



## Review

# The Dual Role of Nanomaterials in the Environment

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**Abstract:** Unquestionably, nanoparticles (NPs) are present in all areas: food, medicine, electronics, industries, and others. The intense use of NPs has increased the concern about their fate in the environment and also the risk they may pose. On the other hand, the NPs are an important tool for environmental remediation and can be used to degrade and decrease of concentration different pollutants, such as toxic metals and also organic compounds. This scenario has motivated this review which aims to discuss the dual role of NPs in the environment by presenting their role as environmental remediators and also the possible effects on the environment such as the transformations that these particles can undergo which can increase or decrease their toxicity.

**Keywords:** nanoparticles, environmental remediation, toxicity of nanoparticles

## 1. Introduction

Nanoparticles (NPs) are particles with at least one dimension at 100 nm and due to the ability to synthesize and manipulate them, they are considered the building blocks of nanotechnology and have pharmaceutical, environmental, catalytic, electronic, and different other applications (Figure 1).<sup>1</sup> The wide application of nanotechnology is observed by the global economic impact of \$3 trillion in 2020, employing 6 million laborers worldwide.<sup>2</sup>

However, the use of nanomaterials (NMs) is not restricted to recent applications, their use dates back to ancient times. The Egyptians were using PbNPs more than 400 years ago for hair dye and also synthesized NPs to the mixture in glass and quartz in order to synthesize pigments.<sup>3</sup>

The sources of nanomaterials can be classified into (i) incidental NMs, when they are produced incidentally such as NPs from the combustion process; (ii) naturally produced which are found in plants and microorganisms; and (iii) engineered NMs which are manufactured with specific size and composition for different applications.<sup>3</sup> Due to the different sources of NPs, consequently, their fate is the environment. They are released into the biosphere intentionally or not occurring by the release of their components during use and by final disposal. The aquatic ecosystem is the main destination in the environment since it is the final fate of NPs introduced in natural systems. Soil, sediments, and air are also the destination of NPs in the environment as illustrated in Figure 2.<sup>4</sup>

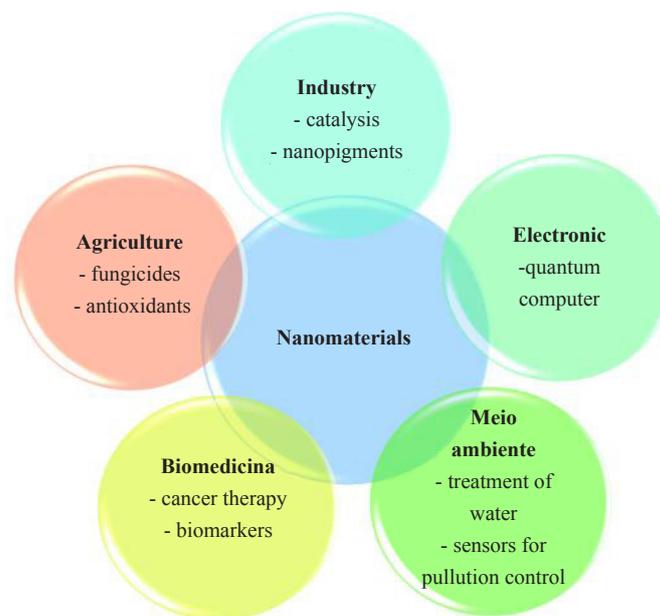


Figure 1. Application of nanomaterials

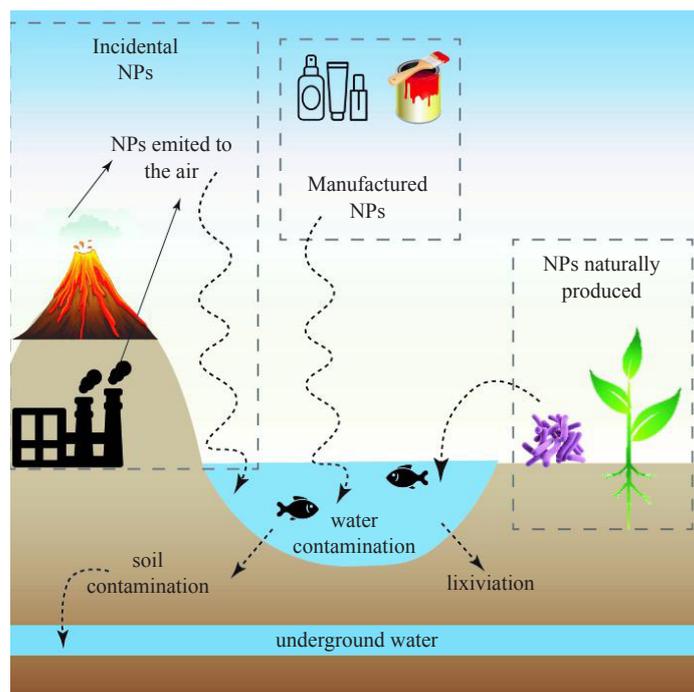


Figure 2. The environmental fate of nanoparticles

After several decades of intense research effort, a large number of synthesis approaches to NMs have been developed and they can be divided into the following categories: (1) physical methods which do not involve toxic chemicals and form a narrow size distribution of the synthesized AgNPs; (2) chemical methods which employ reagents in the synthesis and (3) biological methods which include fungi, plants, and bacteria in synthesis and it is considered a green methodology since it does not employ toxic reducing agents.<sup>5</sup>

Because of the facility to synthesize NPs, the possibility to control their size, composition, and their functionalization, and also due to their characteristics to have a large surface area and high reactivity, NPs are getting attention as potential adsorbents for different applications such as adsorbent for environmental contaminants as some studies have demonstrated.<sup>6-9</sup>

Although the NPs have been extensively used, a new concern emerged: the possible harmful effects on the environment since they can directly affect biota, change the bioavailability of toxins and/or nutrients, and also change environmental microstructures.<sup>10</sup>

Considering the wide range of applications of NMs and also their large consumption of them, it is important to take into account their role in the environment: are they effective in environmental decontamination? Can they represent a risk for living organisms? In this context, this review aims to present the two faces of the same coin of the NPs in the environment: their role as environmental remediator and their harmful effects on living organisms in the environment.

## 2. Nanoparticles as environmental remediator

Environmental pollution is undoubtedly one of the major concerns for society today and anthropic action accelerates this issue by increasing the concentration of different pollutants such as organometallic contaminants, inorganic metal ions, and organic compounds. Since the use of NPs may be able to offer solutions to overcome this issue, their application in the environment is increasing, as well as the number of studies about this theme (a search on google academic provided 16,900 results for 2022 for the keywords “nanoparticles remediation in the environment”).

### 2.1 NPs as remediators of toxic metal(oid)s in the environment

The sources of toxic metal(oid)s are wastewater from mines, smelters, sewage, battery industries, dyes, alloys, and electronic factories and the concern about these pollutants is because they do not degrade easily and persist longer in aqueous systems.<sup>11</sup> Considering this problem, NPs emerged as a promisor and efficient option for their remediation.

Arsenic is a toxic element that causes, in long-term exposure, liver cancer, skin, lung, kidney, and other noncancerous illnesses. Because of this, the World Health Organization (WHO) established the maximum concentration of As in drinking water as  $10 \mu\text{g L}^{-1}$  to avoid harmful effects on health.<sup>12</sup> In view of this fact, the use of different NPs has been studied to investigate their efficiency. The most used NPs for As removal is iron-based NPs, which can be magnetic NPs<sup>13,14</sup>, zero valent NPs<sup>15,16</sup>, oxides NPs<sup>17</sup>, and also iron NPs combined with different compounds<sup>18-20</sup>. Das et al. made a comparative study of different iron-based NPs for As remediation and they reported that Zero-valent Fe NPs removed arsenic better than the magnetite-based ones and graphene oxide-nano Fe<sup>0</sup> presented the best efficiency for As removal.<sup>21</sup> Not only iron-based NPs are effective for As remediation, but gold NPs (AuNPs) and ZnO decorated zirconia was synthesized by Hua in order to investigate the efficiency in As removal and it was reported that optimized AuNPs/ZnO-ZrO<sub>2</sub> exhibited the best adsorption capacity for arsenic at concentrations lower than  $8 \text{ mg L}^{-1}$ .<sup>22</sup> Recently, Guo et al. investigated the use of polymorphous magnesium oxide NPs (MgONPs) and achieved higher arsenate adsorption capacity ( $98 \text{ mg g}^{-1}$ ).<sup>23</sup> According to Stanicand Nujic<sup>12</sup> other different NPs such as TiO<sub>2</sub>-based NPs, CaO<sub>2</sub> NPs, Aluminum oxide NPs, Zirconium oxide NPs, AgNPs were investigated and were effective for As removal.

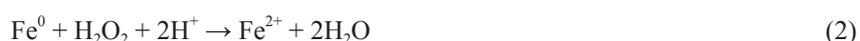
The most commonly used toxic metals are Zinc (Zn), Copper (Cu), Nickel (Ni), Lead (Pb), Cadmium (Cd), Chromium (Cr), and Mercury (Hg), which can cause harmful effects such as kidneys, bones, brain, pancreas, lungs, cardiovascular system, and liver damage, anemia, Alzheimer's disease, and Parkinson's disease and in high exposure carcinogenic effects are reported. In view of this fact, the regulatory agencies established the maximum concentration for these toxic metals in order to avoid environmental contamination.<sup>24</sup>

Toxic metals can also be remediated using NPs. Khooso and co-workers achieved high removal efficiencies of Cr(VI), Pb(II), and Cd(II) obtained 89%, 79%, and 87% respectively by using nickel ferrite NPs.<sup>12</sup> Almomani et al. synthesized eco-friendly and low-cost magnetic nanoparticles (MNPs) grafted on hyperbranched polyglycerol (HPG) for toxic metal removal from industrial effluent. These NPs achieved a maximum adsorption capacity of 0.700, 0.451, and  $0.790 \text{ mg mg}^{-1}$  for Cu, Ni, and Al, respectively, indicating good efficiency removal.<sup>25</sup> Recently, according to Song et al., sulfur-ferromagnetic nanoparticles (SFMNs) adsorbed spontaneously Pb and Cd with maximum adsorption capacities of Pb<sup>2+</sup> and Cd<sup>2+</sup> of 0.36 and 0.32 mmol/g, respectively.<sup>26</sup>

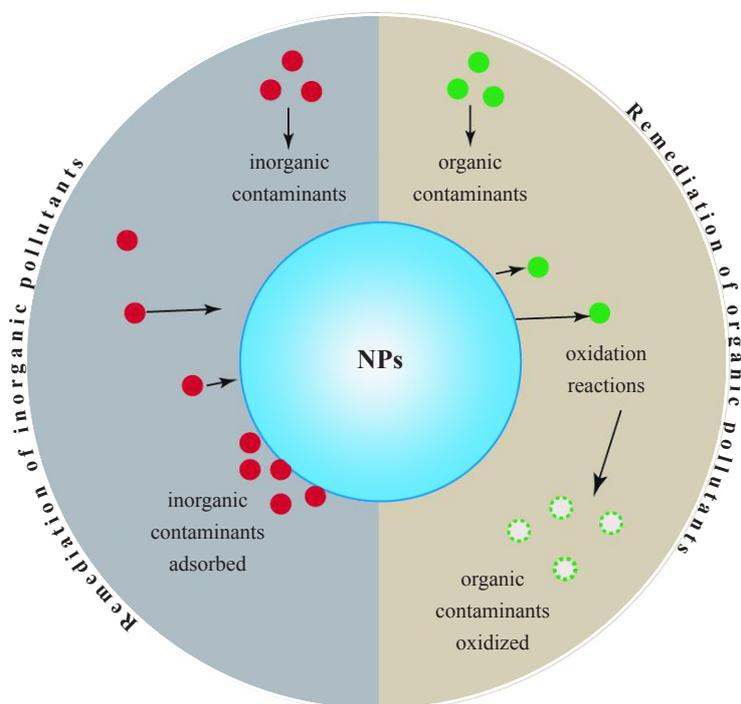
## 2.2 NPs as remediators of toxic organic pollutants in the environment

Organic pollutants can also cause serious harmful effects on the environment and health and their toxic effects range from neurotoxic to teratogenic, carcinogenic, and endocrine disruptive effects. Furthermore, the lipophilic properties of these pollutants favor their storage in the fat tissue of organisms leading to bioaccumulation through the food chain.<sup>27</sup> The typical organic contaminants include pesticides, organic dyes, detergents, phenolics, halogens, and aromatics from industrial wastes.<sup>28</sup>

Because of the characteristics of NPs, they offer a promising solution for the remediation of organic contaminants. One of the most used NPs for organic remediation is zero-valent iron nanoparticles (ZVINPs) as described by different authors<sup>29-33</sup>, since they are Fenton-like catalysts as shown in the following equations<sup>33</sup>:



Kheshtzar et al. synthesized ZVINPs with sizes ranging from 5 to 20 nm and reported that the concentration of methyl Orange decreased by more than 50% from the initial value after 2 h.<sup>31</sup>



**Figure 3.** Representation of possible mechanisms for remediation of organic and inorganic contaminants by NPs.

Different other NPs have been employed for the remediation of organic pollutants besides ZVINPs. Recently, Xiao et al. synthesized AgNPs immobilized on an amine-functionalized metal-organic framework (MOFs) (Ag/UiO-66-NH<sub>2</sub>)

as a robust catalyst for the remediation of 4-nitrophenol (4-NP) in water. Besides de good degradation efficiency, the authors reported an excellent outstanding cyclability (10 recycling runs), and observable long-term durability.<sup>34</sup> AgNPs, synthesized by a green method, also presented photocatalytic activity according to Singh. These AgNPs showed a potential degradation of 88% and 86% for reactive blue 19 (RB19) and reactive yellow 186 (RY186), respectively after 180 min.<sup>35</sup>

Due to the photochemical properties of TiO<sub>2</sub>, NPs of this oxide have been used for the degradation of organic compounds. The combination of TiO<sub>2</sub>NPs and Fe<sup>3+</sup> showed good efficiency in the removal of para-nitrophenol as reported by Sood et al., achieving a maximum degradation rate of 92% in 5h.<sup>35</sup> Vatanpour and co-workers associated TiO<sub>2</sub>NPs in the membrane to investigate the photocatalytic degradation of Reactive Orange 29 (RO29). At optimized conditions with the addition of urea and 450 °C, the efficiency of degradation of RO29 achieved 84%.<sup>36</sup>

The Figure 3 summarizes the possible mechanism for inorganic and organic remediation by the NPs.

### 3. Environmental nanotoxicity

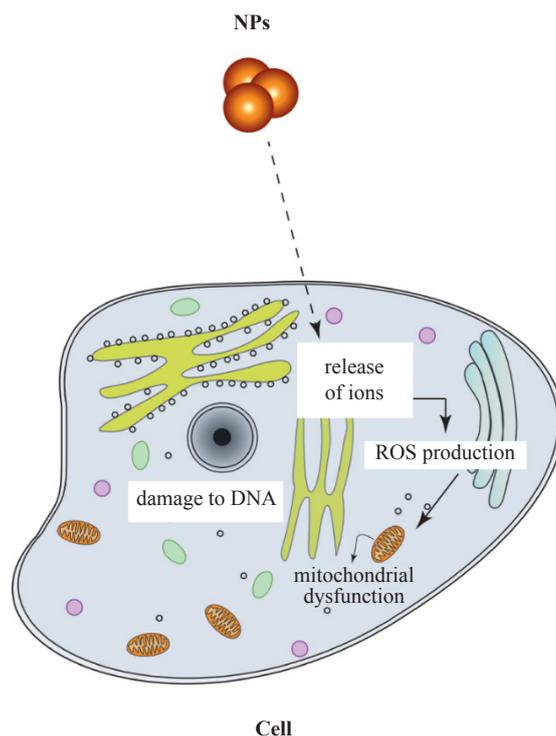
#### 3.1 Nanoparticles categories in the environment

The NPs can be present in different categories in the environment. As stated by Hansen and co-workers, NPs can be categorized according to their structures: bulk or free particles.<sup>37</sup> In the environment, the free particles can be presented suspended in the aquatic ecosystem, airborne, and also in solid phase (such as soil and sediments) suspended or on the surface. Furthermore, the NP also can be classified according to other characteristics: (1) chemical composition, (2) size, (3) shape, (4) crystal structure, (5) surface area, (6) surface chemistry, (7) surface charge, (8) solubility, and (9) adhesion, and all these characteristics can influence in their toxicity. Different studies<sup>38-41</sup> reported that the size of NPs has an important role in the toxicity: due to their ability to release ions, higher reactive surface, and also the possibility to penetrate cells, the smaller sizes are in general more toxic than larger ones. The surface charge also impacts the toxicity: Djurišić and co-workers reported that the toxicity of NPs can be related to the electrostatic interaction between the cell and NPs: negatively charged cell membranes attract the positively charged NPs favoring their attachment onto the cell surface and redox reactions on the surface of membrane.<sup>42</sup>

#### 3.2 Environmental nanotoxicity and effects of environmental transformation on the toxicity

The wide use of NPs meant that their final destination was the environment, which can pose potential risks to ecosystems. Many studies reported the toxicity of different NPs to the environment.<sup>43-46</sup> Souza and coworkers investigated the toxicity of silver NPs (AgNPs) to the aquatic plant *Lemna minor* and reported that many factors must be taken into accounts such as differences in size and concentration. In their study, it was observed that the lower AgNPs (30 nm) presented the most toxic response (equivalent to the death of the plants in a shorter period) and this toxic response is lower for larger AgNPs even for the highest concentrations (50 mg L<sup>-1</sup>).<sup>38</sup> Lopes et al. studied the toxicity of zinc NPs (ZnNPs) to *Daphnia magna* and they reported that ZnNPs with 30 nm affect the feeding activity, showing that NPs play an important role in the feeding inhibition of *D. magna*.<sup>47</sup> According to Rajput et al. copper, NPs (CuNPs) also presented an ecotoxicity effect on *Hordeum sativum* by affecting the germination rate, root and shoot lengths, and transpiration rate.<sup>47</sup>

Some mechanisms of toxicity of different NPs were proposed, but in most cases, the toxic effect is due to the formation of reactive oxygen species (ROS).<sup>40</sup> In the case of AgNPs, the most widely accepted hypothesis to explain the cytotoxic effect is called “Trojan horse mechanism” in which the AgNPs are internalized and Ag<sup>+</sup> ions are released into the cytoplasm. Ag<sup>+</sup> ions damage the lysosomes, depolarize the mitochondrial membrane and inactivate enzymes, and as a consequence, ROS concentration is increased harming the cell membrane and DNA.<sup>5</sup> Iron oxide NPs showed toxicity to the aquatic plant *Lemna minor* in different concentrations due to the formation of ROS (such as OH·) in a dose-dependent manner, i.e., the higher the concentration of iron oxide NPs, the higher the ROS production, which promotes the lipid peroxidation causing harmful effects to the lipid membrane.<sup>48</sup> Djurišić et al. also reported the toxic effect of TiO<sub>2</sub> and ZnO NPs related to the formation of ROS in bacteria and fungi.<sup>42</sup> Figure 4 illustrates the possible mechanism of NPs toxicity in cells.

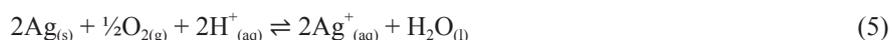


**Figure 4.** Schematic representation of the mechanism of toxicity of NPs

Although these studies have demonstrated the potential toxic risks for different NPs is important to take into account that once exposed to the natural environment, the physicochemical properties and toxicity of NPs can be changed due to some physical, chemical, or biological transformations that NPs can suffer which will define the behavior of NPs in environment.<sup>49,50</sup>

The chemical transformation covers dissolution, redox, and photochemical processes, physical transformation involves aggregation, agglomeration, sedimentation, and deposition; and biological transformation can be biomodification and biodegradation.<sup>50</sup>

The pH of the environment is a factor that contributes to the transformation of NPs. AgNPs, for example, can suffer dissolution under acid pH, according to the following equation:<sup>5</sup>



The dissolution of NPs in the environment release ions that can enhance ecotoxicity. The release of  $\text{Ag}^{+}$  ions from AgNPs is a problem since they interact with NADH dehydrogenase from the respiratory chain inducing a collapse of proton motive force due to their binding in the transport proteins.<sup>5</sup>

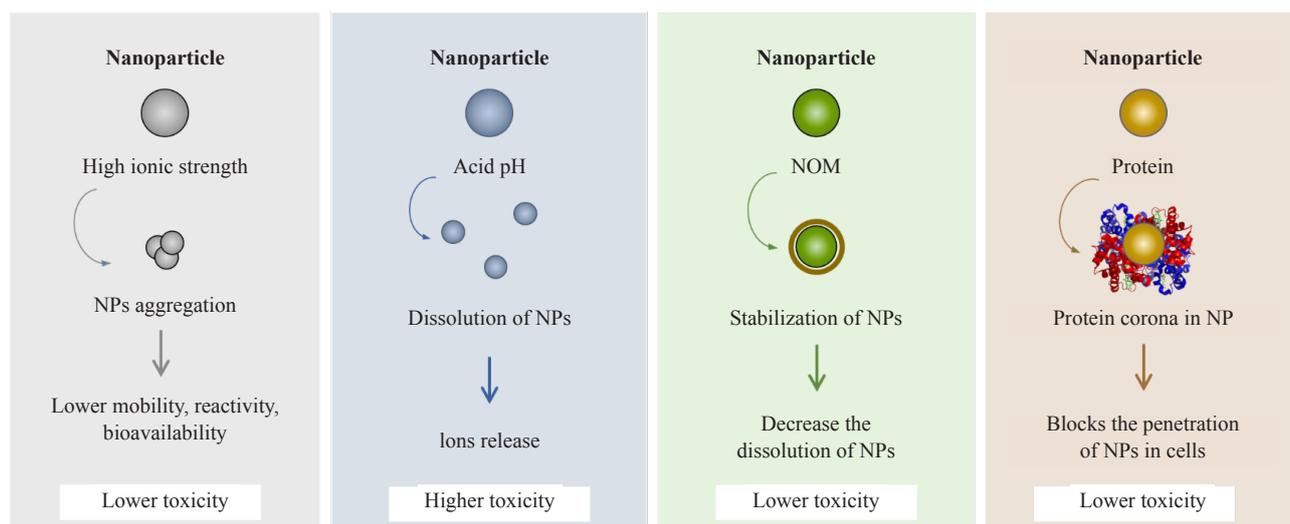
The aggregation of NPs is another transformation that occurs in the environment and this agglomeration can be classified as homo-agglomeration (interaction between NPs) or hetero-agglomeration (NPs interaction with organic and inorganic colloids). In terms of toxicity, the agglomerated NPs have less surface area which decreases their mobility, and reactivity, and consequently decreases their bioavailability.<sup>51</sup> Furthermore, Angel and co-workers reported the difference in toxicity of  $\text{Ag}^{+}$  ions, AgNPs (with the average size of 4.2 nm), and AgNPs aggregates micron-sized to different algae (*Pseudokirchneriella subcapitata*, *Phaeodactylum tricornutum*, *Ceriodaphnia dubia*) and toxicity was in the order micron Ag < AgNPs <  $\text{Ag}^{+}$  ions.<sup>52</sup>

The ionic strength and natural organic matter (NOM) also are involved in the transformation of NPs: high concentrations of ions such as  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  promote the aggregation of particles while NOM in the environment can be adsorbed in the NPs surface promoting steric and electric stabilization of NPs.<sup>5</sup> According to Angel and co-workers,

the NOM also reduced the toxicity of algae since NOM decreases the dissolution of NPs.<sup>52</sup>

Proteins also interact with NPs in biological mediums and also can transform them by alteration in their surface due to the adsorption of proteins. The protein coating is called protein corona (PC), which can enhance the agglomeration of NPs.<sup>5</sup> Furthermore, the PC layer can block the direct contact and penetration of NPs with the cell membrane which decreases the harmful effect on the cell membrane.<sup>53</sup>

The transformations and effects on toxicity are illustrated in Figure 5.



**Figure 5.** NPs transformation and effects on toxicity

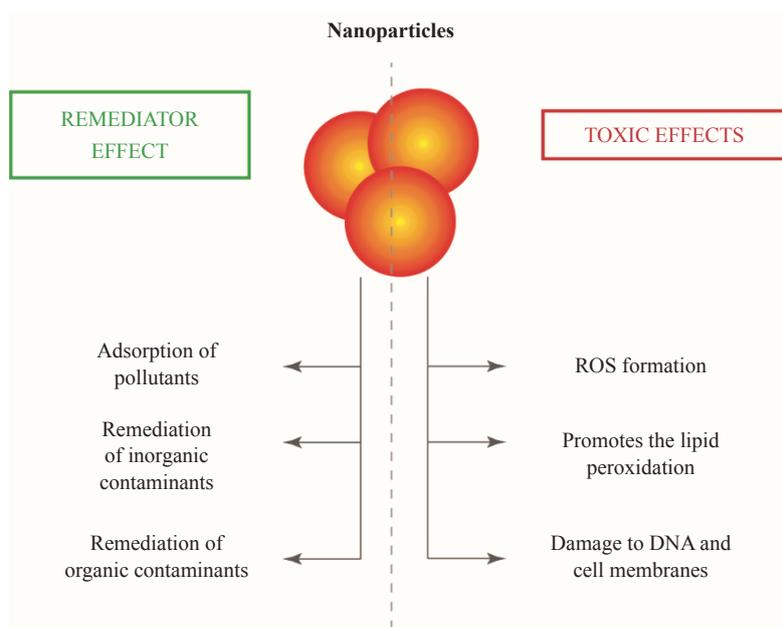
Considering that NPs can be transformed in the environment, their toxicity also can be changed as mentioned before. Besides the effects of proteins, NOM, and ionic strength, which all these factors decrease the toxicity of NPs in the environment, sulfidation is another factor that can decrease the toxicity of NPs. Levard and co-workers reported the decrease of AgNPs toxicity by sulfidation to different species such as aquatic and terrestrial eukaryotic organisms: *Danio rerio* (zebrafish), *Fundulus heteroclitus* (killifish), *Caenorhabditis elegans* (nematode worm) and aquatic plant *Lemna minuta*. The authors associate the toxicity reduction with the decrease of  $\text{Ag}^+$  release by the formation of  $\text{Ag}_2\text{S}$  with lower solubility.<sup>54</sup>

Surfactants also can decrease the NPs toxicity as reported by Oleszczuk and co-workers, which observed the reduction of toxicity of ZnONPs and  $\text{TiO}_2$ NPs to *D. magna*. by using hexadecyltrimethylammonium bromide (CTAB) and triton X-100 (TX100), respectively. The possible reduction of toxicity was related to the formation of NPs aggregates in the presence of surfactants inhibiting the availability of NPs to *D. magna*.<sup>55</sup>

## 4. Final considerations

As presented in this review, NPs has a wide range of applications including as environmental remediator. However, it is important to take into account that the same NPs which act as a remediator can cause harmful effects on the environment and health (Figure 6). An example is the use of iron-based NPs in environmental remediation.

Another relevant point is the synthesis of NPs, which can be a source of environmental contamination due to toxic compounds employed during the synthesis. This issue is getting more attention and many efforts are being made to synthesize green NPs.<sup>56</sup> These green NPs are synthesized employing non-toxic substances or they can be produced by biosynthesis using plants or microorganisms.



**Figure 6.** The dual role of NPs in the environment

Considering that NPs can have this dual role in the environment it is imperative to think about the rampant use of nanoparticles. Firstly, in the case of employing NPs for environmental remediation, it is necessary to develop a study of the risk of toxicity to answer these points: are these NPs toxic? Can this size cause toxic risks to the environment? Does the synthetic route employ toxic reagents? If these topics do not represent concern, the risks are minimized and the NPs can play the role of one of the most potential promisor compounds for environmental remediation.

## Conflict of interest

The author declares no competing financial interest.

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