

Review

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Review

Synthetic Nanoparticles in Aquatic Systems: Hidden Ecotoxicity and the Sustainability Challenge

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Abstract

Synthetic nanoparticles (NPs) have emerged as versatile materials in a range of industrial and biomedical applications. However, their release into aquatic systems raises growing concern due to their unique physicochemical transformations and ecotoxicological impacts. This review critically explores how nanoparticle properties—such as crystallinity, size, surface reactivity, and light sensitivity—influence their environmental behavior, bioavailability, and toxicity, particularly toward primary producers like microalgae. We highlight recent findings on the mechanisms of nanoparticle-induced photosynthetic inhibition and oxidative stress at the cellular and molecular levels. A key contribution of this review is the introduction of the “Green Synthesis Paradox”, a concept that challenges the assumed environmental safety of green-synthesized nanomaterials by demonstrating their potential hidden toxicity in real ecosystems. We argue that sustainability in nanotechnology must be assessed across the full life cycle of nanoproducts, from synthesis to environmental fate. By integrating ecotoxicological perspectives into the design and regulation of nanomaterials, this review calls for a paradigm shift toward responsible innovation in nanoscience.

Keywords: nanoparticles; aquatic ecosystems; toxicity; primary producers; environmental transformations; regulation; green synthesis

1. Introduction

Nanoparticles (NPs) are nanometer-sized particles of natural or synthetic origin that have revolutionized numerous research fields. The wide variety of available nanomaterials and their continuous expansion, with compositions that cover practically all the elements of the periodic table, have allowed the implementation of NPs in applications as diverse as drug delivery, biomedicine, improvement of services and products for the population, among others [1–3].

Globally, nanotechnology has represented a significant technological leap, driving innovation in materials and industrial products [4–6]. However, in other parts of the world (e.g., Latin America), a gap persists between industrial development that uses nanotechnology and the regulation of associated environmental risks. The lack of an adequate regulatory framework and information gaps generate uncertainty regarding the possible impacts of nanoproducts on the environment [7].

Nanoparticles are engineered and manipulated at the molecular level, adjusting their physicochemical properties by processes such as high pressures, extreme temperatures, or doping with surfactants. This gives them unique characteristics such as high reactivity, photocatalytic properties, agglomeration ability, and surface areas with specific reaction sites [8–10].

The aforementioned properties make nanoparticles especially attractive for their use; however, for a decade now, it has been evident that nanoparticles and the products containing them can have adverse effects on both human health and ecosystems, once they reach them as final disposal. Concentrations of nanoparticles have been detected in surface water bodies near sewage treatment plants, soils connected to landfills, and even in the atmosphere, as a result of the incineration and combustion of materials containing nanocomposites [11–14].

Currently, understanding the effects of nanoparticles on ecosystems is complex, since the innocuousness of these materials in conventional disposal processes, such as wastewater treatment, was not considered in their conception. In view of this problem, the present review aims to examine the physicochemical properties of nanoparticles, describing how these characteristics can influence their environmental toxicity, especially in aquatic ecosystems where their final destination was not contemplated from their initial synthesis.

2. Characteristics of Synthetic Nanoparticles

2.1. Crystalline Structure.

In nature, crystalline forms predominate because their atoms and molecules are arranged in three-dimensional repetitive patterns with well-defined symmetries, such as translation, reflection, and rotation. This arrangement, known as the crystal lattice, constitutes the fundamental principle in the structural basis of nanoparticles [15,16]. Given the variety of existing crystal configurations and shapes, these have been classified into 14 geometrical structures called Bravais lattices [17].

A key feature of nanoparticles is that the repetition of their basic structural unit provides a complete description of the final structure. This organizational capability makes nanoparticle engineering a versatile tool, as it allows their synthesis and controlled manipulation through adjustments in physical parameters such as temperature, light, and electromagnetic fields.

In addition, the crystal structure influences the functional properties of nanomaterials. The wave functions of the atoms in a nanocrystal retain, in part, the individual characteristics of the atoms, which determine their use and application in specific nanoproducts. This phenomenon is key to optimizing the physical and chemical properties of nanoparticles according to their industrial and environmental applications.

2.2. Size

The size of nanoparticles has been defined as an intermediate scale between a single atom or molecule and up to approximately 100 nanometers (nm) in molecular diameter [18]. However, the International Organization for Standardization (ISO), through the technical committee TC 229, defines a nanomaterial as a material with at least one external dimension at the nanoscale (1-100 nm), or that presents an internal or surface structure at this same scale [19].

Size reduction at the nanoscale confers unique properties to materials, mainly derived from their large specific surface area and quantum effects. These properties include changes in melting point, optical, magnetic, and mechanical characteristics, which are not observed in larger materials [20,21]. For example, at the nanometer scale, quantum confinement effects can give rise to atypical electronic and catalytic behaviors, enabling advanced applications in different fields.

A prominent example of these properties is the dispersion of cuboidal quantum dots in nematic liquid crystals, which results in faster electrical switching and anisotropic photoluminescence [22]. Similarly, suspension of insulating nanoparticles such as TiO_2 and Si_3N_4 in liquid crystals significantly reduces the density of moving ions, transient currents, and threshold voltage [23].

On the other hand, adding semiconducting nanoparticles such as ZnO enhances not only the intensity of moving ions but also the electrical conductivity of nanocrystals [24,25]. These findings reflect the importance of nanometer size in optimizing physical and chemical properties, expanding the range of applications of functional materials.

2.3. Electric and Magnetic Properties

Due to their small size and high surface-to-volume ratio, nanoparticles possess unique electronic and magnetic properties. This allows them to interact with energy differently compared to larger materials. These changes originate from electronic structure modifications and increasing surface influence, making nanomaterials particularly sensitive and suitable for applications such as sensors (Nie et al., 2020).

Nanoparticles' small size and morphology cause specific effects in their interaction with electromagnetic energy. For example, gold and silver nanoparticles (40-100 nm in diameter) exhibit visible color changes, creating yellow or red hues due to the excitation of surface plasmon resonances [26].

On the other hand, ferromagnetic nanoparticles such as iron, nickel, cobalt, and certain oxides, with sizes of approximately 10 nm, exhibit superparamagnetism. This implies that they respond strongly to an external magnetic field without possessing a permanent magnetic moment, as thermal energy induces fluctuations in the magnetic dipole of each particle [27]. These properties are applied in medical diagnostics, such as in contrast enhancement in magnetic resonance imaging and in magnetic hyperthermia therapies, where tumors are destroyed by inducing localized heat [28].

These characteristics are inherent to metallic nanoparticles, especially noble metals, known for their excellent electrical and magnetic conductivity. These properties have enabled the development of advanced applications, such as biomarkers, chemical and biological sensing, optoelectronics, thermal phototherapy, biological imaging, DNA labeling, microscopy, and photoacoustic imaging [29].

2.4. Nanoparticles and Surfactants

Combinations between nanoparticles and surfactants are an essential foundation in industries such as extractive and pharmacy medicine. Zeta potential measurements can define the adsorption areas of specific components, whether biological molecules or contaminants, facilitating removal processes or controlled interaction [9].

Surfactants play a key role in the synthesis of nanoparticles since they allow for the control of their formation by adjusting the concentration and type of surfactant used. Systematic investigations have shown that different surfactant structures can significantly influence nanoparticle size, morphology, and organization. For example, the formation of basic nanostructures with diameters between 20 and 80 nm has been observed, which can subsequently cluster into particles of final size between 1 and 5 μm , adopting mushroom, cube, and sphere shapes [30–32]. A relevant example is the use of sodium dodecylbenzenesulfonate, a surfactant that facilitates the synthesis of nano-spindles, nano-ellipsoids, nano-spheres, and nano-polyhedra of uniform sizes. These results are achieved by adjusting parameters such as reaction temperature, additive amount, and reagent concentrations [33].

The versatility of surfactants in the manipulation and synthesis of nanoparticles makes it possible to obtain materials with controlled properties, which broadens their applications in various industrial and technological fields.

3. Physicochemical Interaction of Nanoparticles in the Aquatic Environment

The presence, distribution, and persistence of NPs in aquatic systems depend on their colloidal stability. NPs can dissolve, aggregate, agglomerate, settle, or remain stable in the aqueous phase. Experimental partitioning studies indicate that a significant fraction of NPs is removed from wastewater during secondary treatment by sorption onto sewage treatment plant sludge [34–36]. However, these NPs adsorbed on sludge may return to the environment if these sludges are used as agricultural fertilizers, generating a potential risk of release into soils and water bodies.

During wastewater treatment processes, nanoparticles can also be chemically transformed. For example, silver nanoparticles (AgNPs) are mainly transformed into silver sulfide (Ag_2S) in both effluent and sludge [37].

Partial disaggregation of nanoparticles can be stimulated by natural events such as seasonal variations in hydrological currents, mixing of aqueous streams of different quality (e.g., wastewater and surface water), precipitation events, or local variations in shear stress within a moving fluid. This disaggregation can form smaller aggregates, which increases their resuspension and mobility within the water column, favoring their dispersal in the aquatic system [38].

In addition, NPs can enter water bodies through terrestrial runoff, reaching subterranean aquifers and eventually flowing into surface water streams. Kim et al. (2009) demonstrated that iron nanoparticles, stabilized with polyelectrolytes, maintained their original properties after 8 months of desorption in sand columns. This finding raises questions about the design of functional coatings that enhance the biodegradation potential of nanoparticles, thereby reducing their persistent effects in the aquatic environment [35].

3.1. Speciation

The speciation of nanoparticles in aquatic systems is determined by complex reactions and relationships, influenced by factors such as organic matter content, ligand or surfactant concentration, pH, and ionic strength of the medium [39]. Zhang et al. (2016) described the complex nature of the physicochemical behavior of silver nanoparticles (AgNPs) in aquatic environments, highlighting the need for further research to fully understand the dissolution kinetics of these nanoparticles. They noted that current assumptions based on Gibbs free energy and Ag^+ ion release fail to describe the actual fate of AgNPs in natural environments accurately.

In a different study, Yu et al. (2015) demonstrated that AgNPs, upon exposure to natural aqueous environments and sunlight, undergo oxidation and reduction simultaneously, leading to the release of Ag^+ ions and the formation of new AgNPs.

Metallic nanoparticles can exist in different oxidation states, which depend on the environment in which they are found. These states could lead to their destabilization, thus increasing the risk of contamination in aquatic environments [40–42].

3.2. Gradients of pH and Organic Matter

pH and organic matter are critical factors that determine nanoparticle colloidal stability and behavior in aquatic environments. Organic matter adsorption on the surface of nanoparticles is favored at low pH values (6.0–6.6), which increases their colloidal stability [43]. Conversely, organic matter adsorption decreases as pH increases, negatively affecting nanoparticle stability.

As organic matter layers do not extend significantly in solution, nanoparticles can interact directly with cells such as microalgae, especially at pH close to 7.5. This could explain the presence of toxicity in aquatic organisms [44].

Specific interactions between nanoparticles and organic matter have been observed in different studies. For example, carbon nanoparticles such as fullerenes and carbon nanotubes [45,46], as well as TiO_2 and ZnO nanoparticles [47], have shown strong interaction with organic compounds.

In the case of AgNPs, the presence of organic matter has a positive effect by stabilizing their colloidal dispersion and preventing their dissolution. However, it can also induce their partial transformation into Ag_2S particles, which are more stable and less reactive [48].

3.3. Heteroagglomeration and Homoagglomeration

In aquatic systems, dissolved organic matter plays a key role in stabilizing residual nanoparticles. Homoagglomeration, i.e., aggregation between similar nanoparticles, is usually the predominant mechanism leading to their sedimentation. However, heteroagglomeration, which

involves the deposition of nanoparticles on natural colloids and solid fractions of the environment, represents the most relevant process in terms of sedimentation [49].

In heteroagglomeration, aggregation and disaggregation processes can occur simultaneously. These phenomena are equally important in determining the behavior and fate of nanoparticles in the aquatic environment. Nevertheless, research on disaggregation processes is considerably less frequent compared to that focused on aggregation. Partial disaggregation can be induced by factors such as humic acid adsorption, a decrease in ionic strength, an increase in organic matter concentration, as well as by variations in temperature or exposure to sunlight [50,51].

These processes are critical when assessing the potential for bioaccumulation in exposed organisms. Agglomerated nanoparticles may still be bioavailable to aquatic biota even if they increase in size. Filter-feeding organisms that process large volumes of water, using their cilia to trap particles, are particularly susceptible to nanoparticle ingestion. This phenomenon is observed even in species that filter particles ranging in size from 0.4 to 150 micrometers [52–56].

It is important to highlight that ingesting agglomerated nanoparticles with sizes greater than 100 nanometers does not eliminate the associated risks. The weak forces that hold particles together in homoagglomeration or heteroagglomeration processes can dissociate under changes in environmental conditions, releasing smaller nanoparticles. This process can even occur inside organisms, amplifying potential risks to exposed biota [57–59].

3.4. Light

The photosensitivity of nanoparticles is closely related to the activity of surface electrons, which can be excited upon interaction with ultraviolet (UV) or visible light. This phenomenon gives rise to the surface plasmon effect, characterized by molecular resonance that induces the generation of energetic electrons (also called hot electrons) and the energetic separation between holes and electrons. In a typical model, surface electrons absorb resonant photons with coincident energies, causing them to oscillate on the surface of metallic nanomaterials. This generates an enhanced local electromagnetic field and simultaneously excites a large number of energetic electrons [60,61].

Visible light-driven photocatalysis has become a prominent area of research due to its potential application in clean and renewable energies. Photosensitive nanoparticles, when activated by sunlight, are used as photocatalysts in air and water purification processes. This has generated significant interest in recent years due to their ability to harness solar energy [62]. However, the low efficiency in utilizing this energy and the short diffusion length of the photogenerated electron-hole pairs limit the effectiveness of these photocatalytic processes [63].

Photosensitive nanoparticles are often doped with other molecules or elements to improve their efficiency. This procedure extends the range of light absorption and reduces the recombination of electron-hole pairs, optimizing their photocatalytic performance [64].

In aquatic environments, nanoparticles interacting with visible and UV light have a marked redox effect, especially when they interact with atoms of high electronegativity. This generates oxygen vacancies on the surface of the crystal lattice, further enhancing the oxidation-reduction processes and favoring nanoparticle reactivity [65,66].

4. Nanoparticles Interactions at Different Levels of Biological Organization

NPs have the ability to anchor and accumulate in cell membranes, penetrating them and altering their fundamental properties. These alterations include collapse of proton pumps, inhibition of DNA synthesis, generation of reactive oxygen species (ROS), inactivation of sulfur-containing proteins and enzymes, denaturation of ribosomes, and degradation of molecules such as lipopolysaccharides [67–69].

Particle size plays a crucial role in nano-ecological toxicity. Studies have shown that smaller nanoparticles possess a greater capacity for cell penetration, thus increasing their toxicity. For example, in a study with CeO₂ nanoparticles, the nanometer form was found to be significantly more

toxic than its micrometer form. An inverse relationship between nanoparticle size and toxicity has been observed, where smaller size tends to decrease EC50 values and increase toxic effects [70,71].

Sendra et al. (2017a) reported that TiO₂ nanoparticles in their nanometer form induce more intense cytotoxic responses due to excessive production of reactive oxygen species (ROS), compared to their bulk form. Differences in nanoparticle size modify their physicochemical properties, affecting their interaction with organisms such as microalgae [72–74].

On the other hand, iron nanoparticles of approximately 20 nm exhibit higher toxicity than larger particles. This has been demonstrated through parameters such as increased malondialdehyde (MDA) content, lipid reduction, peroxidation, and cell deformation, in addition to a higher tendency to agglomerate [71]. In general, smaller nanoparticles are more toxic because they penetrate cell walls more easily, whereas larger particles have limited penetration ability [75].

However, nanoparticles with sizes of 30-50 nm have been found to show higher internalization efficiency compared to smaller (15-30 nm) or larger (70-240 nm) particles, probably due to more effective interactions with cell membrane receptors [76].

Finally, microalgal cells, which exhibit a negative charge, can reduce the bioavailability of nanoparticles. Nevertheless, this interaction may cause direct injury to algal cells, exacerbating the toxic effects on these organisms [77].

4.1. Nanotoxicity on Primary Producers

Microalgae, as key photosynthetic organisms in surface waters, are particularly vulnerable to the presence of NPs. These particles can anchor to the cell wall, penetrate it, and cause severe damage such as loss of flagella, cell swelling, and alterations in cell function [78].

One of the main toxic effects of nanoparticles in microalgae is the shading effect, which directly affects the chloroplast membrane, where light is captured for photosystem II (PSII), key in the production of ATP and NADPH. TiO₂ nanoparticles, for example, are able to enter cells and aggregate on the chloroplast membrane, inhibiting ATP and NADPH synthesis, which significantly reduces cell proliferation due to a lack of energy for growth [79].

Studies have shown that exposure to nanoparticles severely affects the photosynthetic activity of microalgae. An 18% drop in PSII activity and a 35% decrease in chlorophyll content induced by nanoparticle exposure have been recorded. Moreover, PSII activity was most affected by nanoparticle dose, while the reduction in chlorophyll content was dependent on both the dose and type of nanoparticle [80].

Photosynthesis, the essential mechanism for microalgae to capture solar energy and transform it into ATP and NADPH molecules, is critical not only for their development but also for the production of carbohydrates, organic compounds, and atmospheric oxygen [81]. Therefore, any alteration in this process puts at risk the food chain, which depends on microalgae as primary producers.

It has been reported, for example, that cobalt and copper oxide nanoparticles cause photoinhibition of PSII and reduce photosynthesis in species such as *Platymonas subcordiformis*, *Chaetoceros curvisetus*, and *Skeletonema costatum*, due to decreased light absorbed by shading and photocatalysis effects [80,82,83]. In *Chlamydomonas reinhardtii*, exposure to cerium oxide nanoparticles (80 nm, 0.01 g/L) has been shown to cause chlorophyll impairment and photoinhibition of PSII [84].

In addition, nanoparticles can modify gene expression in microalgae. For example, a reduction in the transcription of genes associated with photosynthesis has been observed in the presence of TiO₂ and ZnO nanoparticles, as well as alterations in the proteosome, ROS production, and enzymatic activity related to cell hydrolysis [85,86]. The release of metal ions by nanoparticles, as in the case of copper oxide, interferes with photosynthetic mechanisms and exacerbates oxidative stress [87].

A recent meta-analysis showed that the accumulation of reactive oxygen species in the presence of nanoparticles increases oxidative stress by 90%, with this effect being influenced by dose, type of nanoparticle, and species of microalgae exposed [88].

On the other hand, diatoms have shown toxic effects similar to those observed in green microalgae when exposed to (NPs). In species such as *Phaeodactylum tricornutum*, titanium (TiO₂) and cerium (CeO₂) nanoparticles form aggregates in the culture media, enveloping and entrapping diatom cells. This phenomenon causes a significant inhibition in the quantum yield of photosystem II (PSII), affecting photosynthetic efficiency.

Simultaneously, an increase in the following parameters has been observed: Chlorophyll a content, soluble sugars, superoxide dismutase (SOD), and peroxidase (POD) enzyme activities.

These increases suggest that diatoms activate antioxidant defense mechanisms in response to nanoparticle-induced oxidative stress [89].

Exposure to nanoparticles under visible light generates an overexpression of reactive oxygen species (ROS) in organisms such as cyanobacteria. This accumulation of ROS damages phycobiliproteins (the main photosynthetic pigment of these organisms) and phycobilins (water-soluble pigments). The alteration of these components is the leading cause of the malfunctioning of the photosynthetic system, which inhibits cell growth [90].

It is worth mentioning that not all photosynthetic organisms absorb the same wavelengths of the visible spectrum. This difference is due to the variability in the photosynthetic pigments involved in the photochemical mechanisms, which prevents direct competition for ecological niches between different groups of photosynthetic organisms [91].

4.2. Aquatic Plants

The influence of nanoparticles (NPs) on aquatic plants has been less researched compared to other photosynthetic organisms. However, recent studies have shown that silver nanoparticles (AgNPs) have the ability to accumulate in the roots of species such as duckweed (*Landoltia punctata*) after 24 hours of exposure. The formation of silver derivatives in roots is attributed to the activation of plant molecular defenses in response to AgNPs uptake [92].

On the other hand, Oukarroum et al. (2013) reported a reduction in cell viability in *Lemna gibba* plants exposed to 1 and 10 mg/L concentrations of AgNPs for 7 days. This phytotoxic effect is associated with uncontrolled production of reactive oxygen species (ROS), leading to severe oxidative stress within the cells. The release of silver ions (Ag⁺) inside the cells contributed to the generation of ROS and the observed negative effects [93].

When exposed to AgNPs and zinc oxide (ZnO) nanoparticles, tissues of *Spirodela punctata*, another duckweed species, showed a similar pattern of oxidative stress. Stressed plants showed higher total antioxidant capacity and elevated superoxide dismutase (SOD) activity compared to untreated controls, reflecting a cellular defense mechanism to nanoparticle-induced stress [94].

Kim et al. (2011) demonstrated that both AgNPs (at low concentrations of 1 ppm) and TiO₂ nanoparticles (at higher concentrations of 250 ppm) inhibited the growth of aquatic plants *Lemna paucicostata* [95].

5. Difficulties in the Risk Assessment of Nanoparticles

Ecological risk assessment is a complex process that involves analyzing the likelihood that the environment (atmosphere, hydrosphere, lithosphere, and biosphere) will be affected due to exposure to stressors. Such ecological effects may involve plants, animals, and ecosystems as a whole, as well as human interactions with these systems [3,96].

Despite these concerns, regulations related to products containing nanoparticles remain limited due to the absence of comprehensive risk assessments that include them. This gap represents a critical challenge in identifying and managing the potential risks of nanoparticles. Grieger et al. (2010) and the OECD (2010) have suggested implementing a prioritized nanoparticle classification, focusing on those with the highest potential risk, in order to encourage immediate research to support the early development of specific regulations [97,98].

The classification proposal takes into account:

- Exposure assessments, based on production and use levels.
- Potential risk, determined by toxicity tests (see Table 1).

Based on available information, nanoparticles identified as requiring priority research include:

- AgNPs (silver nanoparticles),
- ZnO (zinc oxide),
- Fe₂O₃ (iron oxide),
- TiO₂ (titanium oxide)

Therefore, current ecotoxicological evaluations **coincide with this trend**, as shown in Table 1, which gathers various results obtained from EC 50 with different types of nanoparticles.

Table 1. Comparative ecotoxicological assessment of engineered nanoparticles: EC₅₀ values across aquatic organisms.

Nanoparticle	Species	EC ₅₀	Reference
TiO ₂	<i>Scenedesmus obliquus</i>	5,5 mg/L	[99]
CdS		21,3 mg/L	
ZnS		94,1 mg/L	
TiO ₂	<i>Heterosigma akashiwo</i>	141,7 mg/L	[100]
SMB3		252,8 mg/L	
SMB24		3,6 mg/L	
CeO ₂ NM-211		8,5 mg/L	
CeO ₂ NM-212		10,9 mg/L	
CeO ₂ NM-213		98,7 mg/L	
TiO ₂ NM-104	<i>Raphidocelis subcapitata</i>	126,9 mg/L	[101]
TiO ₂ NM-105		4,7 mg/L	
TiO ₂ Eu-doped		0,36 mg/L	
TiO ₂ Fe-doped		3,6 mg/L	
TiO ₂ No doped		0,06 mg/L	
	<i>S. acuminatus</i>	0,0385 mg/L	
AgNPs	<i>C. gracilis</i>	0,0243 mg/L	[102]
	<i>D. lumholtzi</i>	0,0576 mg/L	
TiO ₂	<i>Dunaliella tertiolecta</i>	24,10 mg/L	[103]
SiO ₂		187,77 mg/L	
CuO	<i>R. subcapitata</i>	12,77 mg/L	[104]
	<i>L. minor</i>	1,9 mg/L	
ZnO	<i>R. subcapitata</i>	4,86 mg/L	
TiO ₂	<i>R. subcapitata</i>	20 mg/L	
SiO ₂	<i>R. subcapitata</i>	20 mg/L	
ZnO	<i>Pseudokirchneriella subcapitata</i>	0,042 mg/L	[105]
TiO ₂		5,83 mg/L	
CuO		0,71 mg/L	
AgNPs	<i>P. tricornutum</i>	163,5 mg/L	[74]
	<i>P. tricornutum</i>	15,23 mg/L	
	<i>T. suecica</i>	11,69 mg/L	
TiO ₂	<i>I. galbana</i>	11,78 mg/L	[106]
	<i>S. obliquus</i>	11,76 mg/L	
	<i>P. subcapitata</i>	29,14 mg/L	
	<i>P. tricornutum</i>	4,41 mg/L	
	<i>T. suecica</i>	4,87 mg/L	
ZnO	<i>I. galbana</i>	1,82 mg/L	
	<i>S. obliquus</i>	6,42 mg/L	
	<i>P. subcapitata</i>	3,59 mg/L	
AgNPs	<i>Chlorella vulgaris</i>	33,63 mg/L	[77]
T-AgNP	<i>Raphidocelis subcapitata</i>	0,163 mg/L	[73]

C-AgNP		0,155 mg/L	
E-AgNP		0,243 mg/L	
P-AgNPs	<i>Chlorella vulgaris</i>	50 mg/L	[107]
N-AgNPs		70 mg/L	
<hr/>			
SMB3 (<i>Mesoporous silicon dioxide without metallic inclusions</i>)			
SMB24 (<i>Mesoporous silicon dioxide with metallic inclusions</i>)			
T-AgNP (tyrosine coating)			
C-AgNP (curcumin coating)			
E-AgNP (epigallocatechin gallate coating)			
P-AgNPs (positively charged, polyethylenimine - PEI - coating)			
<hr/>			
N-AgNPs (negatively charged, citrate coated – Cit)			
<hr/>			

If we observe, we can understand the different effective concentrations that have been experimented with for more than a decade in primary producers. However, it is true that most are in a range of milligrams per liter; this varies when synthetic nanoparticles have their physicochemical properties modified. For example, for TiO₂, it is observed that undoped TiO₂ has an EC₅₀ of 0.06 mg/L, indicating a high toxicity compared to other forms of TiO₂. On the other hand, doping with Fe (Fe-doped TiO₂) and Eu (Eu-doped TiO₂) affects the toxicity, with EC₅₀ values of 3.6 mg/L and 0.36 mg/L, respectively. This suggests that chemical modification may alter bioavailability and toxicity mechanisms, possibly by modifying the generation of reactive oxygen species (ROS).

Similarly, a variation in toxicity can be observed with Ag nanoparticles, which show considerably higher toxicity compared to TiO₂. For example, in *S. acuminatus*, *C. gracilis*, and *D. lumholtzi*, the EC₅₀ values are extremely low (0.0385 mg/L, 0.0243 mg/L, and 0.0576 mg/L, respectively), indicating high toxicity even at minimal concentrations. This is largely due to the release of silver ions, which can generate oxidative stress and affect essential cellular functions.

In addition, the toxicity of AgNPs varies according to the type of coating. Tyrosine-coated AgNPs (T-AgNP) show an EC₅₀ of 0.163 mg/L in *Raphidocelis subcapitata*, while those coated with curcumin (C-AgNP) have an even lower EC₅₀ (0.155 mg/L). Those coated with epigallocatechin gallate (E-AgNP) show a slight increase in their EC₅₀ (0.243 mg/L), suggesting that certain coatings may modulate toxicity by affecting the stability of nanoparticles and their interaction with the environment.

Another relevant aspect is the difference between the EC₅₀ values reported for different species. For example, *Scenedesmus obliquus* presents a relatively high toxicity for TiO₂ (5.5 mg/L), while *Dunaliella tertiolecta* shows an EC₅₀ value of 24.10 mg/L. These differences may be due to the physiology of each organism and its ability to tolerate or bioaccumulate nanoparticles.

A clear example is SiO₂ nanoparticles. These exhibit relatively low toxicity compared to TiO₂ and Ag, with EC₅₀ values in the range of tens to hundreds of milligrams per liter. However, the inclusion of metals in the SiO₂ structure significantly alters their toxicity.

Mesoporous silicon dioxide without metal inclusions (SMB3) shows an EC₅₀ of 252.8 mg/L, indicating low toxicity. However, when metal inclusions (SMB24) are incorporated, the EC₅₀ decreases drastically to 3.6 mg/L, significantly increasing toxicity. This suggests that metals present in the structure may modify the solubility of the nanoparticle or facilitate the generation of ROS, which increases cell damage in aquatic organisms.

This difference in toxicity highlights the importance of considering structural and chemical modifications in the risk assessment of nanoparticles, since the simple incorporation of metals can transform a relatively inert nanoparticle into a highly toxic one.

The data analyzed demonstrate that physicochemical modifications in nanoparticles can significantly alter their toxicity, from doping in TiO₂ to coatings on AgNPs or the inclusion of metals in SiO₂. These variations underscore the need for detailed characterization prior to their

environmental or biomedical application, as well as the urgency of strategies that reduce their negative impact. In its role, the OECD has proposed a more extensive list of representative nanoparticles, with the aim of better understanding the measurement methods, toxicology, and risk assessment associated with other nanostructured materials (ENMs) [98,108].

Current environmental challenges include a mismatch between rapid innovation in nanotechnology and current environmental regulations, especially in Latin America. This discrepancy has created regulatory gaps that hinder the effective management of the ecological risk associated with the use and release of synthetic NPs. In addition, nanoparticles experience complex and diverse physicochemical interactions in aquatic ecosystems, which makes it extremely difficult to assess their environmental impacts accurately. This generates uncertainty, complicating the implementation of adequate strategies for their prevention and mitigation. There are no internationally validated standardized methodologies to address this problem, which further limits the ability to assess the risks of the impact of nanoparticles in a consistent manner. In addition, nanomaterial synthesis processes are highly toxic, with persistent residues, sometimes with supernatant products that do not precipitate due to their size and are discharged into water tributaries. This widespread lack of friendly approaches represents a significant threat to the sustainability of aquatic ecosystems, not only because of the synthesis, but also because the massive use of commercial products using nanomaterials is on the rise, as industrial synthesis methods increasingly have greater control over size and shape, at an ever-increasing scale of production.

In this context, green synthesis, or the development of nanoparticles with lower toxicity and greater environmental compatibility, has been widely promoted as an innovative strategy, addressing regulatory challenges and fostering a more sustainable approach to nanotechnology. Nevertheless, this perspective should be viewed with caution, as the mere adoption of greener synthesis strategies does not per se guarantee a reduced environmental impact in the final disposal of the material. The sustainability of nanoparticles obtained by green synthesis can only be validated if their degradability, toxicity, and persistence in the environment are evaluated comprehensively, thus avoiding reductionist interpretations that could divert the focus from a holistic assessment of the life cycle of these materials.

6. Review of the Synthesis of Environmentally Friendly Nanoparticles

6.1. Principles and Fundamentals of Green Nanoparticle Synthesis

Green synthesis of nanoparticles has emerged as a viable alternative to reduce the environmental impact and toxicity of traditional methods, promoting the production of safer and more environmentally friendly materials [109,110]. This approach seeks to minimize the use of hazardous reagents and decrease waste generation by using reducing agents of biological origin instead, such as plant extracts, microorganisms, and biopolymers [111].

Conventional nanoparticle synthesis methods often require extreme temperature and pressure conditions, in addition to the use of potentially toxic precursor chemicals. In contrast, green synthesis is based on sustainable chemistry principles, employing biomolecules such as flavonoids, terpenoids, and polysaccharides to reduce and stabilize nanoparticles [112]. Several studies have shown that biogenic synthesis of metal nanoparticles and metal oxides yields functional materials applicable in critical areas such as biomedicine, catalysis, environmental remediation, and electronic device development, on the same level as nanoparticles produced through traditional synthesis methods [113,114]. In particular, plant extract-mediated biosynthesis has emerged as a highly efficient strategy, in which secondary metabolites present in plants play a dual role as reducing and stabilizing agents, favoring greater colloidal stability and optimizing reaction kinetics [115]. These advantages not only consolidate the feasibility of biogenic synthesis but also reinforce its potential as a sustainable approach without compromising the quality or functionality of the resulting nanoparticles. However, the main benefits of this strategy are not that natural extracts are the final

product but that the reactive means are the ones that replace traditional chemical methods and minimize contamination by chemical waste from the synthesis process [116].

6.2. Benefits and Applications of Green Synthesis in Industry

The implementation of green nanoparticle synthesis in industry has addressed multiple challenges associated with pollution and environmental safety. Among the main successful applications on an industrial scale are:

Antimicrobial coatings in medical devices: Silver nanoparticles synthesized by ecological methods have been implemented in bandages, catheters, and biomedical materials to prevent bacterial infections, reducing the use of antibiotics [117].

Ecological cosmetics and sunscreens: Zinc oxide nanoparticles obtained through green synthesis have been incorporated into cosmetic products such as safe UV filters, reducing the environmental impact of conventional sunscreens [118].

Ecological fertilizers and pesticides: Biogenic copper nanoparticles have been used in sustainable agriculture to improve crop protection without generating toxic residues [119].

Treatment of contaminated water: Iron nanoparticles synthesized from plant extracts have been applied in environmental remediation processes, removing organic pollutants and heavy metals from water bodies [120].

Other biosynthesis applications: Green tea (*Camellia sinensis*) leaf extract [121] has been used to synthesize AgNPs by biological reduction of silver ions, taking advantage of its phenolic compounds as natural reducing agents. Neem (*Azadirachta indica*) leaves for the synthesis of Ag, Au, and bimetallic Au@Ag nanoparticles [122] and also aloe vera [123], both have been widely studied due to their antioxidant and ecological metal reduction properties. Fresh leaf extracts of *Ocimum basilicum* L. (basil), *Origanum majorana* L. (marjoram), *Satureja mexicana* Briq. (mint), *Mentha piperita* L. (peppermint) and *Eucalyptus globulus* have also been used to synthesize AgNPs [124,125].

The synthesis of nanoparticles has been widely studied using isopolymers or natural biomolecules such as chitosan [126], cellulose [127], or natural proteins such as albumin or gelatin [128]. These are used as stabilizing and reducing agents, significantly reducing toxicity and environmental impact compared to traditional chemical methods. Filamentous fungi such as *Aspergillus niger* and *Penicillium chrysogenum* have also been used in the biosynthesis of silver nanoparticles. In addition, *Penicillium chrysogenum* has been used to synthesize CuNPs and CuO NPs, showing potential antimicrobial and environmental bioremediation applications [129].

On the other hand, the green synthesis approach not only focuses on the use of biological reduction or oxidation agents, but also on obtaining zinc oxide and titanium dioxide nanoparticles that are synthesized in aqueous routes at low temperature, avoiding the use of organic solvents and high temperatures, decreasing energy consumption and reducing toxic waste [130], in addition to microwave-assisted synthesis systems, because they allow obtaining nanoparticles under mild experimental conditions, in short reaction times with lower energy consumption and significant reduction in the use of toxic solvents [131].

These practices demonstrate good progress in the concept of green synthesis, emphasizing environmentally responsible, efficient and safer alternative processes in the industry.

6.3. Ecotoxicological Gaps in Sustainable Nanomaterial Innovation: Between Green Synthesis and Real Environmental Impact

Despite the above, the accumulation and interaction of nanocontaminants in the environment continues to be one of the main concerns in the scientific field. In this context, it is crucial to redirect the focus towards the final product - the nanoparticles - and not solely towards the synthesis process [132]. Adopting an environmentally responsible approach in the design of nanoproducts would allow moving towards extended producer responsibility, thus mitigating the potential ecotoxicological effects in situ. For this, it is essential that the green synthesis incorporates ecotoxicological assessments of the final product through representative analyses of the receiving ecosystems, which

would contribute to reducing the release of persistent chemical compounds in aquatic, terrestrial, and atmospheric environments.

Thus, as the synthesis of nanoparticles through ecological routes consolidates as an attractive alternative to conventional methods, several studies have reported advances in designing nanomaterials as products that promise natural and biocompatible residues with different environmental matrices. However, a detailed analysis of the literature shows that most of this research lacks ecotoxicological evaluations that support the environmental safety of the materials.

For example, Kulkarni et al. (2023) highlight the advantages of biogenic nanoparticles in biomedical applications, emphasizing their biocompatibility and low toxicity. However, the authors themselves acknowledge the lack of information on their degradation, distribution, and ecotoxicological effects in the receiving environment, which limits their application beyond the laboratory [133]. Similarly, Kucuk et al. (2025) propose nanoparticles obtained from plant extracts for sensors in biological and pharmaceutical environments, but omit to consider their potential impact once released into natural ecosystems [134].

Even in applications designed for environmental remediation, such as those proposed by Wu et al. (2025) with titanium nanoparticles to remove pesticides in water, no in situ studies assessing bioaccumulation or effects on aquatic organisms are reported [135]. Khatri et al. (2023) present green electrospinning as an innovative strategy to produce biodegradable nanofibers applicable in medicine, remediation, and sustainable packaging, but their analysis focuses on technical aspects of the process, without incorporating environmental toxicity assessments under real conditions [136].

Likewise, Keçili et al. (2025) develop sensors based on materials such as graphene oxides and carbon quantum dots obtained by environmentally friendly methods for detecting antibiotics in food. Although they stand out for their analytical efficiency and sustainability in their synthesis, the adverse effects that could result from their release into the environment are not addressed. In the biomedical field [137], Anwar et al. (2021) highlight the potential of biodegradable nanoparticles for the release of drugs and vaccines. However, they acknowledge that commonly employed polymers, such as PLGA or PEG, can generate acidic by-products for which the environmental toxicity has not been explored outside the clinical context [138].

These examples highlight a critical gap in the development of sustainable nanomaterials. Although significant progress has been made in terms of synthesis and functionality, there is still a lack of comprehensive environmental validation to ensure their ecological safety. Overall, the literature reflects a worrying trend: “green” nanomaterials are promoted as safe and sustainable without standardized studies that assess their toxicity under real environmental conditions. This omission limits the ability to anticipate ecological risks associated with their extensive use and underlines the urgent need to integrate representative ecotoxicological testing from the early stages of nanoparticle design.

6.4. Limitations and Challenges of Green Nanoparticle Synthesis

Despite its many advantages, green synthesis faces limitations that hinder its large-scale implementation, such as low reproducibility associated with variability in size and morphology of the obtained nanoparticles, poor industrial scalability due to unresolved technological barriers, and generally longer reaction times compared to conventional chemical methods [109,112,118].

Even though green synthesis proposes methodologies with lower environmental impact due to the advantages mentioned above, such as mild conditions in the synthesis processes, the use of biological agents or renewable resources, and/or the use of heating and self-reduction systems when microwaves are used, critical challenges remain. Due to their physicochemical nature, the generated nanoparticles can also transform, accumulate, and cause significant ecotoxic effects in aquatic ecosystems. This means that, although the production process may appear environmentally friendly and clean, it does not necessarily guarantee that the final product will be harmless. This paradox implies that the environmental approach should not be limited only to the stages of the synthesis process, but should also consider the entire life cycle of nanoparticles, including their interaction and

subsequent transformation in ecosystems. This raises the need to develop synthesis methods to obtain nanoparticles by ecological routes and by containing intrinsic properties that make them less toxic and environmentally compatible.

As authors, we have called the above effect “The Green Synthesis Paradox”, which refers to the phenomenon whereby nanoparticles sintered using methods considered ecological or green can still represent a high ecotoxicological risk once they are released into the environment. In other words, an environmentally friendly production process does not automatically guarantee ecological safety throughout the life cycle of the material, so it is necessary to comprehensively consider the stability, toxicity, and environmental behavior of nanoparticles and any nanomaterial from the early stages of their design to their final disposal. This paradox shows that initial or apparent sustainability does not necessarily guarantee long-term environmental harmlessness, underlining the need for comprehensive and preventive ecological impact assessments throughout the life cycle of any technological innovation. In this sense, it shows how good intentions and 'green' approaches in early stages may not be sufficient to ensure real and lasting sustainability, especially when unexpected negative effects are manifested after implementation or release into the environment.

6.5. Recommendations for the Nanoparticle Industry

Progress in nanoparticle synthesis has traditionally been focused on process optimization. However, in the current sustainability and environmental regulation context, shifting the focus towards the final nanoproduct is imperative. A key objective is to obtain nanoproducts with higher biodegradability and lower environmental persistence, which will mitigate the risk of bioaccumulation and long-term ecotoxicological effects. To achieve this transition, it is essential for the industry to adopt strategies that not only reduce the environmental impact of synthesis but also guarantee the safety and functionality of the final product throughout its life cycle.

To encourage the adoption of green synthesis in the production of nanoparticles, the following is recommended to the industry:

Optimizing the use of renewable sources: As mentioned in previous sections, integrating plant extracts, microorganisms, and biopolymers as reducing and stabilizing agents in the synthesis of nanoparticles ensures that these components not only minimize the process's toxicity but also positively influence the degradability of the final nanoproduct [139].

Establishing strict environmental regulations: Implementing regulations that not only evaluate the toxicity of nanoparticles in their synthesis stage, but also consider their persistence and effects in different environmental compartments before their commercialization [110]. Unlike other pollutants, such as microplastics, which are an environmental waste product of the accumulation and degradation of plastics used for decades, nanoparticles can have an eco-friendly vision from their inception, and that is a problem that can be avoided beforehand, considering all the possible effects exposed, so adopting a preventive vision before environmental regulations is imperative to achieve objectives established by the UNEP.

Promoting the scalability of green synthesis: Investing in technologies that enable large-scale production without compromising the sustainability of the final product, ensuring that the transition to green nanotechnology is technically, economically and environmentally feasible [113].

7. Conclusions

Current research on NPs in the environment has demonstrated their increasing presence in aquatic ecosystems. However, important knowledge gaps remain regarding their fate, transformations, and toxicological effects on primary producers.

This review critically evaluates the most recent findings on the interaction of NPs with aquatic systems, demonstrating that current ecotoxicological assessments may underestimate actual environmental risks due to simplified experimental conditions and inadequate regulatory frameworks. The influence of surface chemistry and aggregation dynamics further complicates toxicity predictions, making a paradigm shift in risk assessment methodologies imperative.

Despite growing awareness of these risks, significant knowledge gaps remain regarding chronic exposure effects, mixture toxicity, and specific responses among species at different trophic levels. Furthermore, although the use of green synthesis methods shows promise, it raises new concerns due to the absence of standardized protocols and effective regulation, which could introduce novel bioactive compounds with unknown ecotoxicological profiles.

In the face of these challenges, it is recommended that future research adopt integrative approaches that combine high-resolution physicochemical characterization, realistic exposure scenarios, and multi-biomarker assessments in environmentally relevant species. Similarly, it is urgent to develop a regulatory framework that considers the complexity of the behavior of nanoparticles as products, including their transformations, trophic transfer, and potential long-term impacts, to ensure the safe design, use, and disposal of nanomaterials in aquatic systems.

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