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ORIGINAL ARTICLE

Fate and toxicity of nanoparticles in aquatic systems

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Abstract

Nanotechnology is a ground-breaking multidisciplinary field across a broad spectrum of basic and applied sciences for producing and applying nano-sized materials for innovative solutions. The use of nanomaterials in industrial applications, medical products, and consumers has increased repeatedly over the last few years, and these applications will likely continue to grow. In an aquatic ecosystem, nanoparticles take entry through a direct route that includes industrial discharge, disposal of wastewater treatment effluents, and indirect runoff from the soil. After reaching the aquatic environment, the nanomaterials are highly affected by their backdrops and subsequently go through various conversions like agglomeration, aggregation, dissolution, sulfidation, etc. The fate and the behavior of nanomaterials in the aquatic system not only depend on their physical-chemical properties but also on the pH, temperature, salinity, water hardness, and concentration of natural organic matter present in receiving water. In this review, emphasis has been given to the toxicological properties and potential risks of nanomaterials in terms of factors contributing to their toxicology, bioavailability, and accumulation in aquatic organisms as well as the environment. Furthermore, we summarize the published data on engineered nanoparticles' effect on aquatic organisms. The issues related to the accumulation and penetration of nanoparticles in the aquatic organism, their toxic effect, and biotransformation along with the food web are also discussed. Since nanomaterials are being increasingly released into aquatic bodies, it is important to pay greater attention to their toxicity and how it affects the aquatic ecosystem. The nanomaterials are bioavailable to plants, resulting in trophic transfer, and they impact other organisms through biomagnification, as discussed in this review. To close the enormous information gap, extensive research on the interactions and impacts of NPs on different species belonging to different trophic levels of the aquatic environment and the destiny of NPs along the food chain of the ecosystem is urgently needed.

Highlights

- The use of nanomaterial is in industrial applications, medical products, and consumers has increased repeatedly.
- The accidental release of NPs in the environment ultimately reaches the aquatic environment.
- A high concentration of these NPs negatively affects the organism at every trophic level.
- The NPs induced toxicity is mainly due to the generation of reactive oxygen species.

1 Introduction

Nanotechnology is a field expanding very fast and has developed many products in every human-oriented area, whether it is electronics, cosmetics, or food industry. Nanoparticles (NPs) are a wide class of materials that include particulate substances, which have one dimension less than 100 nm at least (Laurent et al. 2010). The properties of nanoparticles such as reactivity and toughness are dependent on their distinct size, shape, and structure (Khan et al. 2019). Because of their large surface area and nano-scale size, NPs also have specific physical (low melting point) and chemical (high reactivity) properties. Due to their unique size-physiochemical property, nanoparticles are widely used in a variety of products (Maurer-Jones et al. 2013). Furthermore, many other parameters, such as morphology and coating agents,

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affect the properties of NPs (Jurasin et al. 2016; Khan et al. 2019).

"The Nanotechnology Consumer Products Inventory" has described the list of most used nano-materials (NMs) among the products, which includes carbon (29 products), i.e., fullerenes and nanotubes (Maynard 2006). Silver was the second most referenced (25 products), followed by silica (14), titanium dioxide (8), zinc oxide (8), and cerium oxide (Kahru and Dubourguier 2010). Nearly 60% of nano-based products (30% medical or pharmaceuticals; 29% chemicals and advanced materials) are directly intertwined in our day-to-day life (Kurwadkar et al. 2015). The widespread use of nanomaterials has inevitably resulted in their release into the environment, either as the original (as-manufactured) nanomaterial or, more likely, as degradants of societal nano-enabled goods. Our particular interest is the aquatic environment, including sediments, which tend to be the ultimate sink for particulate contaminants like NMs (Selck et al. 2016). Nanoparticles can be added to the aquatic system directly through industrial discharges or from the clearance of wastewater treatment effluents and indirectly through surface runoff. The occurrence of NPs in the aquatic system associated with excessive usage has led researchers to investigate their different properties, sources, behaviors, and toxicological impact (Bundschuh et al. 2018). The release of nanoparticles into aquatic environments may result in various transformational processes which subsequently control their impact on the ecological system (Petosa et al. 2010). Currently, many kinds of research are ongoing on the effect of NPs on the environmental and ecotoxicological issues of nanomaterials (Handy and Shaw 2007). However, the toxicological impact of nanoparticles depends on various factors related to the nanoparticle themselves, their surrounding environment, and the tested model organism (Gatoo et al. 2014; Turan et al. 2019).

With the increasing use of NMs since early 2000, the question of whether they pose a risk to the environment has loomed large. Because the toxicity level for every organism is different, some organisms can survive at the same level while others may be negatively affected. This study is motivated by these questions of environmental risk because of the predicted rapid increases in environmental concentrations, the known bioavailability and deleterious biological effects, and the consequent complexities of risk assessment (Taylor et al. 2016; Laux et al. 2018). However, the absence of information, the lack of defined guidelines for storage, transport, and disposal, and an evolving regulatory perspective have made it difficult to comprehend, manage, and mitigate the environmental risks due to the occurrence of nanoparticles in the environment. When we talk about the whole ecosystem, the problem is more complicated and needs more concern. Understanding the sources, routes, and exposure pathways and the inherent toxicity of nanoparticles can help safeguard the environment against the release of nanoparticles in the environment. Thus, we attempted to highlight the enormous increase of NMs in the global market with accompanying risks to the aquatic environment. Furthermore, this review summarizes the major sources of NPs including their fate and transport. Moreover, we intend to present a systematic overview of NPs in aquatic systems on different species belonging to different trophic levels of the aquatic ecosystem, including phytoplankton, micro-organisms, invertebrates, and fish, and their toxicological responses. Additionally, the mechanism of nano-toxicity in aquatic organisms is also discussed.

2 Sources, fate, and uptake of nanoparticles

2.1 Sources of nanoparticles in aquatic ecosystem

The sources of nanoparticles have a history and are not new, with the understanding that the life of Earth itself. Nanoparticles can be generated from natural (biogenic, geogenic, atmospheric, pyrogenic) and anthropogenic sources as engineered or byproducts. The nanoparticles could be categorized into two categories based on their production: (i) naturally formed nanoparticles which include humic & fulvic acid, organic acids, carbon nanotubes, nanospheres, and metals like silver, gold & Fe-oxides, and (ii) manufactured nanoparticles comprises carbon black, functionalized fullerenes, polyethylene glycol, platinum, metal phosphates, zeolites, and ceramics, etc. (Luther and Rickard 2005; Nowack and Bucheli 2007; Renzi and Guerranti 2015).

The intentional release of nanoparticles is mostly related to the use of engineered nanoparticles for drug production, groundwater remediation, biomedical imaging, and other applications whereas the unintentional one is related to activities such as burning fossil fuels, vehicle exhaust, mining, and demolition (Turan et al. 2019). The accumulation of nanoparticles in the water matrices begins once they are discharged into the environment (Iavicoli et al. 2014). Furthermore, in the aquatic environment, NPs can enter either through nonpoint sources such as atmospheric release and water infiltration or the deliberate discharge of NPs (Weinberg et al. 2011). The presence of NPs in sewage or effluents from treatment plants has an environmental risk once mixed with the marine ecosystems. Furthermore, the NPs that are present on land contaminate soil, solid wastes, and wastewater effluent discharges directly or indirectly into the marine system by wind or rainwater runoff (Stephen et al. 2008). Numerous nanoparticles are present in industrial waste and products dumped into landfills, are regularly washed off into water bodies, and thus are another entry point into

Table 1 Types, sources, and concentration of nanoparticles (NPs) in the aquatic system

Types of NPs	Sources	Concentration	Reference
Silver NPs	Clothing, cosmetics, medical devices, paints, humidifiers and refrigerators	< 1 ng L^{-1}	Azimzada et al. (2021)
		0.088 to 2.16 ng L^{-1} (PEC)*	Gottschalk et al. (2009)
Titanium dioxide NPs	Skincare products	< 10 μg L^{-1}	Azimzada et al. (2021)
		0.03 L^{-1} to 1.6 μg L^{-1} (PEC)	Gottschalk et al. (2013)
		8.8 μg L^{-1} (Thames region seaside, U.K.)	Johnson et al. (2011)
Zinc oxide NPs	Skincare products	0.008 to 0.055 μg L^{-1} in Europe and 0.001 to 0.003 μg L^{-1} in US (PEC)	Gottschalk et al. (2009, 2013)
CeO_2 NPs	Skincare products	< 100 ng L^{-1}	Azimzada et al. 2021
		5.1 to 54.2 μg m^{-3} (PEC)	O'Brien and Cummins (2010)
n-C60	Pharmaceutical industry	5 to 20 ng L^{-1} (Waste water of Spain)	Farre et al. (2010)
		4 to 20 ng L^{-1} (PEC)	Gottschalk et al. (2009, 2013)
CNT	Electronics products	0.0005 to 0.0008 μg L^{-1} (PEC)	Mueller and Nowack 2008

*Predicted environmental concentrations (PEC)

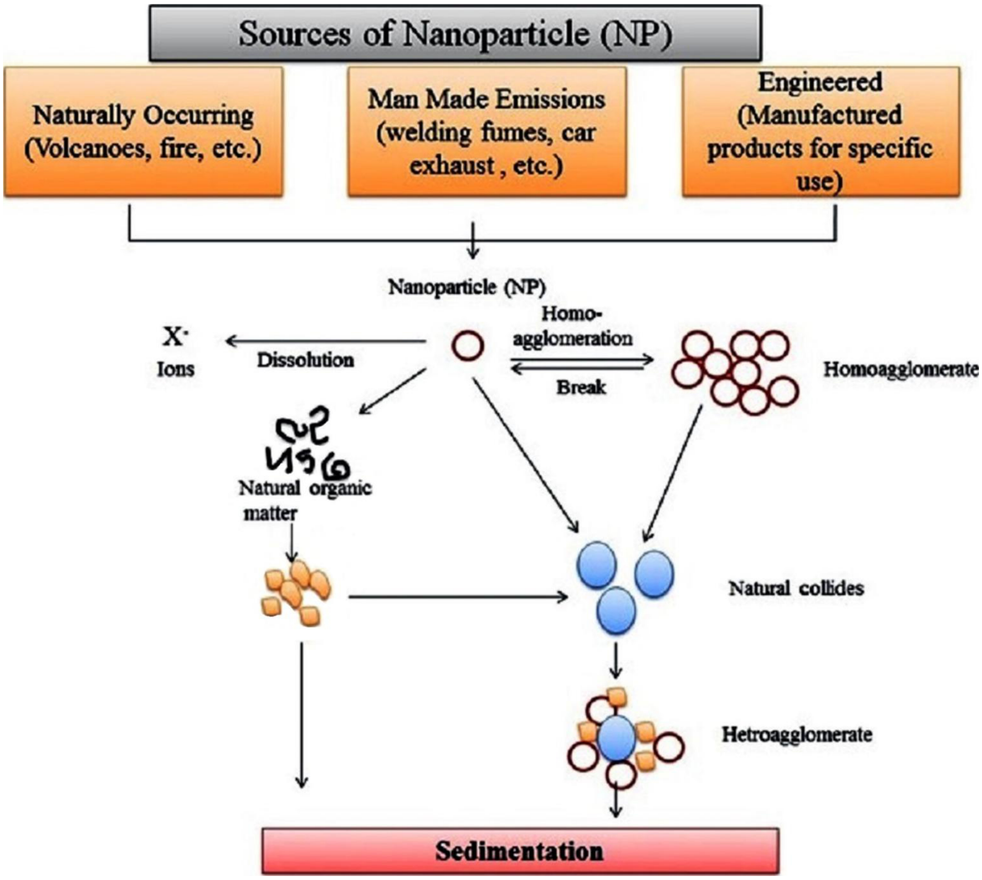
the aquatic environment (Moore et al. 2006). Subsequently, nano-based industries begin to come online with mass production, making the entry of nano-products and byproducts into the aquatic environment unavoidable (Howard 2004; Moore et al. 2006; Royal Society and Royal Academy of Engineering 2004). Approximately 60% of nanomaterials are used in medical/pharmaceutical and industrial applications; thus, they are likely released into wastewater (Kurwadkar et al. 2015). The variety of sources through which nanoparticles can enter wastewater include commercially available consumer products containing metallic silver and titanium dioxide, industrial processes, and waste streams resulting from the cleaning of production chambers viz. textile, photography, and electronics industries (Turan et al. 2019; Azimzada et al. 2021). In addition to this, a large fraction of sewage sludge is being used as fertilizers in the agricultural field in countries like the United Kingdom and the United States of America (Nicholson et al. 2003), while in other nations, such sewage wastes are burned (Gottschalk et al. 2009). A detailed description of the main sources of nanoparticles in the environment is summarized in Table 1. The worldwide production of silver nanoparticles (Ag NP) is estimated at 500 tons per annum (Mueller and Nowack 2008). However, the environmental conventions will ultimately limit the entered amount of NPs waste in the aquatic system via accidental release. The release of such NPs into the main water stream creates a new ecological problem that needs to be studied on a large scale shortly.

2.2 Fate of nanoparticles in aquatic ecosystem

The NPs present in the aquatic system are aquatic colloids; hence they are never in thermodynamics equilibrium like chemicals (Elimelech et al. 1995) and are subject to several transformational processes (Lowry et al. 2012; Nowack et al. 2012; Stone et al. 2010). In an aquatic ecosystem, the crucial processes which influence the fate and behavior of nanomaterials are categorised into three categories (i) Physical processes which cover homo/hetero aggregation, agglomeration, sedimentation, and deposition, (ii) the chemical processes encompass photochemical reaction, dissolution and oxidation and sulfidation (Lowry et al. 2012; Nowack et al. 2012; Stone et al. 2010), and (iii) Microbial mediated biodegradation and bio-modification processes are the main examples of the biological processes (Lead et al. 2018). These properties are important for the understanding of the transformation behaviors as well as the risk assessment and management plans (Lead et al. 2018). Details related to these critical and universally agreed properties that characterized NPs are discussed in the section below and presented in Fig. 1 (Klaine et al. 2008; Bhatt and Tripathi 2011; Lowry et al. 2012).

Agglomeration: It is how nanoparticles get aggregated into large particles that could be removed from the water bodies and then transported to the sediments. The term "aggregate" is used for particles containing multiple strong bonding with smaller surface areas than individual ones, while "agglomerate" is defined as the collection of loosely bound aggregate. Surface charge controls the stability of nanoparticles, which in turn controls the agglomeration and toxicity of nanoparticles (Gatoo et al. 2014). Moreover, the agglomerate formation or aggregation is affected by the surface charge as a response to the exposure of organisms to nanoparticles (Hoshino et al. 2004). Particle aggregation is influenced not only by the surface charge but also by the particle size and composition. Due to aggregation, the toxicity of nanoparticles decreases with the increase in the concentration of nanoparticles at higher concentrations (Gatoo et al. 2014; Pietroiusti et al. 2011). Various factors like the composition of medium, ion strength, pH, and concentration of naturally present organic matter are known to affect the agglomeration process.

Fig. 1 Diagrammatic representation of fate of NPs in aquatic ecosystem



Nanoparticle coating and aging: The surface modification and functioning play a controlled role in the electrostatic stabilization of nanomaterials. The surface coating may eliminate or induce toxicity according to the nature of the coating used (Gatoo et al. 2014). For instance, nanoparticles having a surface coating of silica induce toxicity associated with the generation of reactive oxygen species (ROS) which in turn has cytotoxic effects (Risom et al. 2005; Sayes et al. 2004). Further, the product containing TiO_2 nanoparticles should have a coating of silicon and aluminum oxide and be emitted to the environment by coating the nanoparticles (Arvidsson et al. 2012). In addition, Label et al. (2010) investigated the age of nanoparticles and concluded that TiO_2-containing nano-composites (often used in sunscreen) altered the dispersive capacity of particles in water and consequently the fate of the environment.

Collision capacity: Aggregation of particles is dependent on attachment efficiency and collision frequency. The attachment efficiency depicts the chance that upon collision of two particles they will stick together and form an aggregate, while the collision frequency depicts the number of collisions between particles that could potentially result in the formation of an aggregate (Phenrat et al. 2010). The cluster of particles is affected by the collision efficiency. No collisions will cause attachment if the collision efficiency is equal to zero, and if the collision efficiency is one, there will be attachments by all the collisions.

Natural organic matter and colloids: In a natural aquatic system, there is abundant organic matter (ranging from small molecules to larger macromolecules), inorganic clay minerals, and natural colloids of varying sizes (Gallego Urrea et al. 2010). It is well recognized that in natural water bodies, the sorption of such nanomaterials is generally mentioned as natural organic matter (Arvidsson et al. 2011). Being a universal component of aquatic ecosystems, natural organic matter may affect the aggregation and/or deposition properties of NPs by influencing the surface speciation and charges of those particles. Buffle et al. (1998) distinguished the natural organic matter into three groups based on their biophysical properties: (1) rigid biopolymers, which include the polysaccharide and peptidoglycan produced by phytoplankton or bacteria (Myklestad 1995), (2) fulvic compounds that contain breakdown products of plants, and (3) flexible biopolymers which covers the degradation product of microbial community. The interaction of released nanoparticles with natural organic matter will change their surface properties by forming a different natural coating that will affect their fate and behavior in water (Biswas and Sarkar 2019).

Sedimentation: The ultimate consequence of aggregation is the sedimentation of these nanoparticle aggregates to the sediment. In addition to aggregation, nanoparticles will deposit on other surfaces, like natural colloids (Petosa et al. 2010; Arvidsson et al. 2011). Sedimentation is well described for agglomerates with spherically dense morphology, while non-agglomerated NPs have an almost negligible sedimentation rate due to their smaller size. All particles with a higher density than water must have a net downward force vector, which leads to a fixed sedimentation velocity for that particle (Elimelech et al. 1995).

Dissolution: Dissolution is an important chemical process that controls the mobility and availability of trace metals in the soil. The amount of dissolution is expected to depend on various factors like pH, presence, and absence of oxygen, oxidants like hydrogen peroxide, and ligand properties (Galloway et al. 2010). As toxic metal ions may release from nanoparticles, the dissolution reaction of those nanoparticles might be expected to play a significant role in enhancing their toxicity (Campbell et al. 2002; Hiriart- Baer et al. 2006). In wastewater treatment plants, the dissolution /transformation of silver or nano-silver into silver sulfide nano form has also been shown (Kim et al. 2010).

Sulfidation and redox behavior: Sulfidation is a major chemical transformation for many metal NPs, particularly in the presence of enhanced sulfide concentrations such as those found in parts of wastewater treatment plants (Kim et al. 2010; Kaegi et al. 2011). The reactions can result in changes in particle size, surface charge, and solubility. Ultimately these changes will influence the fate, bioavailability, and effects of the NPs. As consequence, the sulfidized form is more toxic to aquatic biota (Li et al. 2015). More generally, oxidation is not a major transformation pathway for most of the NPs, although it is an essential step in the dissolution of metals such as Ag, whereas redox transformations of metal oxides such as FeO and ceria are important in determining the behavior of NPs in the aquatic system (Lead et al. 2018).

2.3 Uptake and bioavailability of nanoparticles in aquatic systems

The uptake of nanoparticles is a major concern in aquatic biota. Studies on bioavailability and uptake are critically important to link the environmental chemistry of NPs to biological effects. The hypothesis is that the presence of nanoparticles in an organism will lead to a biological response, and this can be understood by how the NPs initially interact with the external surfaces of the organism. Further, the properties and behaviors of NPs are important factors in bioaccumulation. For instance, particle size may not be revealing the exposure of aggregate, though it has been shown to influence bioaccumulation. In addition to this, particle size and composition, the shape of the NPs, and their synthesis method can affect bioaccumulation (Dai et al. 2015; Ramskov et al. 2015). Many studies have shown that bulk or micron-size particles are less bioavailable to invertebrates than their nano-sized counterparts (Pang et al. 2013; Cozzari et al. 2015). The prokaryotes are protected against nanoparticle uptake since they don’t have any mechanism for the bulk transport of colloidal particles. However, in eukaryotes (i.e. protists and metazoans), well-developed cellular processes like endocytosis and phagocytosis are present for the internalization of nanoscale particles; hence the situation is very different (Na et al. 2003; Panyam and Labhasetwar 2003). The possible routes for nanoparticle regeneration include epithelial boundaries such as direct penetration or penetration through body walls, gills, or olfactory organs (Brigger et al. 2002; Farkas et al. 2011). In fish, the liver is likely to be targeted by endocytotic transport to the intestinal epithelium in the liver portal blood system (Smedsrud et al. 1984). In addition, nanoparticles are potential targets in the case of invertebrates for internalization of the immune system, intestinal epithelium, and digestive or midgut gland (Moore 1990).

3 Impact of nanoparticles on aquatic ecosystems

On the grounds of the extensive use and clearance of engineered nanomaterials in our everyday life, ecosystems, especially aquatic ecosystem, becomes a major victim of environmental pollution. The toxic impact of nanomaterials on aquatic organisms is important to study because most contaminants released in the environment are consumed by aquatic species. Griffitt et al. (2008) conducted a study to assess the toxicity of metallic nanoparticles in aquatic organisms. Additionally, irregularities in behavior patterns and the mortality rate of these organisms have also been observed (Lovern and Klaper 2006; Templeton et al. 2006; Roberts et al. 2007). The nano-toxicological studies, as well as various risk assessments, have been carried out on algae and bacteria (Wang et al. 2008; Jiang et al. 2009), nematodes and crustaceans (Wang et al. 2009; Heinlaan et al. 2008), fish and rats (Griffitt et al. 2008; Elgrabli et al. 2007). Exploration of biological effects involved in (i) in-vitro and (ii) in-vivo studies. For the uptake of engineered nanoparticles released from the environment, surface sediment and filter-feeding Molluscs are thought to be major candidates; meanwhile, Molluscs are already identified to accumulate the sediments and suspended particles.

3.1 Impact on phytoplankton / primary producer

The phytoplanktons are the dominant primary producer in the aquatic ecosystem, having a size of 40–80 µm (Arturo et al. 2012). Nanomaterials released in the aquatic environment can potentially interact with photoautotrophic organisms, thus hampering key ecological processes, particularly photosynthesis, which decreases primary productivity. The small particles showed a concentration-dependent effect, while large particles showed less toxicity (Hund-Rinke and Simon 2006). Algal exposure to dissolved NPs results in reactive oxygen species (ROS) production leading in turn to an important reduction in the chlorophyll content, algal cell growth, and viability (Oukarroum et al. 2014; Sirelkhatim et al. 2015). It was also reported that the ionic form accumulation of some NPs in algal cells underlies the mechanism of toxicity. The unfavorable impact of fabricated NiO-NPs on the microalgae *Chlorella vulgaris* has been reported by Gong et al. (2011), and according to them, cells of *C. vulgaris* inhibited the overall growth as a result of plasmolysis, and membrane leakage at 72 h and showed EC50 values of 32.28 mg NiO L^{-1}. In the same way, the effect of pH on Ag-NPs induced cellular toxicity in *Chlamydomonas acidophila* has been determined by Oukarroum et al. (2014). They stated that the size distribution of Ag-NPs was pH-dependent, and a higher solubility was observed at pH-4 compared to pH-7. In addition, the results indicated that 24-hour exposure to Ag-NPs causes decreased cell viability and reduction in chlorophyll content attributable to the pH-dependent dissolution and production of reactive oxygen species. Also, in another study on *Spirodella polyrrhiz*a, Movafeghi et al. (2016) broadened the toxic effect of TiO_2-NPs and observed a significant reduction in the activity of particular oxidative stress controlling enzymes and in growth parameters and photosynthetic pigment contents. The nanoparticles are bioavailable to plants, causing trophic transfer, and have an impact on other organisms via biomagnification.

3.2 Impact on microorganisms

Apart from aquatic plankton, NPs also caused major toxicity to aquatic microorganisms, which are very small organisms with a size of 0.1 micron. Microbes are the root source of the ocean food web and play an important role in nutrient cycling by decomposing organic matter (Fasham 1984). They are also known to regulate the metabolism of the aquatic ecosystem through disruptive activities, alkalinity, pH, and redox circumstances (Fasham 1984; Trombetta et al. 2020). The rapid use of nanotechnology has increased the potential risks for microorganisms. Among different microorganisms, bacteria which are the ubiquitous members of ecosystems, serve as the basis for the food web and support environmental functions. Bacteria are generally less affected by the NPs toxicity in comparison with other living organisms in the aquatic environment due to their ability to overcome stress conditions and develop their defense systems (Freixa et al. 2018). The interaction between nanomaterials and biomolecules, directly or indirectly, may give rise to strong antimicrobial activity, as it is proved by current reports exposing the side effects of nanomaterials on microorganisms (Niazi and Gu 2009). The excess production of ROS can cause bacterial cell membrane dislocation and/or damage, changes in membrane permeability, and subsequent cell death (Choi and Hu 2008; Nair et al. 2009) (Table 2).

3.3 Impact on plants

In all ecosystems, plants are vital components and play a crucial role in the fate and behavior of nanomaterials despite their sessile nature. Plants have been taken into consideration by scientists due to their interface with soil, water, and air which may include manufactured nanoparticles, consequently generating nanotoxicity. However, the toxic effects on aquatic plants from NMs have not been well documented, and a very few number of reports are accessible in the literature. In the ecosystem, there is a broad range of plant species. Most of the nanotoxicity work so far has been focused on plants used for human consumption, such as maize (Birbaum et al. 2010), wheat (Ma et al. 2010), soybean (Priester et al. 2012), tobacco (Sabo-Attwood et al. 2012) and many fruits and/or vegetables such as pumpkin (Zhu et al. 2008), cucumber (Lin and Xing 2007; Ma et al. 2010; Wang et al. 2012) and radish (Lin and Xing 2007; Ma et al. 2010; Atha et al. 2012). Further, some other studies concentrated on the effect of Ag-NPs on *Lemna minor* and demonstrated the inhibition in plant growth and chlorophyll synthesis after exposure to Ag-NPs (Pereira et al. 2018). In addition to this, many studies have been performed on hydroponic plants, where NPs are presented in an aqueous phase compared to more realistic nanoparticles through irrigated soil or sand. Sabo-Attwood et al. (2012), while experimenting on tobacco seedlings treated with Au-NP under hydroponic conditions, reported that the smaller-sized NPs are capable of translocating into leaves while the NPs with larger sizes are restricted to the root periphery only.

3.4 Impact on animals

In aquatic organisms, invertebrates are normally in the habit of measuring the potential hazard effects of chemicals in ecosystems, as they act as representatives of different food webs in aquatic systems (Ruppert et al. 2004). The largest

Table 2 Effect of different types of nanoparticles (NPs) on microbial community and invertebrate species

Studied Organism	Type of Nanoparticle	Concentration	Impact on Organism	References
Nitrifying bacterial community	Ag	0.10 mg L^{-1}	No change in the membrane fouling rate but increased concentration of extracellular polymeric substances (EPS).	Zhang et al. (2014)
N-related microbial community	Ag	50 to 200 µg L^{-1}	Disturbed enzymatic activities were observed after Ag NPs application.	Huang et al. (2019)
River microbial community	Ag	200 µg L^{-1}	Change in structure of bacterial community was observed after NPs exposure.	Londono et al. (2019)
Juvenile *Epinephelus coioides*	CuO	20 to 100 µg L^{-1}	Significantly lower growth parameters were observed after CuO NPs exposure. No mortality was observed.	Wang et al. (2014)
Marine invertebrates Worms: *Hediste diversicolor* and *Scrobicularia plana*	CuO	10 µg L^{-1}	No significant effects were shown for the markers of neurotoxicity or oxidative damage. Enzymatic biomarkers: GST, CAT and SOD are activated by CuO NPs in *Scrobicularia plana*	Buffet et al. (2011)
N-related microbial community	CuO	1 mg L^{-1}	Bacterial genera depleted by CuO NPs were related to carbohydrate and glycan biosynthesis and metabolism, and biosynthesis of other secondary metabolites.	Miao et al. (2019)
N-related microbial community	CuO	1 mg L^{-1}	CuO NPs decreased the nitrogen removal efficiency, anammox rate, and relative abundance of anaerobic ammonia-oxidizing bacteria (AAOB).	Zhang et al. (2018)
Mesocosms (phytoplankton, zooplankton, macroinvertes, macrophytes, and fish)	TiO_2	25 and 250 µg L^{-1}	The biomass of Rotifera was significantly reduced after exposure to TiO_2 NPs while biomass of *Cladocera*, *Copepoda*, phytoplankton, macrophytes, chironomids, and fish was unaffected.	Jovanovic et al. (2016)
Microbial communities	TiO_2	700 µg L^{-1}	No significant effect on distribution and the structure of the microbial communities was observed at this concentration of NPs.	Londono et al. (2017)
N-related microbial community	TiO_2	1 mg L^{-1}	Decrease in nitrogen removal efficiency was observed, and the relative abundance of anaerobic ammonia-oxidizing bacteria was found to decrease under application of TiO_2.	Zhang et al. (2018)
Periphyton	TiO_2	0.05 mg L^{-1}	No detectable effects on algal cell density, chlorophyll-a, or periphyton mass was observed.	Wright et al. (2018)
Tegillarca granosa, mollusc	TiO_2	0.1 to 10 mg L^{-1}	TiO_2 NPs were neurotoxic to the blood clam as indicted by increased neurotransmitter concentrations, as well as the down-regulated expression of Neurotransmitter related genes.	Guan et al. (2018)
Caenorhabditis elegans	TiO_2	1 µg L^{-1}	A decrease in the locomotion behavior of wild nematodes was observed which could be due to the significant increase in intestinal ROS Production	Dong et al. (2018)

invertebrate phylum, Arthropoda consists of the two largest groups of insects and crustaceans. Crustaceans are the most important group of invertebrates; are mostly used as model organisms to assess ecotoxicological tests of hazardous materials in water ecosystems (Ruppert et al. 2004). Crustaceans also can sequester toxic metals in their tissues, i.e., granules of the hepatopancreas and other tissues. Oberdorster et al. (2006) analyzed the impact of NM, i.e., fullerenes on *Daphnia magna*; which results in altered moulting and decreased reproductive output, and increased mortality rates (Oberdorster et al. 2006). NPs can enhance the toxicity of particular chemicals by interacting with them and also work as a carrier of co-existing contaminants toward *Daphnia magn*a. Baun et al. (2008) suggested using crustaceans as representatives to study the impact of NPs or any other chemicals in the aquatic ecosystem for further knowledge in nano-ecotoxicology using in-vitro and in-vivo analysis. With these tests, we can analyze the behavior and bioavailability of NPs and also their bioaccumulation in the food chain of the aquatic ecosystem. Heinlaan et al. (2008) said that *Daphnia magna* could be a model organism to study the toxicity of nanoparticles in aquatic ecosystems. From the above study, we can say that NPs at high concentrations can negatively affect the crustacean i.e. *Daphnia magna*, in particular, is the representative fauna of the aquatic environment.

Molluscs, also known as bivalves, can filter plenty of water; due to this reason, any contaminant present in the water tends to accumulate in the different tissues of molluscs. Laura et al. (2012) have reported the stimulation of lysozyme enzyme release and reactive oxygen and nitrogen species which can ultimately lead to oxidative in response

Table 3 Effect of different types of nanoparticles (NPs) on fish species

Fish species	Type of Nano Particles	Concentration	Main effects	Reference
Oreochromis niloticus and *Tilapia zillii*	Ag-NPs	2 and 4 mg L^{-1}	Ag-NPs at higher concentration i.e. 4 mg/L have deleterious effects on brain antioxidant system.	Afifi et al. (2016)
Oreochromis mossambicus	Al_2O^{3-}NPs	120 to 180 mg L^{-1}	NPs were accumulated in the fish liver and caused major histological anomalies such as structural alterations in the portal vein, necrotic hepatocytes, vacuolation, aggregation of blood cells and melanomacrophages	Murali et al. (2017)
Apistogramma agassizii and *Paracheirodon axelrodi*	Cu-NPs	-	An increase in reactive oxygen species (ROS) levels.	Braz-Mota et al. (2018)
Oncorhynchus mykiss, Pimephales promelas, and *Danio rerio*	Cu-NPs	-	Caused damage to gill filaments and gill pavement cells, with differences in sensitivity for these effects between the fish species studied	Song et al. (2015)
Rutilusrutilus caspicus	Cu-NPs	0.1 to 0.5 mg L^{-1}	Histological changes occur in liver and kidney. The result of the study showed that copper nanoparticles could cause severe damages in the vital tissues of Caspian roach; *Rutillus rutillus caspicus* and have lethal effects for fish.	Aghamirkarimi et al. (2017)
Prochilodus lineatus	TiO-NP	1 to 50 mg L^{-1}	Ti accumulated in the liver, muscle, and brain and decreased muscular AChE activity	Carmo et al. (2019)
Cyprinus carpio L.	ZnO-NPs	-	ZnO NPs might affect kidney and liver function.	Chupani et al. (2018)
Oreochromis niloticus	ZnO-NPs	1 and 2 mg L^{-1}	mRNA expression of antioxidant enzymes were significantly decreased	Abdelazim et al. (2018)

to the uptake of nanoparticle agglomerates. A nanoparticle enters the cell by the process of endocytosis in the digestive gland cells of blue mussels and cockles. C60 fullerene induces cytotoxicity in *Mytilus edulis* hemocytes (Laura et al. 2012). Marine bivalves also take nanoparticles by endocytosis, such as *Mytilus edulis* (Moore 2006). Mussels and oysters more efficiently capture and ingest nanoparticles incorporated into agglomerates than freely suspended (100 nm) nanoparticles (Ward and Kach 2009). Exposure of C60 fullerene in oysters (*Crassostrea virginica*) can alter the development of larvae and digestive gland lysosomal negatively (Laura et al. 2012). Similarly, the accumulation of CuO nanoparticles in marine bivalve *Scrobicularia plana* increased the activities of SOD, CAT, and GST (Buffet et al. 2012). The impact of NPs on microorganisms and invertebrates has been summarized in Table 2.

Fishes are also very sensitive to nanoparticles due to gills. An early study suggested that C60 fullerenes (tetrahydrofuran as C60 solution) at very low aquatic exposure levels could induce fish brain changes (Oberdorster 2004). This significantly enhances lipid peroxidation in the brain of largemouth bass after 48 h of exposure to 0.5 mg / l of uncoated C60 fullerene. Fishes exposed to fullerenes have shown lipid peroxidation in the brain (Stephen et al. 2008). The toxicity of Ag ion has been studied in some freshwater fish species at a concentration of 0.8 μg L^{-1} (LC10) (Birge and Zuiderveen 1995; Janes and Playle 1995; Wood et al. 1996). Ag ions in solution can reach the bronchial epithelial cells via the Na^+ channel coupled to the proton ATPase in the apical membrane of the gills, travel to the basolateral membrane of the gill, and block the Na^+ K^+ ATPase affecting ion regulation of Na^+Cl^- ions across the gills (Bury et al. 1999). An adverse effect of nanoparticles on the fish has been presented in Table 3.

Amphibians are sensitive toward nanomaterials because of their biphasic life cycle and the high permeability of eggs, skin, and gills. Many works have been done to analyze the toxicity of ENMs on amphibians. Amphibian larvae may form micronuclei by genome mutations which can be used as biomarkers to analyze the impacts at the biochemical, physiological, and genetic/molecular levels in response to ENMs (Mouchet et al. 2007, 2008).

4 Mechanism of nano-toxicity

In general, toxicity in a living organism is produced by the excess generation of reactive oxygen species (ROS); in normal conditions, these ROS are effectively scavenged by the antioxidant defense system (Bashri et al. 2018). In a similar way to other toxicants, NPs also generate ROS at high concentrations and produce oxidative stress in the affected organism (Fig. 2). Many studies reported a large generation of ROS even under small amounts of CuO or ZnO NPs in the incorporated cells (Chang et al. 2012; Toduka et al. 2012). NPs can induce ROS directly when they come in contact with the organelles of exposed cells and the major sites of ROS production in mitochondria where any

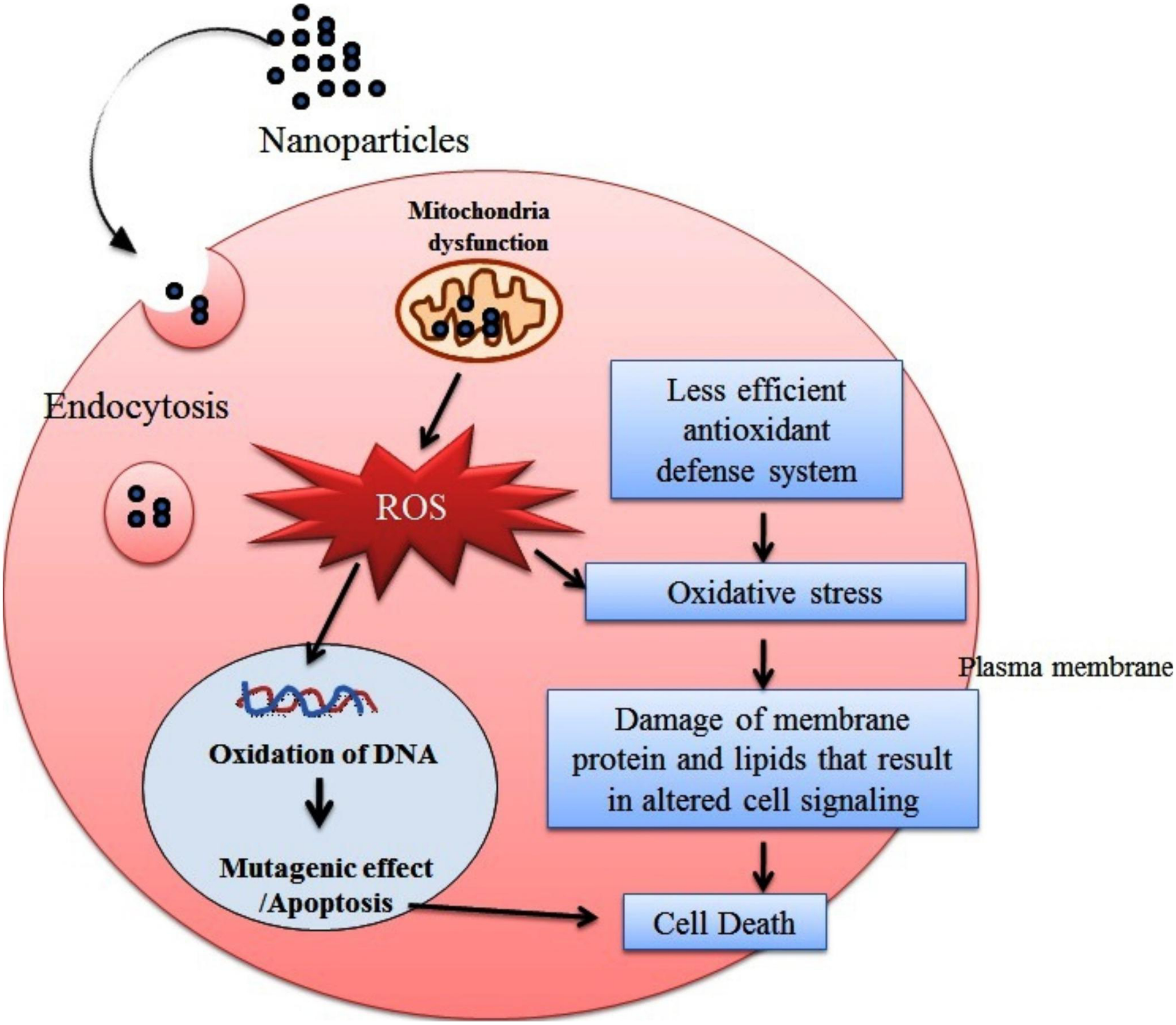


Fig. 2 Schematic representation of NPs induces generation of reactive oxygen species (ROS) that lead to oxidative stress in cells that may cause cell death

disturbance in the electron transport chain leads to the generation of superoxide radical (Nohl and Gille 2005; Zhang and Gutterman 2007). NPs have a specific property, i.e., large surface area; due to this reason, they can easily cooperate with the biomolecules that enrich CuO or ZnO NPs with high electronic density (Pisanic et al. 2009). According to published data on metallic and metal oxide NPs, oxygen is frequently required for the generation of reactive oxygen species (ROS) in AgNPs and nano-zero valent iron, whereas illumination is required for ROS generation in TiO_2 and ZnO NPs (Yang et al. 2013). Ag-NPs are probably toxic to microbes due to both the release of silver ions (ion-free) and the production of reactive oxygen species (Zhang et al. 2016). Consequently, the formation of excess superoxide oxide ($O_2^{\bullet-}$) induces ROS accumulation and causes oxidative stress (de Berardis et al. 2010). Superoxide radical ($O_2^{\bullet-}$) is converted into hydrogen peroxide by the action of the enzyme superoxide dismutase. In the middle of this, chemical reactions occur, known as Fenton's reaction. This hydrogen peroxide can convert into the most toxic hydroxyl radicals in the presence of transition metals by the reaction of Heiber Veis and Fenton's (Yamakoshi et al. 2003). These generated ROS can react with biomolecules and cause the oxidation of lipids and proteins, causing an imbalance in biological systems (Xia et al. 2008; Yang et al. 2009; Xiong et al. 2011) studied the oxidative stress induced by metal oxide in zebrafish, which causes damage to biomolecules in the absence of light. It has also been proved that oxidative stress represents a common mechanism for NP-induced cell damage (Pulskamp et al. 2007), and the mechanism has been authenticated in many NPs' toxicity studies (Yang et al. 2009). But above any toxicant, the generation of ROS exceeds its scavenging process which results in the oxidative burst, and it also results in intracellular Ca^{2+} release, which leads to mitochondrial perturbation and cell death (Xia et al. 2008). Meanwhile, with increased ROS production, NPs can also alter and damage the DNA and disturb protein synthesis (Yang et al. 2009). Similarly, Singh et al. (2009) documented that the increased level of ROS induced by NPs in lysosomes could be one of the reasons for DNA point mutations.

5 Conclusion and future perspective

Nanotechnology is the fastest growing industry, which gives us many products of daily use and many benefits in terms of medicine and its technology. But the accidental release of NPs in the environment ultimately reaches the aquatic environment, which may harm living organisms and sensitive ecosystems. The NPs reached the aquatic system through wind, rivers, etc. A high concentration of these NPs can negatively affect the organism of every trophic level in the aquatic ecosystem, such as phytoplankton, microorganism, plants, and animals. This negative impact of NPs on living organisms is due to the excess generation of reactive oxygen species due to altered balance with an antioxidant defense system that can lead to cell death. Thus, although development is an essential feature of a growing society, it should be done with the proper management not to alter the environment. For this, there should be sustainable methods to overcome the harmful impact of these NPs on the environment. On the way to sustainable nanotechnology, it is evident that the expertise from different disciplines must contribute to a greater understanding of nano bio-interaction. However, there is much need for more studies and research to better understand the impact of NPs on particular organisms. A complete study of the interactions and impacts of NPs on various species belonging to various trophic levels of the aquatic ecosystem, along the food chain and food web of the ecosystem, is urgently needed to close the enormous knowledge gap. This study could help researchers to make regulations that forbid companies to spread nanoparticles into aquatic environments.

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Declarations

Conflict of interest The authors declare no conflict of interest.

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