



Nanoparticles in wastewaters: Hazards, fate and remediation



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ABSTRACT

The increasing use of nanoparticles will inevitably result in their release into the aquatic environment and thereby cause the exposure of living organisms. Due to their larger surface area, high ratio of particle number to mass, enhanced chemical reactivity, and potential for easier penetration of cells, nanoparticles may be more toxic than larger particles of the same substance. Some researchers have been showing some relations between nanoparticles and certain diseases. However, the doses, surface shapes, material toxicity and persistence of nanoparticles may all be factors in determining harmful biological effects. In order to better evaluate their risks, potential exposure route of nanoparticles has to be taken into consideration as well. Finally, a brief summary of techniques for nanoparticle removal in waters and wastewaters is presented, but it seems that no treatment can absolutely protect the public from exposure to a large-scale dissemination of nanomaterials.

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1. Introduction

Particles in the nano-sized range, for example soot and organic colloids, have been present on earth for millions of years. Recently, however, nanoparticles have attracted a lot of attention because of our increasing ability to synthesize and manipulate such materials [1]. The Woodrow Wilson Database listed an inventory of 1317 consumer products containing engineered nanoparticles (March 2011) currently on the market, which has grown by nearly 521% since March 2006. The largest product category is health and fitness (including cosmetics and sunscreens), with a total of 738 products, followed by home and garden (209), automotive (126), food and beverage (105).

Commercially important nanoparticles include metal oxide nanopowders, such as silica (SiO₂), titania (TiO₂), alumina (Al₂O₃) or iron oxides (Fe₃O₄, Fe₂O₃), and other nanoparticle materials like semiconductors metals or alloys. Besides these, molecules of special interest that fall within the range of nanotechnology are fullerenes and dendrimers (tree-like molecules with defined cavities), which may find application for example as drug carriers in medicine [2].

Nanowires, nanotubes or nanorods as linear nanostructures can be generated from different material classes. As one of the most promising

linear nanostructures, carbon nanotubes can be expected to find a broad field of application in nanoelectronics, catalysis, design of novel gas sensors, enzymatic biosensors, immunosensors and DNA probes, and also as fillers for nanocomposite materials with special properties [3–5].

Nanolayers are another important topic within the range of nanotechnology. Through nanoscale engineering of surfaces and layers, a vast range of functionalities and new physical effects (e.g. magnetoelectronic or optical) can be achieved. Moreover, the surfaces and layers of nanoscale are often needed to optimize the interfaces between different material classes (e.g. semiconductors on silicon wafers), and to have the desired special properties [3]. In addition, nanolayers can also be coated to fight erosion, corrosion in metals.

Nanoporous (usually called mesoporous) materials with the pore-size in the nanometer range have a broad range of industrial applications due to their outstanding properties [2]. Their large surface area which generally certifies large quantities of active centers, as well as their narrow pore size distribution makes mesoporous materials widely used in shape-selective catalysis, membrane filtration and energy storage [6–9].

The reasons that make these nanomaterials so different and so intriguing may be as follows. The extremely small feature size at the nanoscale is of the same scale as the critical size for physical phenomena. Fundamental electronic, magnetic, optical, chemical, and biological processes are different at this level. Surfaces and interfaces are also important in explaining nanomaterial behavior. In bulk materials, only a relatively small percentage of atoms will be at or near a surface or interface (like a crystal grain boundary). In nanomaterials,

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the small feature size ensures that many atoms, sometimes half or more in some cases (size < 5 nm), will be near interfaces. Surface properties such as energy levels, electronic structure, and reactivity can be quite different from bulk ones, and then give rise to quite different material properties [10].

Such exceptional properties of nanomaterials might not only favor their applications, but also cause their novel toxicity. In fact, the reactive surface of ultra-small particles can result in the direct generation of harmful oxyradicals (ROS): these can cause cell injury by attacking DNA, proteins and membranes [11–13]. Furthermore, the ability of these particles to penetrate the body and cells (e.g., via fluid-phase endocytosis and caveolae) provides potential routes for the delivery of nanoparticle-associated toxic pollutants to sites where they would not normally go [13]. Nanoparticles can then behave like a vector on which hazardous compounds are concentrated. It is worth knowing that medicinal applications of nanoparticles benefit the same property to deliver drugs to diseased cells in order to improve the bioavailability of a drug; but biodistribution of some nanoparticles may not be known exactly, so they may accumulate in the body over time, leading to potential dangers.

Summarily, as the nanotechnology industries start to come on line with larger scale production, it is inevitable that nanoscale products and by-products will enter the aquatic environment [13,14], since industrial products and wastes tend to end up in waterways (e.g., drainage ditches, rivers, lakes, estuaries and coastal waters) despite safeguards. Accidental spillages or permitted release of industrial effluents in aquatic systems could lead to direct exposure to nanoparticles for humans via inhalation of water aerosols, skin contact and direct ingestion of contaminated drinking water or particles adsorbed on vegetables or other foodstuffs [14]. More indirect exposure could arise from ingestion of organisms such as fish and shellfish (i.e. mollusks and crustaceans) as a part of the human diet.

2. The potential hazards of nanoparticles

Although the risks of nano- or ultrafine particles seem to be plausible, hazards relevant to humans and other mammals have been studied. Much of this research has been done with experimental mammals, but animal experiments cannot be the only basis for precise quantitative estimates regarding actual risk for humans because of the differences between experimental animals and humans that make extrapolations uncertain [15,16].

2.1. Risks of inhaled nanoparticles

The high deposition efficiency of inhaled nanoparticles in the pulmonary region increases in people with asthma or chronic obstructive lung disease [17]. Inflammation of the lung is often seen as a response to the inhalation of nanoparticles as well. In addition, exposure to carbon nanotubes can give rise to the formation of interstitial granulomas in animal experiments [15].

2.1.1. Metal oxide nanoparticles (TiO₂ and SiO₂)

In vivo pulmonary toxicity studies in rats, Warheit et al. [18] demonstrated that ultrafine TiO₂ had low inflammatory potential and lung tissue toxicity. Studying the effect of ultrafine carbon and TiO₂ particles ranging from 12 to 220 nm, Möller et al. [19] saw evidence for impaired defense ability in the rat lung. Renwick et al. [20] showed that ultra fine TiO₂ and carbon black particles impaired phagocytosis by alveolar macrophages more strongly than fine particles of the same materials. There was also evidence that nanoparticles might act as an adjuvant for allergic sensitization [15].

Moreover, submicron and nanoscale amorphous silica spheres and rods as model materials were synthesized by Brown et al. [21] for shape-driven toxicological experimentation. Their results showed that

shape-driven agglomeration may be a factor in the pathogenesis of particle-induced lung disease.

2.1.2. Carbon nanotubes and carbon nanoparticles

In the studies of Möller et al. [19] and Renwick et al. [20] in 2.1.1, ultrafine carbon particles have been proved to be toxic to some extent. Deckers et al. [22] further compared the toxic effect of aluminum oxide, titanium oxide nanoparticles to multi-walled carbon nanotubes. Carbon nanotubes were more toxic than metal oxide nanoparticles. They also demonstrated significant difference in biological response as different functions of nanomaterials. Prevailing theories suggested that acicular or fiber-like particles induce enhanced toxicity over isotropic materials through hindrance of phagocyte-mediated clearance mechanisms and through the aggravation of proximal cells via mechanical interactions. Moreover, Lundborg et al. [23,24] found that rat and human alveolar macrophages had impaired function due to aggregates of ultrafine carbon particles, which may be linked to increased infection risk and decreased protection of sensitive lung cells.

2.1.3. Quantum dots (QDs)

Recently, researchers are more and more focused on the influence of size, crystalline structure, and chemical composition of nanoparticles in the investigation of their toxicities. Clift et al. [25] studied the uptake, kinetics and cellular distribution of different surface coated QDs and demonstrated that surface coating has a significant influence on the mode of nanoparticle interaction with cells, as well as the subsequent consequences of the interaction.

2.2. Risks of contacted nanoparticles

2.2.1. Metal oxide nanoparticles (TiO₂ and ZnO)

Apart from exposure by inhalation, dermal penetration of nanoparticles is a matter of interest for humans. The application of TiO₂ and ZnO nanoparticles in sunscreens, currently the most important use of ultrafine metal oxide particles in personal care products highlights the dermal penetration of nanoparticles. TiO₂ and ZnO particles sized ~15 to 50 nm can be photocatalytically active on exposure to sunlight [15]. According to a study of Dunford et al. [26], this also holds for coated particles that are actually applied in sunscreens.

Menzel et al. [27] demonstrated in experiments that TiO₂ nanoparticles can penetrate pig skin through the stratum corneum into the underlying stratum granulosum within the first 8 h after application. And studies with ZnO suggest that ZnO nanoparticles may penetrate deep into the rat and rabbit skin [26]. ZnO and TiO₂ nanoparticles may also become involved in damaging nucleic acids and other cell components by photocatalytic reactions on exposure to sunlight due to penetration into the stratum granulosum [26]. TiO₂ nanoparticles may furthermore become involved in causing allergic reactions [15,27].

Wu et al. [28] evaluated the potential toxicity of TiO₂ nanoparticles in hairless mice and porcine skin. Their results indicate that TiO₂ nanoparticles can penetrate through the skin, reach different tissues and induce diverse pathological lesions in several major organs. Topical application of nano-TiO₂ for a prolonged period can induce dermal toxicity, most likely associated with free radical generation, oxidative stress, and collagen depletion that can lead to skin aging.

2.2.2. Carbon nanotube

Dermal exposure of humans may also be important in handling nanoparticles in laboratories or industries. Glove deposits of single-walled carbon nanotube during handling were estimated by Maynard et al. [29]. They showed that substantial deposits on skin or gloves could originate in handling carbon nanotubes, and presented evidence that (unrefined) carbon nanotubes may cause dermal toxicity due to oxidative stress [15].

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