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Environmental dynamics of metal oxide nanoparticles in heterogeneous systems: A review

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HIGHLIGHTS

- Influence of contaminants on the mobility of metal oxide nanoparticles (MNPs).
- Synergistic effects of MNPs in the presence of contaminants.
- Effect of environmental factors on the transformed MNPs.
- Research direction on the toxicity modeling assessment of heterogeneous systems.

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ABSTRACT

Metal oxide nanoparticles (MNPs) have been used for many purposes including water treatment, health, cosmetics, electronics, food packaging, and even food products. As their applications continue to expand, concerns have been mounting about the environmental fate and potential health risks of the nanoparticles in the environment. Based on the latest information, this review provides an overview of the factors that affect the fate, transformation and toxicity of MNPs. Emphasis is placed on the effects of various aquatic contaminants under various environmental conditions on the transformation of metal oxides and their transport kinetics – both in homogeneous and heterogeneous systems – and the effects of contaminants on the toxicity of MNPs. The presence of existing contaminants decreases bioavailability through hetero-aggregation, sorption, and/or complexation upon an interaction with MNPs. Contaminants also influence the fate and transport of MNPs and exhibit their synergistic toxic effects that contribute to the extent of the toxicity. This review will help regulators, engineers, and scientists in this field to understand the latest development on MNPs, their interactions with aquatic contaminants as well as the environmental dynamics of their fate and transformation. The knowledge gap and future research needs are also identified, and the challenges in assessing the environmental fate and transport of nanoparticles in heterogeneous systems are discussed.

1. Introduction

Production of ENMs has grown continuously and is expected to reach 58,000 tons per year by 2020 according to an estimate by the United Nations Environment Programme [1]. Over the last decade or so, ENMs have found wide applications in various fields such as medicine, manufacturing, pigments, and photo-catalysis. Among numerous ENMs, MNPs are produced in large quantities and have been used widely in industry, agriculture, consumer products, and household goods [2–10].

As most spent ENMs will end up being released into environmental media [11], there have been significant concerns about their release into the aquatic environments via wastewater discharge

Abbreviation: ENMs, engineered nanomaterials; MNPs, metal oxide nanoparticles; CeO_2 NPs, cerium oxide NPs; SiO_2 NPs, silica dioxide NPs; NOM, natural organic matter; SOM, soil organic matter; DOM, dissolved organic matter; IS, ionic strength; ROS, reactive oxygen species; EPS, extracellular polymeric substances; SWCNTs, single wall carbon nanotubes; MWCNTs, multi-walled carbon nanotubes; PAA, polyacrylic acid; HMP, hexametaphosphate; CFT, colloid filtration theory; NOL, natural organic ligands; AONPs, aluminum oxide NPs; CoO NPs, cobalt oxide NPs; OM, organic matter; PAHs, polycyclic aromatic hydrocarbons; OECD, organization for economic co-operation and development; SRNOM, suwannee river-natural organic matter; IEP, isoelectric point; XDLVO, extended derjaguin-landau-verwey-overbeek; HUVEC, human umbilical vein endothelial cells.

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and runoff [12]. For instance, zinc oxide and TiO_2 NPs have been extensively used in skincare products, with more than 33,000 tons of sunscreens produced containing up to 25% of ZnO NPs [13–15]. According to Danovaro et al. [16], at least 25% of the sunscreen used (~4000–6000 tons/year) was released in reef areas [16]. As a result, the discharge volume of ZnO NPs was estimated the second largest, only to that of TiO_2 NPs [17].

CeO_2 NPs constitute one of the most widely used nanomaterials, with uses including oxygen sensors, solid oxide fuel cells, polishing solutions, and petrochemical processing [18–23]. Consequently, large amounts of CeO_2 NPs have been found in wastewater treatment plants [24]. With an annual global production rate of 1000 tons [25], CeO_2 NPs have been feared to pose toxic effects on the ecological health, in particular, on plants and beneficial soil bacteria [26–31]. The primary concern around CeO_2 NPs is the significant discharge to waste streams during the manufacturing processes (coating, polishing, painting) of consumer products [32]. SiO_2 NPs are widely used in industrial products, packaging, ceramics, drug delivery, remediation of contaminants, food processing, ultrasound medical imaging, and biosensors [33–35].

A recent study showed that the presence of CuO NPs led to decline in the microbial biomass of a flooded paddy soil as well as composition and diversity of the soil microbes. The underlying mechanisms included the release of Cu ions from the NPs and the generation of free radicals [36,37]. Studies also indicated that the deposition of Fe_3O_4 and CuO on the soil can reduce its porosity and hydraulic conductivity [38,39].

Various factors have been reported as affecting the potential toxicity of MNPs, including exposure dose and time, SOM, pH, Eh (oxidation/reduction potential), IS, and moisture content [38–42]. According to the OECD, MNPs (e.g., TiO_2, ZnO, CeO_2) are of particular concern due to their unique properties and wide, versatile uses, yet information regarding the toxicity mechanism of various MNPs has been lacking [43]. While significant acute health issues may not occur at levels detected in the environment, sub-lethal effects were noted with dissolution of metal ions (e.g., Ag, Zn, Cu), which may result in chronic health impacts [44].

Adsorption and accumulation of ENMs may depend on the environmental media as the ultimate sink. Several studies using exposure modeling showed significant accumulation of NPs in soil and sediment, others detected ZnO NPs in the concentration range from 10 to 500 ng/L in surface waters and sewage sludge [17,45,46].

Table 1 summarizes MNPs commonly used in consumer products. In heterogeneous systems, different types of contaminants will undergo various transformations that can alter the mobility, fate, and toxicity of MNPs. Understanding various factors that affect the environmental dynamics (fate, transport, transformation) of MNPs is essential to understand interactions between NPs and environmental conditions, and to evaluate the environmental impacts of MNPs.

Systematic information is therefore needed concerning the environmental dynamics of MNPs in heterogeneous systems. This article reviews all aspects of MNPs in terms of fate, transport, transformation processes, and toxicity, with an emphasis on their interactions with contaminants and offers an update on the latest development in this relatively new research avenue. The article will offer information useful to a wide audience, including, but not limited to, scientists, policy makers, consultants, and product design engineers.

This review aims to: (1) examine the environmental conditions (e.g., contaminants, pH, IS, NOM) that affect the fate, transport, and transformation of MNPs, (2) analyze the effects of coexisting contaminants on the release and the transformation mechanisms of MNPs in heterogeneous systems, (3) assess the influence of environmental conditions on the toxicity of MNPs, especially in the presence of common contaminants, and (4) evaluate the potential toxicity impacts of MNPs in heterogeneous systems. Based on the comprehensive review, knowledge gaps are identified and future research needs are proposed.

2. Factors affecting fate of MNPs

Relatively few studies have investigated factors that influence the fate of NPs, especially MNPs in complex and heterogeneous systems. Common environmental contaminants may interact with MNPs, potentially altering the physicochemical properties and/or being transformed through sorption, chemical, or biological processes.

2.1. Effects of contaminants on MNPs

A few studies [52–55] have investigated how different types of contaminants influence the fate of NPs, particularly MNPs in the environmental media, and what the underlying mechanisms are. Researchers have found the extent of the contaminant effects may depend on the affinity of contaminant molecules. For instance, because of the higher affinity of Cd(II) toward TiO_2, higher Cd toxicity was observed in the presence of TiO_2 NPs [52]. Studies have shown that the presence of Cd(II) significantly affects the fate of TiO_2 NPs due to the stronger adsorption capacity of TiO_2 NPs for Cd compared to sediment particles [52]. According to their study, the Cd concentration in carp (μg/g dry weight) increased by 146% than that in the absence of nano-TiO_2 over bioaccumulation time (d), estimated from the equation:

$$C_t = k \times C_{Ti} + C_d$$

[C_t: Cd concentration in carp (μg/g dry weight), C_{Ti}: TiO_2 concentration in carp (mg/g dry weight), k: transport coefficient, C_d: dissolved Cd ions during exposure time (d)].

And vice versa, the fate of TiO_2 could influence contaminants in terms of their removal and the resultant toxicity, by which the deterioration of nano-TiO_2 (e.g., surface modification) can affect the affinity of Cd adsorption along with the toxicity.

Adsorption of arsenic to iron oxide NPs was found nearly proportional to the specific surface area of the MNPs [54,55]. As more adsorption sites are occupied by arsenic and other contaminants, the characteristics of the MNPs would alter, which could not only affect continued removal of the contaminants, but also the behavior of the MNPs. Depending on the mobility, stability and adsorption properties of the MNPs, such contaminants-NPs interactions may either enhance or reduce the mobility of the contaminants. However, the influencing factors have not been well understood, especially in complex heterogeneous systems.

The fate of MNPs could be influenced by the particle size, which, in turn, is a function of contaminants (e.g., metals and ligands) and the contaminant concentration. In a wastewater treatment process (sequencing batch biofilm system), the removal efficiency of total nitrogen (TN) decreased from 75% to 60% when the concentration of CeO_2 NPs increased from 1 to 50 mg/L, due to generation of ROS from large quantities of CeO_2 NPs adsorbed onto the biofilm (i.e., 40% increase of ROS production when CeO_2 NPs concentration increased to 50 mg/L from 1 mg/L) [56]. The results indicate that both concentration and type of MNPs could affect the removal of contaminants adsorbed on MNPs in wastewater treatment processes.

The contaminants adsorbed on NMPs not only affect their removal, but also physicochemical properties of the NMPs. This was well illustrated by one of several recent studies [57], which reported that adhesion of *Escherichia coli* to γ-Al_2O_3 and α-Fe_2O_3 NPs decreases with increasing pH and decreasing ionic strength. The observation indicates that the surface electrostatic charge was

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