



Effects of alginate on stability and ecotoxicity of nano-TiO₂ in artificial seawater



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ABSTRACT

The large-scale use of titanium dioxide nanoparticles (nano-TiO₂) in consumer and industrial applications raised environmental health and safety concerns. Potentially impacted ecosystems include estuarine and coastal organisms. Results from ecotoxicological studies with nano-TiO₂ dispersed in salt exposure media are difficult to interpret due to fast flocculation and sedimentation phenomena affecting the dispersion stability. The goal of this study was to investigate the stabilisation effect of alginate on uncoated nano-TiO₂ in artificial seawater dispersions used in ecotoxicity bioassays. The most effective stabilisation was obtained at alginate concentration of 0.45 g/L after sonicating dispersions for 20 min (100 W). The size distribution remained constant after re-suspension, indicating that no agglomeration occurred after deposition. Ecotoxicity tests on *Artemia franciscana* and *Phaeodactylum tricornutum* did not show any adverse effects related to the presence of alginate in the exposure media, and provided evidence on possible reduced bioavailability of nano-TiO₂. The suitable concentration of alginate is recommended to occur on a case-by-case basis.

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1. Introduction

The increasing application of titanium dioxide nanoparticles (nano-TiO₂) in consumer products raised environmental, health and safety concerns (Donaldson et al., 2004; Gao et al., 2008; Handy et al., 2008; Ju-Nam and Lead, 2008; Klaine et al., 2008; Nel et al., 2006). The introduction of nano-TiO₂ in the environment may occur during its whole life cycle including production, use and disposal (Hagendorfer et al., 2010; Kaegi et al., 2008, 2010; Corsi et al., 2014). High concentrations of nano-TiO₂ were detected in surface waters (i.e. 10 mg/L) after a simulated rainfall release from outdoor walls (Kaegi et al., 2008). Rain water can be conveyed and treated in wastewater treatment plants, which do not effectively remove nanoparticles from the effluent discharge (Kiser et al., 2009). Nano-TiO₂ entering surface freshwater is likely to be stabilised and transported to the sea under conditions of low ionic strength and high levels of natural organic matter (Domingos et al., 2009; Jiang et al., 2009; Keller et al., 2010; Petryshyn et al., 2010; Zhang et al., 2008). Being coastal water and sediment the

final sink for nano-TiO₂ particles (Gottschalk et al., 2009, 2010), marine organisms-like crustaceans and algae-may be exposed to them. As a consequence, it is necessary to assess the potential hazards of nano-TiO₂ for these target species.

According to some standard ecotoxicological protocols (e.g. ASTM, 2004), culture and exposure media for marine organisms, i.e. artificial seawater (ASW), must have about 35‰ salinity and 0.7 M ionic strength generated by a mixture of selected salts. The high salt concentration of ASW and the pH of 8.00–8.40 form favourable conditions for nano-TiO₂ to agglomerate and rapidly settle (Keller et al., 2010, Petosa et al., 2010). As a result, the tested organisms are exposed to material concentrations and size distributions dynamically changing over time throughout various non-equilibrium states; these variations affect the generation of robust test results (e.g. realistic concentration–response relationships), as well as their proper interpretation (Hund-Rinke et al., 2010; Kahru and Dubourguier, 2010; Pace et al., 2010; Strigul et al., 2009; Velzeboer et al., 2008).

The introduction of a stabilising agent in the exposure media appears acceptable if the selected substance occurs naturally in the environment and is not hazardous for the tested species. It is well known that natural organic matter (NOM) can stabilise

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colloids (Tiller and O'melia, 1993). The mechanism was initially thought to be solely an electrostatic repulsion due to the negative charge of the NOM coating (Hunter and Liss, 1982; Beckett and Lee, 1990; Wilkinson et al., 1997). Indeed, it has been shown that there may be a steric component to the stabilisation (Sander et al., 2004). It has also been shown that NOM may also destabilise colloids under certain conditions through bridging flocculation (Wilkinson et al., 1997; Chen et al., 2007).

Other recent investigations suggested the use of organic substances to stabilise nanoparticle dispersions in freshwater media. Several examples of stabilisation of carbon based and metal-based nanoparticles by humic substances have been published (Chen and Elimelech, 2007; Diegoli et al., 2008; Abe et al., 2011). Tiraferri et al. (2008) tested guar gum, alginate and potato starch on bare iron nanoparticle (nano-Fe) dispersions. The effect of these polymers was preliminarily analysed in the range of 1.3–4.0 g/L in presence of 1 mM NaCl and it was observed that guar gum (0.5 g/L) was more effective in preventing sedimentation of 1.5 g/L nano-Fe under low ionic strength at neutral pH, despite the fact that the other two polymers were not investigated in detail. Liu et al. (2010) reported the effects of Suwannee River humic acid (15 mg/L) and alginate (4.4 mg/L C) on 10–20 nm boron nanoparticles (50 mg/L) in electrolyte solutions. Alginate solutions did not significantly stabilise the dispersions in presence of NaCl (0.05–0.3 M), while in MgCl₂ solutions low stabilisation effect was observed (0.5–8 mM), while agglomeration was prevented in CaCl₂ solutions in the range 0.5–1.3 mM and enhanced in the range 1.3–10 mM.

In natural waters, the major classes of Natural Organic Matter (NOM) biopolymers are seasonally varying with higher concentrations during and after plankton blooms (Buffle et al., 1998). It is believed that most biopolymeric NOM are exudates from algae and bacteria and are rich in protein and acid polysaccharide components (Aluwihare and Repeta, 1999). The structure of these exudates have been shown to be fibrillar in both freshwater and seawater (Wilkinson et al., 1999; Santschi et al., 1998; Stolpe and Hassellöv, 2009). This rigid fibrillar characteristic in combination with the charge distribution is believed as important both for steric stabilisation and bridging flocs depending on specific conditions. Although the natural exudates are complex mixtures, different model macromolecules have been used in experiments such as alginate, xanthan, gum Arabic and guar gum.

Among natural polysaccharides, alginate occurs as a structural component in marine brown algae (*Phaeophyceae*) and capsular polysaccharides in soil bacteria; it is a linear chain copolymer consisting of (1→4)-linked α -L-guluronic acid and β -D-mannuronic acid repeating units that are randomly arranged (Andriamanantoanina and Rinaudo, 2010). Alginate is commonly applied as additive in food, pharmacy, agriculture and environmental industries (Ertesvåg and Valla, 1998; Fayaz et al., 2009). The concentration of dissolved organic carbon is well known in seawater and range from as low as 40 μ M in the open ocean to several hundred μ M in coastal waters with high freshwater input (Pettine et al., 1999). The bulk chemical composition of NOM in seawater revealed that total polysaccharides accounted for approximately 50% of the NOM in surface seawater (Benner et al., 1992), but the different fractions of unaltered macromolecules are much less well quantified due to lack of methods. Another significant source of NOM is the direct effluent discharge into seawater from the sewage treatment plants (STPs) that is one of the major routes for the entry of manufactured nanoparticles in the marine environment being extremely rich in OM both from the sewage and from the exudates of the microbial treatments. It is therefore plausible that the nanomaterials will be exposed to a very high NOM concentration within and shortly after the wastewater treatment before excessive dilution in the receiving water. Recently, about the

use of stabilisers in ecotoxicity testing, OECD (2014) stated that the inclusion of NOM into test dilutions and not within stocks is still open to further discussion due to the batch-to-batch required approach; indeed, depending on the type of NOM, engineered nanomaterials (ENMs) can be stabilized or destabilised after NOM adsorption. Currently, no harmonisation of NOM management procedure is available.

The objective of this work is to assess the effectiveness of alginate in stabilising nano-TiO₂ in crustacean (ASW-1) and algae exposure media (ASW-2), used in ecotoxicity testing. In particular, the size distribution, agglomeration, and sedimentation behaviour under centrifugal forces of nano-TiO₂ particles in the presence of alginate were determined using different polymer concentrations and sonication dispersion periods. The most effective alginate solution, that means the lowest treatment solution to obtain an adequate nano-TiO₂ stabilisation, was studied in great detail in order to assess the possibility to introduce some modifications to the toxicity testing exposure media. Ecotoxicity tests on the anostracan crustacean *Artemia franciscana* and on the unicellular diatom alga *Phaeodactylum tricornutum* were carried out according to the standard methods APAT and IRSA-CNR (2003) and UNI EN ISO 10253 (2006), respectively. Bioassays assessed the potential ecotoxicological effects of nano-TiO₂ dispersed both in the standard media (< 5 mg/L total organic carbon) and alginate rich suspensions.

2. Materials and methods

2.1. Nanoparticles

Aeroxide[®] P25 uncoated titanium dioxide powder (declared primary particle size of 21 nm) was obtained from Evonik Degussa Corporation. The material consists of a crystalline state with phase composition of approximately 80% anatase and 20% rutile. The pristine material was stored at room temperature in the dark.

2.2. Dispersion media

Ultrapure water (18.2 M Ω cm minimum resistivity) was produced by a Milli-Q water purification system (Millipore). Two artificial seawater solutions (ASW-1, ASW-2) were used as dispersion media and prepared according to the standard protocol E 724-98 (ASTM, 2004), using analytical grade salts (purity > 99.8%) (Sigma-Aldrich). Their exact compositions are reported in Table S1. The solutions were prepared by dissolving salts in deionised water under magnetic stirring at room temperature. After completing the salt dissolution, they were aerated with a stream of laboratory air over 12 h, in order to stabilise the pH to 8.2 \pm 0.2. The solutions were filtered using 0.45 μ m glass fibre filters (Whatman International Ltd.) and stored at 4 \pm 1 $^{\circ}$ C in the dark.

2.3. Alginate solutions

The alginate (Fluka Code 71240, Fluka – Milan, Italy) is characterised by an average molecular weight of 345 kDa (Serp et al., 2000). The alginate solutions were prepared by dispersing the polymer in ASW with initial concentrations of 0.1, 1, and 10 g/L sodium alginate. The solutions were vigorously shaken for 60 s and left at 4 \pm 1 $^{\circ}$ C for two days in order to achieve complete dissolution of the alginate powder. The undissolved alginate was removed by sequential filtration through 1 μ m, 0.45 μ m, and 0.22 μ m glass fibre filters (Whatman International Ltd.). Once prepared, the alginate solutions were stored at 4 \pm 1 $^{\circ}$ C in the dark. Prior to use, they were kept at room temperature for at least 2 h and then vigorously shaken.

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