



Review

Fate of engineered nanoparticles: Implications in the environment



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ABSTRACT

The increased flux of engineered nanoparticles (ENPs) in consumer and commercial products has become a viable threat, particularly if their release affects the environment. The aim of this paper is to review the recent literature results pertaining to the underlying mechanisms initiating the transformations of ENPs for both biotic and abiotic processes. The transformation of ENPs is necessarily interrelated to multiple environmental aspects and many concepts overlap. Physicochemical, macromolecular, and biological pathways contribute to assessing the impact of the altered activities of ENPs on the surrounding environmental matrices. Transformations involving both organic and inorganic ligands are vital in soil and water systems. Energy-efficient biocatalytic pathways can easily facilitate biotransformation involving enzymatic reactions and biomolecules. The relationship between physicochemical and biological parameters triggers transformation, greatly affecting the bioavailability and aging of ENPs to various extents. Therefore, the interaction of ENPs in environmental matrices is significant in understanding the risk of potential exposure and/or uptake by biota.

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1. Introduction

It is well known that engineered nanoparticles (ENPs) are used widely in medical, energy, electronics, and environmental applications [1]. The extensive commercial application and production volume of ENPs raises concerns about their impact on the environment [2]. According to Amara's law, the growth of ENPs is predicted to form a large number of nano-products and, consequently, nano-wastes (Fig. 1) [3]. Therefore, exposure assessment is important, at least for the popular ENPs, because their environmental impact is poorly understood. ENPs are released into the biosphere, whether inadvertently or intentionally. For example, occupational or residential exposure to Ag nanoparticles (NPs) from consumer and hospital products has impacts on the aquatic environment through oxidative dissolution and sulfidation. Likewise, nanozerovalent iron (nZVI) is injected into groundwater polluted with chlorinated solvents at remediation sites where ENPs are released directly into water and soil [4]. Therefore, the influx of ENPs is a matter of balancing reward and risk in the environment.

The complex interaction between environmental matrices and ENPs is important. Abiotic and biotic pathways influence transformation, altering bioavailability and the aging process [5]. Different hydro-chemical parameters such as pH, ionic strength (IS), hardness (e.g. Ca^{2+} and Mg^{2+} ions), and O_2 -limiting conditions change aggregation kinetics [6]. Similarly, natural organic matter (NOM) alters stability through electrostatic and steric interactions [7,8]. Moreover, the (ad)sorption of molecules in surrounding environmental matrices indicates macromolecular level transformations [9]. ENPs are often functionalized by surface coatings for specific use, which results in altered activities [10]. For example, TiO_2 NP (Ti NP) composites showed hydrophilicity during the aging process and formed aggregates due to the oxidation and desorption of amphiphilic surface-coated molecules in an aqueous environment [11]. In addition, photochemical reduction of Ag^+ ions shows that ionic Ag bound to NOM facilitates the formation of Ag NPs under ambient light conditions in an aquatic system [12]. Similarly, biotic pathways including cellular degradation in matrices containing NOM, protein/polypeptide, and polysaccharide can alter the bioavailability of ENPs [13]. Bioavailability process controls the potential for transfer of ENPs from the environment to ecological receptors. So ENPs are not only affected by soil and water quality parameters but also by the presence of biomolecules including the biomass of plants and (micro)organisms [14]. Therefore, ENPs can

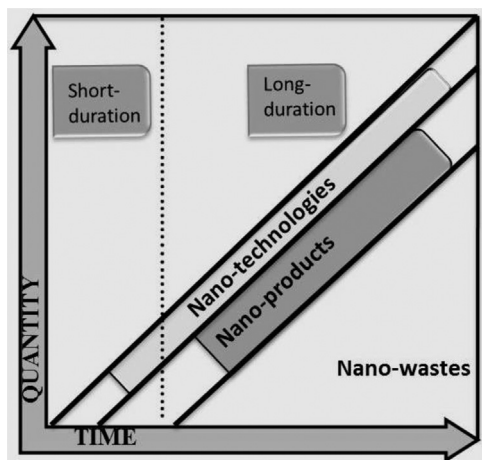


Fig. 1. Relationship of ENPs growth over time (Amara's law correlation of nanotechnological growth).

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change their behavior after being released into the environment by abiotic and biotic interactions [15].

The environmental implications and risks associated with nanotechnology have been addressed by various researchers. For example, specific reviews on silver [16], biotic mechanisms [17], and nanomaterial behavior and their fate [18–22] are a few of the valuable contributions to this field. This paper reviews the recent results in the wider literature concerning the mechanisms initiating the physicochemical, macromolecular, and biological transformations of ENPs through both the biotic and abiotic processes.

2. Transformation of ENPs

The characteristics of both the environment and ENPs are important in controlling the behavior of the released ENPs. The nature and degree of the transformation can be perceived in physicochemical, macromolecular interaction and biologically mediated reactions.

2.1. Physicochemical transformation

Abiotic pathways are generally based on physicochemical transformations. For example, the aggregation, stability, dissolution and deposition of ENPs are interrelated process. The natural pathways of sunlight-driven photochemical reactions are significant in controlling photo transformations. The adsorption of molecules readily occurs in the surrounding matrix of a natural system showing macromolecular transformations. The aerobic and anaerobic environment can also potentially alter the behavior of ENPs by differential affinity to the ligands, such as sulfidation in O_2 -limiting conditions.

2.1.1. Aggregation kinetics and stability

The colloidal stability of ENPs and their aggregation are explained through the interactions of colloid particles and adhering surfaces by the Derjaguin–Landau–Verwey–Overbeek (DLVO) theory [23]. According to this model, the aggregation of ENPs is dependent on interaction forces such as electrostatic repulsion and van der Waals attraction. Non-DLVO theory interactions namely steric hindrance, magnetic and hydration forces may have significant influence on the adhering surface efficiency. According to the International Organization for Standardization (ISO, 2008), nanomaterials in the size range of 1–100 nm are nanosized in different dimensions, such as nanoparticles, nanoplates and nanofibers which are nanosized in all three-dimensions, one-dimension and two-dimensions, respectively [24]. ENPs are much smaller than conventional colloid particles ($<2 \mu\text{m}$) and may not necessarily be spherical. They demonstrate wide variations in shape, such as triangular, icosahedral, ellipsoidal, and cylindrical forms. Two types of aggregation are relevant to ENPs in the environment: homoaggregation and heteroaggregation, which are the aggregations of similar and dissimilar ENPs. For example, aggregation of Ag NPs with Ag NPs is a homoaggregation whereas aggregation of Ag NPs with clay minerals is a heteroaggregation. Considering natural environment systems, heteroaggregation plays a significant role for ENPs transformation. Therefore core–shell structure, surface properties (which varies from hydrophobic to hydrophilic coatings), and the degree of transformation all alter the DLVO justification of the aggregation and stability of ENPs [25].

2.1.1.1. Effect of ionic strength.

2.1.1.1.1. Studies related to critical coagulation concentration. Ionic strength (IS) is known for its capability of ENPs transformation. The critical coagulation concentration (CCC) explains the 'required minimum electrolyte concentration' for favorable aggregation of ENPs by eliminating the electrostatic energy barrier.

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