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REVIEW

Nanoparticles in the Aquatic Environment: The Risks Associated with Them and the Possibilities of Their Mitigation with Microalgae

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Abstract—Nanoparticles (NPs) are dangerous micropollutants that exhibit biotoxicity even in low (ng/L range) concentrations. Apart from direct toxicity to living organisms, NPs can absorb and transfer organic or inorganic toxicants as well as potentiate the toxicity of other micropollutants. Increasing use of NPs in industrial and domestic applications leads to their increased production and discharge into the environment giving rise to diverse risks for ecosystems. These risks are exacerbated by the resilience of NPs to biodegradation in natural ecosystems and traditional wastewater treatment plants. Efficient NP removal technologies are complex and expensive, so they cannot be affordably replicated in common wastewater treatment plants. Despite the risks associated with NPs, humanity will not abandon their use in the nearest future, since NPs are now at the foundation of many modern technologies. The biodestruction and biosorption of NPs using microalgae cultures and algal-bacterial consortia are considered promising approaches regarding environmental safety and the conservation of natural resources. However, the progress of this approach is hindered by the paucity and fragmentary nature of the information about the effects of NPs on microalgae cells and microbial communities. This review attempts to fill this gap, at least partially, by considering common industrial NP types based on metals and their oxides as well as carbon nanomaterials. The pathways of their entry into aquatic ecosystems, toxicity to living organisms, accumulation and biotransformation in cells, synergistic effects of NPs in combination with heavy metals and antibiotics, as well as methods for the bioremoval of NPs and nanomaterials from aquatic ecosystems using microalgae are discussed.

Keywords: nanoparticles, microalgae, biotoxicity, bioremoval, wastewater, micropollutants
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INTRODUCTION

Pollutants exhibiting biotoxicity in low (on the order of ng/L) concentrations have received a special name: emerging/hazardous micropollutants (HM) [1]. They are represented by drugs, antiseptics, personal hygiene products, food additives, pesticides, plasticizers, natural and synthetic hormones, heavy metals, and nanoparticles (NPs). Metallic and metal oxide NPs of silver (Ag) [2], zinc oxide (ZnO) [3], and titanium dioxide (TiO_2) are the most widely used [4]. Nano zero-valent iron (nZVI) [5], copper (Cu) and copper oxide (CuO) [6], aluminum (Al) and aluminum oxide (Al_2O_3) [7], and gold (Au) nanoparticles [8], as well as a number of other substances, are continuously mentioned in the literature [9].

NPs and nanomaterials are increasingly used for industrial and domestic purposes, which entails a steady increase in their production. The expected

annual growth of the world market for NPs made of metal oxides and metalloids will amount to 7% in the period of 2020–2025 [10]. Annual global production of TiO_2 and ZnO-based NPs exceeds hundreds of tons [11]. Accordingly, the emissions of NPs into the environment are growing and, at the same time, the risks of adverse effects on natural systems are increasing. The studies of the influence of NPs on aquatic and terrestrial ecosystems is attracting more and more attention. NPs can not only directly affect living organisms but also serve as carriers of organic and inorganic pollutants as well as enhance the toxic effects of other HM. Resistance to biodegradation in natural ecosystems and traditional treatment facilities exacerbates the problems associated with the accumulation of NPs in the environment. Nevertheless, despite the risks associated with NPs, humans will not stop using them in the near future since they are widely used in modern technologies.

Effective technologies for the removal of HM (including NPs) based on chemical sorption and oxidative destruction are complex and expensive; therefore, their widespread introduction into wastewater treatment plants is not yet possible. The products of HM oxidation reactions, which can be even more toxic, are also dangerous. On the other hand, biodegradation and biosorption (bioconcentration) using microalgae cultures and microalgal-bacterial consortia (MBC) is considered one of the most promising approaches from the point of view of environmental safety and the conservation of natural resources. However, the development of this approach is hindered by the lack and fragmentation of information on the effect of NPs on microalgae as well as including microbial communities in natural and artificial ecosystems. The data on the distribution, effects, and transformation of antibiotics and other pharmaceuticals in nature and in wastewater treatment plants is not yet possible. The products of HM oxidation reactions, which can be even more toxic are fairly well systematized, unlike the information on NPs. An analysis of recent reviews on the effect of metallic NPs on ecosystems, including aquatic ecosystems [12–15], indicates that, despite active research, there are gaps in our knowledge due to the lack of modeling and field research results. The main source of uncertainty is the lack of data on the concentrations of NPs in the environment and the dosimetry of NPs in general [13]. This review attempts to fill this gap, at least partially. The article discusses common industrial NP types based on metals and their oxides as well as carbon nanomaterials. The pathways of their entry into aquatic ecosystems, toxicity to living organisms, accumulation and biotransformation in cells, synergistic effects of NPs in combination with heavy metals and antibiotics, and methods for the bio-removal of NPs and nanomaterials from aquatic ecosystems using microalgae are discussed.

SOURCES OF NANOPARTICLE ENTRY INTO THE ENVIRONMENT

There are three possible scenarios for the entry of NPs into natural ecosystems, including aquatic ones: during production, during operation, and after the disposal of products containing NPs. Out of the nanomaterials produced, 63–91% eventually end up in landfill sites, 8–28% in soils, 0.4–0.7% in natural water bodies, and 0.1–1.5% in the atmosphere [16]. Thus, it was shown that 1 m^2 of commercially available self-cleaning cement releases 18.7–33.5 mg TiO_2 NPs after 168 h of leaching [17], and facade paints with TiO_2 NPs under the influence of atmospheric conditions, release these NPs, which are then transported by sewage into water bodies [18]. The use of low-frequency TiO_2 and ZnO in cosmetic products also leads to their entry into water bodies [19]. Thus, using electron microscopy, it was possible to identify TiO_2 NPs from sun-protection creams in suspended matter of the Old Danube Lake (Vienna, Austria); their content increased in the summer season [20]. The popularity of textiles containing NPs with bactericidal properties, releasing these NPs, for example, during washing, is increasing [21]. Thus, microscopy showed that silver particles with a diameter of 10 to 500 nm are released into the washing water from socks containing nanosilver [22].

NPs formed as a result of natural phenomena, such as volcanic activity, and during industrial processes, such as cutting, grinding, melting, casting, welding, etc., also enter the aquatic environment [23]. For example, NPs with abnormally high concentrations of Cu, Zn, Ag, Cd, Sn, Sb, Hg, Pb, Tl, and Bi were found in road dust [24]. Such NPs can enter aquatic ecosystems with wastewater. Emissions of metallic NPs are also possible as the result of their use for the remediation of soils and groundwater, as in the case of zero-valent iron [25], as well as when plants are treated with NPs-based growth regulators and pesticides [26].

Carbon nanostructures are nanoscale allotropic modifications of carbon, including representatives of zero- (quantum dots, fullerenes), one- (nanotubes), and two-dimensional (graphenes) NP types, are now widespread and actively produced. They are used in many branches of industry, agriculture, and medicine. Due to a wide variety of structures and unique physicochemical properties, carbon NPs are used to develop agents for targeted drug delivery; photo-, radio-, and gene therapy [27, 28]; antibacterial drugs [29]; biosensors [30]; sensors for monitoring pollution [31]; adsorbents for wastewater treatment [32]; etc. All this significantly increases the volume of these NPs entering the ecosystems. Carbon NPs can be transferred to the aquatic environment from aerosols formed as a result of forest and steppe fires, burns, volcanic eruptions, the burning of agricultural waste, and the use of hydrocarbon fuels at power plants. Natural oil and bitumen can act as sources of NPs [33]. There-

fore, all living organisms experience their effect to one degree or another. In the last decade, NP sources included wastewater treatment plants [34] and industrial facilities where carbon nanostructures are synthesized or used [34]. Currently, there are no precise data on the concentrations of carbon NPs in the aquatic environment; however, the calculated concentrations of carbon nanotubes (CNTs) and graphene in natural environments are 0.001–1000 μg/L [35].

Thus, the increase in the emissions of NPs based on metals, their oxides, and carbon nanomaterials into the aquatic environment due to the widespread distribution of nanoindustry products, as well as due to natural and man-made processes, is a general trend that can lead to unpredictable environmental effects.

TOXIC EFFECTS OF NANOPARTICLES ON HUMANS AND ANIMALS

Metal and metal oxide NPs can affect the human body both when they are deliberately used in nanomedicine, taken with food or as part of personal hygiene products [36], and as a result of unintentional exposure during industrial, natural, and other processes, when NPs are used in agriculture, etc. [10]. The number of studies on the direct effect of metal and metal oxide NPs on human health is low. However, many studies devoted to the effect of NPs on human cells and experimental animals in in vitro and in vivo experiments indicate their potential danger to humans. Metal and metal oxide NPs are cyto- and genotoxic, causing oxidative damage to DNA and cell death [37]. In vivo research showed that various types of metallic NPs tend to form deposits in the liver, causing toxic effects [38]. In addition, NPs can accumulate in the digestive tract, lungs, heart, spleen, cardiac muscle, and kidneys [39, 40]. It was found that metal NPs can be transported to the central nervous system through a damaged blood-brain barrier and stimulate the activation of glial cells for the release of proinflammatory cytokines and the generation of reactive oxygen species (ROS) as well as the production of nitric oxide, which leads to neuroinflammation [41].

The biosecurity of carbon nanomaterials is also debatable. Due to their stability and mobility, these nanostructures are capable of bioconcentration and migration along food chains [42]. Both the general toxic effect and the selective toxicity of CNTs for the respiratory [43], digestive [44], and reproductive [45] systems of mammals have been confirmed many times. Graphene also has a toxic effect on mammals, since its NPs are capable of aggregating in tissues and causing oxidative stress damaging cells of the lungs, liver, spleen, kidneys [46], and the cornea [47].

Thus, metal and metal oxide NPs, as well as carbon nanomaterials, exhibit proven toxicity for mammals and, in some cases, for humans. In this regard, the search for means reducing the content of NPs in the environment is of particular relevance.

EFFECTS OF NANOPARTICLES ON AQUATIC ORGANISMS

The effect of NPs on aquatic organisms is determined by the chemical composition of water, including the content of dissolved organic matter (DOM), ionic strength, and pH [48] as well as illumination and temperature [49]. DOM can be adsorbed on the surface of NPs, forming thin films, changing their functional surface and increasing their aggregate stability [50]. A DOM coating can limit the release of ions from NPs into water [51], increase the ability of NPs to migrate and diffuse [52], and affect their toxicity [53]. The ionic strength and pH of water bodies can change the parameters of aqueous suspensions of NPs, which also affects the adsorption of DOM [49].

Temperature is an important determinant of the growth and productivity of primary producers, such as microalgae. It was shown that an increase in temperature increases the rate of NP suspension [54]. This can increase their toxicity to microalgae. In addition, some NPs (TiO_2, ZnO) are semiconductors with photocatalytic and photodynamic properties. Such NPs can generate ROS, which have a toxic effect on microalgae cells when irradiated with ultraviolet radiation [55]. NPs, such as ZnO particles, can penetrate into the cytoplasm, damaging organelles and subcellular structures, including chloroplasts, vacuoles, endoplasmic reticulum, Golgi apparatus, and mitochondria, or altering their functionality [56].

There is information about the toxicity of carbon nanostructures for aquatic organisms. It is believed that NPs rarely exhibit acute toxicity towards microalgae; however, there is evidence of structural and negative functional disorders of microalgae cells (upon prolonged contact with NPs). Thus, reduced graphene oxide with attached ZrO_2 induced a cytotoxic effect in microalgae *Chlorella pyrenoidosa* causing oxidative stress and functional changes in cell membranes [57]. Graphene oxide and reduced graphene oxide slowed down cell division, damaged cell membranes of *C. pyrenoidosa*, and also reduced the bioavailability of nutrients for microalgae due to adsorption on the surface of NPs [58]. Fullerenes in sublethal concentrations reduced chlorophyll content and Mg^{2+}-ATPase activity, inhibiting cell division of *Scenedesmus obliquus* [59]. Double-walled CNTs already inhibited the cell division of *Thalassiosira pseudonana* diatoms and the growth of *Tigriopus japonicus* crustaceans at a concentration of 0.1 mg/L, while a 50% effective concentration (EC_{50}) of NPs was only 1.86 mg/L [60]. A delay in growth and development was also observed in experiments with *Pseudokirchneriella subcapitata* (EC_{50} = 17.95 and 10.93 mg/L for pure and oxidized double-walled CNTs, respectively) [61]. Both direct

damage to cellular structures and the impairment of trophism and photosynthesis due to adhesion of carbon nanostructures to the surface of microalgae cells are considered as a mechanism of the toxic effect on algae.

Growth and development retardation under the action of CNTs was also observed in *Daphnia pulex* (LC_{50} = 2.81 and 4.45 mg/L for pure and oxidized double-walled CNTs, respectively) [61]. Graphene, fullerene C_{60}, single- and multiwalled CNTs at low concentrations stimulated the growth and reproduction of *D. magna* probably due to the adsorption of nutrients on the surface of NPs, which contributed to an increase in their absorption by daphnia. However, with an increase in NP concentration, an increase in toxicity was observed, manifested as the suppression of growth and reproduction [62]. Some studies did not reveal the acute toxicity of CNTs and fullerene C_{60} for *D. magna* but NPs remained in the intestines of daphnia even after 48 h [63], which increases the likelihood of the transfer of carbon nanostructures to the next trophic level of the food chain. Multilayer CNTs with 28 days of exposure at a concentration of 0.01–1 mg/L had a neurotoxic effect on *Ruditapes philippinarum* mollusks [64]. Graphene oxide at a concentration of 0.4–1 mg/mL caused significant embryonic mortality, delayed hatching, cardiotoxicity, and the development of cardiovascular defects in *Danio rerio* fish embryos [65]. Reduced TiO_2-graphene oxide composite at a concentration of 30 μg/mL did not have a toxic effect on *D. rerio* embryos; however, with an increase in concentration to 1 mg/mL, teratogenic and cardiotoxic effects were observed [66]. Chronic graphene oxide exposure of adult *D. rerio* induced the generation of ROS in cells, damaging the gills and liver [67]. The toxic effects of graphene in *D. rerio* were observed in other studies [68]. Growth suppression was observed in *Oryzias melastigma* under the action of 10 mg/L of double-walled CNTs [60]. However, it should be noted that the toxicity of carbon nanostructures for fish is lower than for other aquatic organisms. Thus, the analysis of literature sources indicates the vulnerability of aquatic organisms to metallic, metal-oxide, and carbon NPs.

SYNERGISM OF DANGEROUS MICROPOLLUTANTS

Aquatic organisms are usually exposed to multicomponent mixtures of HMs, including various NPs. Metal and metal oxide NPs are an effective adsorbent for various HMs, including ions of other heavy metals and antibiotics [69]. The high sorption of HMs on metal NPs is due to the presence of coordination center particles on their surface (protrusions, edges, bends, or corner areas) [70]. Thus, the presence of TiO_2 NPs at a concentration of 1 mg/L increased the toxicity of Zn^{2+} ions for cyanobacteria *Anabaena* sp.; however, with an increase in the concentration of TiO_2 up to 10 mg/L, toxicity of the Zn^{2+}/TiO_2 system decreased due to the adsorption of a majority of the Zn^{2+} on the TiO_2 surface [71–73]. Dichloro-dihydrofluorescein diacetate assay (H_2DCF-DA) showed an increase in the level of ROS in microalgae cells under the influence of the Zn^{2+}/TiO_2; with increase in Zn^{2+} concentration above 0.7 mg/L, cell destruction was observed [71]. Similar results were obtained in experiments on assessing the toxicity of arsenic in the presence of TiO_2 NPs towards *Ceriodaphnia dubiac* [72]. A decrease in the toxicity of heavy metals for green microalgae in the presence of TiO_2 NPs has been shown [73]; however, NPs did not affect the absorption and toxicity of Cd^{2+} in an experiment with *D. magna* and *Lumbriculus variegatus* [74].

The analysis of the publications available to the authors of the review suggests that NPs, being an effective sorbent, can reduce the toxicity of heavy metals. The adsorption of antibiotics on Al_2O_3 [75] and TiO_2 NPs [76] was demonstrated. However, in contrast to complexes of NPs with heavy metals, complexes of NPs with antibiotics are more toxic than antibiotics and NPs separately [77]. The action of antibiotics (azithromycin, cefotaxime, cefuroxime, phosphomycin, and chloramphenicol) against *Escherichia coli* increased in the presence of Ag NPs, but the antibacterial effect of Ag NPs with oxacillin and neomycin antibiotics against *Staphylococcus aureus* was significantly weaker than the effect of antibiotics alone [78]. The combinations "tetracycline + Ag NPs," as well as "neomycin + Ag NPs," more strongly inhibited the growth of *Salmonella typhimurium* DT104 in comparison with the effect of the antibiotic alone; at the same time, no enhancement of the antibiotic effect on this bacterial strain was observed in the combination of "penicillin + Ag NPs." The potentiation of the antibiotic action was probably due to an increase in bacterial binding of Ag NPs under the action of tetracycline or neomycin but not penicillin [79]. The combination of carvacrol with ZnO NPs increased the antimicrobial effect against *Campylobacter jejuni* [80]. It was assumed that NPs promote the penetration of antibiotics into the cell, changing the membrane permeability, and then, together with them, destroy the cell wall [80]. Another mechanism of the toxic action of the NP + antibiotic complex can be mediated by the generation of ROS. The "NP + Ag-kanamycin" complex generated significantly higher amount of ROS compared to a system containing only an antibiotic or only NPs [81].

Unmodified carbon nanostructures can be safe for living organisms [82]; however, the surface functionalization or interaction with other pollutants can provide a synergistic effect, significantly increasing their bioavailability and toxicity [83]. At the same time, the behavior of nanostructures upon interaction with

other pollutants is rather difficult to predict. For example, CNTs in an aqueous medium at a high rate adsorb Cd ions on their surface, tripling the toxicity of Cd for *D. magna* [84]. The herbicide diuron in the presence of various multilayer CNTs (industrial, purified, nonfunctionalized, and oxidized) was actively adsorbed on the CNT surface, remaining bioavailable for green microalgae *C. vulgaris*, which led to a fivefold increase in the toxicity of the herbicide [85].

The surface properties of functionalized multiwalled CNTs variously affected the toxicity of lead for *D. magna* [86]. Negatively charged carboxylate multiwalled CNTs markedly reduced lead toxicity (LC_{50} increased from 0.15 to 1.08 mg/L in the presence of 10 mg/L of multiwalled CNTs). In contrast, positively charged multilayer CNTs modified with polyethyleneimine had only a minor effect on the toxicity of lead (LC_{50} increased from 0.15 to 0.16 mg/L under the same conditions). The decrease in lead toxicity was associated with a decrease in the bioavailability of the free metal form (Pb^{2+}) upon adsorption on the surface of multilayer CNTs [86].

Despite the fact that both CNTs and Cu NPs in an aquatic environment inhibited the growth of microalgae *Skeletonema costatum*, CNTs were capable of adsorbing Cu NPs, thereby reducing its toxicity [87].

Due to their high specific surface area and sorption capacity, carbon nanostructures, especially graphene and CNTs, are increasingly considered as sorbent materials with an antibacterial effect for wastewater treatment. Their ability to adsorb surfactants [88], heavy metals [89], organic substances and dyes [90], antibiotics [91], and radioactive waste [92] has been experimentally proved. Studies have shown that multiwalled CNTs can remove up to 99% of Zn^{2+} from an aqueous solution [93].

The analysis of the above publications allows us to conclude that NPs and nanomaterials are capable, depending on the properties of the NPs themselves, environmental conditions, and the presence of other substances, both to enhance or to weaken the toxic effect of other pollutants in the aquatic environment, such as heavy metals and antibiotics.

POTENTIAL OF MICROALGAE FOR THE REMOVAL OF NANOPARTICLES FROM WASTEWATER

The ability of algae to adsorb the NPs of metals and their oxides has been shown in a number of studies [94–96]. Mariano et al. detected internalized Ag NPs inside large vacuoles of *C. vulgaris*; these NPs were not released into the environment even after 1 week and were not biotransformed [97]. After a 4-h incubation of *C. vulgaris* with Ag NPs at a concentration of 2 mg/L, the content of these Ag NPs in microalgae cells reached 1200–3300 μg/g dry weight [98], and microalgae *Raphidocelis subcapitata* accumulated Ag NPs in the amount of 45 and 93.7 μg/g dry weight after 24 h incubation with these NPs at a concentration of 15 and 30 μg/L, respectively [99].

For the penetration into the microalgae cell, NPs should penetrate through the cell wall containing cellulose and other polysaccharides, as well as glycoproteins, and the cytoplasmic membrane. It was found by scanning electron microscopy that CuO NPs were attached to the surface of microalgal cells and interacted with the exopolysaccharide matrix, which promotes the adsorption of NPs by microalgal cells. Transmission electron microscopy revealed a fourfold thickening of the exopolysaccharide layer after exposure to NPs, which indicates a possible protective role of this layer of the cell wall of microalgae. However, despite the thickening of the exopolysaccharide layer, NPs penetrated through the cytoplasmic membrane by endocytosis and were deposited in the cell vacuoles [49, 56].

Inside the cells, metal NPs can undergo changes, including oxidation–reduction and complexation [100], or dissolve in the acidic medium of lysosomes [101]. The latter mechanism ensures the transport of toxic metal ions into cells. For microalgae, the entry of Ag NPs into the periplasmic space after 48 h of incubation with NPs has been described [102]. Using synchrotron X-ray absorption spectroscopy, it was established that Ag is present inside the cytoplasm in both crystalline and amorphous forms, identified as β-Ag_2S and silver thiolates. These studies convincingly proved the ability of microalgal cells to internalize and biotransform Ag NPs.

Carbon nanostructures entering aquatic ecosystems are involved in various transformation processes, including homo- and heteroaggregation, agglomeration, sedimentation, oxidation, sulfidation, as well as biodegradation and biomodification processes, which affects their properties [103]. There is evidence of the bioaccumulation of carbon nanostructures by cells of microalgae, protozoa, mollusks, crustaceans, and fish [104]. The biodegradation of carbon nanostructures in the natural environment occurs using enzymatic catalysis [105], for example, with the involvement of peroxidases in the corresponding subcompartments of hydrobiont cells [105].

CONCLUSIONS

This review is an attempt to concisely systematize information on the most common types of NPs, associated risks, entry into the aquatic environment, and pathways of biotransformation in aquatic cells. Even such a brief examination shows large gaps in our knowledge about these processes. The need to fill these gaps becomes more acute the faster and more widely technologies using NPs and nanomaterials are distributed. At the same time, NPs are a "double-edged weapon" that can be both a dangerous toxicant

and a powerful means of removing pollutants from wastewater and the environment. Special attention in the review is devoted to the potential of using unicellular oxygenic phototrophs (eukaryotic microalgae and cyanobacteria) as a basis for creating biotechnologies providing effective and economically affordable bioremediation of HMs. Potential pathways for the binding (bioconcentration) and elimination of NPs using microalgal cells include the uptake and accumulation of NPs in cell compartments, aggregation, sedimentation, chemical modification (oxidation, reduction, sulfidation, and complexation), and enzymatic biodegradation. In this case, important factors are the initial concentration of NPs, the pH of the medium, and the metabolic and physiological plasticity of microalgae cells. However, unlocking the potential of microalgae as components of biotechnology for reducing the risks associated with NPs requires a large amount of research for the elucidation of the mechanisms of NPs tolerance and search for effective strains performing bioconcentration and biodegradation of these particles.

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COMPLIANCE WITH ETHICAL STANDARDS

The authors declare that they have no conflict of interests. This article does not contain any studies involving animals or human participants performed by any of the authors.

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