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The effect of nanohydroxyapatite on the behavior of metals in a microcosm simulating a lentic environment

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ABSTRACT

In the environmental science and engineering community, nanohydroxyapatite (nHAp) has been widely applied for the remediation of contaminated soil and purification of wastewaters polluted with heavy metals for its strong ability to fix these contaminants. Based on this process, the aim of the present study was to evaluate the impact of nHAp in sorption/desorption of Cu, Zn, Fe and Mn in microcosm experiments, considering different environmental conditions and investigating the effects of pH, contact time and influence of natural organic matter and contamination with Cu and Zn. Due to its relevance as a regional water supply source, the environmental scenario of Juturnaíba reservoir (Rio de Janeiro State, Brazil) was chosen as basis for the microcosm experiments. It was observed that nHAp had an effect on Zn and Cu behavior, acting as a captor and promoting the reduction of their dissolved concentration in the water treatment sludge after water contamination with these metals. However, this behavior was modified by the addition of humic acid and acid to the microcosm system. On the other hand, the behavior of Fe and Mn was impacted by these nanoparticles in an opposite way.

1. Introduction

In the last years, nanotechnology has become a worldwide keyword, once it gathers different areas of science with an interdisciplinary approach (Groso et al., 2010). Nanoscale implies the size range from approximately 1–100 nm (ISO, 2008; Lövestam et al., 2010); however; the concept of nanomaterials is evolving; overcoming the definitions of operational nature (ABDI, 2013). Currently one of the most accepted definitions is outlined in ISO TC 229 [2]; in which nanomaterials must contain at least one of the following aspects: i) understanding and control of matter and processes in nanoscale; typically; but not exclusively; below 100 nanometers in one or more dimensions where the onset of size-dependent phenomena enables new applications; ii) the use of the material properties in nanoscale that are different from the properties of individual atoms; molecules or macroscopic materials; by creating materials; devices and systems that better exploit these new properties. Consequently; nanomaterials should be classified as new substances for evaluation and regulation effects.

Considering the generation of nanoparticles of different chemical compositions, innovative and in depth studies are demanded for a detailed evaluation of possible impacts related to their routine disposal in the sewage system.

Although the use of nanoparticles can be beneficial in several areas, including industry, medicine and electronics, it is still necessary to evaluate the environmental risks of these materials, considering their behavior and possible toxicity in different systems (Baalousha et al., 2011; Bystrzejewska-Piotrowska et al., 2009; Dickson et al., 2012; Handy et al., 2008). The most significant processes and transfer pathways of the nanoparticles into the environment are represented in Fig. 1. Nanoparticles are easily transported by air and they may enter into the food chain, influencing the biosphere, pedosphere and hydrosphere. Thus, their disposal in association with sewage sludge on landfills and agricultural areas may produce a relevant exposure pathway to man and biota which must be evaluated.

Nanomaterials may also become mobile in the environment, where they can have detrimental effects on aquatic organisms and humans (Kanel and Al-Abed, 2011; Nowack and Bucheli, 2007). Environmental impacts of manufactured nanoparticles have been studied by many

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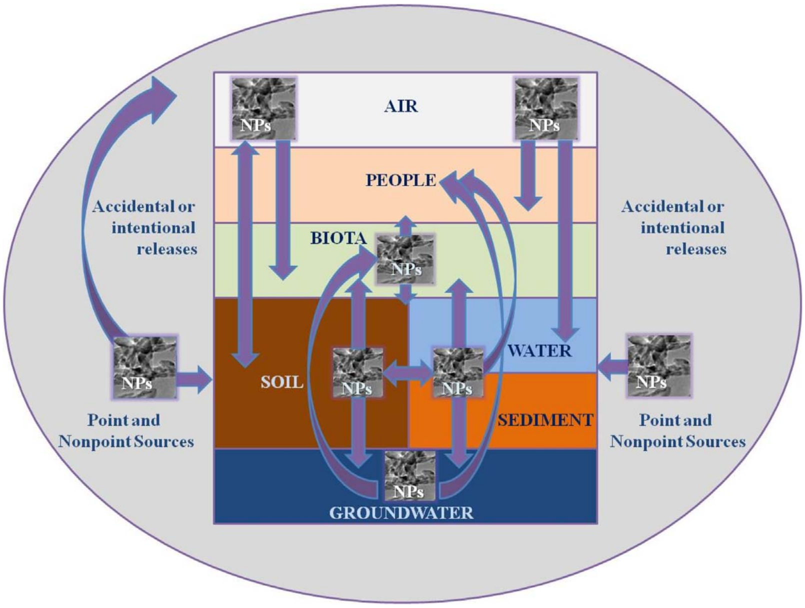

Fig. 1. Main nanoparticles transfer pathways (NPs) in the environment and exposure of humans (adapted from Nowack et.al, 2007).

researchers that focused on aggregation (Jassby et al., 2012; Labille and Brant, 2010; Omar et al., 2014), pH influence (Alias et al., 2010; Baruah and Dutta, 2009; Shafaei et al., 2010), and interactions with natural organic matter (Akaighe et al., 2012; Ma et al., 2012; Palomino and Stoll, 2013). Nevertheless, there are several scientific evidences suggesting that some of these nanoparticles are being deliberately released and accumulated into the environment (residual waters, soils, and sediments), at risk of being transported to the flora and fauna, and that both destination and transformation are difficult to be evaluated and controlled (Brar et al., 2010; Dasari and Hwang, 2010; Weir et al., 2012).

Some studies pointed out the application of nanohydroxyapatite $[Ca_{10}(PO_4)_6(OH)_2]$ as biocompatible adsorbent for the adsorption and immobilization of toxic metals. This application has become relevant due to its special chemical composition and crystal structure. (Yang et al., 2016). In nuclear medicine, the radiolabelled nanoparticles of hydroxyapatite with Technetium–99 m have been also used for targeting cancer and therapy as drug delivery due to its nontoxicity, biocompatibility, and biodegradability.

In the environmental science and engineering community, nHAp has been also widely applied for the remediation of contaminated soil and purification of wastewaters for its strong ability to absorb heavy metals (Chen et al., 1997; Hodson et al., 2000; Laperche et al., 1996; Ma et al., 1993; Mavropoulos et al., 2002; Smiciklas et al., 2008). In China, nHAp has been widely used as an ideal candidate for remediation of soils contaminated with heavy metals such as Cu^{2+}, Zn^{2+}, Pb^{2+}, Cd^{2+} (Wang et al., 2011). Many studies related to remediation in contaminated areas have confirmed the efficiency of nHAp in immobilizing heavy metals in water, sediment or soil (Corami et al., 2007; Ma, 1996; Mavropoulos et al., 2002; Smiciklas et al., 2008; Wang et al., 2011; Yang et al., 2016). The suggested immobilization mechanism of hydroxyapatite, consider ion exchange process, surface complexation, dissolution, precipitation and coprecipitation. However, there is limited information regarding the long-term effects of nHAp applications as drug delivery and its final disposal in sewage system. According to (Lin et al., 2005), the environmental risk of nHAp has been neglected because it has displayed good cytocompatibility.

Considering the world scenario of production, large-scale use and disposal, studies of manufactured nanoparticles fate and impact in the environment are becoming important due to the discharges already occurring to the environment. The apparent increase in discharges from industries and the immense gap in our knowledge lead to difficulties in risk assessment and management of these materials (Handy et al., 2008). Moreover, agencies do not have sufficient data, tools and mechanisms for detection, monitoring, and controlling of manufactured nanoparticles and even less to remove them from the environment.

In this direction, this exploratory study has the main objective of identifying, the potential impact caused by discharge of nHAp, that is used in nuclear medicine as drug delivery, into sewage system on the chemical behavior of contaminants (Cu and Zn) and natural metals (Fe and Mn). The chosen study area was the Juturnaíba reservoir (Rio de Janeiro, Brazil), that has been negatively impacted due to the population growth. The microcosm assays were built with the aim to reproduce as accurately as possible the real conditions of the lentic environment present in the Juturnaíba reservoir. Changes of pH, contact time, influence of natural organic matter (humic acid) and contaminants (Zn and Cu) were also induced, simulating anthropic and natural changes in the system.

2. Materials and methods

2.1. Study area description

The Juturnaíba lagoon is located at Silva Jardim municipality in Rio de Janeiro State, Brazil. This reservoir is the main water supply source for the São João River Basin and supplies water to a population of more than one million people. However, the environmental impacts resulting from the use and occupation of the soil around the reservoir, the accumulation of waste and the disposal of domestic effluents directly in the spring, threaten the water quality of the reservoir, generating excessive nutrient and sediment supply in the environment.

According to Almeida (2016) during the last years, several studies have been carried out at the Juturnaíba reservoir, among them a water quality monitoring study, which registered high levels of Fe and Al dissolved in water at some periods of the year. Previous studies also observed a homogeneous distribution of Cu, Fe and Al and a high mobility of Al, Cu, Mn, Pb, Zn and Fe, pointed out the potential impact of the presence of residues generated in Water Treatment System on the dynamics of metals in the sediments of the Juturnaíba Reservoir (Almeida, 2016).