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Toxicity of solid residues resulting from wastewater treatment with nanomaterials

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ABSTRACT

Nanomaterials (NMs) are widely recommended for wastewater treatments due to their unique properties. Several studies report the different advantages of nanotechnology in the remediation of wastewaters, but limited research has been directed toward the fate and potential impacts of the solid residues (SRs) produced after the application of such technologies. The present work aimed at investigating the ecotoxicity of SRs resulting from the treatment of three effluents (OOMW, kraft pulp mill, and mining drainage) with two NMs (TiO_2 and Fe_2O_3). The invertebrate *Chironomus riparius* was selected as test organism and exposed to the residues. The effect on percentage of survival and growth was assessed. Results showed that the SRs from the treatments nano-TiO_2(1.0 g L^{-1})/H_2O_2(0.5 M) and nano-Fe_2O_3(1.0 g L^{-1})/H_2O_2(1.0 M) from OOMW and nano-Fe_2O_3(0.75 g L^{-1})/H_2O_2(0.01 M) from kraft pulp mill effluent exhibited lethal toxicity to *C. riparius*. Only the exposure to SRs resulting from the treatment with nano-Fe_2O_3(0.75 g L^{-1})/H_2O_2(0.01 M) applied to the kraft pulp mill effluent significantly affected the growth rate based on the head capsule width. In terms of growth rate, based on the body length, it decreased significantly after exposure to the SRs from the treatments nano-TiO_2 (1.0 g L^{-1}) and nano-Fe_2O_3(0.75 g L^{-1})/H_2O_2(0.01 M) of kraft paper mill effluent and nano-Fe_2O_3(1.0 g L^{-1})/H_2O_2(1.0 M) of OOMW. According to our study the SRs can promote negative effects on *C. riparius*. However, the effects are dependent on the type of effluent treated as well as on the organic and inorganic compounds attached to the NMs.

1. Introduction

Surface and ground water resources are continuously facing profound changes and quality deterioration, caused by several anthropogenic activities. Industrial activities, in particular, are often responsible for the direct discharge of effluents containing organic pollutants and metals into aquatic ecosystems deteriorating the quality of water (Kanu and Achi 2011). In an effort to combat the problem of water pollution the research for new wastewater treatment technologies is increasing worldwide. In the last few years nanotechnology has become a hot topic for application in water and wastewater treatment due to the production of nanosize materials with their unique properties (Mohmood et al., 2013). The physical and chemical properties of nanomaterials (NMs) such as high activity for adsorption and photocatalysis (high surface to volume ratio), antimicrobial properties for disinfection, magnetism, or other unique optical and electric properties make them excellent candidates for wastewater treatment (Qu et al., 2013). A plethora of reports have been published reporting the efficient application of nanoparticles for water and wastewater treatment purposes (Hua et al., 2012; Xu et al., 2012; Bora and Dutta, 2014). However, the use of NMs for wastewater treatment will inevitably result in the production of sludge containing NMs and several other chemicals bound to them. Further, some NMs may persist in suspension, which can ultimately be released into the aquatic environment and thereby pose risks to organisms. But to the best of our knowledge, no data about the fate and potential impacts of the solid wastes produced during the wastewater treatment exists

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in previous reports. There is an important knowledge gap on the assessment of the risks associated with this type of residuals to the ecosystem, in particular to the sediments compartment that needs to be addressed.

In aquatic ecosystems, sediments play an important role, as they represent the sink for several lipophilic contaminants (organic and inorganic) entering into water resources (Bettinetti et al., 2012). Moreover, the concentration of contaminants in sediments could be several orders of magnitude higher than in the overlying water. Sediments also provide a habitat and food source for a large number of benthic organisms, which themselves are important links in food chain (Bettinetti et al., 2012). Chironomids represent a large fraction of benthic communities, being one of the most ubiquitous freshwater benthic invertebrates with a worldwide distribution and ecologically relevant to the aquatic food chain (Galluba et al., 2012; Hale et al., 2014). The larvae of the midge *Chironomus riparius* are widely employed as test organisms to evaluate sediment toxicity (Grabow, 1996; USEPA 2000; OECD, 2004). Since *C. riparius* are sediment-dwelling and deposit-feeding organisms, they have a high probability of bioaccumulating high concentrations of contaminants through sediment ingestion (Oberholster et al., 2011), including contaminants like nanoparticles. Although in the last few years important reports have been released concerning the ecotoxicological effects of NMs to benthic fauna (Oberholster et al., 2011; Waissi-Leinonen et al., 2012; Nair et al., 2013; Bour et al., 2015), the knowledge is still scarce and the topic needs to be addressed further. However, to the best of our knowledge there is no report in the literature about the ecotoxicological effect of NMs bound to contaminants after the treatment of real hazardous organic and inorganic effluents to the *C. riparius*.

The objective of this study was to investigate the extent to which the solid residuals (SRs) produced during the treatment of three effluents (olive oil mill, kraft pulp mill, and mining drainage) with two (TiO_2 and Fe_2O_3) NMs impacts the survival and growth of *C. riparius*. The SRs used in this study resulted from our previous studies with wastewater treatment and were chosen from the treatments that showed best performances in ameliorating the chemical characteristics and the toxicity of each effluent. For this purpose, a shortened and adapted version of OECD standard method 218 (Grabow, 1996) was used to test short-term effects on *C. riparius* (survival and growth) by exposing first instar larvae for 10 days to artificial sediment spiked with solid residues containing nano-TiO_2 (239.6–383.2 mg SR Kg^{-1} d.w. of soil) and nano-Fe_2O_3 (195.8–336.3 mg SR Kg^{-1} d.w. of soil) attached to organic and inorganic compounds.

2. Materials and methods

2.1. Solid residue formation

In our previous studies, advanced oxidation processes (AOPs) with NMs (nano-TiO_2/UV, nano-Fe_2O_3/UV, nano-TiO_2/H_2O_2/UV and nano-Fe_2O_3/H_2O_2/UV) were applied to treat OOMW (olive oil mill wastewater), kraft pulp mill effluent and a mining drainage (Nogueira 2015; Nogueira et al., 2015a,b). The influence of different concentrations of nano-TiO_2, nano-Fe_2O_3 and hydrogen peroxide (H_2O_2) was studied. The suspensions (effluent + catalyst) were placed in an orbital shaker (100 rpm) overnight to attain the adsorption–desorption equilibrium of the organic compounds on the surface of the catalyst. After this period a UV lamp (Spectroline XX15F/B, Spectronics Corporation, NY, USA, peak emission at 312 nm) was switched on after the addition of H_2O_2 (when testing the treatments nano-TiO_2/H_2O_2/UV and nano-Fe_2O_3/H_2O_2/UV), and left for 2 h. During irradiation, magnetic stirring was maintained to keep suspensions homogenous. After that, the samples of the treatments that showed best performances in ameliorating the chemical characteristics and the toxicity of each effluent were left to settle. The SRs produced were measured (Table 1).

Table 1
Mass (mg Kg^{-1}) of the SRs containing nano-TiO_2 and nano-Fe_2O_3 in the spiked sediment.

Effluent	Treatment	Mass (mg Kg^{-1})
Olive oil mill (OOMW)	TiO_2 1.0 g L^{-1}/H_2O_2 0.5 M	356.90
	TiO_2 1.0 g L^{-1}/H_2O_2 1.0 M	361.47
	Fe_2O_3 1.0 g L^{-1}/H_2O_2 0.5 M	335.70
	Fe_2O_3 1.0 g L^{-1}/H_2O_2 1.0 M	336.33
Kraft pulp mill	TiO_2 1.0 g L^{-1}	325.40
	TiO_2 0.75 g L^{-1}	232.90
	TiO_2 0.75 g L^{-1}/H_2O_2 0.01 M	242.30
	TiO_2 0.75 g L^{-1}/H_2O_2 0.075 M	239.63
	Fe_2O_3 0.75 g L^{-1}/H_2O_2 0.01 M	218.43
	Fe_2O_3 0.75 g L^{-1}/H_2O_2 0.075 M	195.80
Mining drainage	TiO_2 $1.0^{g L^{-1}}$	383.23
	TiO_2 0.75 g L^{-1}	293.30
	Fe_2O_3 1.0 g L^{-1}	334.13
	Fe_2O_3 0.75 g L^{-1}	275.90

2.2. Characterization of the organic and inorganic content of SRs

The organic (i.e. organic compounds attached to nanoparticles) and inorganic content of SRs produced after the chemical treatment of OOMW, kraft pulp mill effluent and mining drainage were quantified in additional replicates obtained. The SRs were dried in an oven at 60 °C until the weight was constant. A known amount of each dry SR was added to porcelain crucibles that were previously washed, sterilized in a muffle furnace for 30 min at 550 °C, and weighed. To measure the amount of organic content the crucibles with SRs were placed in a muffle furnace at 550 °C for 3 h, cooled at room temperature in desiccators and weighed to the nearest 0.00001 mg. The difference between the oven-dry SR mass and the SR mass after combustion gave us the organic content. The inorganic content in the samples was then determined by heating at 1050 °C for 4 h in the muffle furnace.

2.3. Chironomus riparius *sediment bioassay*

In this study, the SRs were directly mixed with the artificial sediment before the addition of the overlying water (as described in OECD (1984)) giving final concentrations of 195.8–383.2 mg SR Kg^{-1} soil (dry weight) depending on the treatment applied to the effluents (Table 1). A 10-day whole-sediment bioassay with *C. riparius* was carried out following, with adaptions, some of the recommendations of standard guidelines (ASTM, 2002; OECD, 2004). Such adaptations were made in order to deal with the reduced amount of SRs produced in each effluent treatment previously performed in batch conditions (please see Section 2.1). The beakers were prepared 72 h prior to the beginning of the test with 150 g (wet weight) of the spiked sediment and 300 mL of reconstituted hard water (ASTM, 2002), to allow the sediment to attain the equilibrium (Oberholster et al., 2011). Three replicates were set up for each SR test consisting of ASTM hard water and the spiked sediment, while the control utilized ASTM and artificial sediment not spiked. Each replicate received 10 first instar *C. riparius* larvae, which were randomly selected and transferred to each beaker using a glass pipette, and after 30 min, aeration was started. The viability of the larvae was checked as they entered in the water column through their swimming action. The bioassays were conducted at 21 ± 1 °C, under a 16:8 h light:dark photoperiod, and water parameters (temperature, pH, conductivity and dissolved oxygen) were monitored in all beakers at the beginning and the end