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Effects of silver adsorbed on fumed silica, silver phosphate glass, bentonite organomodified with silver and titanium dioxide in aquatic indicator organisms

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ABSTRACT

In order to reduce the level of transmission of diseases caused by bacteria and fungi, the development of antimicrobial additives for use in personal care, hygiene products, clothing and others has increased. Many of these additives are based on metals such as silver and titanium. The disposal of these products in the environment has raised concerns pertaining to their potential harmfulness for beneficial organisms. The objective of this study was to evaluate the influence of the shape, surface chemistry, size and carrier of three additives containing silver and one with titanium dioxide (TiO_2) on microcrustacean survival. *Daphnia magna* was used as a bioindicator for acute exposure test in suspensions from 0.0001 to 10,000 ppm. *Ceriodaphnia dubia* was used for chronic test in TiO_2 suspensions from 0.001 to 100 ppm. *D. magna* populations presented high susceptibility to all silver based additives, with 100% mortality after 24 hr of exposure. A different result was found in the acute experiments containing TiO_2 suspensions, with mortality rates only after 48 hr of incubation. Even on acute and chronic tests, TiO_2 did not reach a linear concentration-response *versus* mortality, with 1 ppm being more toxic than 10,000 ppm on acute test and 0.001 more toxic than 0.01 ppm on chronic assay. Silver based material toxicity was attributed to silver itself, and had no relation to either form (nano or ion) or carrier (silica, phosphate glass or bentonite). TiO_2 demonstrated to have a low acute toxicity against *D. magna*.

Introduction

Due to the known antimicrobial characteristics of silver (Ag) and titanium dioxide (TiO_2), the use of these elements is increasing in many industrial fields and consumer use materials (*e.g.*, surface coating, electronics, clothes, cosmetics, shoes, keyboards, toothpaste, sunscreen) (Dankovic et al., 2007; Kalbassi et al., 2011). However, while these elements may provide a manner to prevent infections by interfering in pathogenic microorganism proliferation, they may potentially impact the environment when released and transported into air, water, and soil ecosystems during their product life-cycle (Ribeiro et al., 2014). In this respect, an assessment of metal particles regarding their effects on human health and environment is necessary (Carlson et al., 2008).

In the aquatic environment, organisms can come into contact with substances that cause chromosomal aberrations, leading to impairment of cell division and tumor formation (Buzea et al.,

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2007). The researches have focused on the toxicity of Ag and TiO_2 particles to organisms, including algae (Navarro et al., 2008; Hartmann et al., 2010), bacteria (Binaeian et al., 2012; Heinlaan et al., 2008), invertebrates such as cladocerans (Heinlaan et al., 2008; Sakamoto et al., 2015) and vertebrates such as fish (Asharani et al., 2008; Zhu et al., 2008; Wehmas et al., 2015). *Daphnia magna* (*D. magna*) is recognized as a key organism in freshwater ecosystems by being important phytoplankton consumer, while they are preferentially preyed upon by fish (Persson et al., 2007). Also, because of their filter feeding mechanisms (Lovern and Klaper, 2006; Griffitt et al., 2008), sensitivity to environmental pollution, small body size and short life spans, *D. magna* is considered the most sensitive organism in the food web (Clément et al., 2013; Bondarenko et al., 2013), being used to assess the health of environments in ecotoxicological investigations (Lam and Wang, 2006; Flohr et al., 2012; Newton et al., 2013).

A wide range of silver modifications have been employed to improve silver antimicrobial capacity, like carbon nanotubes with silver (Rangari et al., 2010), silver/silica nanocomposites (Egger et al., 2009), zeolites doped with silver (Ferreira et al., 2012), and silver nanoparticles (Kong and Jang, 2008). The mechanisms reported about metal particles' toxicity have been variable depending on the carrier, surface coatings, size and system (Gatoo et al., 2014). Since nanoparticles (Nps) can interact in unpredicted ways with biological systems, a better understanding of the behavior of metal particles with different characteristics and interactions with key aquatic species is required (Albanese et al., 2012). Ag can be ranked after Hg (mercury) as having a high potential cumulative into daphnid bodies (Lam and Wang, 2006). Also, the ionic form Ag^+ is described as being the most harmful to aquatic organisms (Benn and Westerhoff, 2008). Silver nanoparticles (NpAg) are reported as more highly reactive and toxic (Allen et al., 2010). On the other hand, TiO_2 microparticles have been reported as being inert, non-toxic and non-migratory (Rosa, 2013), with a lethal concentration (LC_{50}) higher than 100 mg/L for nanoform and non-nanoform TiO_2 (Wiench et al., 2009). Though, studies with nano TiO_2 have described EC_{50}–48 hr around 8 mg/L in acute test (Dalai et al., 2013) and LC_{50}–48 hr of 7.75 mg/L (Das et al., 2013).

Reckoning with this fact, this study aims to investigate the toxicity effects of nanosilver, silver ions and titanium dioxide (TiO_2) particles toward aquatic crustaceans *Daphnia magna* (*D. magna*) and *Ceriodaphnia dubia* (*C. dubia*). The silver additives tested have three different forms: silver nanoparticles on fumed silica (NpAg_silica), silver phosphate glass (Ag^+_phosphate) and bentonite organomodified with silver (Ag^+_bentonite). The goal of comparing Ag and TiO_2 was to reveal potential differences in toxic mechanisms between these elements. Additionally, *C. dubia* reproduction was investigated after the exposition to TiO_2.

1. Material and methods

1.1. Characterization of the particles

Four additives were tested; nanosilver adsorbed on fumed silica ("NpAg_silica"), silver ions supported in phosphate glass ("Ag^+_phosphate"), bentonite organomodified with silver (Ag^+_bentonite") and a commercial rutile titanium dioxide ("TiO_2").

Determination of mineral composition was held by qualitative analysis by X-ray diffraction, in a PanAnalytical X'pert PRO (PanAnalytical, The Netherlands) and software X'PertHighScore (PanAnalytical, The Netherlands). Particle size distribution was determined by laser diffraction, the equipment used was a CILAS 1180 (Cilas, Orleans, France) particle size analyzer, with scanning range between 0.04 and 2500 μm. NpAg_silica, Ag^+_phosphate and TiO_2 were predispersed in deionized water using ultrasound (60 sec), Ag^+_bentonite was predispersed in isopropyl alcohol.

For transmission electron microscopy (TEM) G2 T20 (Tecnai), samples were dispersed in ethanol by ultrasound for 30 min. The samples were prepared by mounting a drop of the ethanol suspension containing the particles on a 300 mesh copper grid carbon film. Image acquisition was through acceleration voltage of 200 kV. The average particle diameter and scale distribution were calculated using ImageJ version 1.40 g software.

The specific surface area (SSA) was measured by nitrogen adsorption using BET method. Measurements were performed by a Quantachrome Nova 1000 (Quantachrome Instruments, Boynton Beach, FL, USA) and surface area analyzer. Samples were dried in an oven at 110°C for 24 hr and then vacuum at 200°C for 3 hr.

The zeta potential (ZP) measurements were carried out using a zeta scaler Zetasizer NanoZ (Malvern Instruments, Malvern, UK). Each sample was dispersed in deionized water to obtain suspensions at 1%. Suspension pH was adjusted to 3, 5, 7, 9 and 11 using NaOH 0.1 mol/L or HCl 0.1 mol/L.

1.2. Daphnia magna preparation to the acute toxicity assays

Acute toxicity tests were conducted according to ABNT NBR 12713:2009. The acute 24 hr and 48 hr toxicity tests were performed using neonate (2 hr and 26 hr old) *D. magna* (Landesamt Für Wasser und Abfall (LWA), Nordrhein-Westfalen, Düsseldorf, Germany). The animals were derived from the laboratory stock culture at the test facility, where they were reared in artificial fully defined M4 medium at 20°C. Culture medium was renewed twice weekly and the daphnids were fed with a suspension of the unicellular green algae *Desmodesmus subspicatus* and fish-yeast compost.

1.3. Preparation of solutions

For stock suspension preparation, appropriate amounts of Ag and TiO_2 particles were suspended in sterilized double distilled water and dispersed by shaking for 30 min (1500 r/min at 25°C) in a magnetic stirrer-SP-160 (Advantec MFS, Inc., Dublin, CA, USA). Working suspensions were made through serial dilution followed by vigorous vortexing when required. During testing the suspensions were not shaken in order to avoid physically damaging the organisms. In the TiO_2 suspensions, further sedimentation of particles was visually observed.

1.4. Exposure

The test suspensions were prepared immediately before use by diluting the particle powder in eight different concentrations (0.001; 0.01; 0.1; 1; 10; 100; 1000; 10,000 ppm). Four replicates per

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