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Physicochemical transformation and algal toxicity of engineered nanoparticles in surface water samples☆

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ABSTRACT

Most studies on the behavior and toxicity of engineered nanoparticles (NPs) have been conducted in artificial water with well-controlled conditions, which are dramatically different from natural waters with complex compositions. To better understand the fate and toxicity of NPs in the natural water environment, physicochemical transformations of four NPs (TiO_2, ZnO, Ag, and carbon nanotubes (CNTs)) and their toxicities towards a unicellular green alga (*Chlorella pyrenoidosa*) in four fresh water and one seawater sample were investigated. Results indicated that water chemistry had profound effects on aggregation, dissolution, and algal toxicity of the NPs. The strongest homoaggregation of the NPs was associated with the highest ionic strength, but no obvious correlation was observed between the homoaggregation of NPs and pH or dissolved organic matter content of the water samples. The greatest dissolution of ZnO NPs also occurred in seawater with the highest ionic strength, while the dissolution of Ag NPs varied differently from ZnO NPs. The released Zn^{2+} and especially Ag^+ mainly accounted for the algal toxicity of ZnO and Ag NPs, respectively. The NP-cell heteroagglomeration occurred generally for CNTs and Ag NPs, which contributed to the observed nanotoxicity. However, there was no significant correlation between the observed nanotoxicity and the type of NP or the water chemistry. It was thus concluded that the physicochemical transformations and algal toxicities of NPs in the natural water samples were caused by the combined effects of complex water quality parameters rather than any single influencing factor alone. These results will increase our knowledge on the fate and effects of NPs in the aquatic environment.

1. Introduction

Advances in nanotechnology have promoted the widespread production and application of engineered nanoparticles (NPs), causing increased discharge of NPs into aquatic environments (Garner and Keller, 2014; Gottschalk et al., 2013). For example, ZnO and TiO_2 NPs are widely utilized in cosmetic, coating, paint, and electronic industries (Dange et al., 2007; Franklin et al., 2007; Hall et al., 2009). Ag NPs are employed in a variety of consumer products due to their antimicrobial activity (Dobrzynska et al., 2014), and carbon nanotubes (CNTs) have a range of applications, such as biomedicine (Cha et al., 2013), sewage treatment (Kar et al., 2012), electronics, and sensors (Bennett et al., 2013). Consequently, environmental concentrations of NPs, though being modeled and/or measured to be in levels of μg/L or much less, were estimated to increase exponentially (Gottschalk et al., 2009, 2013). Moreover, environmental concentrations of some NPs in their application or deposition area could be extremely high, e.g., 0.75–50 g/L zero valent iron NPs were used in *in situ* field scale remediation of contaminated soil and groundwater (Grieger et al., 2010). More and more case studies indicated that the discharged NPs could pose serious risks to aquatic organisms (Ma et al., 2013; Schultz et al., 2014).

In aquatic environments, various environmental parameters, such as pH, ionic strength, and dissolved organic matter (DOM), will alter the physicochemical properties and the colloidal behaviors of NPs. It was reported that the aggregation of ZnO NPs increased with increasing ionic strength and was much stronger at

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the pH close to the point of zero charge (pH_{pzc}) of NPs (Bian et al., 2011). In addition, the dissolution of ZnO NPs was observed at both low and high pH and was enhanced by humic acid at high pH (Bian et al., 2011). The aggregation and dissolution of Ag NPs increased with increasing ionic strength (Chambers et al., 2014) but was inhibited in the presence of Cl^- (Lin et al., 2015). CNTs demonstrated enhanced stability in the presence of DOM (Lin and Xing, 2008; Lin et al., 2010a), which was greatly dependent on pH and ionic strength as well (Lin et al., 2009, 2012a). Water-chemistry-dependent homoaggregations of TiO_2 NPs (Lin et al., 2015) and other NPs (Chekli et al., 2015; Conway et al., 2015) have also been reported. In spite of the intensive investigations of the effects of well-controlled water quality parameters on the physicochemical transformations of NPs, the understanding of their fate and behavior in natural water is still in its infancy (Lowry et al., 2012). The combined effects of diverse environmental factors may make the behaviors of NPs in natural water different from those in artificial waters. It is necessary to strengthen the research on the physicochemical transformation of NPs in a real water environment for the scientific assessment of environmental behaviors and biological effects of the NPs.

An increasing number of studies have reported the toxicity of NPs to aquatic organisms with a focus on the effect of water chemistry (Schultz et al., 2014). The higher toxicity of Ag NPs to algal cells was observed in acidic media (Oukarroum et al., 2014) and media with high ionic strength (Chambers et al., 2014), owing to the increased release of silver ions. However, the inverse phenomenon was reported in several studies where Ag NPs demonstrated decreased toxicity in media with higher ionic strength (Gao et al., 2009; Harmon et al., 2014). Mitigated bactericidal effects of ZnO NPs (Li et al., 2013) and TiO_2 NPs (Lin et al., 2014) were also observed in media with high pH or ionic strength. DOMs generally alleviated the nanotoxicity, owing to their complexation with the NP-released toxic ions, the hindrance of NP-organism contact, and/or the reduced generation of reactive oxygen species (Kim et al., 2013; Lin et al., 2012b; Zhao et al., 2013). Enhanced nanotoxicity, however, was also observed in the presence of DOMs (Wang et al., 2011; Zhang et al., 2015). Until now, most studies have been conducted in artificial waters, which are dramatically different from natural waters with complex compositions. Very few studies have investigated the toxicity of NPs toward aquatic organisms including algae in natural water samples (Bhuvaneshwari et al., 2015; Dalai et al., 2013). The complex water chemistry of natural waters would complicate the toxicity of NPs, which merits more investigation.

We hypothesize that there may be no clear correlation between the physicochemical transformation and toxicity of NPs and the water chemistry of natural waters because of the coexistence of multiple water quality parameters. Aggregation, dissolution, and algal toxicity of NPs in five natural water samples with distinct physicochemical properties were, therefore, investigated. Nanoscale TiO_2, ZnO, CNTs, and Ag particles were used as the typical NPs because of their extensive usage. The unicellular green alga (*C. pyrenoidosa*), a widely used model aquatic organism, was selected as the test organism. The correlations between water chemistry and aggregation, dissolution, and algal toxicity of the NPs were specifically discussed. We believe that our findings will increase the knowledge on the fate and effects of NPs in the aquatic environment.

2. Materials and methods

2.1. Collection and characterization of water samples

Five surface water samples with distinct physicochemical properties were collected in October 2013 from a fish pond in Tangxi town (TX, N 30°28′26″, E 120°11′19″) of Hangzhou city, a countryside river in Dongyang city (DY, N 29° 17′ 23″, E 120° 14′ 30″), the Dongjiang river in Shaoxing city (SX, N 30°4′25″, E 120°27′29″), the Taihu lake (TH, N 31°5′55″, E 120°15′56″), and the East China Sea at Taizhou city (TZ, N 28°13′54″, E 121°24′20″) of China. The collected water samples were centrifuged (3500 *g*, 15 min) to remove large particles, filtered through 0.45 μm polytetrafluoroethylene filters to remove microorganisms, and then stored at 4 °C in dark. The five water samples represented various water environments: TX being a fishery-affected water body, DY standing for the freshwater far away from cities, SX representing the river water passing through a city, TH being the freshwater from one of the biggest lake in China, and TZ being the seawater in an estuary mixed with freshwater.

The conductivity of the samples was analyzed with a conductivity meter (DDS-11A, Yoke Instrument Co., China). The content of total organic carbon (TOC) was measured by a TOC analyzer (TOC-VCPH, Shimadzu, Japan) to reflect the DOM content. The pH and zeta potential were determined using a pH meter (Mettler Toledo, Columbus, USA) and a Zetasizer (Nano ZS90, Malvern Instruments, UK) at 25 °C, respectively. Inductively coupled plasma mass spectrometry (ICP-MS, 7500 Series, Agilent, USA) was applied to determine cation concentrations in the surface water samples after acid digestion. Anions excluding CO_3^{2-} in the samples were analyzed using ion chromatography (861 Advanced Compact IC, Metrohm, Switzerland). The concentration of CO_2^{3-} was expressed as the inorganic carbon content as measured by the TOC analyzer.

2.2. Characterization of the NPs in the water samples

The used ZnO (20 ± 5 nm) and anatase TiO_2 (12 ± 4 nm) NPs were purchased from Zhejiang Hongsheng Materials Technology Co., China. Ag NPs (46 ± 25 nm) were obtained from Beijing Daoking Technology Ltd., China. The multiwalled CNTs (70 ± 9 nm in the outer diameter and 3.2 ± 0.9 μm in length) were from Shenzhen Nanotech Port Co., China and were further purified by HCl solution before use. We had previously characterized and used all the NPs in other studies (Ji et al., 2011; Long et al., 2012; Lin et al., 2015), and their selected properties are summarized in Table S1 in the Supporting information.

The NPs (100 mg/L) were sonicated (100 W, 40 kHz, 25 °C) into the water samples for 30 min, and their zeta potentials and hydrodynamic sizes were measured by the Zetasizer at 25 °C. To determine the dissolution of ZnO and Ag NPs in the water samples, the concentrations of metal ions in the supernatants of the NP suspensions collected after the centrifugation (2500 g, 15 min) and the filtration through 0.22 μm polytetrafluoroethylene filters were quantified by the ICP-MS.

2.3. Settling experiment

NP–NP and cell–cell homoaggregations and NP-cell heteroagglomeration in the water samples were investigated following the procedures described in our previous study (Ma et al., 2015). Briefly, algal cells and NPs were individually suspended or mixed in the water samples; the individual suspensions or mixtures were immediately transferred to cuvettes, and their absorbance at 660 nm (Lin et al., 2012b; Long et al., 2012) was thereafter monitored. Since the CNTs were more hydrophobic and settled much faster than the other NPs, the absorbance of CNT suspensions was monitored at intervals of 1 s within 2 h, whereas the absorbance of ZnO, TiO_2, and Ag suspensions was recorded for 12 h at intervals of 15 min. The settling curves, normalized absorbance vs. settling time curves, were subsequently plotted. The co- (mix) and additive-