



Molecular transformation of natural and anthropogenic dissolved organic matter under photo-irradiation in the presence of nano TiO₂



Jitao Lv^a, Dan Li^b, Lei Luo^a, Tong Wu^b, Shuzhen Zhang^{a, c, *}

^a State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

^b School of Environmental Science and Engineering, Hebei University of Science and Technology, Hebei, 050018, China

^c University of Chinese Academy of Sciences, Beijing, 100049, China

ARTICLE INFO

Article history:

Received 24 March 2017
Received in revised form
23 August 2017
Accepted 23 August 2017
Available online 26 August 2017

Keywords:

Dissolved organic matter (DOM)
Sewage sludge
Peat
Photo-transformation
TiO₂
FT-ICR-MS

ABSTRACT

Photochemical transformation of dissolved organic matter (DOM) plays a very important role in the cycling of organic carbon in aquatic systems. Increasing release of photoactive nanoparticles such as titanium dioxide nanoparticles (nano TiO₂) into surface water may impact this process. The present study employed Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS) to examine the molecular transformation of natural DOM (peat DOM, DOM_p) and anthropogenic DOM (sludge-derived DOM, DOM_s) under photo-irradiation as affected by nano TiO₂. Differences in molecular components between DOM_p and DOM_s were observed. DOM_s contained more heteroatom formulas (76%) with low aromaticity and low carbon oxidation state than did DOM_p (22%). The presence of nano TiO₂ resulted in significant decreases in both DOM content and molecular diversity under photo-irradiation. Consistent alterations were observed between DOM_p and DOM_s such that high molecular weight compounds, high aromaticity and/or heteroatom S-containing compounds were more easily photodegraded in the presence of nano TiO₂; whereas the average carbon oxidation state decreased in DOM_p but increased in DOM_s, likely due to the significant differences in O abundance, especially in the contents of carboxyl moieties, between DOM_p and DOM_s. The findings of the present study suggest that the release of nano TiO₂ into aquatic environment will accelerate the consumption of dissolved organic carbon and the attenuation of molecular diversity for both DOM in waters.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

Among the commercially available engineered nanoparticles (NPs), titanium dioxide nanoparticles (nano TiO₂) are the most widely used engineered nanomaterials to date (Troester et al., 2016). Nano TiO₂ materials have been produced on a large scale for applications in pigments, coatings, and sunscreen cosmetic additives, as well as environmental applications such as removal of various contaminants in water, air and soils by adsorption and/or photo-catalytic degradation (Lee and Choi, 2002; Luo et al., 2010; Pena et al., 2006; Zhang et al., 2007). As a result, the release of nano TiO₂ into the environment is unavoidable, particularly into waters, and the amount will continue to increase (Klaine et al.,

2008; Nowack and Bucheli, 2007). Therefore, the contents of nano TiO₂ in waters are expected to be much higher than other engineered nanoparticles (Gottschalk et al., 2010, 2009). Model studies have predicted that the production of nano-TiO₂ would exceed 2.5 million tons per year by 2025 (Robichaud et al., 2009). Once released into waters, nano TiO₂ will interact with dissolved organic matter (DOM), which universally exists in natural water. In the past few years, many researchers have demonstrated that DOM plays a critical role in the stability and mobility of NPs, including nano TiO₂, in aquatic environments (Domingos et al., 2009; Aiken et al., 2011; Zhu et al., 2014; Adam et al., 2016). These studies have demonstrated that the bond of DOM on nano TiO₂ will significantly reduce the aggregation of nanoparticles in aqueous systems. Therefore, the presence of DOM will not only enhance the mobility but also impact the distribution of nano TiO₂ in waters.

Another important fact is that TiO₂ is a photoactive nanomaterial. Studies have demonstrated that TiO₂-based photo-catalytic oxidation can induce the destruction of natural organic

* Corresponding author. Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, P. O. Box 2871, Beijing 100085, China.

E-mail address: szzhang@rcees.ac.cn (S. Zhang).

matters (Eggins et al., 1997; Li et al., 2002; Liu et al., 2008a, 2008b; Wiszniewski et al., 2003). Most of these studies attempted to monitor the changes in concentration and spectral features of dissolved organic carbon (DOC) in waters in the presence of nano TiO₂. Some investigated the changes in the molecular weight and hydrophobic fractions of DOM by using size exclusion chromatography (SEC) and resin fractionation (Liu et al., 2008a, 2008b; Wu et al., 2016). However, these analytical techniques failed to clarify the photocatalytic transformation of DOM at the molecular scale. The great advance in high-resolution mass spectroscopy technique namely electrospray ionization coupled with Fourier transform ion cyclotron resonance mass spectrometry (ESI-FT-ICR-MS) provided the unique opportunity to detect thousands of individual molecules in DOM (Kim et al., 2003), which has greatly improved our understanding of the chemical features of DOM at the molecular level (Reemtsma, 2009; Minor et al., 2014), although it has difficulties with quantitative analysis. Recently, FT-ICR-MS has been used to investigate the molecular transformation of river and ocean DOM induced by sunlight irradiation (Gonsior et al., 2009; Stubbins et al., 2010). The molecular characteristics of photo-resistant, photolabile and photo-produced fractions in Congo River DOM were described by Stubbins et al. (2010).

Characterization of anthropogenic DOM such as the ones derived from wastewater, sewage or farm wastes etc (Meng et al., 2013), at the molecular level using FT-ICR-MS has been very limited (Gonsior et al., 2011; Li et al., 2015; Tseng et al., 2013). In a previous research using FT-ICR-MS, Gonsior et al. (2011) found that DOM in effluent displayed a much more complex molecular diversity than the ones in natural water, notably the presence of an unexpected amount of sulfur-containing molecular formulas. Li et al. (2015) used FT-ICR-MS to further investigate the molecular transformation of DOM in refinery wastewater from water treatment processes. However, clarification of molecular transformation in wastewater- and sludge-derived DOM induced by photochemical or other biogeochemical process has not been achieved.

Sludge is an important sink of engineered nanoparticles. Previous studies have revealed that TiO₂ accumulates in dry sludge at concentrations ranging from 1 to 6 g Ti/kg (Kiser et al., 2009; Gottschalk and Nowack, 2011). Furthermore, organic matters are also prone to sequestration in sludge. As a result, the coexistence of nano TiO₂ and sludge-derived DOM is widespread. The aim of the present study was to investigate the molecular transformations of natural and anthropogenic DOM under photo-irradiation in the presence of nano TiO₂ using ESI-FT-ICR-MS. The results will extend our understanding of the environmental and ecological risk of photoactive nanomaterials such as nano TiO₂ as well as the fate of DOM in the environment.

2. Materials and methods

2.1. Peat and sewage sludge dissolved organic matter

Water-extractable organic matter extracted from a commercially available fen peat (Klasmann, Germany) was selected as the representative of natural DOM (peat DOM, DOM_p), and water-extractable organic matter extracted from sewage sludge (sludge-derived DOM, DOM_s) generated in a wastewater treatment plant in Beijing was selected as the representative of anthropogenic DOM. Briefly, the DOM was extracted by shaking dry peat or sewage sludge with ultrapure water at a ratio of 1:10 for 24 h at room temperature. The leachate was obtained by centrifugation of the above peat or sewage sludge suspensions at 5000 rpm and filtered through 0.22- μ m Nylon filters. The extraction procedure was repeated three times. The final DOM_p and DOM_s solutions were kept in the dark at 4 °C until further use.

Structural characteristics and carbon-functional-group contents in DOM_p and DOM_s were measured with solid-state ¹³C NMR using cross-polarization and magic angle spinning (CP/MAS) techniques. Spectra were recorded on a 400 MHz NMR Unity Inova Varian spectrometer using the same method as a previous study (Rodriguez-Zuniga et al., 2008).

2.2. Photochemical experiment

A typical photochemical experimental procedure was adopted in this study. Aqueous solutions of DOM, set at 40 mg L⁻¹ TOC, higher than their normal environmental levels, and commercial-grade TiO₂ (Aeroxide P25, 80% anatase and 20% rutile, 100 mg L⁻¹) were put into a 250-mL glass-lined vessel under constant stirring. The pH of the suspension was adjusted to 7.0 using diluted HCl (0.1 M) and then equilibrated in the dark under stirring for 2 h before illumination. The extent of DOM adsorption onto nano-TiO₂ was found to be insignificant in the dark control (about 1.2% of DOC adsorbed) due to the low ratio of nano-TiO₂ to DOC loaded. Simulated solar irradiation experiments were performed in a CEL-APR photochemical reactor (Cealight, Beijing, China) equipped with a 300 W xenon lamp placed in a quartz cooling well. An AM 1.5 filter was used to best match the total solar spectrum, with average illuminance of about 1.2×10^5 lux. Dark control samples were processed under the same conditions except for photo-irradiation. At given time intervals, a certain amount of suspension solution was collected, centrifuged and filtered through pre-rinsed 0.22 μ m Nylon membranes, and the filtered supernatants were used for further analysis. The absorbance spectra of the filtered supernatants from 200–650 were determined using a Shimadzu UV-2600 UV–vis spectrometer. All batch experiments were conducted in triplicate.

2.3. ESI-FT-ICR-MS analysis

Selected samples before and after photo-irradiation were further analyzed by ESI-FT-ICR-MS. Sample entrapment and desalination were performed on all the samples by solid phase extraction (SPE) according to Dittmar et al. (2008) using Varian Bond Elute PPL cartridges (500 mg/6 mL). Briefly, the cartridges were rinsed with 6 mL of methanol (MS grade) and pure water respectively prior to use. The samples were acidified to pH 2 with HCl (32%, ultrapure), and then passed through the cartridges by gravity at a flow rate of approximately 2 mL min⁻¹. Cartridges were rinsed with three volumes of 0.01 M HCl for the removal of salts, dried with a stream of N₂ and immediately extracted with three volumes of methanol (MS grade). Eluted samples were blow-dried with N₂ and kept in the dark at –20 °C. The extraction efficiencies of DOM_p and DOM_s by PPL-based SPE were about 72% and 61% according to their TOC recoveries, respectively. Some highly hydrophilic compounds such as carbohydrates and proteins may be lost during SPE (Riedel et al., 2012); therefore, the identified DOM is actually SPE-DOM. These dried samples were dissolved in 50:50 methanol/water (v/v) for ultrahigh resolution mass spectrometry analysis. Ultrahigh resolution mass spectra were acquired using a Bruker Solarix FT-ICR-MS equipped with a 15.0 T superconducting magnet and an ESI irradiation ion source under the same conditions as the previous report (Cao et al., 2015; Lv et al., 2016).

2.4. Molecular formula assignment

All possible formulas were identified with Bruker Data Analysis software based on the requirement that the mass error for a given chemical formula between measured mass and calculated mass was ≤ 0.5 ppm. Molecular formulas were assigned to peaks with a

Download English Version:

<https://daneshyari.com/en/article/5758791>

Download Persian Version:

<https://daneshyari.com/article/5758791>

[Daneshyari.com](https://daneshyari.com)