nitride (g-C₃N₄), and bismuth-based compounds have been investigated. ZnONPs are particularly notable for their high electron mobility, which contributes to the efficient photodegradation of dyes like methylene blue (MB) under both UV and visible light (Nemiwal et al., 2024). Similarly, bismuth oxychloride (BiOCl) has garnered attention due to its unique layered structure, which promotes effective charge separation and enhances its photocatalytic performance when it comes in contact with visible light (Liu and Peng, 2020).

The development of hybrid photocatalysts combining different materials also holds great promise. For instance, composites of TiO_2 and graphene oxide have demonstrated superior photocatalytic properties, which enhances their degradation of persistent organic pollutants such as phenols and pesticides under sunlight (Qasim, et al., 2024). These hybrid systems leverage the strengths of the individual components used to make them to achieve high efficiencies when used in treating wastewater. In the study by Kamali et al. (2019) the sustainability criteria for assessing the applicability of nanotechnology in wastewater treatment applications was presented. Kumar et al. (2023) also carried out a study on the use of bionanoparticles obtained from agricultural waste for waste water treatment.

Reactive green nanostructures are thought to be viable alternatives for water treatment because they have potential features which make them more efficient in converting hazardous/harmful materials into toxic-free substances when used to treat industrial effluents (Gurushantha et al., 2015), thus encouraging responsible consumption and production- SDG 12). Nanomaterials (NMs) and NPs have recently been used in pollution control and environmental monitoring and sensing (Grünberg et al., 2001; Huang et al., 2014a; Huang et al., 2014b). Some nano-catalytic membrane systems and nano-sorbents such as TiO_2 , Au, Pd, Ag, Cu, Fe_3O_4 , etc. are not cost-effective or environmentally friendly, hence, they are not used on a large scale to treat wastewater.

Over the past few decades, natural resource-based extracellular bio-conjugated metal NPs (Sudhparimala and Vaishnavi, 2016) which involve the use of capping and reducing agents made from plant-based materials such as proteins, seeds, plants, biomass, starch, fruits (Rupa et al., 2018), leaves (Wang, 2013), and seeds have been studied as potential/sustainable, economically viable, and aesthetically pleasing alternatives relative to chemical production techniques for water treatment applications (Sudhparimala and Vaishnavi, 2016; Ullah et al., 2017). According to a study, the use of a water-soluble carbohydrate as capping agent gives rise to the green synthesis of metal NPs with impressive superficial characteristics (Markova et al., 2014). Plant extracts containing enzymes, reducing sugars, proteins, alkaloids, polyphenols, amino acids, and flavonoids may be involved in stabilizing metal NPs in the course of reducing metal ions to metal NPs

in aqueous solution (Harshiny et al., 2015). Antimicrobial activities against human pathogens and other diseases have been recorded for NPs with plant caps, which have resulted in the emergence of green nanomaterials (NMs) with high activity/efficiency, low impact on the environment, low cost, and easy application (Vijayan et al., 2018). Therefore, green-fabricated NMs can be considered viable options for photo-catalytic reactions in real-world water treatment systems (Njagi et al., 2010), albeit, further in-depth study of their use cannot be undermined (Husein et al., 2019; Gawande and Jenkins-Smith, 2001).

Traditional physico-chemical methods for fabricating nanomaterials have employed flammable and potentially dangerous substances, which have prompted researchers to investigate more sustainable options, such as safer, more cost-effective, bioinspired, biogenic methods for creating efficient and novel nano-scale catalysts and adsorbents that can be used to remove and degrade a wide range of contaminants in water (Gawande and Jenkins-Smith, 2001). Numerous phenolic antioxidants found in plants and other microorganisms serve as reducing and capping agents in the manufacture of NMs in numerous geometrical forms (Ramesh et al., 2018) including rods, flowers, tubes, and wires. Plant extracts contain biomolecules (i.e., polysaccharides, enzymes, vitamins, proteins, amino acids, and organic acids/citrates) that can pair with metal ions to bio-reduce them to their corresponding metal atoms/NPs (Banerjee et al., 2017); this process is chemically complex but benign to the environment.

This critical review examines the state of the art future potential of green-synthesized nano-catalysts and NMs for water and wastewater treatment. Cleaner and more sustainable methods of removing contaminants and metal ions from aqueous solutions like wastewater, groundwater, and drinking water have led to the development of cutting-edge biogenic NMs and novel nano-sorbents, however, a pool of such discourses and their contextual applications are rarely available in literature. In addition, potential applications for wastewater treatment and purification, as well as recent advances, current challenges and future prospects in the use of green-synthesized nano-catalysts and NMs in wastewater treatment are discussed; these clearly situate the insights provided in the contextual framework of this review-paper. For industries that generate chemically-laden waste waters that are hazardous and toxic, the development of new environmentally friendly treatment methods should be seen as a crucial component. In the light of this, this review focuses on synthetically sustainable green NPs obtained from plants, their toxicity assessment techniques and their applications in wastewater treatment. The discourse also centers around recent advances and future considerations for wastewater and water treatment applications of green synthesized NPs alongside the probable challenges associated with their use.

2 Methods for synthesizing inorganic NP and green NPs

2.1 Methods for NP synthesis

The top-down and bottom-up techniques are two ways by which NPs can be synthesized. The top down approach involves the physical break down of large materials into smaller ones, which

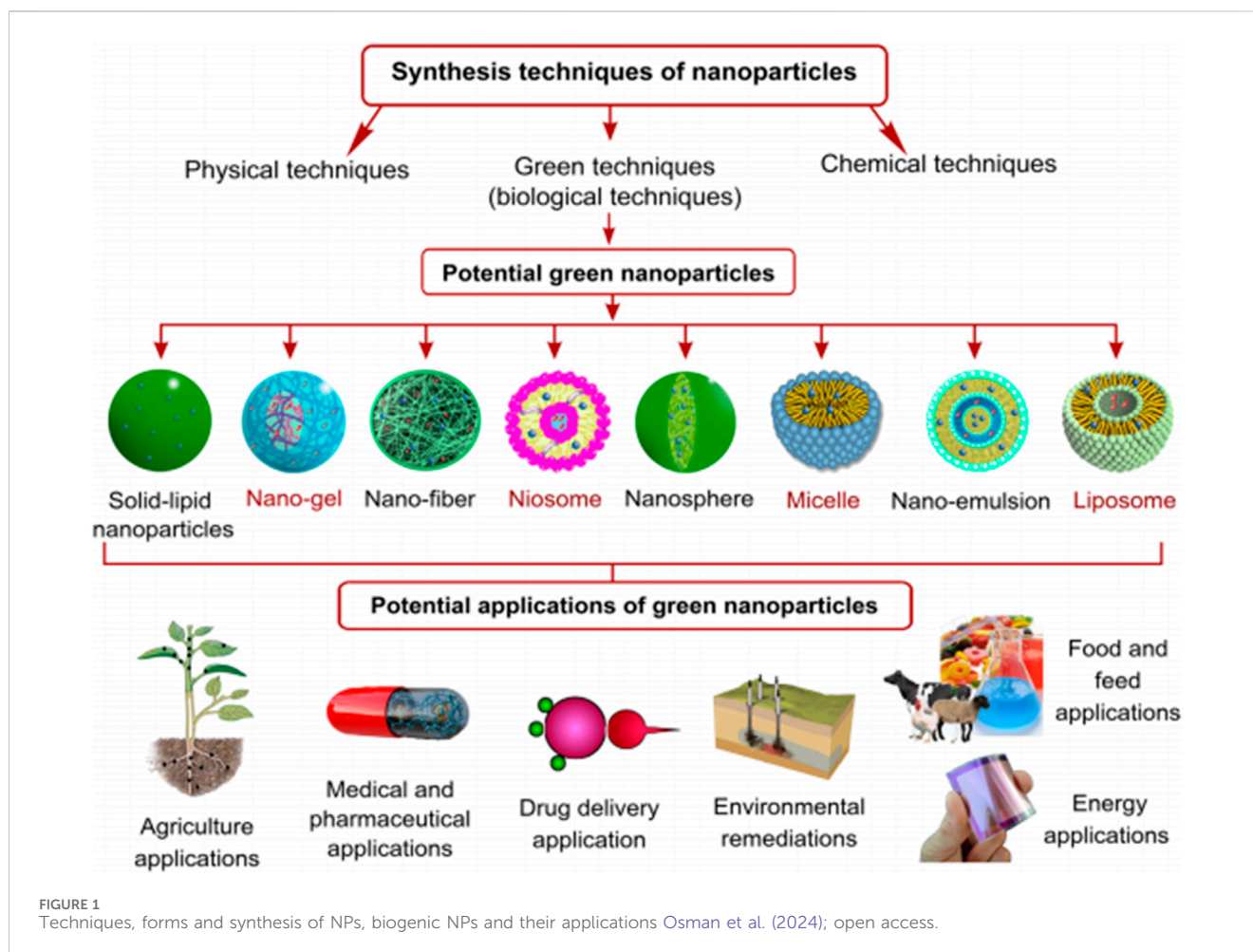
is accompanied by sequential evaporation-condensation or laser ablation. In contrast, the bottom-up approach, involves growing NPs from assembled atoms into nuclei. The synthesis of NPs via biological and chemical processes is an example of a bottom-up approach. A wide variety of biological, physical, and chemical methods have been used to produce NPs of precisely controlled specifications and forms (Rosbero and Camacho, 2017; Salem and Fouda, 2021).

2.2 Physico-chemical techniques for synthesizing NPs

Several scientists have worked out numerous physical and chemical means of synthesizing NPs that have several applications. Some new methods that have recently emerged to generate NPs with specific geometries include nanoimprint lithography, microcontact printing, photolithography, evaporation-condensation, ion beam lithography, dip pen lithography and electrochemical synthesis. Some mechanical methods that are capable of achieving a few desired geometries have also been discussed (Ahluwalia et al., 2016). In contrast, chemical processes begin by controlling the mass of the source-atoms after reducing the corresponding metal ions to metal atoms (Karlsson et al., 2005; Ahluwalia et al., 2016). Because of their specificity and ability to produce monodisperse NPs, both physical and chemical approaches have often been adopted for the synthesis of other kinds of NPs (Figure 1). A number of techniques have been employed for the production of metal nanoparticles, these include sodium borohydride conversion, gamma-ray irradiation, sol-gel technique, solvothermal synthesis, microwave-assisted synthesis, laser ablation and microemulsion, the use of hydrazine, hydrazine hydrate, and electrochemical reduction. The most popular methods for synthesizing inorganic NPs are associated with a number of drawbacks including energy inefficiencies, high operating costs and toxicity (Soenen et al., 2011; Zoroddu et al., 2014). However, the only meaningful approach to limiting their toxicity is by adopting permissible concentrations that are non-toxic and hazardous but this can only be ascertained by optimizing the process conditions involved in their synthesis. Toxic chemicals, costly machinery, and a number of treatment processes including temperature, pressure, and pH variation are often prevalent in these procedures. Furthermore, other by-products that are harmful to the ecosystem are also produced by these methods. This is because a number of polar and non-polar solvents are part of the chemical toolbox for a wide range of so-called bottom-up NP creation strategies which in turn lead to the synthesis of a wide variety of metallic NPs of various compositions, sizes and shapes (Rosbero and Camacho, 2017). The available physical and chemical methods for NP synthesis are not only expensive, but also generate compounds that are very harmful and hazardous, thus posing severe risks. As a result, there is an immediate advocacy for the adoption of green NPs as viable alternatives (Zhou et al., 2016).

2.3 Methods for synthesizing green NPs

Producing green NPs at moderate pH, temperature, pressure and at a much-reduced cost using plants, bacteria, fungi (Sastray et al., 2003) and other biological materials, helps to circumvent



many of the supposed detrimental characteristics associated with those produced by conventional techniques (Harshiny et al., 2015; Korbekandi et al., 2014; Zhou et al., 2016). Actinomycetes, algae, yeast, bacteria, fungus (Bansal et al., 2004), and plant extracts (Iravani, 2011) have been used to synthesize NPs in an environmentally friendly manner (Aswathi et al., 2022). The production of Mg, Ti, Au, Ag, Cu, Zn, and alginate NPs from a variety of bacteria, microbes, and fungus have been studied (Shen et al., 2017). Viruses, bacteria, *actinomycetes*, and fungi have also proven to be viable sources of bio-synthesized metal NPs such as those of Pt, Au, quantum dots, Te, Ag, Zr, Zn, Se, Ti, magnetite and Cu.

When adopting the bottom-up approach for green NP production, biomolecules including sugars, enzymes, carbs, protein, etc. bring about the release of metallic ions during the oxidation/reduction process, which then leads to the formation of the NPs (Nadaf and Kanase, 2016). Since different types of microbes interact with metal ions in different ways, knowledge-gaps on the mechanisms behind the use of microbes in the synthesis of NPs are yet to be uncovered. The shape, morphology, and size of the synthesized NPs from biomolecules are ultimately impacted by the processing technique, interactions within the microbe, as well as the environmental conditions (temperature and pH) (Arora et al., 2014). Consequently, the following are some of the most important obstacles that could pose delays in the adoption of green synthetic

routes for biogenic NP synthesis. Since it is known that the biological activities of green NPs mirror the optimization procedures that are necessary for their green production, a comprehensive chemical analysis of the biological biomass filtrate is also necessary for identifying the function of each component involved in the bio-fabrication of the resulting green NPs. In addition, future research works are to focus on economic considerations for scaling-up green NP application for industrial wastewater treatment. Furthermore, in order to create innovative commercially viable green nanomaterials, multidisciplinary research collaborations across various disciplines must be prioritized as no one discipline has all it takes to pull this through. Figure 2 is an illustration of the synthetic sources and pathways for biogenic NPs.

3 Nature/characteristics of green Nps in water/wastewater treatment

Heavy metals, halogenated recalcitrant pollutants, toxic textile dyes, pigments, pharmaceutical/personal care products (PPCP), pesticides (Yadav et al., 2015), refractory organic micro-pollutants and pathogenic microorganisms have been eliminated from contaminated waters using biogenic nanoparticles (BNPs) made from various bacterial species (Bousselmi et al., 2004; De Gussemme et al., 2011; Furgal et al., 2015; Hatamifard et al., 2015; Xiao

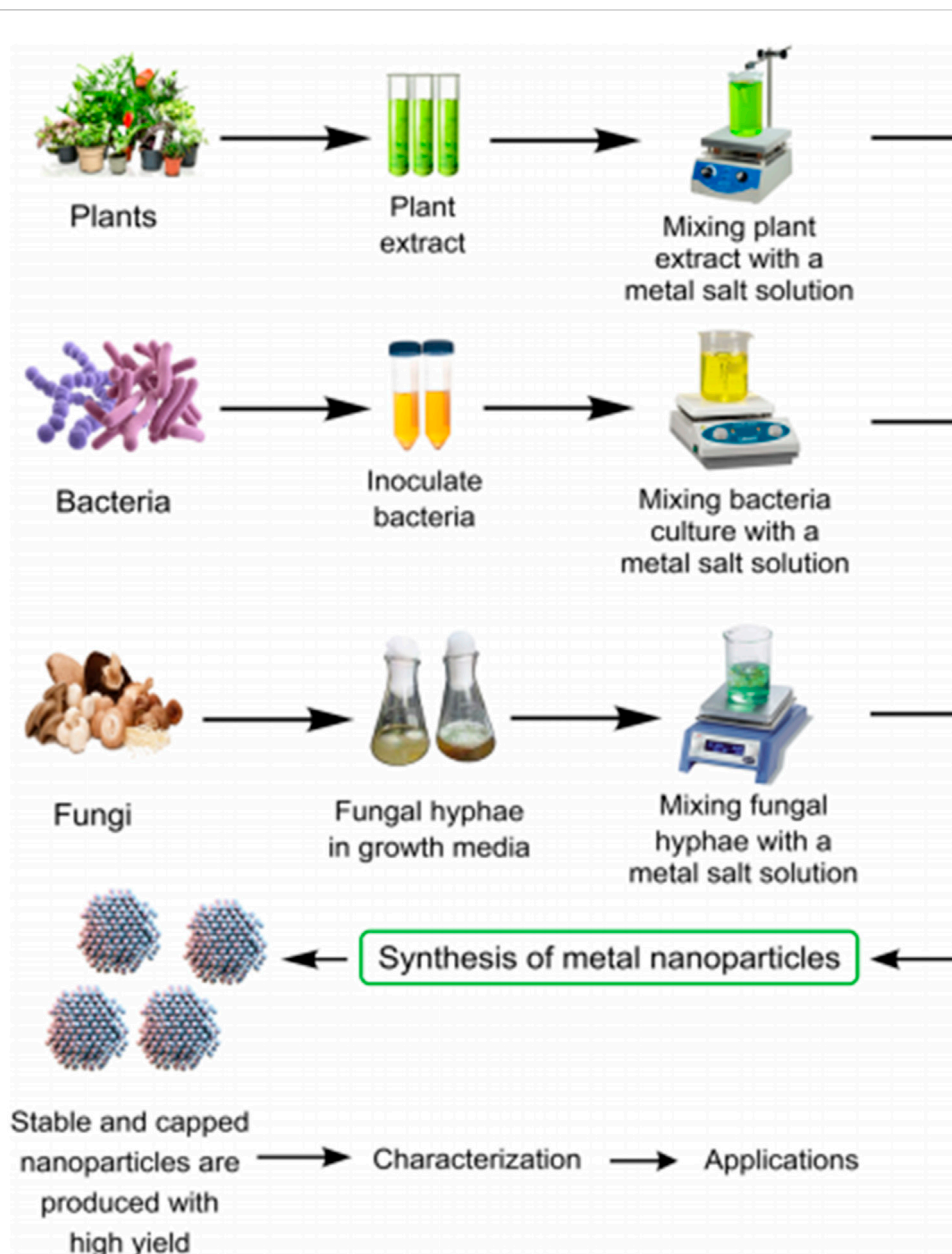


FIGURE 2
Synthetic sources and pathways of biogenic NPs Osman et al. (2024); open access.

et al., 2015b; Hatamifard et al., 2016; Xiao et al., 2016; Zhou et al., 2015; Zhou et al., 2016; Martins et al., 2017; Qu et al., 2017; Gautam et al., 2019). De Corte et al. (2012) also found that wastewater and their sediments can be used to generate power and recover useful resources such as metal ions. One promising avenue for recovering resources from polluted water is the capacity of microorganisms to alter the oxidation state of metals (Kashefi and Lovley, 2000; Kim et al., 2007; Kim et al., 2009; Kim et al., 2012).

It is possible to recover used BNPs from wastewater using microbes rather than using a solution of the metal ions (Ahluwalia et al., 2016; Kim et al., 2001). The presence of high specific surface areas, opposing charges, unique sizes, high reactivity, and the availability of bacterial cell matrix make these synthesized BNPs prominent for various applications (e.g., as adsorbents,

catalysts, antibacterial agents, fabrication of anti-biofouling membranes, etc. (Sureshkumar et al., 2010; Chokkareddy and Redhi, 2018; Dauthal and Mukhopadhyay, 2016; Dhanker et al., 2023). BNPs have the ability to biodegrade harmful micro-pollutants in water and wastewater when used as adsorbents (Ali et al., 2015; Ali et al., 2019).

3.1 As bio-adsorbents

In some investigations biogenic adsorbents were used as eliminators of contaminants from contaminated waters. This is due to the fact that the rate controlling step in the adsorption process provides clues to the removal mechanism on how this works

(Jain et al., 2016a; Jain et al., 2016b). Adsorption isotherms and kinetic models were employed, and the estimated R^2 values were used to compare the results. According to Table 1, the majority of the studies confirm that the adsorption kinetics and isotherm data conformed to the pseudo second-order kinetic model as well as the Langmuir isotherm. The results shown in the available publications mostly corroborate the chemisorption hypothesis in relation to the elimination of contaminants/pollutants from the water. According to Jain et al. (2016a), the availability of the functional groups (hydroxyl, carboxyl, amino, etc.) on the BNPs were crucial for the adsorptive removal of contaminants/pollutants via ion exchange and electrostatic interactions. On the other hand, based on some findings, the adsorption of contaminants/pollutants may be caused by surface precipitation (Kim and Baek, 2019), co-metabolism of microbes, oxidation/reduction (Kandasamy, 2017), intraparticle diffusion, chemical monovalent ion exchange, or pseudo first order reaction (Watts et al., 2015a; 2015b). Table 1 supports the fact majority of researches involving adsorption isotherms, assumed that the contaminants or adsorbates were adsorbed on a solid surface characterized by a monolayer, thus giving credence to the Langmuir model.

The adsorptive elimination of toxic heavy metals such as $Ni(II)$, $Cr(IV)$, Mn^{2+} , $Co(II)$, $Pb(II)$, Ag^+ , $Cu(II)$, Zn^{2+} , and Cd^{2+} via the use of BNPs are as contained in Table 1. The occurrence of certain functional groups—such as hydroxyl, carboxylate, methyl, and amide I, II, and III, as well as a range of reducing substances produced by bacterial cells, which had charges opposite to the metallic ions are responsible for the removal of the toxic metals. Ion exchange and electrostatic attraction were the main mechanisms by which the metallic ions were removed, with the -OH-groups playing a particularly active role. The surface precipitation that aided the removal of the harmful metal ions was likewise facilitated by carboxylate groups (Watts et al., 2015a). Watts et al. (2015b) noted that the existence of electrostatic contact may cause the H^+ ions released by bacterial cells to bind to metallic ions on the surface of an adsorbent. Nevertheless, it was also observed that various BNPs produced by different microbes in salt solutions exhibited varying degrees of adsorption of the metal ions. This variation is attributed to the capabilities of the individual functional groups and the presence of various cell metabolites in the BNPs (Iwohari et al., 2014). In addition, the Langmuir isotherm model was used to determine the maximum daily adsorptive capacity and removal of the heavy metals. Moreover, the metal-ions removal efficiency of the BNPs varied with the metal-types and circumstances surrounding the adsorption process, which may be explained by the presence of the negative charges on the surfaces of the BNPs or the selective adsorption of hazardous metal ions onto BNPs imposed by the smaller ionic radius of the metal and its electronegativity/larger ionization potential. Noting how easily BNPs produce metal hydroxyl species or acetate complexes is another way to track their relative preferences for adsorbates (Tuo et al., 2013).

Factors such as pH, contact time, initial pollutant/contaminant concentration, and adsorbent dosage are known to influence the performance of BNPs (Kumar et al., 2016; Deng et al., 2017). Although, BNPs have the potential to operate throughout a wide pH range, however, their efficacy would differ depending on the specific BNP type and the pollutants in question (Table 1). While utilizing biogenic SeNPs, a maximum of 95% adsorptive removal of

Cu^{2+} ions was obtained at a pH of 5, whereas, at a pH of 12, bio-*Pd* was found to remove 64% of $Cr(VI)$. According to several studies, the adsorptive removal/performance of BNPs may be affected by changes in pH, which in turn affect the attraction and repulsion between the pollutants and BNP surface-sites (Jain et al., 2016; Watts et al., 2015a; Mystrioti et al., 2016). The effectiveness of BNPs in eliminating certain contaminants may also be affected by factors such as contact time and adsorbent dosage (Fredrickson et al., 2000). More than 96% of the $Cr(VI)$ was eliminated in 24 h, according to the research conducted by Tuo et al. (2013) via biogenic *Pd(0)* produced by *Geobacter sulfur-reducers*. The results showed that the biogenic *Pd(0)* surface and the *G. sulfurreducens* cells were metabolically active in reducing $Cr(VI)$. Also, adding anthraquinone-2,6-disulfonate (AQDS) to the cells, increased the amount of biogenic *Pd(0)* and also raised the cell's dry weight with an improvement in $Cr(VI)$ removal.

3.2 As green catalysts/photocatalysts

According to Table 2, BNPs have been proven to have good catalytic efficiencies when it comes to removing various organic contaminants, including those that are hazardous or difficult to break down. Pesticides, organic/inorganic solvents, medicines, hazardous metals, and other industrial activities are the primary sources of these contaminants. To charge or activate a biogenic catalyst, a reducing agent like formate or hydrogen gas is often used (Durán et al., 2015). On the other hand, there have been instances when bio hydrogen donors were created by using certain strains of microbes or organisms that are grown by fermentation. Furthermore, this choice makes the technology economically viable while also lowering the treatment's running expenses. Biodegradation or reduction of pollutants mostly includes a combination of biosorption which results from electrostatic interactions, microbial co-metabolism induced by functional groups (Hazarika et al., 2017) and a redox process.

Bio-*Pd* made from wastewater containing bacteria was reported by Deplanche et al. (2014) to completely remove $Cr(IV)$ from wastewater. Using bio-*Pd* as catalyst and *in situ* bio hydrogen as an electron donor, Suja et al. (2014) reduced the concentration of $Cr(IV)$ completely within a day. Table 2 shows that BNPs can successfully remove harmful pigments and colours from wastewater. According to these results, the presence of various reducing chemicals produced by bacterial cells helped to biodegrade these harmful colours via co-metabolism of the BNPs and bacterial cells. It should be noted that the use of different bacterial strains and BNPs of different kinds resulted in different biodegradation rates of the same harmful dye. Nevertheless, the total quantity of dye elimination was high. In the study by Xiao et al. (2015a), rhodamine B (RhB), was completely biodegraded after being exposed to UV light for 3 h. Biogenic *ZnSNPs* were produced when artificial wastewater was treated with the bacterium *Shewanella oneidensis MR-1*. In addition, it was recounted that photogenerated holes, and not eOH radicals were the primary culprits in the decolourization of the dye. The insufficient power of the photogenerated holes by the biogenic *ZnS* under UV irradiation alongside the produced OH^-/H_2O and eOH radicals were seen as the proposed reason for the occurrence.

TABLE 1 A brief summary of the adsorptive performances of biogenic nanoparticles (BNPs).

Contaminant(s)	BNPs	Microbe(s)/ strain	Initial concentration (C _i)	Concentration of biogenic NPs (C _{BNPs})	R.E/q _e ^a /Y	t _e ^b	T (°C)	pH ^b	Model ^s	Isotherm ^e	Shape/ Size	Removal mechanism	Ref(s)
Toxic metals													
Pb ²⁺	BMO/Zeolites	<i>Pseudomonas putida</i> Strain MnB1	300 mg/L 0.975 mmol/L 1.79 mmol/L 0.08 mmol/L	0.2 g 17.69 mg BMO/g	0.71 mmol/g, 72.5%	2.5 h	30	4–7	P-1	L	2.43–185.5 nm	Mixture of ion exchange and precipitation	Roy et al. (2010)
Cd ²⁺					0.92 mmol/g, 71.5%								
Zn ²⁺					1.41 mmol/g, 79.1%								
Ag ⁺	BMO	Marino-bacter sp.Mni7-9	0.7 mmol/L	0.7 g	8.01 mmol/g, 92%	7 min	35	4–9	P-3	L	—	Electrostatic attraction	Sinha et al. (2013)
Cr(VI)	Biogenic-palladium Pd (0)	Geo-bacter sulfur reducen	400 μM	38 mg/L	94%	12 h	35	8.0	—	—	22 nm	Decrease in metabolic activity	Lee et al. (2014)
Co ²⁺	Biogenic	Geo-bacter	0.2 mM	—	29 mmol/mol	—	28	7.4	—	L	<35 nm	Ion exchange and electrostatic interaction	Arora et al. (2014)
Mn ²⁺	Mn	LAR9-2and Geo-bacter			28 mmol/mol								
Ni ²⁺	NPs	Sp. EB1			27 mmol/mol								
Zn ²⁺					69 mmol/mol								
Cr(VI)	BnM	Geo-bacter sulfur-reduce	17 mg/L	—	35 mg/g, 75%	320 min	-	15	P-1	—	10–25 nm	Mixture of surface precipitation and electrostatic interaction	Das et al. (2012)
Zn ²⁺	BioSNPs	Anaerobic granule (UASB)	300 mg/L	0.25 g/L	70 mg/g, 80%	5 h	40	7.5	—	L	165–190 nm spherical	Mixture of surface precipitation and electrostatic interaction	Mittal et al. (2013)
Cd	BioSNPs	Anaerobic granule (UASB)	199 mg/L	0.70 g/L	180.8 mg/g	965 min	40	7.5	P-2	F	165–190 nm spherical	Mixture of surface precipitation and electrostatic interaction	Jadoun et al. (2020)
Cu	BioSeNPs	Anaerobic granule (UASB)	80 mg/L	0.28 g/L	48 mg/g, 90%	965 min	40	5.5	—	—	—	Mixture of surface precipitation and electrostatic interaction	Nadaf and Kanase (2016)
Cd					115.9 mg/g			7.9					
Cu					79.9%			5.8					

(Continued on following page)

TABLE 1. (Continued) A brief summary of the adsorptive performances of biogenic nanoparticles (BNPs).

Contaminant(s)	BNPs	Microbe(s)/strain	Initial concentration (C _i)	Concentration of biogenic NPs (C _{BNPs})	R.E./q _e ^a /Y	t _e ^b	T (°C)	pH ^b	Model ^s	Isotherm ^e	Shape/Size	Removal mechanism	Ref(s)
Cr (VI)	CuS	<i>Shewanella oneidensis</i>	40 mg/L	0.08 g	95.1%	50 min	—	—	—	—	Nanorods, D 18.4 nm, L 90.9 nm	Mixture of surface precipitation and electrostatic interaction	Dauthal and Mukhopadhyay (2013)
Toxic dyes and recalcitrant pollutants													
MO	bi-(Pd)	<i>Caldicellulosiruptor</i>	50 mg/L	400 g/L	90%	—	—	—	—	—	—	—	—
Diatrizoate	NPs	Saccharolytic	50 mg/L	—	90%	40 min	80	—	—	—	15–25 nm	Reduction	Shen et al. (2017)
MB	MR-GO	<i>Shewanella nonevidences</i>	50 mg/L	0.45 g/L	154 mg/g, 100%	50 min	—	—	—	—	—	—	—
MG	—	MR-1	—	0.6 g/L	77.4%	50 min	30	6.7	P-2	L	10.6 nm, cubic	Electrostatic attraction	Cao et al. (2016)
CV	—	—	—	0.66 g/L	97.8%	—	—	—	—	—	Spinel crystal	—	—
MB	Na ₃ MnPO ₄ CO ₃	MOB	6 mg/L	0.5 g/L	77.1% 20.8 mg/g1	10 min	—	7.5	—	—	Amorphous	Mixture of O ₂ , and ion exchange	Hou et al. (2018)
17α-(EE2)	BMO	<i>Pseudomonas putida</i>	0.5 mg/L	7 mg/L	90%	2.5 h	30	5.6	—	—	110 nm (L)	Mixture of O ₂ , and ion exchange	Konishi et al. (2007)

This is because the valence band edge (VB) voltage of the biogenic ZnS was 1.92 V versus that of the semi conductor edge (SCE) voltage, which is lower than the normal voltage potential of 2.7 V for the OH[•]/OH. Ahluwalia et al. (2016) attempted to enhance the catalytic performance of Bio-Se by impregnating ZnS with Se through a calcination process. This resulted in the degradation of methyl orange (MO) by the nanophotocatalyst (Se-ZnS). After 160 min of UV irradiation, the dye removal rate was approximately 95%. As the degree of MO degradation rose, its removal fitted the pseudo-first-order kinetic model, and the emission of CO₂ grew steadily. Alvaro et al. (2007) observed that photocatalytic performance could be enhanced by photoexcited semiconductor electrons generated from a metal organic framework (MOF), while Xiao et al. (2015a) observed that the extra energy levels of an impregnated Se boosted its photocatalytic performance. By subjecting ZnS to ultraviolet light, electrons were energized and paired with holes in the valence band, which then migrated to the covalent band. Due to their extreme instability, the excited electrons may return to the valence band in a matter of seconds, thus leading to electron-hole pair recombination and the inability of the catalyst to produce the necessary ·OH radicals and superoxide ions for organic pollutant destruction. The results also show that Se may have improved the semiconductor’s electron-hole pair separation by acting as either an electron/hole trap. However, its electrical arrangement would have been upset if it managed to capture the electrons such that the resulting superoxide radical was transported quickly to an oxygen molecule while further degrading the MO. Moreover, the Se can trap the hole and maintain its stable electronic state, thus influencing the adsorption of the resulting ·OH radicals onto the surface of the ZnS. Moreover, the degradation of the organic contaminants was mostly accomplished by the hydroxyl radicals and the superoxide ions. In the study by Yue et al. (2016), biogenic PbS in combination with H₂O₂ helped to degrade 100% of methylene blue (MB) in only 20 h when the medium bearing the PbS was exposed to UV light. Also, by manipulating the polyethylene glycol (PEG) content in the microbial system, a novel approach was established for the fabrication of high-quality biogenic PbS. The results showed that, rather than the specific surface area of the BNPs, the number of the available crystal planes was the primary factor responsible for the catalytic degradation of the MB. In addition, azo dyes (such as Congo red, orange II, and Evans blue) were degraded with over 80% degradation efficiency in only 4 h of contact time when Bio-Pd was immobilized on an anaerobic granular sludge (Quan et al., 2015). The results demonstrated that glucose, formate, ethanol, acetate, and lactate were the electron and hydrogen donors that triggered the breakdown of the azo dyes. A thorough investigation was carried out by Qu et al. (2017), on the use of biogenic AuNPs in breaking down harmful dyes produced by *Trichoderma* sp. *WL-Go* and *Aspergillum* sp., respectively (Table 2). Other properties of green NPs include, lower toxicity, biocompatibility, small surface area to volume ratios, size tunable features, uniform morphology and high penetration strength through cells, etc.

3.2.1 Advantages/benefits of biophotocatalysts and biogenic nanomaterials for wastewater treatment

The benefits or advantages of green nanomaterials/nanophotocatalysts/nanomaterials used in wastewater treatment include:

TABLE 2 Brief summary of the catalytic performances of biogenic nanoparticles (BNPs) in the removal of toxic and emerging pollutants (T&EPs).

Contaminate(s)	BNPs	Microbe/strain	C _i	C _{BNPs}	R.E/ q _e ^a /Y	t _e ^a	T (°C)	pH ^b	Shape/ size	Mechanism for removal	Properties	Ref(s)
Diatrizoate	<i>Pd</i> -NPs	<i>Shewanella- oneidensis</i> <i>MR-II</i> <i>Bacter braakii</i> <i>Klebsiellia</i> <i>pneumoniae</i> <i>C-bacter braakii</i>	30 mg/L 30 mg/L 30 mg/L 60 mg/L 90 mg/L	20 mg/L 20 mg/L 20 mg/L 20 mg/L 60 mg/L	99% 0.50 ± 0.05 h ⁻¹ 0.25 ± 0.05 h ⁻¹ 5.50 ± 0.66 h ⁻¹ 10.22 ± 0.05 mg/mg	5 h — — — 20 h	—	9 —	25 nm —	Electrostatic interaction	XRD, SEM, TEM EDX	Mittal et al. (2013) Ullah et al. (2017) Luo et al. (2016)
Diatrizoate, TC	<i>Pd</i>	<i>C. braakii</i>	90 mg/L	60 mg/L	10.10 ± 0.05 mg/ mg Pd	20 h						
Diclofenac	Bio-MnO + Bio-Ag	<i>P-putida</i> <i>MnB6</i>	6 mg/L	Bio-Ag (15 mg/L) + Bio-MnO (6.90 mg/ L) Bio-MnO (8 mg/L)	90% ± 0.5% 80% ± 9%	140 h 140 h	24	—	—	Mixture of microbial/ redox and biomass sorption		Paul et al. (2016) Yaqoob et al. (2020)
2-				+ Bio-Ag								
APA												
Diclofenac	Bio- <i>Pd</i>	—	2 mg/L	10 mg/L	96% ± 5%	24 h	—	7.8	—	Mixture of O ₂ , co- precipitation and metabolic		Vennila and Prabha, (2015)
Direct brown MR dye	<i>ZnS</i> -NPs	<i>P-aeruginosa</i>	50–300 mg/ L	ZnNPs was 120 mg/L + NPs 150 mg/L	97% and 92%	150 min	28	11	11–12 nm Spherical	Oxidation/reduction	TEM, XRD, SEM	Rao et al. (2013)
4-N-phenol	Ag nanoparticles + NaBH ₄	<i>Cylindrladium</i> <i>floridanum</i>	10 ⁻⁴ mol/ dm ³	13.2 E10 ⁻⁵ mol/dm ³ + 6.7 × 10 ⁻³ mol dm ³	7 × 10 ⁻² min ⁻¹		40		30 nm Spherical	Oxidation/reduction	SAED, UV-US, TEM, EDX	Manjari et al. (2017)
Mn (II)	(Bio- <i>MnOx</i>) <i>Y-Mn₃O₄</i> biocatalyst multi- <i>Cu</i> <i>Escherichia coli</i> strain (<i>ECueO</i>)	<i>E. colistras K-12</i> <i>substr. Mg165AND</i> <i>Bl2</i>	14 mM		33.4% 91.0%	8 days 10 d	45	8.0	200–300 nm	Oxidation/reduction- redox process	XPS, XRD, TEM.	Kaviya and Prasad (2015)
Cr(VI)	<i>Pd</i> NPs	<i>Gram-negative/ positive strains</i>	4 mL	0.7 mg/12 mL	95%	40 min (150 min)			45 nm	Enzymatic reduction	TEM	Mittal et al. (2013)
Cr(VI)	Bio- <i>Pd</i> + H ₂	<i>Microbial granules</i>	4 mM 0.5 mM	—	96% 70% and 90%	300 min	—	—	4.5 nm Short rods	Mixture of reduction/ oxidation	XRD, SEM	Cao et al. (2016)

(Continued on following page)

TABLE 2 (Continued) Brief summary of the catalytic performances of biogenic nanoparticles (BNPs) in the removal of toxic and emerging pollutants (T&EPs).

Contaminate(s)	BNPs	Microbe/strain	C _i	C _{BNPs}	R.E/ q _e ^a /Y	t _e ^a	T (°C)	pH ^b	Shape/ size	Mechanism for removal	Properties	Ref(s)
2,4- dichloro- Phenol	Nano-MnO	<i>Pseudomonas</i> sp.	25 mg/L	60 mg/L +6 g/L	90% 99%	10 h 5 h	25	8	2 nm	Mixture of reduction/ oxidation	XPS, XRD, EDX	Arora et al. (2014)
Rhodamine B (RhB)	ZnS	<i>Shewanelli oneidensis MR-1</i>	25 mg/L	55 mg/55 mL	90%	4 h	—	—	6 nm Spherical	Oxidation and reduction	XRD, TEM SEM	Konishi et al. (2007)
CR	Bio-Pd AGS	<i>Anaerobic Granules</i>	70 mg/L	450 mg/L	87%	2 h (6 h)	40	—	0–7 nm	Mixture of oxidation and reduction	SEM-EDX TEM	Gan et al. (2018)
Orange II		(UASB)			98%					Mixture of oxidation and reduction	TEM	Salehi et al. (2019)
Evans Blue					85%							

Coomassie brilliant blue (CBB), picric acid (PA), methyl red (MR), 3-nitrophenol (3-NP), 4-nitrophenol (4-NP), methyl orange (MO), eosin-Y (EY), cresol red (CRR), phenol red (PR), aniline blue (AB), and tetracycline (TC), Methylene blue (MB), 4-nitroaniline (4-NA), rhodamine B (RhB), 2-nitrophenol (2-NP), rhodamine 6G (Rh6G), acridine orange (AO), congo red (CR), azo violet (AV), eriochrome black T (EBT) and methyl green (MG).

- availability of clean water: nanoparticles/biogenic nanoparticles of permissible concentrations are able to render contaminated wastewater free from contaminants (ionic salts, heavy metals, expired drugs, toxic chemicals etc.) (Devi and Ahmaruzzaman, 2016; Lingamdinne et al., 2017) such that the pH of the purified water assumes that (6.8–7.0) which is safe for drinking (Table 3).
- less environmental pollution: bionanocomposite membranes/biosorbents such as multiwalled carbon nanotubes have been used as adsorbents or hybrid-adsorbents to rid off contaminants from wastewater (Lloyd and Macaskie, 2000; Sathyanarayana and Hübner, 2013; Khodadadi et al., 2017a; b; Sanni et al., 2022a; b; Kumar et al., 2023).
- reduced sicknesses and mortality: nanoparticles (encapsulated graphene and reduced graphene oxide nanocomposites) have proved their worth in terms of eliminating and detecting toxic contaminants that are cancerous and capable of causing lung infection which can lead to death or high mortality if not diagnosed early (Sanni et al., 2021; Sanni et al., 2023a; Sanni et al., 2023b).
- improved health: several communities where contaminated water is used on daily basis are prone to incessant cases of diarrhoea, cholera, dysentery and other water-related sicknesses which in turn lead to deteriorated health and low productivity since evidence has it that, many rural community dwellers depend on farming for their daily existence.
- preservation of aquatic life and secondary hosts: many contaminants such as microplastics that have high tendencies for bioaccumulation in fish tissues including their stomachs, livers and gills as well as reduce the average life expectancy of the fishes and in turn cause adverse effects in humans when such fishes are consumed by humans, can be trapped by BNPs from such waters.
- improved food production: in biotechnology and agriculture, efforts are in place regarding the use of bionanoparticles as soil supplements (Machado et al., 2013a; Machado et al., 2013b) or composites of membranes used as seed coats for CO₂ capture which aid plant photosynthesis as well as boost food production.
- reduced extinction and preservation of the current biodiversity in oceans, rivers, lakes etc.: many aquatic organisms have gone extinct as a result of their ingestion of poisonous contaminants or pollutants in wastewaters; today, a number of marine-habitat species are no longer in existence due to anthropogenic activities that have led to the destruction and elimination of such lives below water. Hence, bionanoparticles/green nanotechnology is an apt technique for securing the current biodiversity.
- Enhancement of equipment service life: The presence of chlorinated salts in fresh/wastewater can lead to the corrosion of submersible pipes lined through such waters. However, the use of nanofluids as corrosion inhibitors has helped to provide protective films that abate corrosion.

3.2.2 Stability and reusability of green synthesized NPS

Based on literature hitherto, it is clear that green-synthesized NPs hold more promises than their conventionally-prepared

counterparts in terms of efficient, safe, nontoxic, clean, and environmental friendliness, and hence their better performance in terms of pollutant removal. The regeneration and reusability of NPs is crucial to the cost-benefit analysis of nano-based water and wastewater treatment technologies and their long-term viability (Grünberg et al., 2001; Ali et al., 2016; Tajbakhsh et al., 2016). Several other studies have shown that NPs have been successfully used as adsorbents with no effluent released/generated (Husein et al., 2019; Prasad et al., 2019; Manjari et al., 2017). The ability of NPs to produce zero-effluent/-industrial wastewater is due, in part, to the presence of organic functional groups on the surface of the adsorbent, which may degrade after a certain amount of time. This phenomenon, however, also reduces the NPs' reusability (Hou et al., 2018). For economic and commercial reasons, it is crucial that NPs be reusable, recyclable, and somewhat stable. Spherical magnetic NPs synthesized using *Lagerstroemia speciosa* bark (LB) extract by co-precipitation method were found to be effective in removing Cr(VI) from aqueous solution (Al-Asfar et al., 2018). Both Langmuir isotherm and the pseudo-second-order models gave good descriptions of the kinetics and equilibrium adsorption. Cr(VI) adsorption using magnetic NPs was found to be more than 93.72% after 11 successive adsorption-desorption cycles, and the NPs were easily collected from the aqueous solution by a magnet after the maximum adsorption of Cr(VI); the results are in sync with the observations of Wei et al. (2017) when iron oxide nanoparticles were used to adsorb Cr(VI) from an aqueous system. Iron oxide NPs were synthesized using *Eucalyptus globulus* plant extract. The results showed that the iron oxide NPs synthesized in the laboratory effectively adsorbed arsenic. However, the As(V) desorption experiments showed that the synthesized iron oxide NPs were readily regenerated in basic solutions of moderate concentrations (Martínez-Cabanas et al., 2016; Farhadi et al., 2017).

However, they asserted alongside Lateef et al., 2016 that more investigations are required to ascertain the effective use of green synthetic nanoparticles in water and wastewater treatment

3.2.3 Limitations of green NPs/biogenic nanomaterials for wastewater treatment

Several agrowastes including those of wheat straw and oat resources are potential sources for the design of sustainable adsorbents for wastewater treatment which do not allow room for any food competition concerns. The development of biowaste materials including cellulose, lignin and hemicellulose into effective, low-cost adsorbents have been discussed (Taleb et al., 2020; Sajjadi et al., 2021). Agriculture prone regions such as North America (Saskatchewan), produce 60% of Canada's grain crops including oat hulls and wheat straw which are abundant, sustainable and renewable. The benefits of torrefaction as a processing technique include its ability to infuse greater polar characteristics alongside uniform particle size/particle distribution. However, studies have highlighted some of the challenges associated with pelletizing wheat straw residue after undergoing torrefaction (Agu et al., 2021). Thus one strategy that is viable for addressing such challenge is to modify the adhesive and mechanical properties of the microwave mildly torrefied materials at 200–300°C and blending them with high density polyethylene (HDPE) residue, all aimed at achieving a

TABLE 3 Biosynthesized metal and metal oxide-based nano-catalysts for the degradation of pollutants in water.

Nanocatalyst	Application	Biogenic source	Refs
Ag NPs	Photodegradation of aqueous Methyl Red (MR)	<i>Piper pedicellatum</i> C.DC leaf	Rambabu et al. (2021)
Ag nanoparticles/clinoptilolite	Reduction of MB, MO, CR and RhB in aqueous solution	<i>Vaccinium macrocarpon</i> fruit	Chen et al. (2017)
Ag-ZnO	Photodegradation of aqueous MB	<i>Azadirachta indica</i> (Neem) leaf	Rong et al. (2020)
Ag/RGO nanocomposite	Reduction of CR, 4-nitrophenol (4-NP) and RhB in aqueous solution	<i>Abutilon hirtum</i> leaf	Solano et al. (2019)
Ag/zeolite nanocomposite	Reduction of MB, 4-NP, CR, RhB and MO in aqueous solution	<i>Euphorbia prolifera</i> leaf	Momeni et al. (2016)
rGO/Ag-AuNPs	Reduction of toxic Cr(VI) in aqueous solution	<i>Albizia Saman</i> leaf	Weng et al. (2016)
ZnO-Ag nano custard apple	Degradation of MB in aqueous solution	Pomegranate peel	
Ag/TiO ₂ NPs	Photodegradation of aqueous MB	Rambutan (<i>Nephelium lappaceum</i> L.) peel	Nadaf and Kanase (2016)
AgNPs	Treatment of industrial euent	<i>Morinda Tinctoria</i> leaf	Coker et al. (2010)
AgPdNPs	Electrocatalytic reduction of H ₂ O ₂ in aqueous solution	<i>Lithodora hispidula</i> (Sm.) Griseb. leaf	Gnanaprakasam and Selvaraju (2014)
Ag/bentonite nanocomposite	Reduction of MB, 4-NP, CR and RhB in aqueous solution	<i>Euphorbia larica</i>	Madhavi et al. (2013)
Ag/MgO nanocomposite	Reduction of MB, 4-NP, MO and 2,4-dinitrophenylhydrazine (2,4-DNPH) in aqueous solution	<i>Acalypha hispida</i>	Garole et al. (2019)
AgNPs	Photodegradation of bromo phenyl blue (BPB) in aqueous solution	<i>Cirsium japonicum</i>	Khan et al. (2016)
Ag nanocomposite hydrogels-based sodium alginate	Removal of MB from aqueous solution	<i>Mukia maderaspatna</i> leaf	Bremner et al. (2009)
Ag-Mo/CuONPs	Photodegradation of MB in aqueous solution	<i>Azadirachta indica</i> leaf	Gopalakrishnan et al. (2015)
AgNPs	Reduction of 4-NP in aqueous solution	<i>Coleus forskohlii</i> root	Harshiny et al. (2015)
Ag@AgClNPs	Degradation of Victoria Blue B in aqueous solution	<i>Aquilaria agallocha</i> (AA) leaf juice	Devi et al. (2016)
Ag-TiO ₂ nanopowders	Photodegradation of MB in aqueous solution	<i>Carambola</i>	Chowdhury et al. (2016)
Au and Ag-AuNPs	Degradation of malachite green in aqueous solution	<i>Bacillus safensis</i>	Ojo et al. (2016)
RGO nanosponge/Ag-NP	Reduction of 4-NP in aqueous solution	<i>Tabebuia berteroi</i> leaf	Vellaichamy and Periakuruppan, (2016)
AgNPs	Degradation of RhB and MB in aqueous solution	<i>Parkia roxburghii</i> leaf	Paul et al. (2016)
Ag/polyphenols-modified graphene	Reduction of 4-NP in aqueous solution	Green tea	Wang et al. (2015)
Ag-SnO ₂ nanocomposites	Degradation of MB, Methyl Violet 6B, Rose Bengal and 4-NP in aqueous solution	<i>Saccharum ocinarum</i>	Sinha et al. (2017)
AgNPs	Photodegradation of Putnam sky blue 39 in aqueous solution	<i>Rosa 'Andeli'</i> double delight petals aqueous extracts	Suárez-Cerda et al. (2015)
Ag/ZnO in montmorillonite	Photodegradation of MB in aqueous solution	<i>Urtica dioica</i> leaf	Tamuly et al. (2014), Sohrabnezhad and Seifi (2016)
AgNPs	Degradation of RB-21, reactive Red-141 (RR-141) and Rhodamine-6GB in aqueous solution	Palm shell	Vanaamudan et al. (2016)
AgNPs/peach kernel shell	Reduction of MB, 4-NP and MO in aqueous solution	<i>Achillea millefolium</i> L	Khodadadi et al. (2017a)
Ag and AuNPs		<i>Citrus aurantifolia</i> peel	Farhadi et al. (2017)

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TABLE 3 (Continued) Biosynthesized metal and metal oxide-based nano-catalysts for the degradation of pollutants in water.

Nanocatalyst	Application	Biogenic source	Refs
	Reduction of 4-nitroaniline in aqueous solution		
Ag@Fe bimetallic NPs	Degradation of bromothymol blue	Palm dates fruit	Al-Asfar et al. (2018)
Ag-Cr-AC nanocomposites	Removal of binary dye system of Reactive Red (RR) and CV from aqueous solution	<i>Azadirachta indica</i> leaf	Jain et al. (2015), Saad et al. (2017)
AgNPs	Reduction of EY and CR in aqueous solution	<i>Synedrella nodiflora</i> leaf	Mittal et al. (2013)
Au-Ag bimetallic nanocomposite	Reduction of 4-NP in aqueous solution	<i>Silybum marianum</i> seed	Gopalakrishnan et al. (2015)
AgNPs	Degradation of MB in aqueous solution	<i>Trichodesma indicum</i> leaf	Kathiravan (2018)
AgNPs	Reduction of 4-NP in aqueous solution	lavender leaf	Kumar et al. (2016)
AgNPs	Reduction of 4-NP, MB, MO and MR in aqueous solution	<i>Stemona tuberosa</i> Lour	Tamuly et al. (2014)
Ag/HZSM-5 nanocomposite	Reduction of MB, CR, RhB and 4-NP in aqueous solution	<i>Euphorbia heterophylla</i> leaf	Machado et al. (2013b)
AgNPs	Reduction of 4-NP in aqueous solution	<i>Ficus hispida</i> Linn. f. leaf	Huo et al. (2018)
AgNPs	Reduction of poisonous nitro compounds in aqueous solution	Extract of date palm	Al-Asfar et al. (2018)
AgNPs	Degradation of CR and MO in aqueous solution	<i>Salvia microphylla</i> Kunth leaf	Lopez-Miranda et al. (2018)
Ag NPs	Reduction of Eosin Blue (EB) and 4-NP in aqueous solution	<i>Sapindus mukorossi</i> fruit	Dinda et al. (2017)
AgNPs	Reduction of 4-NP in aqueous solution	Citrus maxima peel	Huo et al. (2018)
AgNPs/almond shell	Reduction of MB, RhB and 4-NP in aqueous solution	<i>Ruta graveolens</i> sleeves	Bordbar (2017)
AgNPs	Reduction of 4-NP in aqueous solution	<i>Allium ampeloprasum</i> L. leaf	Sebastian et al. (2018)
Au, Ag and Ag/Au alloy NPs	Reduction of 4-NP in aqueous solution	<i>Guazuma ulmifolia</i> L. bark	Karthika et al. (2017)
AgNPs	Photodegradation of MB in aqueous solution	Mortiño berry	Kumar et al. (2019)
PdNPs	Reduction of 4-NP in aqueous solution	<i>Frimiana simplex</i>	Peng et al. (2019)
AgNPs	Photodegradation of Coomassie Brilliant Blue G-250 in aqueous solution	<i>Coccinia grandis</i> leaf	Arunachalam et al. (2012)
AgNPs	Degradation of MB in aqueous solution	<i>Plectranthus amboinicus</i> leaf	Zheng et al. (2017)
AgNPs	Photodegradation of MB in aqueous solution	<i>Biebersteinia multifida</i>	Miri et al. (2018a)
Ag/CuNPs	Degradation of toxic chlorpyrifos pesticide in aqueous solution	<i>Carica papaya</i>	Huang et al. (2011a)
Ag NPs	Photodegradation of MB in aqueous solution	<i>Trichodesma indicum</i> leaf	Kathiravan (2018)
Au@Ag@AgCl core-double shell	Reduction of 2,4,6-trinitro phenol and in aqueous solution	<i>Momordica Charantia</i> leaf	Devi and Ahmaruzzaman (2017)
AuNPs	Degradation of CR and MB in aqueous solution	Cellular extract of <i>Bacillus marisflavi</i>	Nadaf and Kanase (2016)
AuNPs	decolorization of aqueous cationic Red X-GRL, Acid Orange II and Acid scarlet GR	<i>Aspergillum</i> sp. WL-Au	Qu et al. (2017)
AuNPs	Reduction of 4-NP in aqueous solution	<i>Aspergillum</i> sp. WL-Au	Shen et al. (2017)
MnO ₂	Removal of bisphenol A	<i>Desmodemus</i> sp. WR1	Wang et al. (2017)
nano-MnO _x	Oxidative degradation of 2-chlorophenol, 2,4-dichlorophenol, and 2,4,6-trichlorophenol from aqueous solution	<i>Pseudomonas</i> sp. G7	Tu et al. (2015)
Dy ₂ Ce ₂ O ₇ nanostructure		<i>Vitis vinifera</i> juice	

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TABLE 3 (Continued) Biosynthesized metal and metal oxide-based nano-catalysts for the degradation of pollutants in water.

Nanocatalyst	Application	Biogenic source	Refs
	Degradation of MO, and RhB and B naphthol in aqueous solution		
$Ln_2Sn_2O_7$ nanostructure	Degradation of EY, eriochrome black T and methyl violet in aqueous solution	Pomegranate juice	Miri et al. (2018b)
Bio-Pt and bio-Pd nanocatalyst	Removal of ciprofloxacin, sulfamethoxazole and 17 β - estradiol from aqueous solution	<i>Desulfovibrio vulgaris</i>	Moulton et al. (2010)
Pd/Au	Dechlorination of aqueous diclofenac	<i>Shewanella oneidensis</i> MR-1	Mukherjee et al. (2001)
PdNPs	Reduction of aqueous organic dyes	<i>Terminalia arjuna</i>	Sweeney et al. (2004), Garai et al. (2018)
Pd/RGO	Reduction of various dyes in aqueous solution	<i>Artemisia abrotanum</i>	Toyao et al. (2013)
Pd/perlite nanocomposite	Reduction of 4-NP, CR, RhB, MO and 2,4-DNPH in aqueous solution	<i>Euphorbia neriifolia</i> L. leaf	Weng et al. (2013)
AuNPs	Degradation of dyes in aqueous solution	<i>Centella asiatica</i>	Das et al. (2010a) and Das et al. (2010b)
Pd/walnut shell nanocomposite	Degradation of RhB, CR, and MB in aqueous solution	<i>Equisetum arvense</i> L	Dauthal and Mukhopadhyay (2013)
Pd/Fe ₃ O ₄ nanocomposite	Degradation of Cr(VI), 4-NP and 2,4-DNPH in aqueous solution	<i>Hibiscus tiliaceus</i> L	Kumar et al. (2013)
Pd/bentonite nanocomposite	Degradation of 2,4-DNPH, Cr(VI), and 4-NP in aqueous solution	<i>Gardenia taitensis</i> leaf	Das et al. (2011)
Pd NPs/sodium borosilicate glass	Reduction of 4-NP, 2,4-DNPH, MO, CR, MB, and Cr(VI) in aqueous solution	<i>Euphorbia milii</i>	Sherin et al. (2020)
Pd NPs	Diatrizoate removal from hospital wastewater	<i>S. oneidensis</i>	Turunc et al. (2017)
Cu/reduced graphene oxide/Fe ₃ O ₄ nanocomposite	Reduction of 4-NP and RhB in aqueous solution	<i>Euphorbia wallichii</i> leaf	Renuka, et al. (2016)
CuO/ZnO nanocomposite	Reduction of 4-NP and RhB in aqueous solution	<i>Melissa Ocinalis</i> L. leaf	Srivastava et al. (2015)
CuNPs	Degradation of MR in aqueous solution	Peel extract of <i>Citrus grandis</i>	Shukla and Iravani (2017), Shukla (2015)
CuONPs	Photodegradation of MB in aqueous solution	<i>Tinospora cordifolia</i>	Vennila and Prabha (2015)
Cu/ZnONPs	Degradation of MB and CR in aqueous solution	<i>Euphorbia prolifera</i> leaf	Gawande and Jenkins-Smith (2001)
CuNPs	Degradation of Bismarck brown in aqueous solution	<i>Tridax procumbens</i> leaf	Jafarirad et al. (2018)
Cu nanoflowers	Degradation of MB in aqueous solution	<i>Ficus benghalensis</i> leaf	Karthiga Devi et al. (2016)
CuONPs	Reduction of 4-NP in aqueous solution	<i>Tecoma castanifolia</i> leaf	Sharmila et al. (2016)
Cu/Fe ₃ O ₄ /eggshell nanocomposite	Reduction of MO, 4-NP, CR, RhB and MB in aqueous solution	<i>Orchis mascula</i> L. leaf	Nasrollahzadeh et al. (2016)
Cu/Fe ₃ O ₄ NPs	Reduction of 4-NP, CR and RhB in aqueous solution	<i>Morinda morindoides</i> seeds	Ramesh, et al. (2018)
CuO nanocrystals	Degradation of MB, MO, MR, EY and reduction of 2-3, and 4-NP in aqueous solution	<i>Psidium guajava</i> leaf	Sreeju et al. (2017)
CuONPs	Reduction of 4-NP in aqueous solution	Fruit extract of plant <i>Fortunella japonica</i>	Singh et al. (2018)
CuONPs	Photodegradation of Acid Black (AB) 210 in aqueous solution	<i>Abutilon indicum</i>	Ijaz et al. (2017)
CuONPs	Degradation of 4-NP in aqueous solution	Rosehip	Raj et al. (2016)
CuONPs	Reduction of CR, MB and 4-NP in aqueous solution	<i>Aglaiia elaeagnoidea</i> flowers	Reddy et al. (2018)
CuONPs	Photodegradation of RhB in aqueous solution	<i>Ferulago angulata (schlecht) boiss</i>	Jafarirad et al. (2018)

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TABLE 3 (Continued) Biosynthesized metal and metal oxide-based nano-catalysts for the degradation of pollutants in water.

Nanocatalyst	Application	Biogenic source	Refs
CuONPs	Degradation of safranin O (SO) in aqueous solution	<i>Calotropis gigantean</i> leaf	Rajendaran et al. (2019)
CuONPs/clinoptilolite	Degradation of 4-NP, RhB and MB in aqueous solution	<i>Rheum palmatum</i> L. root	Andjelkovic, et al. (2017)
Cu-doped ZnONPs	Degradation of Acid Black 234 in aqueous solution	<i>Clerodendrum infortunatum</i> and <i>Clerodendrum inerme</i>	Khan et al. (2018)
CuNPs	Removal of nitrate	Extract of <i>Hibiscus sabdariffa</i> flowers	Andjelkovic, et al. (2017)
CdS	Removal of Cd from aqueous solution	<i>P. aeruginosa</i> JP-11	Raj et al. (2016)
Se	Removal of Zn(II) from aqueous solution	Anaerobic microbial consortium	Jain et al. (2015)
Se	Removal of Hg ⁰ from aqueous solution	<i>Citrobacter freundii</i> Y9	Wang et al. (2018)
Mn	Removal of Pb(II), Cd(II), and Zn(II) from aqueous solution	<i>Pseudomonas putida</i> MnB1	Zhou et al. (2015)
MgO	Removal of Ni(II), Pb(II), Cd(II), Cu(II), Zn(II), Co(II) and Mn (II) from aqueous solution	<i>Acacia</i> sp	Srivastava et al. (2015)
ZnONPs	Degradation of Synozol Navy Blue-KBF textile dye in aqueous solution	<i>Trianthema portulacastrum</i>	Khan et al. (2019)
ZnO nano-flowers	Photodegradation of MB, EY and Malachite green (MG) in aqueous solution	Panos	Kaliraj et al. (2019)
ZnONPs	Degradation of CR in aqueous solution	<i>Artocarpus Heterophyllus</i> leaf	Plachtová et al. (2018)
ZnONPs	Degradation of Alizarin Red-S in aqueous solution	<i>Carica papaya</i> milk (CPM) latex	Thapa et al. (2017)
ZnONPs	Photodegradation of MB in aqueous solution	<i>Hydnocarpus alpina</i> Wt	Ganesh et al. (2019)
SnO ₂ -ZnO	Degradation of MO in aqueous solution	Gel of <i>Aloe vera</i> plant	Jafarirad et al. (2018)
ZnONPs	Degradation of RhB and MB in aqueous solution	Seeds extract of <i>Parkia roxburghii</i>	Paul et al. (2017)
ZnO/MgO nanocomposite	Degradation of MO, MB and 2-NP in aqueous solution	<i>Musa paradisiaca</i> bract	Maruthai et al. (2018)
ZnO/NiFe ₂ O ₄ NPs	Photodegradation of MB in aqueous solution	<i>Mangifera indica</i> leaves	Poguberović et al. (2016)
ZnONPs	Photodegradation of RhB in aqueous solution	<i>Cyanometra ramiflora</i> leaf	Varadavenkatesan et al. (2019)
ZnONPs	Photodegradation of MB	<i>Thymus vulgaris</i> leaf	Zare et al. (2019)
ZnONPs	Degradation of MO, CR, RhB and MB in aqueous solution	<i>Abelmoschus esculentus</i> mucilage	Prasad et al. (2019)
Fe-ZnONPs	Photodegradation of naphthalene in aqueous solution	<i>Amaranthus dubius</i> aqueous leaf	Shivaji et al. (2020)
ZrO ₂ /rGO nanocomposite	Photodegradation of RB 4 dye in aqueous solution	Cinnamon	Gurushantha et al. (2017)
Hollow microspheres Mg-doped	Photodegradation of RhB in aqueous solution	<i>Aloe vera</i> gel	Thapa et al. (2017)
ZrO ₂ NPs rGO/TiO ₂ /Co ₃ O ₄	Degradation of MB and CV in aqueous solution	<i>Shutteria involucreta</i> leaf	Nasrollahzadeh et al. (2016), Ranjith et al. (2019)
α-Fe ₂ O ₃ /TiO ₂	Degradation of MB in aqueous solution	Flax seed	Paul et al. (2016), Mohammed et al. (2019)
SnO ₂ NPs	Photodegradation of MB, MO and erichrome black T in aqueous solution	<i>Erwinia herbicola</i>	Srivastava and Mukhopadhyay (2014) Zinatloo-Ajabshir et al. (2018)
Au NPs	Reduction of 4-NP in aqueous solution	<i>Trichoderma viride</i> and <i>Hypocrea lixii</i>	Mishra et al. (2014)

more efficient biocomposite adsorbent for wastewater treatment with better adsorptive properties over those of the pristine oat and wheat waste. Figure 3 is an illustration of the potential limitations in the application of green NPs.

Chitosan, a highly abundant biopolymer/biomaterial, which has >50% glucosamine units is a versatile polysaccharide which can be obtained by the deacetylation of chitin, (Ahmed and Ikram, 2017; Mohammadzadeh Pakdel and Peighambaroust, 2018). The degree of deacetylation influences its physicochemical properties, especially those that are related to adsorption (Fierro et al., 2008; Dey and Ghosh, 2020; Tavares et al., 2020). Due to the covalently modified forms of chitosan, its entrenched abundant functional groups can be tailored to form biocomposites of varying structural stability towards the attainment of the controlled adsorption of several friendly/toxic chemical species (Steiger et al., 2021; Parandhama et al., 2016; Parandhama et al., 2019). Also, evidence has it that, kaolinite, an inorganic aluminosilicate clay, interacts favourably with chitosan for improved stability owing to the infused synergistic effects offered by its individual components when pelletized or disintegrated into nanoparticles or nanomaterials which afford them higher surface areas to volume ratios for enhanced adsorption. The establishment of chemical interactions (i.e., electrostatic or H-bonding) between kaolinite and the additive components make it an efficient binder for bionanocomposites (Chen et al., 2013). In a study, kaolinite was employed as a proposed filler/binder in ternary pelletized biomaterials (Bezerril et al., 2006) which then informed its merit as a biomaterial with cation exchange capacity and adhesive properties that are needed in chitosan-based bionanocomposites (Unuabonah et al., 2008). The use of physically blended kaolinite, chitosan and agro-waste materials have been exploited as adsorbents for lead-ion removal from drinking water (Mohamed et al., 2022); despite the quantity of Pb removed, evidence has shown that such adsorbents are more effective when they are used as bionanocomposites of the blended components. The authors also proposed an optimum use of 40 wt% agro-waste based on the estimated stability limit of the composite pellets upon immersion in aqueous media. However, when used in their nanoforms, the measure of stability might drop except if compatible supports are used as reinforcement materials for the nanoadsorbents. To address stability limitations in such bionanocomposites, the extended weights and concentrations of the agrowaste may also become feasible owing to the size reduction effect of the nanosized materials/particles relative to the pellet forms; this helps to provide for improved uptake capacity of the effluent dye/contaminant.

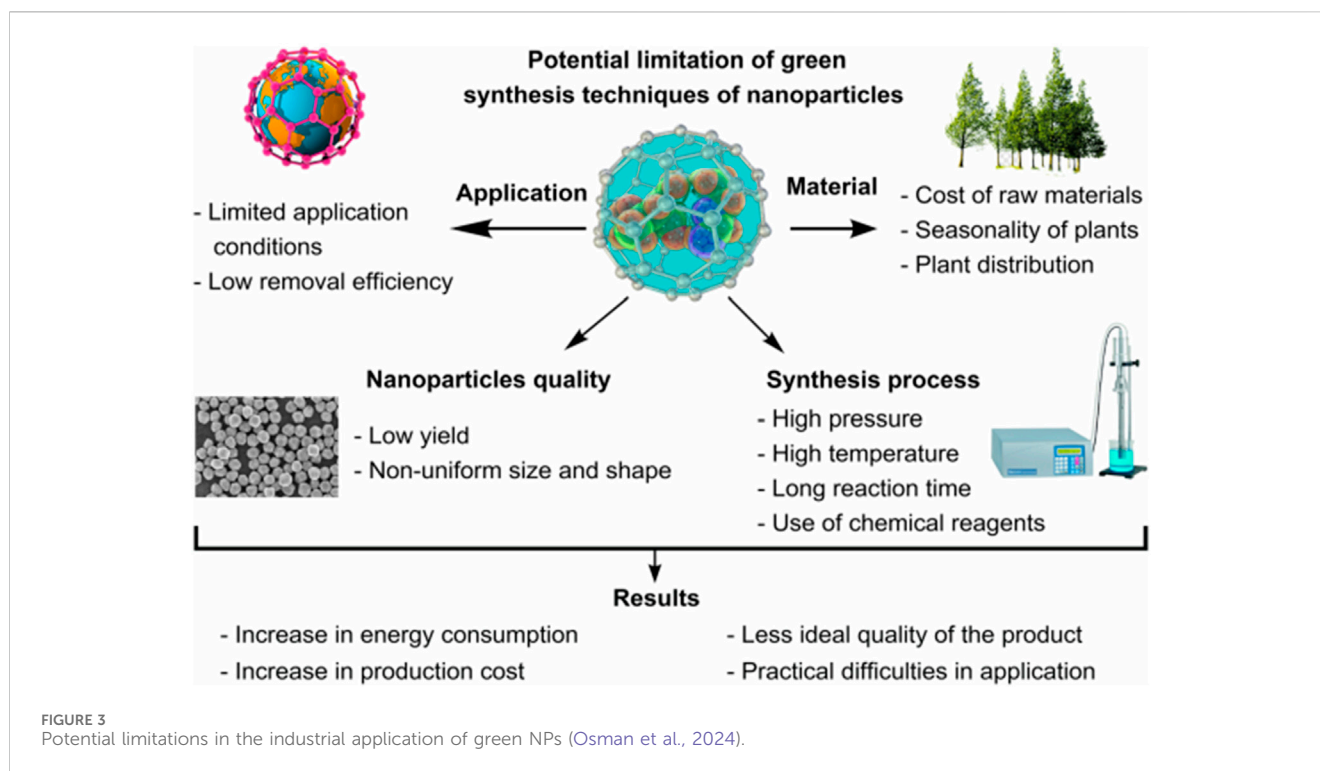
In terms of economics, the cost and adsorption properties of adsorbents made from agro-waste sourced from industrial crops were compared with those of spent coffee grounds (SCG) in order to evaluate the valorization potential of agro-waste composites as sustainable adsorbent materials for cationic pollutants (Sabzevari et al., 2018; Kong and Wilson, 2020). In the study by Steiger et al. (2023), it was affirmed that a facile and bottom-up design strategy of biocomposite materials leads to the valorization of agro-waste biomass yields of functional adsorbents with tailored properties (Mohamed et al., 2020). Therefore, their modified pelletized or nanosized forms will provide better adsorptive properties within the circular economy model for agro-waste derived adsorbent materials for wastewater treatment (Nadagouda and Varma, 2008; Omran and Baek, 2022).

3.2.4 Benefits and applications of biophotocatalysts

The Fenton process is one popular approach that uses an acidic medium to induce the reaction between ferrous ion and H_2O_2 to generate $\bullet OH$ groups for the effective degradation of various recalcitrant natural organic pollutants. The slow rate of generation of ferrous ions in the Fenton process provides for a more effective nanocatalytic degradation aided by the ions which eventually leads to increased higher sludge production in the treatment step (Ahmadi et al., 2021; Nidheesh, 2015; Guterrez et al., 2022). This drawback can be partly controlled with the use of heterogeneous catalysts (Karim et al., 2022). Various synthetic heterogeneous nanocatalysts such as FeO NPs (nZVI) (Puiatti et al., 2022; Nadagouda et al., 2010), Fe_2O_3 (Shahwan et al., 2011; Buarki et al., 2022), mixed iron oxides (Jain et al., 2021), PdNPs (Narasaiah et al., 2017) and bimetallic NPs were biosynthesized using green technology for the degradation of pollutants such as dyes (Sajadi et al., 2018; Zhang et al., 2018; Hassan et al., 2020; Jain et al., 2021), antibiotics (Stan et al., 2017; Ouyang et al., 2019), and nitro-benzene. The photo-Fenton (Puiatti et al., 2022), electro-Fenton, and sono-Fenton (Prakash et al., 2021) operations of different fenton nanocatalysts have been reported alongside their antibacterial activities (Buarki et al., 2022) in several adsorption studies. In addition to the preparation of these nanocatalysts, some synthetic minerals and carbon residue ensue at their production stages which has led to the concentration of efforts in the recent development of Fenton catalyst/ Fe_3O_4 supported on mesoporous carbon or other mineral supports such as bauxite (Al_2O_3). Also, bentonite-supported on nZVI has also been employed in the chemical degradation of organic pollutants in wastewater (Hassan et al., 2020). Materials such as leaf extract (Ayodhya and Veerabhadram, 2017; Maryami et al., 2016; Maryami et al., 2017; Puiatti et al., 2022), tea extract (Hassan et al., 2020), tea polyphenols (Ouyang et al., 2019), waste-lignin, fruit-peel extract (Jain et al., 2021), flower (Buarki et al., 2022), and plants have been adopted in the green synthesis of Fenton catalysts and it was observed that the green materials acted as reducing agents (Puiatti et al., 2022), stabilizing agents (Puiatti et al., 2022), and capping agents. Franco et al. (2021) examined the catalytic potential of green Fe_3O_4 NPs produced by thermal treatment of *Cammelia sinensis* (black tea) extract and Fe^{3+} salt for the removal of azo dye/methyl orange from aqueous solution. Thermal heating aided the removal of tea polyphenols. An illustration of the comprehensive thermal phase transformation of the generated and exposed rare nano $\beta-Fe_2O_3$ phase of the catalysts at 400°C preceded its subsequent conversion to $\alpha-Fe_2O_3$ as the temperature increased. Table 4 contains some information on some photocatalysts that have been used for wastewater treatment.

4 Potential risks associated with the use of green NPs, their long-term environmental impact and their bioaccumulation potential

Due to rapid industrialization and urbanization activities, a quantum of wastewater containing toxic chemicals and heavy metals is generated consistently, which constitutes high environmental nuisance, thus affecting the average life



expectancy/wellbeing of the global populace. The recent advancements in sustainable cost-effective wastewater treatment technologies have attracted more attention from policymakers, to legislators as well as the scientific community. In the study by Kumar et al. (2023), the application of biochar and green NPs obtained from agro-waste were employed in removing refractory pollutants from water and wastewater; the contemporary application, and mechanism of the biochar-supported advanced oxidation process (AOP) incorporated the use of green NPs for the effective removal of organic and inorganic pollutants [noxious chemicals/compounds such as (HMs)] (Bolan et al., 2022a; Bolan et al., 2022b), endocrine disrupting compounds (EDCs) (O'Connor et al., 2022), polyaromatic hydrocarbon (PAHs) (Kumar et al., 2021), personal care products (PCPs), micropollutants (micro-nano-plastics) (Sridharan et al., 2021), pesticides (Sun et al., 2020), etc. from contaminated streams/wastewater. Although, green synthesized NPs/NMs offer significant benefits such as cost-effectiveness/ease of application (Hano and Abbasi, 2022), they also help avoid the use of harmful chemicals/solvents, which allows for the accurate fabrication of NMs/NPs with consistent shapes and sizes, with minimal or no waste generation (Harish et al., 2023). However, one of their shortcomings include the fact that they are useful within low temperature and pressures (i.e., may lose their potency at high temperatures and pressures) compared to their counterparts which are synthesized via traditional methods, however, these conditions reduce the tendencies for unforeseen incidents/events (Dikshit et al., 2021). Green NPs/NMs also facilitate the use of sustainable raw-materials in large-scale production systems (Soltys et al., 2021). Nonetheless, existing literature lacks sufficient information on considerations for human health and the risks associated with *in-vivo* and *ex-vivo* nanotechnology deployments. Furthermore, researches on environmental toxicity and bio-accumulation of

green NPs/NMs are quite inadequate, however, their existence in very small sizes facilitates their influx into humans, thus causing respiratory disfunction and severe sicknesses (Pietrousti et al., 2018). Also, the industrial application of green NMs/NPs is relatively limited, as a result of issues related to difficulty in controlling their sizes, shapes and instabilities (Dikshit et al., 2021). In essence, comprehensive toxicological assessments/genetic modifications may necessitate the enhanced synthesis and application efficiency of NMs or NPs. This is because there is a dearth in knowledge/information on universally acceptable plants and seasonal factors that affect the growth of such plants alongside the synthesis of biogenic NPs/NMs, which therefore poses constraints that hinder the widespread application of green NPs/NMs.

5 Bioaccumulation of green NPs and their plausible long term environmental impacts

Due to the nature of the origin of green NPs that are used as reactive adsorbents, they have a low measure of bioaccumulation potential, this is because of their high reactivity or potential to degrade wastewater contaminants or pollutants (Shafey, 2020), hence they may not constitute any nuisance since they end up interacting with contaminants to produce new/value adding products (Oni et al., 2023). This in turn reduces their potential for bioaccumulation except when they are used as catalysts. Catalysts are known to cause reactions to take place without them undergoing any form of consumption all through the entire process; therefore, nanocatalysts that are employed in wastewater treatment have a higher risk of bioaccumulation compared to

TABLE 4 Iron based biogenetic nanoparticles resource for the removal of heavy metals and dyes from contaminated waters and other fluids.

Biogenic resource of Fe	Size and shape of nanoparticle	Heavy metals/dye remove	Reference
<i>Aloe vera</i>		As(V)	Lloyd and Macaskie (2000)
<i>M. oleifera</i>	250–474, spherical	Nitrate	Bonigala et al. (2018), Katata-Seru et al. (2018)
<i>C. sinensis</i>	5–25, Cuboid/Pyramidal	As(V) and As(III)	Farhadi et al. (2017)
<i>M. ferrooxydans</i>	100–130, Rope like	As(III) and As(V)	Ali et al. (2016)
<i>E. globules</i>	-, spherical	As(V)	Ullah, et al. (2017)
<i>Amaranthus spinosus</i>	58–530 nm, spherical	MB, MO	Ravikumar et al. (2019) and Ravikumar et al. (2020)
<i>Eucalyptus</i>	20–60 nm, spherical agglomerates	Direct black G	Zhuang et al. (2015)
Omani leaf	15 ± 2 in length and 3.0 ± 0.2 nm dia	Heavy oil viscosity moderation	Al-Ruqeishi et al. (2016)
<i>S. jambos</i>	5–60, Oval, spherical	Cr(VI)	Karthiga Devi et al. (2016)
<i>E. globules</i>	50–80, spherical	Cr(VI)	Andjelkovic et al. (2017)
<i>P. granatum</i>	100–200, irregular	Cr(VI)	Ullah, et al. (2017)
<i>C. sinensis</i> , <i>S. aromaticum</i> , <i>M. spicata</i> , <i>P. granatum</i>	50–60, spherical	Cr(VI)	Karthiga Devi et al. (2016)
<i>Eucalyptus</i> leaf	20 and 80 nm, amorphous	Cr(VI), Cu(II)	Weng et al. (2016)
Green tea	5–15 nm, spherical	Bromothymol blue	Ali et al. (2016)
<i>Eucalyptus</i>	50–80 nm, spherical	Cr(VI)	Thapa, et al. (2017)
<i>C. (L.) Cuss</i>	~45.4, irregular	Cr(III) and Pb(II)	Karthiga Devi et al. (2016)
Oolong tea	40–50 nm, spherical	Malachite green	Machado et al. (2013b)
Green tea	70–80 nm, spherical	Malachite green	Ullah, et al. (2017)
<i>Eucalyptus</i> leaf	80 nm, spherical	Phosphate	Naraginti and Sivakumar (2014)
Vine leaves, black tea, grape marc	15–45 nm	Ibuprofen	Muthukumar and Matheswaran (2015)
<i>E. globules</i>	80–90 nm, spherical	Phosphate	Nair and Pradeep (2002)
<i>E. globules</i>	~80, spherical	Nitrate	Nair and Pradeep (2002)

when they are merely used as adsorbents that have high biodegradation potentials which in turn increases their tendencies for bioaccumulation, thus influencing soil fertility, air quality, food production, etc., when they are discarded after use. In another regard, one approach via which this problem can be addressed is by the adoption of nanocatalysts synthesized (whether from chemical constituents or from plants) at optimal/permissible concentrations which are nontoxic and can bring about the conversion of pesticides such as 4-chlorophenol into several multiple useful chemicals to mankind (Sanni et al., 2022a). Also, in another context, the bioaccumulation of bionanocatalysts encapsulated in membrane coated seeds are stable and quite beneficial as potential fertilizers for the stimulation of plant growth. Therefore, for catalysts used as fertilizers, their long term environmental impact may be quite beneficial in terms of their role in boosting food production or the conversion of toxic compounds to value adding products. However, if the nanoparticles do not have high selectivity for the target-toxic compounds in host systems, there may be high risks of bioaccumulation which may in turn result in more complex situations. Even in situations where the NPs can trap

the toxic components from such systems, one feasible long term solution to abating issues related to bioaccumulation is the use of nanoparticles of permissible concentrations that are non toxic/within the optimum requirement while ensuring they have a good measure of stability such that they can be recycled for use or have a long reusability span which will help reduce the quantities used per continuous operation during contaminant removal (Verónica et al., 2024); this then implies that the system will be such that it is a continuous and not a batch process, where the nanomaterials and photocatalysts are used and dislodged after the first run for clean ups before being used in another batch of contaminant removal; this will also help to ensure some measure of commercial viability for the green NPs. In addition, since biological wastewater treatment processes rely on biological entities to degrade and remove their inherent contaminants and pollutants, they are prone/vulnerable to high toxicity levels. However, considering the fact that several toxicity measurement methods have been proposed for wastewater treatment processes, most of the known techniques are performed off-line, and are usually not adaptable to on-line monitoring systems, especially in terms of providing early warning

signals for potential risks to water treatment operators, systems and the environment (Xiao et al., 2015b). Nonetheless, the past decade has recorded a rapid growth in the research and development of biosensors for the toxicity assessment and effective treatment of contaminated aquatic environments and wastewater. In clear terms, it is needful to begin to consider examining the sensitivity of assays by sensor-based NPs sourced from single organisms that will match one or more toxic contaminants as targets, or better-still, consideration can be given to the development of a matrix of biosensors or a biosensor incorporated with NPs synthesized from multiple organisms, such that they have the potential of eliminating a range of contaminants from wastewater. This can be achieved by testing the micro fuel cell (MFC)-based biosensors with real life-contaminated wastewater and comparing the results with well-established toxicity assays/detectors including those based on oxygen uptake rate (OUR) or CH₄-uptake for the detection of biogenic/green NPs (Au, Ag, Pd, etc.), with integrated advanced data acquisition and processing methods for interpreting the on-line toxicity sensor results in real life which reduces the disturbances associated with the fluctuations in the quality and quantity of wastewater. The only challenge here is that biosensors are quite expensive but their long term viability cannot be overemphasized.

6 Challenges associated with scaling up green NP synthesis for industrial application, significant barriers to commercialization and strategies for overcoming them

Over the years, the remarkable advances in the use of green NMs and NPs, have positioned them as top-contenders across various domains/industries/sectors including agriculture (i.e., boosting soil fertility and crop production), medicine (nanovesicles as drug carriers for efficient drug delivery) (Sengani et al., 2017; Sanni et al., 2022c), environment (abatement of environmental pollution), food (food packaging), sensor technology (smart technologies for the identification of nanotoxic materials), electronics, etc.

Despite the fact that, the fabrication and application of agricultural waste-derived biogenic NPs hold great prospects as a green approach for wastewater treatment, however, prior to scaling up their production and industrial application processes, their toxicological and life-cycle challenges must be taken into account when used in biosensors (Sanni et al., 2023b) or evaluated using correlations that can estimate/measure and detect their toxicity/hazard levels while bearing in mind the process economics, cost-effectiveness and life-cycle assessment of the entire production route of the bio-nanoengineered materials which are often exploited in the generation of green catalysts/adsorbents/materials with enhanced treatment potentials for wastewater treatment (Kumar et al., 2023).

Nanomaterials, such as cellulosic-nanofibrils and nanocrystals have assisted in revolutionizing the era of biobased nanomaterials due to their surface, optical (Lin and Maggard, 2008), crystalline, mechanical, stiffness versatility, light weight, low toxicity, gelation and biodegradability (Kumar et al., 2023). The development of nanomaterials is often faced with challenges ranging from particle agglomeration to limited scalability of the production

methods, environmental impacts and human health, hence the need to explore different approaches or options for their broad use on a large scale in the industrial sector.

Other barriers or challenges posed by biogenic NP use in water treatment include, the lack of data on their biotoxicity, scale-up, storage, bioaccumulation/biodistribution, quantity control, loading onto systems, etc. Critical to overcoming the aforementioned challenges bedeviling the industrial production and commercialization of nanomaterials include the availability/low-cost of the raw materials, environmentally friendly manufacturing processes, low production cost, the use of economical means of drying nanoparticle suspensions to recover the particles, avoiding redispersion ambiguities, adherence to international standards of toxicity measurements, adopting rapid/inexpensive characterization techniques, collaboration amongst producers and users as well as the efficient coordination of efforts by the government, industry and academia towards controlling market forces while ensuring an efficient market-pull for nanoproducts. With all of the aforementioned in place, alongside the availability of the needed resources, research and development, cum industrial-scale production of nanomaterials/nanoparticles will guarantee competitive production costs.

Despite issues related to instability of nanocatalysts or biogenic NPs, the stability and reusability of green NPs used in large scale water treatment processes can be ensured by ensuring that biogenic sources to be used for green NP production are sustainable and cultivated on large farm lands which will also culminate in high availability of the capping and stabilizing agents to be optimized during green NP-synthesis since bacteria, plants, algae and fungi are known to possess capping and stabilizing abilities for green NP synthesis. For the NPs used as catalysts, they can be produced on supports which help to increase the service life of each catalyst.

7 Toxicity assessment of nanoparticles/bionanoparticles

Nanoparticles' sizes range from 1 to 100 nm (Nel et al., 2006). Advancements in technology has led to a drastic increase in their applications (Robertson et al., 2010; Thomas, 2014; Vinay et al., 2017), such as, as additives in paints, foods, ceramics, food packages, paper, drug delivery, cancer therapy and biosensors (Yang et al., 2010), as tumour detectors (Qian et al., 2008), paclitaxel (Gibson et al., 2007) as well as radiotherapy dose enhancers (Hainfeld et al., 2010; McMahon et al., 2011). Their increased demand is due to their small sizes and high surface area-to-volume ratios (Caruthers et al., 2007) which results in high chemical reactivity/reactive oxygen (ROS) production (Choi and Hu, 2008; Zoroddu et al., 2014). In recent times, nanoparticles/nanomaterials have attracted great attention due to their effects in the environment during production/disposal of consumer products containing them (Behra and Krug, 2008). Nanoparticles easily penetrate cell membranes and interfere with intracellular/metabolic activities (Hanley et al., 2009). The identification, detection and measurement of reactive oxygen species (ROS) is one suitable mechanism for determining nanoparticle toxicity (Wang et al., 2014a; Wang et al., 2014b; Elsaesser and Howard, 2012). Nanoparticle interaction with cells induce pro-oxidant effects that

lead to the secretion of NADPH-dependent enzymes as well as mitochondrial respiration/ROS generation (Regoli and Giuliani, 2014; Jomova et al., 2012; Chen et al., 2011). Studies have also recorded that nanoparticle internalization/ingestion, leads to phagocytosis-induced production of ROS (Soenen et al., 2011). Some studies on nanoparticle toxicology/toxicity include toxicity assessments of nanoparticles to environmental microorganisms (Hegde et al., 2016), TiO_2 -NP toxicity (Berghe et al., 2013), AuNP toxicity (Berghe et al., 2013), risk monitoring of inhaled NPs (Bakand and Hayes, 2016), AgNP-induced mitochondrial toxicity (Maurer and Meyer, 2016) and toxicities of single-walled (Jain et al., 2012) and multi-walled carbon nanotubes (Kerfahi et al., 2015). Each article focused on a single nanoparticle's toxicity on an organ without providing any detailed information on the toxicity assessments of higher organisms/cell lines. Elaborative discussions on the toxicity imposed by nanoparticles on organisms (rat, mouse, pig, guinea pig, human cell lines and humans have been discussed). Figure 4 is an illustration of different biogenic NPs and the experimental models adopted for their toxicity assessment.

Toxicity assessment of nanoparticles can be classified as *in vitro*/*in vivo* assessments (Huang et al., 2004; Huang et al., 2011a; Huang et al., 2011b; Schiavo et al., 2016). Some advantages of the *in vitro* assessment scheme include, low costs, short time requirement and lesser ethical considerations (Huang et al., 2015). *In vitro* assessment can be subdivided into proliferation, necrosis, oxidative stress, apoptosis and DNA damage assay (Huang et al., 2017).

7.1 Proliferation assay

This employs 3-(4,5-Dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT) salt for its *in vitro* toxicity assessment of nanoparticles (Sayes et al., 2007) and in turn measures cellular metabolism via the assessment of metabolites/active cells in response to bioNPs (Beveridge and Murray, 1980; Beveridge et al., 1996). The approach accommodates minimal model cell manipulation and gives fast/reproducible results (Marshall et al., 1995). The assay-measurements target tetrazolium salt and may sometimes encounter alterations in the measurements caused by changes in the prepared culture-additives (Molinari et al., 2003), pH (Jabbar et al., 1989), ascorbate (Natarajan et al., 2000) and cholesterol (Abe and Saito, 1999). Since MTT-assay produces formazan, assays such as XTT/WST-1 that can generate soluble synthetic dyes are preferred. Alamar Blue (AB) measures cellular redox potential compared to MTT-assay because of its simplicity in terms of sample preparation (Punshon et al., 2005). However, literature has it that the success of (AB) may be hindered as a result of the unavailability of the assay's biochemical stimulation of the interaction between non-porous silicon and (AB) in the absence of these cells (Low et al., 2006). The cologenic assay is another type of assay which makes room for proliferating cell-counts by visual inspection upon exposure to bioNPs (Casey et al., 2007).

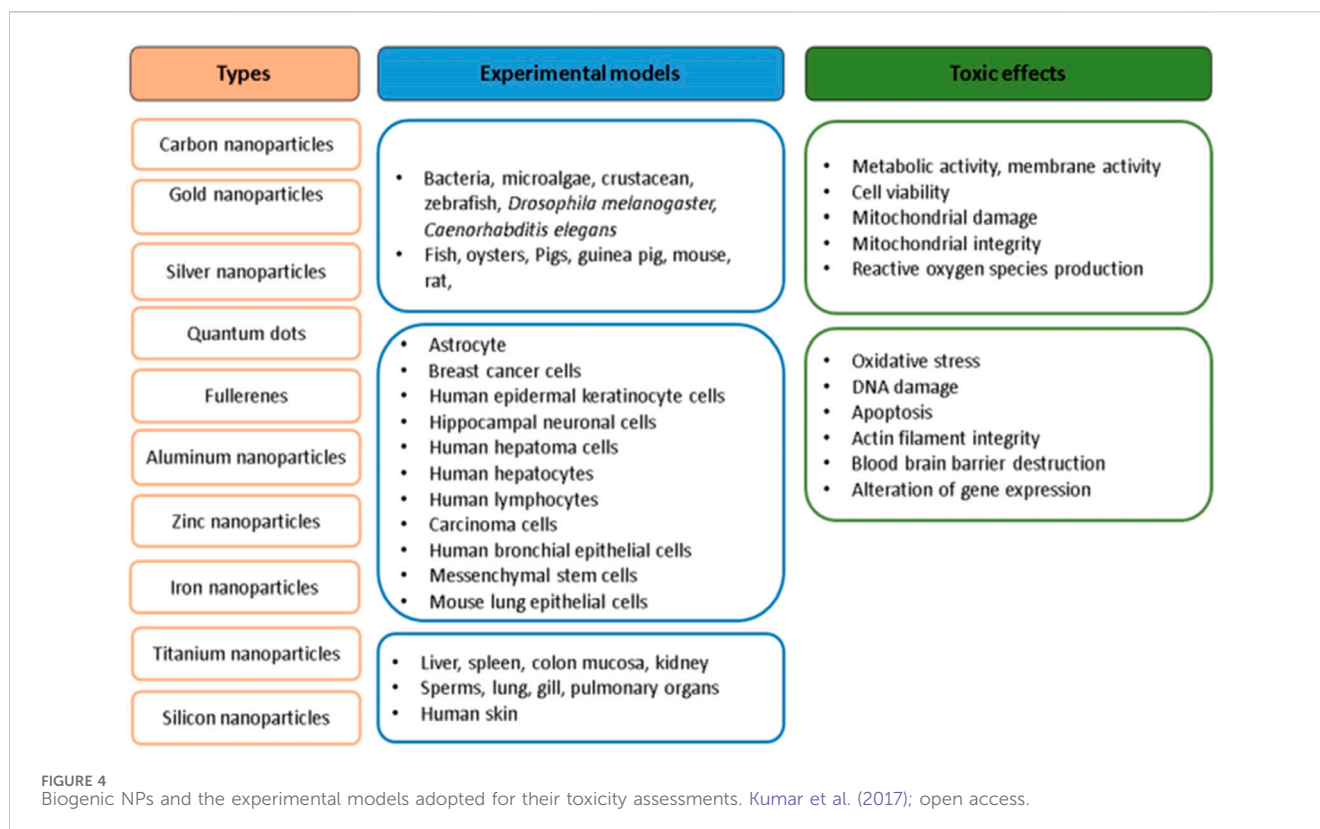
7.2 Apoptosis assay

This happens to be one of the main markers that is usually observed in *in vitro* NP-toxicity assessment. DNA damage, oxidative

stress in cell cultures and apoptosis induced by BNPs are often caused by excessive free radical generation (Bortner et al., 1995; Collins et al., 1995; Ryter et al., 2007; Li and Osborne, 2008; Kumar et al., 2013a; Kumar and Dhawan, 2013b). In an *in vitro* study, apoptosis in the embryonic stem cells of a mouse was found to be induced by AgNPs (Ahamed et al., 2008). Apoptosis markers (i.e., caspase-3 and -9) were used to examine the larval tissue treatment of *Drosophila melanogaster* with AgNPs of 50–100 µg/mL at 24 and 48 h. In a later study, the findings revealed AgNP-interference within the apoptotic pathway of *D. melanogaster* (Ahamed et al., 2010). Upregulation of p38 protein expression occurred as a result of the timely and increased dosage of AgNPs in *D. melanogaster*; when this effects extended to the genes and DNA of the organism, they induced cell death/a cascaded apoptosis pathway (Liang and Clarke, 2001; Sherr, 2004). Methods for apoptosis assessment include Annexin-V (Lee et al., 2007), Comet (Jin et al., 2007), TdT-mediated dUTP-biotin nick end labeling (TUNEL) assays (Mo and Lim, 2005) and morphological change inspection (Pan et al., 2007). In addition, the DNA laddering technique aids in the visualization of the products of apoptosis of endonuclease cleavage (Wyllie, 1980; Arends et al., 1990; Suman et al., 2012). Irregular size reduction of cells coupled with DNA-fragmentation can initiate the inducement of apoptosis (Kerr et al., 1972; Abdel-Khalek, 2016). Annexin-V/propidium iodide (PI), an impermeable dye, is a cell death marker employed in toxicity studies. When Annexin-V binds to phosphatidylserine, it causes increased fluorescence which results in plasma membrane externalization of the organism, which is induced by the caspase-dependent pathway activation. PI is a dye that stains the nucleus when the cell membrane's integrity is lost, and hence, is likened to the latter stage of apoptosis (Silva, 2010). In an investigation involving the AgNP treatment of human HepG2 hepatoma cells, changes in the nucleus/morphology with apoptosis induction were observed (Lu et al., 2011) and measured by Annexin V/PI in the AgNP treated HeLa cell lines (Miura and Shinohara, 2009; Baharara et al., 2016).

7.3 Single cell gel electrophoresis (SCGE) assay/comet assay

A tool that detects a test material's/BNP's mutagenic potential (Henderson et al., 1998; Kisin et al., 2007), alongside the induced *in vitro* and *in vivo* single-/double-stranded DNA breaks in the individual cells (Fairbairn et al., 1995; Singh and Stephens, 1997; Bajpayee et al., 2013; Kumar et al., 2013a). It quantifies DNA-DNA or DNA-protein cross-links, oxidative DNA damage (Lemay and Wood, 1999) as well as basic and alkali-labile sites (Kumar and Dhawan, 2013b; Dusinska and Collins, 2008; Pavanello and Clonfero, 2000). Based on the working principle of the assay, damaged DNA (tail) fragments and undamaged DNA (the head) imposed by BNPs will migrate out of a cell or remain immobile in the nucleus, when an electric current is applied to the cell. The degree of DNA-damage correlates the size/shape of the tail and fragmented DNA (head) in the comet (Malyapa et al., 1998). In this approach, the referred cells are lysed to expel cellular protein while the damaged DNA then migrates from the nucleus via electrophoresis. The samples are stained using DNA-specific fluorescent dye whose gel is then analyzed for the measure of



fluorescence inherent head, tail and tail-length (Singh and Stephens, 1997). The toxicity of ZnONPs of 25 mg Zn/L of *D. tertiolecta* was assessed using comet assay. The results indicated 55% damage in the cell-nuclei. A similar investigation was conducted with SiO₂NPs in *D. tertiolecta* (125 mg/L) using comet assay and it was observed that after 72 h, the results revealed an increase in genotoxic effects as observed in another investigation by Pavanello and Clonfero (2000), whereas, when TiO₂NPs were placed in *D. tertiolecta*, >72% nuclei damage was recorded after 72 h (Handy et al., 2012).

7.4 In-situ TUNEL (IT) assay

A method for detecting, apoptotic cells and DNA damage in *in-situ* TUNEL staining (Gavrieli et al., 1992). It is a method for staining cells in post-apoptosis programmed cell death/internucleosomal DNA-fragmentation (Loo, 2002). TUNEL assay uses the terminal of the deoxynucleotidyl transferase enzyme incorporated with labeled dUTP which generates free 3'-hydroxyl termini induced by DNA-fragmentation. DNA-destruction, caused by non-apoptotic events (i.e., necrotic cell death caused by the exposure to toxic compounds/biogenic nanomaterials or nanoparticles can be assessed using IT assay (Ansari et al., 1993) which have also been used to stain cells undergoing active DNA repair (Kanohe et al., 1999). TUNEL assay of pancreatic β -cells were used in the estimation of the islet function of the pancreas of *Goto Kakizakirats* upon treating them with daily insulin-loading of 25 IU/kg SeNPs for one fortnight. In another study, a decline of 17.6%–2.3% in apoptotic cells of similar rat species was observed after subjecting the cells to IT assay (Deng et al., 2017).

7.5 Necrosis assay

This assay assessment method is rapid, reliable, reproducible and inexpensive. It measures necrosis as a nanoparticle-screening criterion by examining the cell membrane integrity (i.e., the uptake of neutral red (Monteiro-Riviere et al., 2005) and trypan blue dyes (Bitensky, 1963) by BNPs which is a function of the cell's viability. Neutral red also known as 2-amino-3-methyl-7-dimethylaminophenazoniumchloride, is a weak cationic dye with a deep red colour at slightly acidic pH. It can diffuse into the plasma membrane, concentrate in the lysosomes and bind to the anionic sites within the lysosome-matrix via hydrophobic electrostatic bonds (Nemes et al., 1979; Wang et al., 2013). However, the fragility of the lysosome may ensue from alterations induced by xenobiotics and nanoparticles in the cell surface (Lüllmann-Rauch et al., 1979; Borenfreund and Puerner, 2017) which may result in low uptake/binding by neutral red, thus making it possible to differentiate dead and viable cells (Borenfreund and Shopsis, 1985). According to an investigation, the endosome-lysosome stability dropped upon exposing the lysosome to 30% AgNPS (Miranda et al., 2017). In situations involving the trypan blue dye exclusion test, the dye enters into dead cells before being removed from the living cells (Strober, 2001). In an investigation involving the evaluation of the stability of a cell membrane, trypan blue dye exclusion assay was adopted, which was later improvised with different ZnNP sizes (i.e., 12, 61, 123, 184, 369 and 737 μ M). The findings revealed that ZnNP concentrations $\geq 369 \mu$ M exhibited considerable cytotoxicity (Kononenko et al., 2017).

7.6 Oxidative stress assay

Nanoparticle exposure to cells can result in the production of reactive oxygen (ROS) and nitrogen species (RNS) (Magder, 2006). ROS/RNS detection entails reacting 2,2,6,6-tetramethylpiperidine (TEMP) with stable oxygen radical whose detection is aided by the X-band electron paramagnetic resonance (EPR) (Zang et al., 1995), however, the application of this method is limited due to high costs. Therefore, the emergence of an alternative/cost-effective approach that makes use of fluorescent probe was proposed (Gomes et al., 2005). Moreover, literature has it that some limitations of the fluorescent probe technique include inefficiency, caused by the high reactivity potential of the fluorescent probe molecules with a plethora of reactive species which may generate results that may be somewhat misleading (Halliwell and Whiteman, 2004). The aforementioned problem can be abated using a non-fluorescent probe [2',7'-dichlorofluorescein diacetate (DCFDA)], which can react with HO, RO, ROO-and H₂O₂ molecules/radicals in the presence of cellular peroxidase (Wagner et al., 2007). In another study, lipid peroxidation C11-BIODIPY and Thiobarbituric acid (TBA) assays for malondialdehyde were combined for the assessment of oxidative stress (Fantel, 1996). Combining several assays during toxicity assessment of BNPs stimulates convenience, some of which include the Amplex Red assay, 5,5'-dithiobis-(2-nitrobenzoic acid) (DTNB) and the Nitro blue tetrazolium assays for the measurement of lipid hydro peroxide, antioxidant depletion (Kora and Rastogi, 2018) and superoxide dismutase (SOD) respectively (Hussain et al., 2006).

7.7 *In vivo* toxicity assessment methods for NPs

In vivo toxicity assessment procedures (biodistribution, haematology, serum chemistry, hispathology and clearance) are usually conducted using animals (mices and rats) (Kim and Baek, 2019).

7.7.1 Biodistribution

In biodistribution studies, the localization route of BNPs in the tissues/organs of dead rats/mices are examined via radiolabels (Kim et al., 2001).

7.7.2 Clearance technique

The clearance technique entails continuous monitoring of NP-excretion and metabolism by the organisms at different times of exposure (Li et al., 2001).

7.7.3 Serum chemistry

For the serum chemistry *in vivo* toxicity assessment, chemistry and cell type of the dead rat/mice were examined upon their exposure to BNPs (Baker et al., 2008). Histopathology of the cell/tissue/organ of the rat/mice is examined so as to ascertain the level of toxicity infused by the NPs (Lei et al., 2008).

7.7.4 Hispathology

The histopathology of exposed tissues (lung, eyes, brain (Delcroix et al. (2009), heart, kidneys, spleen and liver) of mice

have been reported by Zhu et al. (2008). Some advanced toxicity assessments include the use of micro-electrochemistry/microfluidics (Ewing et al., 1983).

7.7.5 Cell viability and lethality

Cell viability and lethal tendency are two basic parameters used to examine BNP-toxicity. Of the available NPs, CNTs (single or multi-walled) are often adopted for viability and lethal assessment of cells as a result of their unique properties which in turn influence their wide patronage in the chemical, industrial and biomedical sectors (Guo et al., 2012; Sathyanayarana and Hübner, 2013; Madani et al., 2013). Some studies have documented the anti-microbial properties of CNTs in bacteria in which they observed that the CNTs infused mechanical damage to the sampled cells (Amarnath et al., 2012; Krause, 2014; Pasquini et al., 2012). Functionalized CNTs have also been found to affect soil-bacteria diversity (Kerfahi et al., 2015).

The toxicity assessment of the effect of SW-CNT in a micro crustacean (*Daphnia magna*), a fish (*Oryzias latipes*) and two freshwater microalgae, (*R. subcapitata* and *Chlorella vulgaris*) revealed hindered growth in *C. vulgaris* and *R. subcapitata* having SW-CNT concentrations of 30.96 and 29.99 m/L, respectively (Sohn et al., 2015).

FeONPs toxicity in human macrophages, murine macrophage (Hainfeld et al., 2010), hepatocellular carcinoma, and human/rat mesenchymal stem cells have been studied. The NPs had toxic effects on the murine macrophage cells bearing 25–200 µgNPs/mL concentration within 2 h of exposure with an attendant decrease in the cell's viability (Naqvi et al., 2009).

Cell viability reduction was also documented for murine macrophage cells exposed to 7-day treatment using 0.1 mg/mL FeONPs (Jeng and Swanson, 2006), while in another investigation, rat mesenchymal stem cells treated with 0.1 mg/mL FeONPs over a period of 2 days revealed a reduction in the stem cell's viability (Delcroix et al., 2009). SiO₂NPs-toxicity to human keratinocytes at concentrations ranging from 30 to 300 µg/mL were evaluated using human keratinocytes (CHK), the results also suggested a reduction in the viability of the cell (Park et al., 2010).

Toxicity effects of SW-CNTs on the cell lines of human HEL 293, HEK, A549, human macrophage and human epithelial-like Hela cell lines have been investigated (Yehia et al., 2007; Fiorito et al., 2006; Davoren et al., 2007). The toxicity of CNTs in CNT treated lung fibroblast has also been evaluated. A549 cells exposed to 250–500 µg/mL SWCNTs over a 72 h period, resulted in oxidative activity/membrane damage induced by inflammatory response (Choi et al., 2009) and *in vitro* suppression of inflammatory mediators (IL-6, IL-8 and MCP-1) (Herzog et al., 2009). The toxicity effect of MWCNTs on human epidermal keratinocytes have also been investigated (Monteiro-Riviere et al., 2005), where they observed that the toxicity induced by the MWCNTs was mediated by pro-inflammatory symptoms facilitated by the transcription nuclear factor (NF-κB and ROS) (Ye et al., 2009). *In vitro* toxicological effects (oxidative stress, DNA damage and apoptosis) of MW-CNTs in the mammalian cell lines alongside VE-cadherin distribution and actin filament integrity in the human aortic endothelial cells have been documented (Cveticanin et al., 2009; Patlolla et al., 2010; Ravichandran et al., 2013; Reddy et al., 2010; Walker et al., 2009). AuNPs in contact with MRC-5 human lung fibroblasts were found to have induced

autophagy and oxidative stress in the referred fibroblasts (Li et al., 2010). The cytotoxicity of Au nanorods and quantum dots/semiconductor NPs on animal cells was assessed based on cellular motility using the electrical cell-substrate impedance analysis. The results were validated using the dark field microscopy and fluorescence techniques (Tarantola et al., 2008). The toxicity of AgNPs coated with starch were observed on human lung fibroblast and (IMR-90) human glioblastoma (U251) cells. The findings revealed dose-dependent decrease in adenosine triphosphate (ATP) content and deoxyribonucleic acid (DNA) destruction which were induced by the deposition of AgNPs that altered the DNA of the cells followed by cell cycle arrest in the G2/M-phase (Asharani et al., 2008).

Cytotoxic examination of AgNPs on the fibroblast NIH3T3 cells revealed the inducement of mitochondria-dependent apoptosis with JNK activation and ROS (Hsin et al., 2008). AgNP toxicity effects on human hematoma cell line HepG2 was conducted using micro-nucleus test, DNA micro-array analysis and viability assay (Kawata et al., 2009). AgNPs in HeLa cells led to the upregulation of ho-1, mt-2A and oxidative stress genes (Miura and Shinohara, 2009). AgNP-treatment of *E. coli* revealed that the risk gene's replication fidelity was compromised (Yang et al., 2009). CdTe quantum dots exposure on live cells over a long period of time revealed intracellular concentration of Cd²⁺ in human breast cancer cells (MCF-7), cysteamine-capped cadmium selenide-zinc sulphide (CdSe-ZnS) NPs, as well as N-acetyl cysteine and mercaptopropionic acid conjugated to cysteamine coupled with lysosomal destruction and ROS production (Lüllmann-Rauch et al., 1979; Cho et al., 2007). Surface coats of carboxylic acid on quantum dots in contact with human epidermal keratinocytes (HEKs) revealed the release of IL-1 β , IL-6 and IL-8. The surface coating was confirmed to be the primary determinant of the immuno- and cyto-toxicity in the HEKs (Ryman-Rasmussen et al., 2007). CdTe, CdTe/CdS/ZnS core-shell-shell quantum dots and CdTe/CdS core shells were stabilized with thiols on the cell lines (HEK293T and K562) and the results showed that the quantum dots were severely toxic (Su et al., 2009). A neurotoxicity study on the effect of CdSe quantum dots using hippocampal neuronal culture model was carried out with the intent of observing the cytoplasmic-calcium and voltage-gated sodium channel-levels; the results revealed an increase in the cytoplasmic-calcium/voltage-gated sodium channel as well as the death of neurons (Tang et al., 2008).

CdSe quantum dot exposure to enterocyte-like Caco-2 cells as model intestine epithelium were investigated. Based on the results, acid treated polyethylene glycol (PEG)-coated quantum dots were seen to accelerate the cells' toxicity (Wang et al., 2008). In vitro-in vivo toxicity assessment of CdTeNPs on human hepatoma HepG2 cells were conducted using AlNPs (Zhang et al., 2007). 1–10 μ M AlNPs in contact with human brain microvascular endothelial cells (HBMVECs), showed that there was a decrease in cell viability and mitochondrial function with an increase in oxidative stress (OS) (Chen et al., 2008).

Mammalian cells treated with 10–400 μ g/mL AlNPs were examined in relation to cell viability as a way of determining their toxic effects on the cells (Radziun et al., 2011). The cell's viability was determined in relation to human bone marrow derived mesenchymal stem cell (HMSC) interaction with 25–40 μ g/mL AlNP, which showed a reduction in the cell's viability (Alshatwi

et al., 2012). Increased concentrations of 500–2000 mg AlNPs/kg rat blood cells for 72 h revealed that the AlNP-toxicity increased with an increase in the NP-concentration (Balasubramanyam et al., 2009; Radziun et al., 2011). Mammalian cell lines were treated with 0–5,000 μ g/mL AlNPs which were found to be responsible for the destruction in the cell's DNA after 2 h (Kim et al., 2009). In addition to the aforementioned toxicity measurement methods, are other viable approaches that include those of well established standards for NP-testing by the Kupffer cell isolation protocol.

8 Global regulatory policies and established frameworks for the use of nanomaterials and nanotechnology-based products

Safety assessment being an integral part of product development also serves as a prerequisite for their release for use by mankind within systems and the environment. Hence, it is imperative to consider these elements early enough within the value chain. Nanotechnology entails product innovation which brings about enhanced material properties, reduction in material consumption, waste alleviation as well as emission reduction in the environment. Sharing research facilities and the results from nano-science/technology-based research, strengthens the science-base for the regulation and use of nanomaterials/nanotechnology-based products (Devasahayam, 2017; 2019; Hodge et al., 2009). Although, major inventions of nanotechnology for food packaging, medicine, agriculture, water-treatment etc., are deemed huge successes in terms of their abilities to meet modern society needs, however, their associated adverse impacts are somewhat ignored, thus resulting in consequential threats to health (Jiang, 2019), the environment and society at large.

Some information on the Global Coalition for Regulatory Science Research (GCRSR) members [which include Argentina-National Administration of Drugs, Food and Medical Devices (ANMAT); Australia- Food Standards Australia Newzealand (FSANZ); Brazil—National Health Surveillance Agency (ANVISA); Canada- Canadian Food Inspection Agency (CFIA); China- National Institute of Food and Drug Control (NIFDC); European Union- European Commission, Joint Research Center (JRC) and European Food Safety Authority (EFSA); Japan- Food Safety and Commission of Japan (FSCJ), Ministry of Health, Labour and Welfare (MHLW) and National Institute of Health Sciences (NIHS); Korea- Ministry of Food and Drug Safety (MFDS); Singapore-Singapore Food Agency (SFA) and United States- US Food and Drug Administration (FDA)] (US Food and Drug Administration, 2020a; US Food and Drug Administration, 2020b) have provided an overview on the regulatory landscape/framework and future challenges associated with the use of green nanotechnology.

EU's nanosafety concept entails safe design and creation of NMs for future use (Lima Da Cuha, 2019). This implies that products of nanomaterials/nanotechnology ought to be safe for use throughout their entire life-cycle, from production through to waste, recycling and reuse (Krageloh, et al., 2018). The safe design concept was established for industrial innovations and formulated for nanomaterials within the confines of the EU flagship project NANoREG (Gottardo et al., 2017). The approach drives

innovation using support mechanisms such as digitalized innovation hubs alongside open innovation test-beds. With research being core, the European Commission in 2017, via the establishment of digital innovation hubs, aims at becoming a one-stop-shop for companies/SMEs start-up/mid-cap companies with a market value in the range of 2–10 billion USD to invest in nanotechnology (i.e., testing instruments, receiving financial advice, adoption of market intelligence and networking opportunities) (European Commission, 2019). The established Open innovation test-bed of the EU provides access to physical facilities/services required for the development/testing and up-scaling of advanced NMs within industries (Lima Da Cuha, 2019). In addition, an independent agency funded by the European Union—the European Chemicals Agency (ECHA), addresses issues related to the safety assessment of chemicals such as manufactured NMs (European Chemicals Agency, 2019; European Chemicals Agency, 2020), under the European Chemical legislation REACH (registration, evaluation, authorisation and restriction of chemicals) EC 1907/2006 (European Union, 2009). The registration of chemicals/nanoproducts is based on information provided by companies, and the evaluation of the referred chemicals by the EU Member States (European Union, 2019). REACH is a part of EU legislation that addresses NMs/BNPs, as these products fall under pieces of legislation pacts on occupational safety, food packaging, feeds, biocides, cosmetics, water and health. In 2018, REACH was amended to include nano-specific information and modern provisions on chemical safety assessment and downstream user obligations (European Chemicals Agency, 2019). Till date, there are about 37 substance registration dossier information on nano-products with no transition phase for the implementation of the new requirements, nonetheless, fully harmonized/standard testing measures may still be lacking in terms of their availability. The ECHA hosts the European Union Observatory for NMs which provides the objectives and desired information on innovation as well as the safety aspects of NMs in the EU market (Sumrein, 2019; European Chemicals Agency, 2020). EFSA assesses the risks associated with food and feed safety (EFSA, 2016; EFSA, 2020a; b), nutrition/health claims, animal health and welfare, biological hazards, contaminants, feed/food additives as well as plant protection/plant health even though some are exploited for use in the synthesis of bionanomaterials/bionanophotocatalysts/biogenic nanoparticles. The EFSA also provides scientific advice to the European policymakers and supports the regulation/implementation of nanomaterial application in relation to human, animal and plant-health. In addition, it adopts an environmental risk assessment measure to explore the possible impact of nanotechnology on the food chain, which in turn affects the biodiversity of plant/animal habitats. To redress issues related to the exploitation of nanotechnologies/NMs, the EFSA's scientific network for risk assessment on nanotechnology application in food was established (EFSA, 2020b) which facilitates information exchange between EU Member States while prioritizing risk assessment activities. With its special team/group on NMs use in food and feed, there are published guidelines on the risk assessment in relation to the application of nanoscience/nanotechnologies within the food/feed chain. Regulatory aspects of nanotechnology in relation to agriculture, feed and the food sectors within the EU and non-EU countries were reviewed by Amenta et al.

(2015). The European Medicines Agency (EMA)- defines nanomedicine as a field that bothers on medicinal products, purposely designed for clinical applications with an integration of at least one component at the nano-scale, that possesses specific definite proprieties/characteristics targeted at providing clinical advantages and other benefits ranging from dosage to drug targeting and reduced toxicity (Perez de la Ossa and Bremer-Hoffmann, 2019). Furthermore, the EU Commission's Green Deal (European Commission, 2019) which drives the new industrial strategy for Europe, is a road-map designed for a climate-neutral/zero-pollution, circular, sustainable and an all inclusive economy (European Commission, 2020a).

Others include those of the US-FDA which define regulatory science as one that devolves new tools/standards and procedures for assessing safety, quality, efficacy and performance of all FDA-regulated products (US Food and Drug Administration, 2020a; US Food and Drug Administration, 2020b; US National Institute for Standards and Technology, 2020), including NMs and green NPs (Goering, 2019). The FDA-regulation on nanotechnology is to ensure that product developers/users accept and promise that risk and uncertainty abatement accompany all emerging forms of nanotechnology. There is a resolve not to introduce new/specific regulations for NMs only, while being hopeful that the existing framework is somewhat sufficient to regulate NMs/products sourced from them. Thus, horizon scanning/internal reviews of nanotech submissions are key components of the FDA approach.

The FDA provides core nanotechnology facilities with capacity for lab-testing which enables the administration of test methods/standards relating to safety assessment of NMs or newly developed biomaterials. The FDA CORES (Collaborative Opportunities for Research Excellence in Science) is a programme that fosters collaborative and interdisciplinary research on product characterization/safety assessment and the evaluation of scientific data and gap analyses for regulatory applications involving nanotechnologies in non-collaborative and collaborative researches. The outcomes of the programme provides for the preparation of documents that guide or support the industrial exploitation of nanotechnology (US Food and Drug Administration, 2020b) with intent on the development and recognition of apt frameworks, all aimed at establishing standard protocols within the nanotech industry/sector. Therefore, with this intent, the FDA in collaboration with other US government departments/agencies via the National Nanotechnology Initiative (NNI) seeks to dialogue with industry at the early product development phase of any nano-driven technology.

NNI comprises of 20 US departments and agencies, under the National Science and Technology Council and the White House Office of Science and Technology Policy Department. Its focus is on six core areas: NM measurement infrastructure, environment, human exposure assessment, human health, risk assessment and management, informatics and modelling. The policy document of the aforementioned department contains guiding information on workers' safety and organized webinars related to the characterization and quantification of NMs (Friedersdorf, 2019). The National Nanotechnology Coordination Office (NNCO) alongside the EU commission, facilitate a science led initiative, which is open to all researchers globally, via the EU-US Nanotechnology Communities of Research (CoRs). This brought about the collaborative project of the EU

Nanomedicine Characterization Laboratory (EU-NCL) – comprising of multiple European key professional laboratories and the US National Cancer Institute of Nanotechnology characterization laboratory (NCI-NCL), which in turn has accelerated the development of innovative therapeutic and diagnostic nanotechnology-based products for patients' benefit across the globe (Borgos, 2019).

The US-FDA also holds bilateral agreements with organizations from Canada, India and other nations across the globe, on the characterization of NMs, amongst others via active participation in technical sessions hosted by the international standards organization. Despite the considerable progress made so far, the number of approved nanotechnology-based products is relatively low. In spite of the much scientific reporting on the findings related to nanotechnology-based products' application in cancer research, there is need to intensify efforts in bringing such products to the market. Evidence has it that the FDA consistently receives new submissions of NMs containing products with many still in their clinical trial phases while some others are already approved for future drugs/medical devices (Tyner, 2019).

8.1 Landscapes/agencies with established frameworks and policies for NP-use in wastewater treatment

8.1.1 Canada

A number of Canadian departments/agencies including Health Canada, Agri-Food Canada, Environment and Climate Change Canada, as well as the Agriculture and Canadian Food Inspection Agency, have developed and established frameworks/protocols for the safe use of nanotechnology, their associated risk mitigation plans using an inventory NM-based product, and their assessment of biological effects bearing in mind a good understanding of how NMs/products containing them are consumed in relation to the products' life-cycle and exposure. Reports have it that the Chemical Management Plan (CMP) of the Canadian Government has doled out regulations on new potentially harmful/existing NMs. Also, The Canadian nanomaterial regulatory protocol follows the mandate of the Organization for Economic Co-operation and Development (OECD) Council on safety testing and assessment of manufactured NMs (OECD, 2020a; OECD, 2020b) under the Canadian Environmental Act. In addition, the: Canadian Food and Drugs Act, Consumer Product Safety and Hazardous Products Act, Fertilizers Act, Pest Control Products Act, Feeds Act, as well as the Health of Animals Act also entail considerations for NMs (Health Canada, 2020). There are a couple of similarities regarding the US and Canadian concepts/classification of NMs, hence the need for the close regulatory council-tie between both countries dubbed, the US-Canada Regulatory Cooperation Council. The council has developed an approach that prioritizes actions on the conduct of a harmonized NM-risk assessment in variance with what obtains with respect to products beyond the nanoscale. Nanomedicine-evaluation, which is aimed at targeting drug delivery/gene therapy and diagnostics, rests within the purview of the Canadian National Centre of Excellence. Canada, a major contributor to the development of nanomedics for chemo and gene therapy, has revealed that

non-viral NP-systems are helpful in the delivery of genetic information which facilitate the drug manufacturing process at lower costs. In lieu of the aforementioned, a couple of regulatory challenges still subsist, especially in cases where these drugs are designed for single or small groups of patients (Cullis, 2019).

8.1.2 Asia

The stipulations of regulatory science in relation to health in Japan is the responsibility of the: Japanese Ministry of Health, Labour and Welfare (MHLW), Agency for Medical Research and Development (AMED), National Institute of Health Sciences (NIHS) and the Pharmaceutical and Medical Devices Agency (PMDA). The PMDA, houses a centre that was established in 2018, which promotes innovative methods/advanced therapies integrated with nanotechnologies which assists regulators in keeping pace with novel developments. Research findings on cutting-edge pharmaceutical nanoproducts are regulated by the Promotion of Healthcare Industries and Advancement of Healthcare Technologies Act. In the year 2019, the Indian government released some guidelines for the evaluation of nanopharmaceuticals with the scientific rationale for developing new/existing drugs, profiled *in vitro* and *in vivo* methods, safety, drug efficacy, toxicity profile, drug dosage/frequency of administration, patient-recovery, cost implications and other benefits (Dinda, 2019). The National University of Singapore, supports drug developers and regulatory bodies in conducting clinical and laboratory tests towards identifying qualitative attributes of nano-medicines/nanovesicles/drugs drawn from clinical trial data which in turn provide information on which *in vitro* and *in vivo* protocols will provide relevant biomarkers for optimal clinical performance. However, some underlying challenges such as the accurate prediction and elimination of long-circulating liposomes, increased the rate of complex *in vitro* models which do not improve clinical performance predictions, and low data availability on the characterization of nano-carriers (Wacker, 2019).

8.1.3 Chile

Similar to a couple of existing citizen-science-project protocols in the EU, including the European Plastics Pirate Project (European Commission, 2020b; European Commission, 2020c), many institutions located on Chile main and Eastern Islands are involved in the 'National Sampling of Small Plastic Debris' in response to a dire need to establish a baseline for nano-based products such as micro/nanoplastics in the marine environment at a fish farming site in southern Chile.

The International Pharmaceutical Regulators Programme (IPRP), organized by the International Council for Harmonisation of Technical Requirements of Pharmaceuticals for Human use (ICH) identified/addressed issues of shared interest that both on pharmaceutical regulation ranging from nanomedicine to NM use in drugs, borderline/combo products alongside procedures for their development and performance-evaluation (International Pharmaceutical Regulators Programme, 2020). The membership/organizers of the IPRP include government/agency representatives from America, Oceania, Asia, and Europe; its objectives include non-confidential information sharing/regulation-harmonization, international regulators' training collaborations and community-outreaches to innovators/other stakeholders in nanomedicine

(Johnston, 2019). It is pertinent to note that what needs to be reported on NMs by regulators include the necessary metrics based on particle size/number/weight, which depends on the applicable regulation in relation to the specific sector's jurisdiction. For instance, particle size distribution/particle spread is a major requirement for identifying NMs/their products based on the EU-REACH legislation, whereas, the weight fractions/concentrations of nanoscale particles determine whether reporting a material with USEPA falls under the US Toxic Substances Control Act (US Environmental Protection Agency, 2017). However, both metrics may be required for the documentation of a nanomaterial within the European Commission Cosmetics Product Notification Portal (CPNP).

9 Proposed policy directions

Considering the fact that there are a few existing frameworks without a globally unified policy on the use of NMs in relation to human subjects and water treatment. The following directives are herein proposed for enforcement:

- ethical approval need be sought prior to conducting studies involving green NP use on human subjects.
- there must be a statement to ascertain the level of toxicity or risks associated with every biogenic NM/green nanoparticle (McNamara and Tofail, 2017; Mech et al., 2020a; Mech et al., 2020b). In lieu of the fact that, most of the toxicity studies reported in literature, did not reveal the sources of the NPs, most of the referred NPs were synthesized from chemical precursors and not from plant or organic sources, hence, studies are still ongoing in a bid to ascertain the toxicity/non-toxicity of biogenic nanomaterials/green/bio-sourced nanoparticles (Lynch, 2019).
- bionanoparticles are perceived to be somewhat biodegradable (Iram et al., 2010), hence exhibit a low level of bioaccumulation potential. Although studies are yet to be conducted to ascertain this fact, efforts can be directed to examine the biodegradability of biosourced NPs/BMPs which will give a clue as to whether they constitute any form of environmental nuisance when discarded or may bioaccumulate in human cells and cause adverse effects when used as treatment aids (Patra et al., 2018).
- every NP-synthetic methodology must comply with global best safety standards/protocols, methodology and procedure.
- Zero-hazard/risk and pollution tolerance: every synthesized biogenic nanoparticle should not be hazardous or pose any health risk but must turn out being a non-contaminant/non-pollutant in soils or environmental waters when they come in contact with these systems (Jeliazkova et al., 2015).
- The government of every nation/management of research institutions must set out guidelines and legal frameworks (Nelson, 2019) that will address the challenges associated with classifying nanoparticles, as well as ensure the safe production and consumption of biogenic nanoparticles/nano, materials (Jantunen et al., 2017). These systems will impose fines, bans, litigation, seizure of production facilities and closure of firms, organization of professional training and jail-sentence for any lack of compliance.

10 Sustainability criteria for Apt implementation of biogenic nanotechnology for wastewater treatment

Considering the variability of the treatment outcomes of nanoparticles and the need for sustainable treatment approaches, Kamali et al. (2019) proposed a Fuzzy-Delphi approach for selecting the best wastewater treatment technique amongst a list of criteria; the criteria can be adopted for selecting the best biogenic nanomaterials/nanoparticles/bionanocatalyst for the treatment of any wastewater sample. Considering the work of Kamali et al. (2019) with a few modifications by the authors of the current study, the criteria for selecting apt/sustainable techniques for treating wastewater can be ranked in the following order of importance: Health and safety risks > Treatment efficiency > Possibility of combining techniques > Ease of implementation > Material/green NP stability > Solid waste generation tendency > Potential for chemical substance release > Potential for CO₂ emissions > Water reuse potential > Potential to recover by-products > Initial investments > Equipment maintenance costs > Operating cost > Odour impact > Noise Impact > Visual impact > public acceptance.

11 Industrial application of Bio-NMs: case studies on large scale industrial use of green NPs for wastewater treatment

11.1 Fe₃O₄ NPs

Fe₃O₄ NPs are being used in various industries including wastewater purification/treatment. They offer advantages ranging from tiny sizes for high molecular absorption to large surface areas for heavy metal-elimination from water (Guitierrez et al., 2022). The small sizes of NPs enable their effective removal of metals from water effluents of industries (mining and manufacturing industries). Reports have shown that coating Fe₃O₄NP with chitosan, derived from chitin, enhances the NPs removal of organic pollutants from water.

11.2 TiO₂NPs

TiO₂NPs have been used extensively as photocatalysts for environmental remediation (Chong et al., 2010), antimicrobial and energy generation applications. They can degrade and eliminate organic pollutants and bacteria found in air/water by the aid of ultraviolet (UV) light (Rathore et al., 2023).

11.3 Co/Co₃O₄NPs

Co/Co₃O₄NPs have been proven to exhibit antimicrobial properties against *staphylococcus* found in water. They have been used in the medical, food, and water industries. Youseffu et al. (2021) investigated the catalytic and peroxidase-semblance of Co₃O₄NPs in the industrial processing of water involving hydrogenation, reduction and oxidation reactions.

11.4 ZnONPs

ZnONPs being essential for both plants and humans have found applications in the cosmetic, electronic, food, medicinal, and process industries. It was discovered that ZnONPs were able to rid off contaminants from wastewater that may likely impede wheat growth (Haidri et al., 2023). Furthermore, ZnONPs have been adopted as antibacterial agents to fight against infectious disease-carrying vectors in water.

11.5 AgNPs

AgNPs are highly active against bacteria by preventing DNA duplication/cell division or multiplication of harmful microbes (*staphylococcus aureus*- ATCC25923, gram negative bacteria (*Ecoli*—25,922) in wastewater (Dhanker, et al., 2023). AgNPs have high catalytic activity due to their large surface area and unique electronic properties (Das et al., 2013). They can act as catalysts for the reduction of harmful pollutants and based on their high surface area to volume ratio, they have been used in the removal of harmful viruses and bacteria during water purification. They have also been incorporated in filters and added to industrial water tanks to prevent bacterial growth.

11.6 Nanaochitosan

Chitosan NPs possess physico-chemical characteristics and specially differentiated structures for the effective catalytic reduction of organic pollutants found in industrial wastewater (Balik and Serdar, 2016; Karthiga Devi et al., 2016; Nakum and Bharracharya, 2022). Other applications of biogenic NPs are as illustrated in Figure 5.

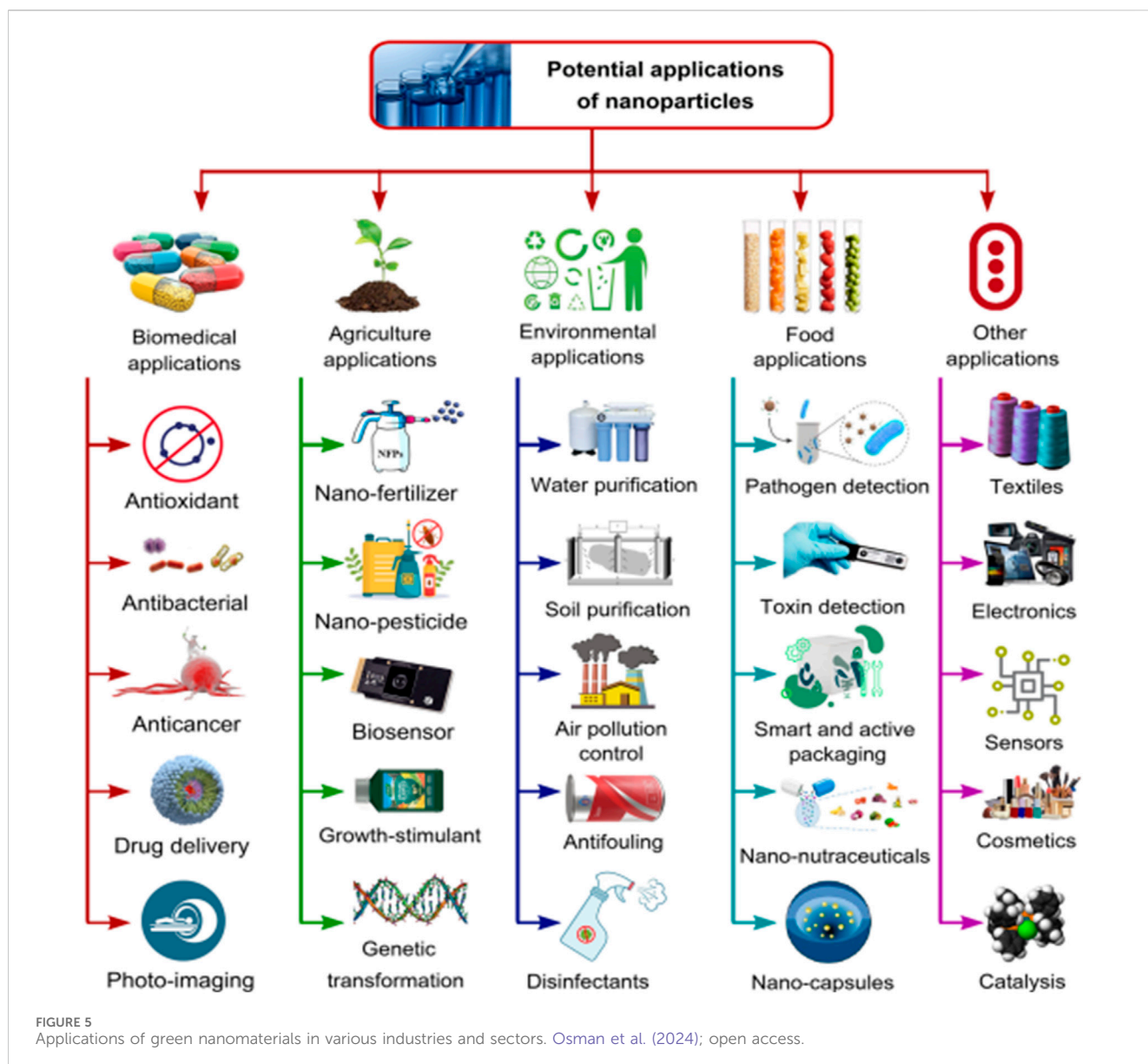
12 Issues related with economics and commercialization of green NPs/NMs for large scale water treatment applications

12.1 Initial investments

Initial investments, such as cost of land, civil works, equipment, etc. Are important in deciding the fate of the industrial relevance of a technology/application, especially as it relates to the treatment of wastewater (Ren et al., 2017; Molinos-Senante et al., 2010; Molinos-Senante et al., 2012; Kalbar et al., 2012; Jozsef and Blaga, 2014). There are relatively few studies on the economic feasibility/viability of various nano-treatment technologies. Buyukkamaci and Koken (2010) treated several types of pulp and paper mill effluents and conducted a detailed analysis on the required initial investment costs. They asserted that, in terms of economic/technical feasibility, the best method for treating medium strength effluents is the up-flow anaerobic sludge blanket (UASB) technique followed by an aeration basin, while for the high strength effluents they proposed the combination of a UASB method with an aeration basin/in

connection to a conventional activated sludge process. With respect to large scale nano-based wastewater treatment technologies, there is the need for more research works on ascertaining the required initial investment costs and this is somewhat lacking in the existing body of literature for nano-based water treatment plants. Therefore, technical specifications may become helpful to determine the amount of initial investment required, where the kinetics of the treatment process can be adopted for design considerations and size of reactor needed alongside the desired nanomaterials (Sathian et al., 2013). Looking at it from a technical point of view, the assumed capital costs/total direct plant cost, such as land, buildings, equipment and the associated indirect costs (i.e., cost of supervision), of the nano-enabled treatment plants can be compared to those of advanced oxidation/Fenton treatment techniques, in order to make rough estimates of the investments required. The comparative investment costs of several chemical oxidation effluent treatment plants from olive oil mills and fine-chemical manufacturing plants was conducted by Cañizares et al. (2009) and they observed that the nature of the effluents had a remarkable influence on the investment cost required, whereas, the associated capital cost of treating the effluent via electrochemical oxidation was worth $€15 \times 10^3/m^2$ in comparison to Fenton oxidation; based on their findings, the capital cost can be taken to mean the rough estimate of treating such effluent using emerging biomaterials (ENMs). However, if enhanced efficiency of the ENM-based treatment is desired, the reactor can be re-sized and made smaller which will also impose a reduction in the capital cost (Adeleye et al., 2016).

For the operating costs, nano-based treatments include costs of purchase/synthesis of ENMs, utilities (i.e., electricity for photocatalytic treatments) and labour. Other costs such as NM-cost have been found to be highly dependent on the source and properties/characteristics including purity (wt%), particle size and surface functionalization of the formed NPs. Reports have it that TiO_2 NPs used in wastewater treatment plants are priced within the range of 0.03- \$1.21/g, with the corresponding treatment costs ranging from 0.50-\$1.00/g pollutant (Adeleye et al., 2016). The low cost (\$0.05–0.10/g) purchase of nano-zero-valent iron (nZVI) NPs is premised on the improvement in the technology involved in its production process. Whereas, in terms of synthesis, micro/bulk zero-valent iron is considerably cheaper (i.e., \$0.001/g pollutant) (Hoag et al., 2009; Crane and Scott, 2012). Magnetite NPs used in a continuous flow process have been estimated to be worth € 0.0035/g by Simeonidis et al. (2015) and *in lieu* of their large scale production costs, finding cheaper feed stocks for the development and synthesis of green and cost effective ENMs at reasonable costs has become a matter of urgency. Also, the possibility of the recovery, recirculation and reuse of NMs via ceramic membranes can potentially reduce the total cost of producing them (Gehrke et al., 2015; Zinatloo-Ajabshir et al., 2018). Pires et al. (2015) compared the cost of different NPs (copper oxide catalysts) on different supports ($\gamma-Al_2O_3$, pillared clay/ TiO_2). CuO supported on $\gamma-Al_2O_3$ was found to be the most cost effective material with an estimated treatment cost of 0.07 \$ at 0.175/g of metal for 80% pollutant-removal. Therefore, comparative treatment costs with different NMs is mandatory in order to decide on the optimized cost for the purpose of commercialization. According to Pirkarami et al. (2014), the



large scale treatment of 1 m³ of dye solution using UV/*Ni-TiO₂* of NM, required an energy consumption of 4 kWh/m³ estimated at 0.042 USD/kWh with a total estimate of 0.168 USD/m³. However, in landscapes where the cost of electricity is high, the use of UV light active NMs (*N-TiO₂*) or solar energy is preferred (Yoshida et al., 2014). While labour costs in relation to NM use in water treatment plants are scarcely available in literature, Long et al. (2018) observed that, for the treatment of wastewater effluents from industrial parks in Taihu and Haihe water basins (China), the associated operating costs of the treatment plants can be ranked in the following order electricity > labor > used chemicals. Li et al. (2017b) also observed that these costs also vary regionally.

12.2 Maintenance costs

Emerging or green NMs for industrial wastewater treatment may impose significant reduction in the plant's maintenance

costs. For instance, when membranes are employed in wastewater treatment plants, membrane-fouling by inorganic suspended solids, dissolved organics/biofilms all add to the overall maintenance costs. However, the single use/incorporation of NMs in the structures of the membranes is one sure way of mitigating against such risks. Lifen et al. (2012) incorporated *TiO₂* in polyvinyl alcohol (PVA) for the treatment of industrial wastewater and found that the composite membrane had improved hydrophilicity/anti-fouling property; they also asserted that low solid waste generation has the potential to reduce maintenance costs that may be incurred from sludge thickening and dewatering systems/facilities. Since green NPs/ENMs used in the treatment of industrial effluents are still far from being evaluated in terms of their negative consequences under real-life scenarios, suggestions are in view to encourage studies in this direction so as to have a holistic/more realistic assessment of the associated maintenance costs of the systems involving their use.

12.3 Environmental considerations

12.3.1 Solid wastes generation

Several treatment technologies (primary, secondary, and tertiary) for industrial effluents have been investigated in terms of their treatment efficiencies and capacity to cut down the quantity of final wastes generated. Activated sludge treatment from industrial effluents generates a large amount of waste (Kamali and Khodaparast, 2015) and generally produces activated sludge which increases disposal costs (Balik and Serdar, 2016). Thus, it is preferable to adsorb pollutants/heavy metals using NMs where the recovery of the adsorbates (heavy metals) and adsorbents (NMs) may prompt the reusability of the latter without the generation of any waste.

CNTs and *nZVI* were used by Vilardi et al. (2018a) to recover hexavalent Cr, Se and Co from aqueous solutions and observed that the NMs or Fenton-like process may yield products such as H_2O and CO_2 with no waste generated; this is in sync with the observations from the photocatalytic degradation of industrial effluents by Yu et al. (2005), Sudha & Sivakumar (2015) and (Kumar et al., 2015). The disposal of NMs is another means of solid waste generation, hence, the need to begin to consider the use of biogenic NPs/NMs with biodegradation potentials/complementary potentials to soils when discarded.

The release of chemical substances/by-products into the treated industrial effluents is another issue that needs attention during NM use in the treatment of industrial effluents. Recently, chemical methods based on the production of hydroxyl radicals which help in eliminating recalcitrant organic pollutants are being discussed. Fenton oxidation which takes advantage of Fe^{2+}/Fe^{3+} generation alongside H_2O_2 , combined with Green NMs have been widely adopted for wastewater treatments due to their short reaction time (Kuang et al., 2013; Koba and Biro, 2015), amid the generation of secondary pollutants caused by the release of Fe^{2+}/Fe^{3+} in the treated effluent (Sze et al., 2005). To resolve this problem, additional treatment techniques may be employed (Kuan et al., 2015), such as the use of other inorganic NMs such as TiO_2 and copper-based NMs, which can induce ferric ion dissolution during the process (Adeleye et al., 2014); other techniques include pH, crystallinity, temperature and particle size moderation/control (Schmidt and Vogelsberger, 2009). Others include CO_2 emission (Chiemchaisri et al., 2007) and water reuse potential of the treated industrial/chemically complex effluents, such as those from metal-works (Jagadevan et al., 2012) including highly toxic compounds with good potential for by-products recovery.

12.4 Social considerations

These include determining the odour impact of industrial wastewater by detecting the smell of malodorous compounds [i.e., volatile fatty acids (VFA)] with adverse olfactory effects (Ronteltap et al., 2011). Some successful applications of green NM photocatalysts for the elimination of odorous compounds include the works of Bordbar, (2017); Bordbar and Mortazavimanes, (2017b); Bordbar et al., 2018, Li et al. (2018), Muthukumar et al., 2017; and Azzouz et al. (2018).

12.5 Noise and visual impacts

Studies have shown that the use of NPs in wastewater treatment plants cited near a crowded neighbourhood may impose social and environmental disadvantages (Zock et al., 2018). The toxic constituents that may ensue from the interactions may result in the release of volatile undesirable products that induce noise nuisances generated from wastewater treatment process units/plants which may affect nearby residents, however, some decibel-coded models can help detect safe and unsafe noise levels within such vicinity (De Heyder et al., 2001).

12.6 Social acceptability

Another criteria that will significantly influence the commercialization of green NM technology for the sustainable treatment of industrial wastewater is the inherent social benefits, besides its technical, environmental/economic viability (Ren et al., 2016). Gupta et al. (2012) received the opinions of respondents in North Western Europe in relation to the factors that may influence the societal acceptability of various NMs. Their conclusion implied the need for any adopted NM technology to be beneficial, useful, and able to address societal needs (clean water availability and abundance).

13 Sustainable approaches and future research directions on the use of green NPs for water purification

Investigations on the use of green-synthesized and biogenic NPs for wastewater remediation in membrane bioreactors, sewage systems, treatment plants, and other water treatment systems help to provide information on dangerous contaminants/pollutants in water resources (Zhang et al., 2019; Philipse and Maas, 2002). Since commercial application of biogenic NPs in water treatment have continued to face difficulties, which are imposed by sedimentation, stability, aggregation, and size control phenomena, such issues can be tackled using nano-films/nanocatalysts, and nano-adsorbents because they are effective in the removal and degradation of pharmaceutical pollutants (Kim et al., 2007; Rizzo et al., 2009) heavy metals, inorganic, organic, radioactive, nitro compounds (e.g., nitroarenes) (Gnanaprakasm and Selvaraju, 2014), nitrophenols (Khoshnamvand et al., 2019), nitrates (Tyagi et al., 2018), phosphates (Xu et al., 2020), and hazardous dyes like rhodamine B (RhB), Congo red (CR) (Vidya et al., 2017), methyl orange (MO) (Robati et al., 2016) and Eosin Y (EY).

The behaviour of NPs in the environment and living cells depend critically on their sizes, shapes, monodispersity, surface charges, plasmonic responses, medical diagnostics, biofunctionality, and catalytic activities as well as the controlled synthesis of the designed green products by safer processes, while maintaining NP efficacy and efficiency, is one of the most difficult and persistent problems to be solved in the development and deployment of novel green NP-synthetic protocols (Lai et al., 2016). Since the organisms used in NP synthesis can range from

simple prokaryotic bacterial cells to complex eukaryotic organisms, developing green, sustainable synthetic routes for the production of metal NPs still requires extensive research and innovative solutions. However these approaches need be refined and optimized for improved efficiencies as occasion demands. It is the diversity of these NP-systems that poses the greatest barrier to their widespread and routine application in sustainable green wastewater treatment operations. Since green extracts vary in terms of type, quality, concentration, alongside reagent ratios, reaction conditions (i.e., time, temperature, and pH), yield, and product characterization which are lacking or inadequate, concerted efforts ought to be made in relation to making accurate comparisons of NP-performances in these systems. The regulation of crystal growth, size and morphology, dispersity, and nanoparticle stability are advantageous to NPs since they induce property modifications for improved wastewater treatments (Dauthal and Mukhopadhyay, 2013). In lieu of the fact that most published studies on green NP synthesis from microbial/plant extracts have provided dependable proofs on the latter's toxicity, only a small number have reported on their comparison with conventionally produced NPs (Naraginti and Sivakumar, 2014; Husein, et al., 2019; Qu et al., 2017). So, it has become pertinent to acquaint with existing techniques and develop new ones for ascertaining the toxicities of green NPs while also exploring ways of mass-producing them safely to meet industrial demands. To this end, researchers need to focus their energy on developing precise and dependable synthetic protocols for detecting, controlling and abating the toxic effects of biogenic NPs (Vellaichamy and Periakaruppan, 2016; Dauthal and Mukhopadhyay, 2015; Renuka, et al., 2016). The properties of green NPs sourced from microorganisms/plant extracts vary greatly, hence, a proper selection of apt reducing agents is vital at the production phase of BNPs (Vennila and Prabha, 2015; Moulton et al., 2010; Bano et al., 2018; Al-Ruqeishi et al., 2016). In order to maintain high reproducibility and thus guarantee good performance of NPs, a large scale synthesis from plant species of the same type, quality and composition must be adopted in each synthetic cycle. Some studies have revealed that different tea extracts of unique compositions of caffeine/polyphenols, acted as both reducing and capping agents during green NP synthesis from the extracts, thus resulting in NPs of controlled shapes and sizes (Al-Ruqeishi et al., 2016; Bonigala et al., 2018; Reddy et al., 2018; De Corte et al., 2012). In addition, the enforcement of standard protocols and guidelines for the characterization and qualitative/quantitative quantification of plant extract-compositions used in NP-synthesis for wastewater treatment will help overcome some of the associated barriers posed by their potential toxins. It is also crucial to take into account the optimization of the influential parameters during green-NP synthesis for qualitative synthesis of NPs (Kaliraj et al., 2019; Peng et al., 2019). High yield and production rates are crucial factors in the successful industrial application of microorganisms or plants for the synthesis of metal NPs. Therefore, it is important to carefully regulate and optimize the extract-to-salt concentration/ratio, as well as the production time, pH, temperature, buffer concentration, and stirring velocity. Nanoparticle size, shape selectivity, and concentration are all controllable by adjusting the amount of green extracts precursors (Shen et al., 2017; Zare et al., 2019). The estimation of the expected NP-features may be difficult/

complex when the green solution composition is high. Most of the time, it is either impossible to completely isolate the components of the green extracts from the extracting solvents, thus leading to contamination of the biogenic NPs; however, this can be abated by employing combined techniques with synergistic or follow-up complementary separability/affinity of the solvent used without jeopardizing the quality of the green NPs. As the stirring time increases, the average particle size also grows an increase in temperature decreases the mean particle size and number of NPs (Ijaz et al., 2017; Bordbar, 2017; Bordbar and Mortazavimanes, 2017b; Bordbar et al., 2017; Bordbar et al., 2018). pH affects the binding of metal ions to biomolecules of green materials, which in turn leads to the formation of particles with a wide variety of shapes at different pH levels. In most cases, lower sized biogenic NPs can be synthesized at lower temperatures and higher pHs, since high temperatures may be undesirable. Nonetheless, since extracting and purifying the synthesized NPs from intra-cellular and extracellular living/non-living biological sources including bacteria (Zhang et al., 1996), fungi, and yeasts is herein a major concern, the development of topnotch intra- and extracellular approaches coupled with less-energy-intensive physical and/or chemical extraction techniques on preference in relation to heating, freezing, thawing, sonication, osmotic shock, as well as multiple centrifugation and washing of the NPs need be established (Andjelkovic et al., 2017; Lloyd and Macaskie, 1996; Karthika et al., 2017) because these processes involve multiple steps that require a great deal of energy and solvent, which may give rise to excessive wastes. As a result, the proposed technique will limit the level of refinement imposed by these wastes on the inherent/superficial characteristics of the NPs (Salehi et al., 2019; Martínez-Cabanas et al., 2016). NPs may form aggregates, sediment, and precipitate under certain conditions, thus resulting in undesirable and uncontrollable properties and behaviours. Enzymatic lysis is one method used in extracting NPs; however, particles formed *in vitro* bacterial cells are typically less stable compared to those formed *in vivo*, and thus, severe aggregation may accompany the extraction step. Additionally, this purification method has not been up-scaled for industrial production because of the anticipated costs. In terms of both production efficiency and ease of purification by filtration/centrifugation, the extracellular method of NP production is preferable hence, strategies for up-scaling this technique with low cost implications must be deployed to address this concern (Ali et al., 2016; Sinha and Ahmaruzzaman, 2015; Mittal et al., 2013; Karthika et al., 2017). For instance, *Pseudomonas* was used in the extracellular synthesis of AgNPs which were precipitated by centrifuging the resulting nano-suspension for 10 min at 12,000 rpm and 25°C (Pradhan et al., 2001; Varadavenkatesan et al., 2019). In this type of synthesis, particle aggregation is quite common, but it should be noted that applying these purification steps can also alter the stability of the NPs. The possession of NP-capping and stability characteristics by plants prevents the aggregation of green NPs (Naraginti and Sivakumar, 2014). When thinking about how to scale-up the process of creating green NPs, it is important to consider how the purification process impacts and alters the NPs' properties. In addition, the toxicity and life cycle assessments of green NPs need be ascertained via quantitative analyses of the cost implications and consequences of adopting these synthetic-protocols (Sreeju et al., 2017; Ali et al.,

2016; Wu et al., 2019). The main limitation of conducting these analyses is the dearth in the specificity of such information. Detailed information on green NP synthetic pathways, toxicity, sources, mechanism, characterization, industrial application, bioaccumulation, environmental and health risks are lacking, and neither is there any experimental data covering all stages of a particular biogenic NPs' life cycle. Since the reduction mechanism of metal ions to NPs has not yet been elucidated, considerations for the reducing agent as a defining factor during NP-synthesis is often excluded from most life cycle analyses-calculations, thus resulting in constrained modeling and, ultimately, an incomplete assessment of such processes (Naraginti and Sivakumar, 2014). Also, the lack of uniform regulations at the national or international levels that would help curb such issues in terms of describing the quality/origin of the materials, restricting the conditions for NP production, standardizing and controlling the quality of the NPs formed, as well as determining their use and long-term effects, further muddles the assessment of the green methods that engender NP-synthesis. Thus, it is a challenging task to design, estimate, and compare the behaviour of NPs based on the different properties exhibited by various green entities. Given these obstacles, more in-depth study is required to establish uniform, safe, and cost-effective green synthetic methods, as well as determine the effects and potential toxicity/innocuousness of the designed and obtained BNPs. In recent times, hybrid NMs have become trendy in wastewater treatment applications, which in turn suggests the need to explore the possibility of adopting the synergistic properties of hybrid nanobiogenics for the production of hybrid nanoparticles which have great prospects in water purification as this will help to curb issues related to the abundance of some species relative to others, thus ensuring longevity and sustainable application of synthetic NMs for water treatment purposes.

Despite the several efforts channeled towards harmonizing the guidelines/analytical approaches for quantifying NMs alongside their risk-assessments, the unprecedented increase in medical nano-based products and their number of agri-/food sector-applications/issues and their associated risks need be given attention by regulatory authorities/sponsors of research. From a technical, regulatory and policy perspective, biogenic NP application is not yet in the market, owing to the fact that researches conducted thus far, are either in their early stages or are technologically oriented, but lack considerations for potential risks and safety/hazards. As the development and application of biogenic nanomaterials/NPs advances, their associated risks and benefits ought to be accounted for. A holistic way of addressing concerns related to the risks and potential benefits associated with the use of complex nanomedicine is necessary if the regulatory/scientific community and research funder must work in synergy, to ensure testing the nanomaterials/nanoproducts rigorously while also ensuring that the methods used in producing the products are reproducible and compare favourably with standard methods and risk assessment plans. Furthermore, specific analytical/complementary equipment need be adopted for the assessment of specific complex products in relation to their toxicities and potency; for instance, every pharmaceutical company needing such products, must ensure that all regulatory authorities are involved at the early stages of the development of the products and not at their final synthetic stages. The need for public-private

partnership cannot be overemphasized, especially with respect to the new nanomedical solutions for patients. Currently, the available legal frameworks begin considerations on the specificity of new nanomaterials and their impacts. However, safe design is an appropriate mechanism or check for such materials, especially with respect to beginning early in the innovation process while balancing safety with functionality of the nanomaterial/nanoproduct. As a way of facilitating the implementation of safe design as a strategy, effective dialogues with stakeholders and regulators must ensue regarding all anticipated innovations in a trusted environment in order to ensure that there is apt regulatory preparedness and governance in relation to the possibility of having cheaper, fast, effective and safe products in the market. With the recent widespread increase in the use of nanomaterials, issues related to definitions, reuse, containment, toxicity and bioavailability are of major concern. However, literature has it that since green NMs and NPs are from biosources, they are generally deemed to have low toxicities or hazard potentials; nonetheless, their actual effects have to be quantified so as to have a clear perspective of their toxicities and hazard potentials. Despite the concerted efforts by researchers to address issues related to terminologies, definitions, characterization, sampling and assessment of their toxicity, hazard potential and impact, the associated regulatory challenges include lack of a globally accepted standardized nomenclature, assessment routines and characterization, which have resulted in a global divergence in regulatory approaches on these fronts. Therefore, apt alignment/harmonization of regulatory and legislative stipulations must be complied with by all stakeholders including scientists, standard organizations, regulators, patient representatives, industries and consumers in creating a globally relevant/harmonized regulatory system/framework for NM/NP production and use. In addition, the GCRSR needs to continue to hold discussions on such crucial matters in their future meetings/summits. Since the JRC is the European Commission's scientific in-house service platform, a partner member of the European and International Research Project (EIRP), as well as a member of the GCRSR, its open/free access nanobiotechnology laboratory infrastructure to academia and small medium enterprises (SMEs) makes room for the ease of investigations related to NM-characterization (European Commission and Joint Research Centre, 2020a; European Commission Joint Research Centre, 2020b).

In order to maximize these efforts (i.e., synergies related to standardization), the establishment of an international working group—placed ideally under the GCRSR to monitor the development of guidelines and global standards that identify priority areas and gaps that need urgent attention must come to bear. The GCRSR will facilitate communications among Green NM/NP-standardization bodies while providing oversight coordination of laboratory-related activities/inter-laboratory validation. Also, it is necessary to mention at this point that nanoscience is still at its developmental phase, hence, scientifically proven and well-established methods/standards of assessment, production and use are still scarce to-date. This then suggests the need for increased research efforts in this area so as to proffer solutions to the myriad of challenges surrounding the commercialization and large scale implementation of biogenic NM/NPs and nanophotocatalysts.

14 Conclusion

In the near future, it is anticipated that the use and commercialization of green/biogenic NPs/NMs/photocatalysts for water treatment will somewhat have a more significant impact on water treatment plants/industries. However, it would be more cost-effective to focus on enhancing the efficiencies of existing treatment methods by maximizing their reusability, stability and non-toxicity. While current wastewater treatment technologies involving chemically synthesized NPs are able to degrade organic and inorganic pollutants in water and wastewater, they neither completely purify them nor render the treated streams fit for reuse, thus making the process more energy intensive and economically unfeasible. However, on the other hand, the imposed capping and stabilizing abilities by green NP-precursors, makes it easier to recover green NPs for reuse compared to their inorganic counterparts that are capped with capping agents of inorganic chemicals with the perceived capabilities. Based on the available information in literature, global standards/protocols for synthesizing biogenic NPs alongside their toxicity assessments need be established in relation to specific NPs as this will provide proper guidance and information on the pros and cons of using a particular protocol or standard; in addition, the aforementioned should be accompanied by penalties for noncompliance. Hybridizing different plants with complementary properties for toxicity control of the constituents of NMs/NPs is also a viable technique that is envisaged to abate the ills associated with the availability of toxins in biogenic NPs. Moreover, large scale industrial application of NPs in treating wastewater can be brought to bear by carrying out apt comparative cost assessments of the initial investments, design costs, operating cost, energy, etc., required for the industrial use of their inorganic counterparts which are produced by conventional means. Biogenic NPs have lower levels of toxicity compared to their inorganic counterparts, which is the reason for their recent consideration for application in biomedicine as this will reduce the levels of complications that may ensue when they are used. Furthermore, using green synthesized NPs for wastewater treatment is not only a green option, but also a promising technology for fulfilling the zero effluent/waste/toxin discharge obligation via low cost and energy adoption. Therefore, it is envisaged that green NPs will play a more dominant/crucial role in water and sewage purification systems. In addition, more studies on the commercial viability of green NPs for water purification and wastewater treatment is also necessary. Nonetheless, it is pertinent to develop and grow several microbial

cultures of prospective microbial precursors which will help ensure a massive production of the desired NPs for sustainable water treatment applications. Therefore, in order to ensure that nanomaterial/particle precursors for wastewater/water treatment applications are highly sustainable, their methods of production, the stabilization process and conditions of synthesis for these systems need be optimized.

Author contributions

SS: Conceptualization, Investigation, Supervision, Writing—original draft, Writing—review and editing. BO: Investigation, Writing—original draft. EO: Investigation, Validation, Writing—original draft. SP: Data curation, Validation, Writing—original draft.

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Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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