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Review Paper

Engineered Nanoparticles (ENPs) in the Aquatic Environment: A Review

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Abstract

Environmental behavior of engineered nanoparticles (ENPs) is an emerging area of research. Due to the widespread utilization and huge amount of production, ENPs will inevitably end up into the environment such as water and soil through waste disposal and unintentional release. So they are vital environmental concerns because they are more toxic and chemically active per unit mass than their bulk counterparts. But environmental fate and behavior of ENPs presents a crucial obstacle in developing a holistic view of the fate and transport of nanomaterials within the environment and therefore environmental exposure. With respect to the aquatic environment, most nanomaterials interact with natural organic matter (NOM) and other materials found in the aqutic systems that influence the fate and transport of ENPs in water and may also be of significance for their effects on biological systems. This review addresses the better understanding of environmental behavior and fate of ENPs in aquatic environments and their physical and chemical characteristics with toxicity factors.

Keywords: Engineered Nanoparticles, Pathways, Toxicity, Behavior, Fate, Aquatic environment.

Introduction

In recent decades engineered nanoparticles (ENPs) have been produced by nano-biotech companies in large quantities to produce inventive products in different fields, including manufacturing, electronics, agriculture, pharmaceuticals, biomedicine and cosmetics[1]. Nanoparticles used in these products may reasonably be expected to end up in soil, avian, and aquatic environments either during their production processes, product uses or disposal[2]. Nanoparticles have unique physical and chemical characteristics. These are because of their extremely small size, large surface area to volume ratio and their size dependent optical properties[3]. The dramatic increase in worldwide production and application of engineered nanomaterials is due to novel and useful material properties that become evident at the nanoscale[4]. Nanoparticles can be found as naturally occurring chemicals in the environment and they are being used intentionally for centuries, the systematic design and engineering of nanoscale materials has only occurred in the last few decades. ENPs are composed of a different variety of materials including metals. They have monodisperse sizes and shapes with a combination of synthetic surface molecules. They are much different from other naturally occurring nanomaterials. These different factors make the ENPs as a particular interest to find out their impacts on the health of ecosystem in the growing field of nanotoxicology[5]. ENPs which are released in aquatic environment inescapably go through numerous water chemistry such as pH, ionic strength, and natural organic matter (NOM), and their fate and transport are highly dependent on the particular environmental conditions[6,7]. Although ENPs have many promising applications and the dominating optimistic projections in technological development, there is chance of environmental damage and impacts on human health through the exposure of some ENPs[8]. Emerging concern over the imminent inadvertent, harmful consequences of ENPs in the environment have generated new research initiatives focused on better understanding of the ecological consequences of ENPs[9].

Engineered Nanoparticles (ENPs) and their Toxicity Factors

Nanomaterials (NM) have one dimension less than 100 nm, whereas nano-objects have two dimensions less than 100 nm, while nanoparticles have three dimensions of less than 100 nm[10]. Mainly there are two types of nanoparticles (NPs), naturally occurring NPs which are produced naturally in volcanoes, forest fires or as combustion by-products and engineered nanoparticles (ENPs) which are deliberately developed to be used in application. These ENPs include carbon black, fumed silica, titanium dioxide (TiO_2), iron oxide (FOx), quantum dots (QDs), fullerenes, carbon nanotubes (CNTs) etc[8]. Now a day's many metal based nanoparticles are being use in consumer products[11]. Metal nanoparticles (MNPs) possess special catalytic properties[12]. Nanoparticles particularly which are less than 20 to 30 nm in size possess this property. This generally produces an excess of energy at the particle surface that makes them highly reactive and thermodynamically unstable[13]. One of the main important determinants of reactivity, transport, and toxicity of nanoparticles is size. The surface to volume ratio of NPs increases exponentially with their decreasing size which makes them more toxic and reactive. In addition, penetration ability into plants and animal tissues of

ENPs increase with their decreasing size[14]. During their dissolution surface area of ENPs might be important; release of metals could be quicker from smaller ENPs[15]. Shape of ENPs is also responsible for their harmful impacts. Shape and charge on NPs can accelerate their translocation process through cell membranes up to 60 orders of magnitude[16]. One major characteristic of NPs is their extremely high reactivity compared to other materials which led them to be used for catalysis and this unusual reactivity makes NPs highly toxic[14,17]. Agglomeration ability of NPs in solutions is another very important factor. Agglomeration rate depends on different variables like shape, size; concentration, charge, temperature, and type of NPs. Agglomerated NPs behave in a different way than the individual dispersed particles mainly because of surface properties changes[14]. Toxicity of NPs influenced by aggregation since this property largely affects cellular uptake. Aggregation rate depends on ionic strength; aggregation rate and extent increase with increasing ionic strength. Increasing bioavailability and toxicity from algae, phytoplankton or detrital feeders might result from the self aggregation of ENPs into greater masses and their further incorporation into aggregate materials[1].

In the presence of natural organic matter (NOM), nanoparticles are stabilized and aggregation is limited at realistic NOM concentrations (1–30 mg of carbon/L). On the other hand when NOM concentration is higher flocculation is observed[18-20]. NOM is a ubiquitous in soil and water environments. They are poorly defined and mainly consist of high molecular weight humic and fulvic acids resulting from plant and animal material decomposition that readily sorbs onto the highly reactive surface of nanomaterials[21]. In addition to organic molecules such as NOM, proteins and carbohydrates, there are other toxic metal ions that are able to absorb onto the ENPs surface. These potentially increase the transport, toxicity and bioavailability of toxic metals in the aquatic environment[22].

Behavior and Fate of ENPs in Aquatic Environment

There are different entries points through which ENPs can enter into the environment. There are many direct applications of ENPs to an environmental compartment either intentionally or through unintentional product degradation, wastewater treatment plant (WWTP) effluent and WWTP sludge[23,24]. ENPs can enter the environment directly through intentional environmental additions or unintentional spills; as the waste byproducts of ENP manufacture; through the liquid waste stream as they are leached from industrial and consumer products; as constituents of solid wastes from biosolids; and through landfill leaching of disposed products or biosolids[9].

Figure-1 shows the possible pathways of environmental exposure to ENPs. The environment may be exposed to ENPs during all stages of their life-cycles: raw material production, transport and storage, industrial use, consumer use, waste disposal[8]. Industrial emissions from raw material production and product manufacturing processes possess the threat of environmental exposure of ENPs. Leakages from ENPs containing products and accidental release during transportation are important sources of exposure. Ultimately, exposure to human caused by using ENPs containing products and disposal as well as recycling activities of such products can aggravate the environmental exposure to ENPs.

The processes that influence NM behavior in the environment include NM surface coating changes, oxidation, dissolution, sulfidation, advection, diffusion, hetero and homoaggregation or disaggregation and sedimentation/resuspension[25]. Generally during transport processes the characteristics and structures of ENPs remain unchanged. Mainly local chemistry of the environment defines the transformation and bioavailability of ENPs. Different transformation reactions may occur either inside the organisms or in the presence of organisms[1,26]. Due to the growing use of consumer products (e.g., sunscreens, cosmetics) the aquatic environment is at more risk to be contaminated with the ENPs[27]. Risk assessment is an important way to find out the predicted environmental concentrations (PECs) of nanoparticles and a number of assessment works have been made by using the current knowledge of NPs transformation and fate to calculate PECs[23,28,29]. Table-1 shows the PECs of highly produced and used NPs in major pathways in the environment.

There are different factors which determine the fate of ENPs in aquatic environment. These factors include aqueous solubility, reactivity of the ENPs with the chemical environment and their interaction with certain biological processes. Settlement of ENPs is generally slow than larger particles of the same material to the bottom due to their lower mass[30]. ENPs could be removed from the water column if they go through the biotic and abiotic degradation in the aquatic environment. Among several abiotic degradation processes, hydrolysis and photocatalysis are of great importance for ENPs. ENPs are exposed to sunlight near to the surface. Photoreactions induced by sunlight can contribute to the removal of some ENPs or may alter their chemical properties[8,31]. In aqueous solution transformation of NPs is mainly favored by their ionic strength and natural organic matter (NOM) present in the aquatic system. In most of the nanomaterials aggregation rate and extent increases with increasing ionic strength and the ionic species are more reactive in aggregation process[5].

It is important to have better understanding of aggregation process as it is significant for characterizing transport of NPs through different environmental pathways. In aggregation dynamics role of NOM is very important. Sorption of NOM onto the surface of nanoparticles may help transformations beyond aggregation. These may include increasing NP size through the reduction of ionic metals at the surface of NP[32].

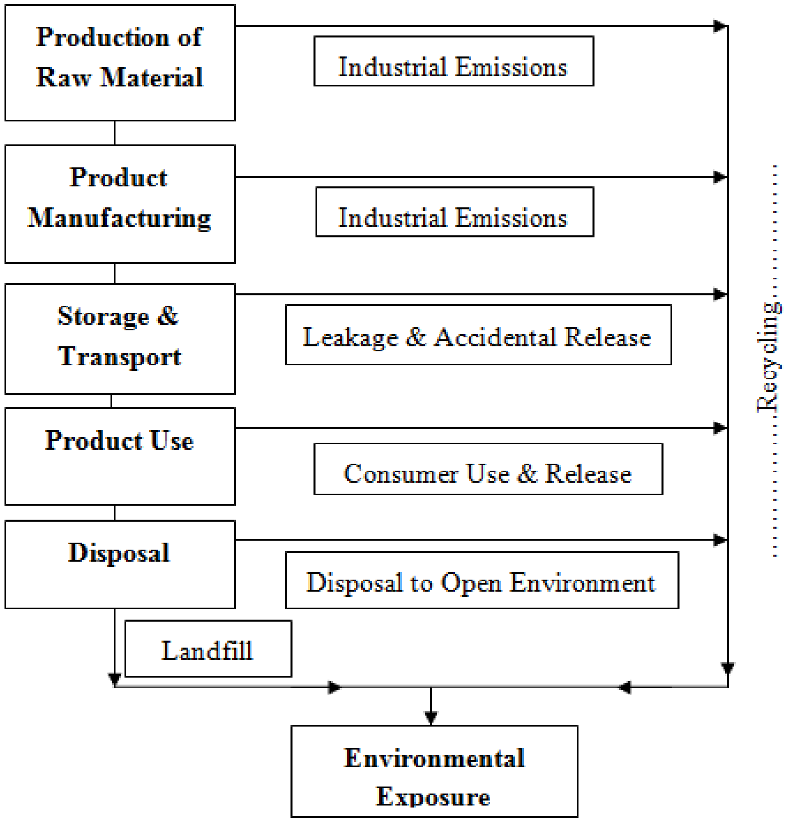

Figure-1
Possible Pathways of Environmental Exposure to ENPs

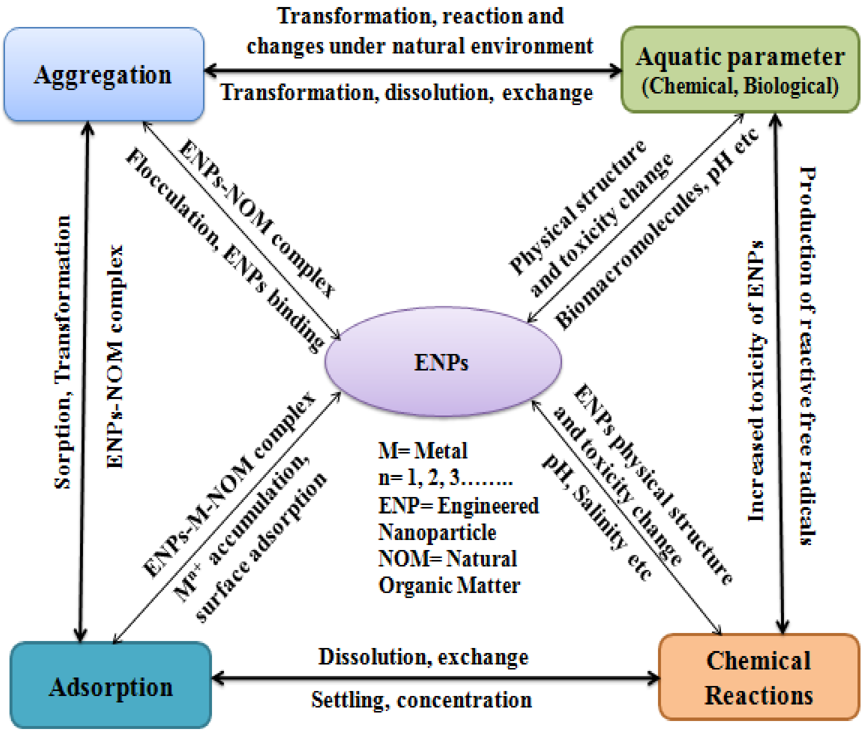

Figure-2
Conceptual diagram of the behavior and fate of ENPs in aquatic environment

Table-1
Predicted Environmental Concentrations (PECs) of some commonly used nanoparticles in three major pathways in the environment[5]

Nanoparticle	PECs
Ag	0.088–10 000 ng/L, surface water 0.0164–17 μg/L, WWTP effluent 1.29–39 mg/kg, WWTP sludge
TiO_2	21–10 000 ng/L, surface water 1–100 μg/L, WWTP effluent 100–2000 mg/kg, WWTP sludge
ZnO	1–10 000 ng/L, surface water 0.22–1.42 μg/L, WWTP effluent 13.6–64.7 mg/kg, WWTP sludge
Carbon-based	0.001–0.8 ng/L, surface water 3.69–32.66 ng/L, WWTP effluent 0.0093–0.147 mg/kg, WWTP effluent

When aggregation is less, it results decreasing sedimentation rates and increasing mobility of ENPs through water column. Aggregation might also be hindered by other processes as surface adsorption of NOM and other macromolecules is affected by oxygen and sulfur atoms present in the aquatic system. Physicochemical properties of aquatic environment may change the transport and fate of NPs. pH, salinity and other chemical properties of the reacting environmental conditions may change the physical characteristics and hence transport and toxicity of ENPs. A conceptual diagram of the behavior and fate of ENPs in water ecosystem is given in Figure-2.

Although there are many past and ongoing research on ENPs, it is not clearly understood the actual behavior of nanoparticle in aquatic environment due to the lacking of characterization in natural environment. In situ real time characterization of ENPs is important in environmentally relevant conditions because of their consequent transfer and toxicity which could be more convoluted by the interactions between different, dynamic transformation processes of them. Present investigative methods yield partial imminent into a subset of these transformations. Significant advancement in this field requires sensitive and appropriate tools for their in situ characterization in various environmental conditions[5].

Conclusion

Although there are many promising prospects for the application of ENPs in future technological advancement and social welfare, they are now a disputed issue for their impacts on different environmental compartments and human health. It is important to identify the characteristic and behaviors of ENPs in nanoscale in different aquatic environment to know their fate and subsequent impacts. In future chemical and biological transformation of ENPs should be addressed in ecotoxicological approaches. Evaluation of their eventual impacts on biological target organisms and the aquatic systems might be an emergent issue. Furthermore, comprehensive risk assessment methodology for ENPs exposure should develop for the wellbeing and protection of human and environment.

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