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EFFECTS OF IRON OXIDE AND TITANIUM DIOXIDE NANOPARTICLES IN AQUATIC ECOSYSTEM

Chemical Science

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ABSTRACT

Recent years have seen an increase in the production of nanoparticles in commercial as well as industrial usage. The uniquely engineered nanoparticles provide a massive advantage to humanity but also come with a certain disadvantage. This has resulted in the exposure of these particles in dangerous amounts to the living organisms in the ecosystem. This paper discusses the effects of Iron oxide(Fe3O4) and Titanium Dioxide(TiO2) nanoparticles on aquatic ecosystems. This is a review of the effects on fauna, emphasising the effects on various body systems, such as the digestive, endocrine, and circulatory systems. It also reviews the flora of the aquatic environment based on past papers, journals and experiments conducted in labs using various model organisms such as algae and nematodes to determine the effects and variations of these particles on their anatomy. The review was done using an online database from Google Scholar and several other reputed websites.

KEYWORDS

Nanoparticles(NPs); pollutants; environment; nematode.

INTRODUCTION

Nanoparticles have existed for millions of years on Earth, and they have been used by humans for thousands of years. Materials made from these particles are called nanomaterials with nanoscale dimensions (less than 100 nm in size). These materials have a wide effect on daily life which is difficult to measure because of the lack of quantitative methods.

Estimates show that the production rate of nanoparticles has increased from 2000 tons in 2004 to more than 58,000 tons in 2020. Such exponential growth in production has led to increased exposure to humans and the environment as a whole. This paper discusses the effects of the interaction between industrial and natural production of nanoparticles and the environment, with special emphasis on the aquatic ecosystem.

Due to the advancement and industrialization in the last few decades, Engineered nanoparticles(ENPs) have been on the rise along with the natural NPs such as clays, minerals and several bacterial products. ENPs in aquatic ecosystems have different results in transformation processes which then control the subsequent impacts on other ecosystems. Understanding this relationship is vital to control and further classify the toxicity and impact of these ENPs. Various factors in play, such as characteristics of the nanoparticles and the environment, further help to determine the toxicity level.

Pollutants in aquatic environment

i) Iron Oxide (Fe2O3 and Fe3O4)

Iron oxide nanoparticles (NPs), with the main forms being magnetite (Fe3O4) and hematite (α-Fe2O3 and γ-Fe2O3), have attracted extensive interest for application because of their superparamagnetic properties and high catalytic abilities. Considerable research has been done to estimate the advantages of iron oxide nanoparticles in biomedical, environmental, and industries. However, they also present possible environmental hazards that were not known until recently.

1. The first study conducted in 2008 reported that pumpkin plants (*Cucurbita maxima*) grown in an aqueous medium containing iron oxide nanoparticles(Fe3O4) could absorb, translocate, and accumulate the NPs in their plant tissues.

2. In 2011, a study reported that iron oxide(Fe2O3) decreased the snout-vent length(SVL) of *Xenopus laevis* tadpoles at concentrations as low as 0.001 mg/L. The SVL increased to 1 mg/L and steadily decreased at higher concentrations(10-1000 mg/L) as it was found that the body length of these tadpoles had significantly reduced compared with the controls.

3. Another study conducted about Indian major carp, *Labeo rohita*, revealed that the Fe2O3 form of iron oxide NPs affected the haematological, biochemical, ionoregulatory, and enzymological parameters even at lower concentrations (1mg/L) upon a 96-hour static exposure. This suggested high potential toxicity of iron oxide NPs in aquatic ecosystems.

4. In 2011, a series of acute ecotoxicity tests were conducted, including phytotoxicity using several plant seeds, aquatic toxicity using *Daphnia magna*, and a bioluminescent test using the bioluminescent marine bacterium *Vibrio fischeri* as a model organism. The results showed that iron oxide (Fe3O4) NPs (at concentrations ≤ 0.67 mg/mL) exhibited low or no toxicity on plant seeds. However, *D. magna* and *V. fischeri* demonstrated extreme sensitivity to iron oxide NPs, which indicates the high toxicity of iron oxide NPs in aquatic environments.

5. Extending this research to aquatic animals and to further assess the toxicity of iron oxide NPs, an early life stage test(ELS) was conducted on zebrafish (*Danio rerio*) embryos and larvae as model organisms. The ELS test is one of the most widely used tools in environmental science research, useful for assessing the toxicity of chemicals that could affect the environment. At concentration levels of 0.1 mg/L to 10 mg/L of nFe2O3, it exhibited no toxicity to zebrafish embryos or larvae. Both 50 and 100 mg/L of nFe2O3 demonstrated toxicity, killing 75% and 45% of the zebrafish embryos/larvae at the end of the exposure. Different concentrations of this NP had different effects on the hatching rate of zebrafish. The nFe2O3-treated embryos showed a dose-dependent effect on the hatching rates under laboratory conditions. Compared with the control group, 0.1–5 mg/L of nFe2O3 did not significantly affect the hatching rate during the 7-day exposure time. However, ≥ 10 mg/L of nFe2O3 displayed significant embryo-hatching delay and toxicity.

ii) Titanium dioxide (TiO2)

Another type of nanoparticle whose use has become prevalent is titanium dioxide. Their use in consumer products has expanded rapidly in the last decade. The release of such NPs from application sites to aquatic environments has many possible risks due to their potential toxicity. The cluster of nano-TiO2 plays an important role in the environmental effects because various characteristics such as size and shape determine the magnitude of any potential toxic effect. The nanoparticles are different in terms of physicochemical properties from their bulk counterparts. Research conducted on how it affects human health revealed that titania has also been linked to Crohn's disease through gastrointestinal intake, and it has been classified as a possible carcinogen. In the environment, less is known about how TiO2-NPs affect organisms, although it has been shown to inhibit the growth of algae and plants and bioaccumulate in Daphnia magna(plant seeds).

1. Algae:

A study on green algae (Desmodesmus subspicatus) was conducted using 25 nm and 100 nm TiO2 particles. Experiments showed that the size and crystalline form determined the toxicity. Smaller particles were found to be more toxic to D. subspicatus (72 hr EC50 = 44 mg L−1) than larger particles (72 hr EC50 >50 mg L−1). A Study was conducted on another species of algae (Pseudokirchneriella subcapitata) using nano-tiO2(25-70 nm) and bulk TiO2. This revealed similar results indicating smaller particles to be more toxic than the bulk ones. Tests like phase contrast microscopy and red fluorescence confirmed the visibility of algal cells. In the case of NPs, larger groups entrapped almost all algal cells. When bulk TiO2 was used in the culture, free algal cells, in addition to cells trapped during the experiment with small TiO2 aggregates, were observed. The grouping of nano-TiO2 reduced the availability of light entrapped to algal cells, which restricted its growth. Further revelations were that adsorption of P. subcapitata onto surfaces of nano-TiO2 carried 2.3 times their weight in TiO2 particles. Maximum adsorption took place in the solution of PH 5.

2. Nematode:

experiments for determining the level of toxicity due to Ti-O2 particles were carried out for nematodes (Caenorhabditis elegans) with Escherichia coli (E.coli) as a food source. As for the bulk Ti-O2 particles (d=285 nm), no toxicity was demonstrated till the concentration was >95.9 mg/L. In contrast, nano Ti-O2 showed toxic effects at just 47.9 mg/L. However, the toxic effects of nano Ti-O2 supernatant at 167.7 mg/L were not very different from their respective controls. Furthermore, the lab tests revealed that exposure to concentration levels of 47.9, 95.9, and 167.8 mg/L of nano-TiO2 gave fewer offspring per worm in contrast to exposure to bulk Ti-O2. Furthermore, tests at Tio2 concentration levels of 20 mg/L and 25 mg/L, representing predicted environmentally relevant concentrations and food concentrations, can be hazardous to work with mutations in sensitive genes using nematodes.

- For exposure to 25mg/L for 24 hours, nematodes had the functioning of both potential primary and secondary targeted organs affected by mutations of these genes. In mutant worms exposed to these particles, mutations of these genes resulted in identical expression patterns of the genes needed for oxidative stress, suggesting that their mechanisms for forming the sensitive characteristic are similar.
- In sod-2, sod-3, mtl-2, and hsp-16.48 mutants, acute exposure to 20 mg/L of TiO2-NPs for 24 hours and 25 mg/L of TiO2-NPs for 0.48 hours or 5.71 hours did not affect the functions of both potential primary and secondary targeted organs. As a result, our findings imply that acute exposure to TiO2-NPs for a short period of time at expected environmental relevant quantities or concentrations similar to those in food is generally safe for nematodes with particular sensitive gene mutations.

3.Rainbow trout:

Recent research and studies about titanium dioxide nanoparticles have shown that these particles present in water or diet of aquatic animals (fishes) can be taken up by them, which accumulate in the internal organs, including the liver. How it affects the liver is unknown. The concern about limited data available about the ecotoxicity of titanium dioxide nanoparticles was raised by Mammalian and *in vitro* studies. A semi-static test system was put in place to expose rainbow trout to either a freshwater control, 0.1, 0.5, or 1.0 mg/L TiO2 NPs for up to 14 days. Exposure to this system showcases some conclusive results. The toxicity of TiO2 NPs showcased-

- Gill pathologies including oedema and thickening of the lamellae
- There is a statistically significant decrease in Na+ and K+ ATPase activity in the gills and intestines.
- A falling trend in the level of enzyme activity in the brain.
- No major haematological or blood disturbances were observed regarding red and white blood cell counts, haematocrit values, whole blood haemoglobin, and plasma Na+ or K+ concentrations.
- Tissue metal levels (Na+, K+, Ca2+ and Mn) were generally unaffected. Exposure to concentration-dependent changes in tissues concerning Cu and Zn levels was observed in the brain.
- Liver cells exposed to TiO2 NPs showed minor fatty change and lipidosis, and some hepatocytes showed condensed nuclear bodies (apoptotic bodies). Fish probably ingested water containing TiO2 NPs during exposure (stress-induced drinking) which may have resulted in some areas of erosion on the intestinal epithelium.

The bottom line is that titanium dioxide nanoparticles are neither a major ionoregulatory toxicant nor a haemolytic toxicant at the concentration and exposure times used. However, respiratory and digestive distress is a concern, along with sub-lethal toxicity, which involves oxidative stress, organ pathologies, and the induction of antioxidant defences, such as glutathione.

CONCLUSION

Researching about this paper, we understand that there is a need to quantify and estimate the amount of nanoparticles released in the environment before we get a proper grasp on its effects. Two main methods for quantification of Fe3O4 and TiO2 NPs are through variations of electron microscopy- TEM(transmission electron microscopy) and EDX(energy dispersive x-ray spectroscopy). In this method, NPs are exposed to an electric field which causes particles of similar polarity to reach an electrode, whereas the remaining particles are deposited on the walls of ESP. Uncharged particles are not affected by the electric field. For this method to be effective, only unipolar-ly charged particles should be introduced in the ESP. As more studies are held on organisms, the effects seem to be far more prevalent and could have a big role in decimating aquatic species in the coming years.

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