



Acute ecotoxicity of coated colloidal goethite nanoparticles on *Daphnia magna*: Evaluating the influence of exposure approaches



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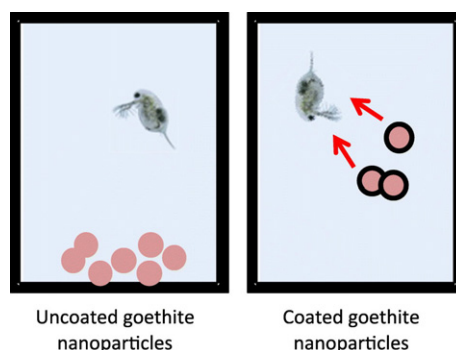
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HIGHLIGHTS

- Toxicity of coated goethite nanoparticles to *D. magna* was explained by interaction organisms-NP.
- Nanoparticle specific effects related to impairment of organisms physiology.
- Filter feeders organisms' behaviour largely varies after interacting with the nanoparticles.
- Humic acid coating favours the colloidal stability of the goethite nanoparticle.

GRAPHICAL ABSTRACT



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ABSTRACT

Synthesized iron oxide nanoparticles have been proposed as an alternative to non-dispersed iron oxides for in situ environmental remediation. Their colloidal properties enable their injection into porous media, i.e. soils and aquifers, and offer a higher efficiency in removing contaminants. However, this dispersed state is also the cause of concerns over their environmental fate and toxicity, e.g., by increasing the exposure time to aquatic organisms in groundwater remediation activities. Therefore, the objective of in situ groundwater remediation is to establish local reactive barriers in the subsurface by injection by means of reactive colloids with a controllable mobility under in situ conditions and present as colloids as shortly as possible.

In this work, we examined the toxicity of humic acid-coated colloidal goethite nanoparticles in *Daphnia magna*. The adaptation of the ecotoxicological standard tests for nanomaterials is intensely discussed to increase comparability and reliability of results. In the present study, the effect of different exposure conditions on goethite nanoparticles colloidal behaviour and acute *Daphnia* immobilization effects was investigated. For this purpose, iron concentration in the water column, aggregation state and acute effects were studied in: i) a standard test, ii) test design with exposure dispersions incubated for a week and iii) water accommodated fraction. Despite the different aggregation and settling of the particles found between the approaches tested, no differences in toxicity were observed. Coated nanoparticles were found clogging up the filtering apparatus, and/or adhered to the exoskeleton, hindering the swimming and molting, and causing the immobilization and death of the organisms at doses of ≥ 943 mg/L (EC50). The data suggests that the toxic potential of these nanoparticles is mainly related to the physical interaction with the daphnids.

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1. Introduction

Iron oxide particles in the micro- to millimetre scale have been widely used in environmental remediation (Cundy et al., 2008). Recently, there is growing interest in the use of iron oxide nanoparticles, because their reduced size renders them suitable for direct injection into porous media, thus making them more efficient in situ remediation strategies than their larger, undispersed counterparts. In aqueous solution, solid particles with small sizes (<100 nm) exhibit a high specific surface area. This together with the fact that Brownian motion dominates over gravity results in highly reactive, dispersed particles. Consequently, the reduced size is likely to modify their environmental fate and toxicity compared with micro- to millimetre scale iron oxides, frequently considered as bulk phase iron oxides. The extent of the impact of size is not totally understood and raises concerns on the intentional introduction of large quantities of these materials to the environment, as in the case of soil and groundwater remediation actions. In ionic solutions, i.e. groundwater and soil solution, synthetic iron oxides nanoparticles are subject to aggregation unless modifications (surface coating, doping with other metals) are conducted that reduce their aggregation (Liu et al., 2012). In the environment, natural organic matter (NOM) and its can be adsorbed onto the surfaces of the nanoparticles (NPs), enhancing their stability and mobility in flowing waters (Chappell et al., 2009). The nanoparticles tested in this study were coated with commercially available humic acid to ensure a temporal stability in ionic solutions, i.e. groundwater. This surface modification allows for a finite mobility of the colloids after their injection into aquifers, which is desirable for the in situ remediation of groundwater by establishing a reactive barrier within the aquifer, which the groundwater has to pass.

In the environment, stabilized nanoparticles may reach surface waters (Baun et al., 2008), causing potential harm to human health or the environment. Surface functionalization might also modulate toxicity of these nanoparticles, by influencing cellular uptake, accumulation, transformation, and elimination (Zhu et al., 2013). Humic substances also reduced the toxicity of nanoparticles (Collin et al., 2014; Fabrega et al., 2009), but mitigation of toxicity is known to be dependent on the actual organic matter composition (Lee et al., 2011; Yang et al., 2014). In the case of CeO₂ and TiO₂ NPs, it has been widely demonstrated that different types of NOM promote their stabilization in aqueous media at typical environmental concentrations (Keller et al., 2010; Yang et al., 2009; Quik et al., 2010) and affect also their toxic effects in aquatic organisms (Van Hoecke et al., 2011). Likewise, commercial organic matter have been proved to interact with these NPs, but the influence on their stability and ecotoxicity is not as clear as that of natural organic matter (Schwabe et al., 2013; Zhu et al., 2014; Wang et al., 2014). Höss et al. (2015) revealed that coating of iron oxide particles with real dissolved organic matter was much more harmful to nematodes than coating of iron oxide with commercial humic acids.

Only very few studies have investigated the effects of iron oxide nanoparticles in aquatic environment, including invertebrates (Filser et al., 2015; Hu et al., 2012; Choi et al., 2014; Baumann et al., 2014; Zhang et al., 2016) and fish (Zhu et al., 2012). Data on the toxicity profile of iron oxide nanoparticles, particularly if coated, should be generated to conclude whether the iron form, size and coating properties of these particles lead to specific hazards in situ remediation of groundwater.

When running the standard aquatic toxicity test (i.e. OECD 202), some dispersed or suspended nanoparticles will subsequently fully or partly dissolve (i.e. for metal-nanoparticles) to their constituent ions and/or partly will aggregate and settle down over the exposure time of the ecotoxicity test resulting in a mixture of different particles forms. The presence of these different forms should be taken into account when interpreting the data from ecotoxicity experiments. Since aquatic exposure to NMs may include both dissolved and/or solid phases (nanoparticles, aggregates, colloids), an additional effort is required to distinguish whether adverse effects are due to one or another

phase. For conventional inorganic compounds, the toxicity is mainly determined by the dissolved forms. However, NPs have the potential to exert toxic effects that are not solely chemical. Physical effects are defined as “mechanical effects not associated with chemical reactions caused by NPs or associated with the dissolution of NPs to ion species” (Skjolding et al., 2016). Physical effects can be manifested as attachment of insoluble material to the exterior of the organism as aggregated particles or a flocculent and can lead to adverse effect from fouled respiratory surfaces or impaired mobility. Besides such physical effects, settled materials included in bioassays may also act as a source of dissolved materials or resuspended particles and potentially alter the system chemistry. Aquatic toxicity testing of nanoparticles is challenging because of their usual instability in the test medium. As a consequence, initial exposure conditions can rapidly change during the test exposure period, making difficult to obtain reproducible results and to correctly interpret the data (i.e., which actual exposure concentration should be used in the risk assessment?). In these cases, the characterization of the nanoparticles during the ecotoxicology test (settling, agglomeration, dissolution...) is needed for an accurate description of the exposure dosage (Petersen et al., 2014). To study the toxicity of these “complex mixtures” in which different individual substances with different solubilities are present, the term of “water accommodation fraction” has been commonly used (Lee et al., 2012). The “water accommodation fraction” arises as the fraction of multi-component substances that is dissolved and/or present as a stable dispersion or emulsion (OECD, 2000).

In this work, we examined the aquatic toxicity of uncoated and humic acid coated iron oxide (goethite) nanoparticles (here called after IONP and ha-IONP, respectively) to *Daphnia magna*. To achieve these goals, *Daphnia magna* immobilization test (OECD, 2004) was performed under three different exposure conditions where contrasting aggregation and settling of the particles was expected.

2. Material and methods

2.1. Iron oxide nanoparticles and humic acids

Colloidal goethite nanoparticles were produced and coated with humic acids, specifically for site remediation, according to US patent 8,921,091 B2 (Meckenstock and Bosch, 2014). Analysis with X-ray diffraction, Fourier-transform infrared spectroscopy, scanning electron microscopy, N₂-physisorption, Laser Doppler velocimetry and elemental analysis revealed that the suspensions consisted solely of low-crystalline goethite, which was arranged in aggregates with comparably broad size distributions (supplementary information: Fig. S1). In contrast to the ha-coated goethite, the major fraction of uncoated goethite was non-colloidal (>> 1 μm). Due to the small size of the single goethite crystallites within the aggregates, the goethite exhibited a very high specific surface area (>250 m² g⁻¹), which exceeded that of common synthetic goethites (Cornell and Schwertmann, 2003). The surface charge was net-positive for uncoated goethite and net-negative for ha-coated goethite at pH ~6.0 (Fig. S1). For experiments, the coated nanoparticles were diluted with deionized water to a concentration of 10 g FeOOH/L for the coated and uncoated iron oxide nanoparticles.

2.2. Exposure approaches and test dispersion

2.2.1. Exposure approaches

A careful experimental design was set up in order to differentiate whether immobilization effects were only attributed to the dispersed colloids and/or colloid aggregates or whether the settled ha-IONP could also affect the organisms.

The typical concentrations of injected slurries at field sites vary from 0.75–1.5 g/L (Elliott and Zhang, 2001) to 10 g/L (Henn and Waddill, 2006; Phenrat et al., 2009). Assuming that the entire injected concentration could reach relevant environmental compartments, a

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