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Effect of humic acid source on humic acid adsorption onto titanium dioxide nanoparticles

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HIGHLIGHTS

- Extent of humic acid adsorption onto nano-TiO_2 depending on HA source
- Preferential HA adsorption onto nano-TiO_2 depending on aromaticity
- Humic acid effects on sedimentation, aggregation and stability of nano-TiO_2

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ABSTRACT

In many studies, different humic acid (HA) sources are used interchangeably to evaluate the effect of organic matter on geochemical processes in the environment. This research looks more specifically at the effect of HA source on HA adsorption onto nano-TiO_2 and how HA adsorption affects the fate and transport of nano-TiO_2. In this study, six humic acids (HAs) were studied which were derived from soils (SLHA), or from sediments (SDHA) all originating from the state of Florida. Humic acid adsorption onto titanium dioxide nanoparticles (nano-TiO_2) and the sedimentation of HA-coated and uncoated nano-TiO_2 were monitored by Ultraviolet–visible (UV–vis) spectroscopy. Synchronous scan fluorescence (SSF) spectroscopy was used to complement the study of HA adsorption onto nano-TiO_2. Phosphate buffer was found to reduce the amount of HA adsorbed onto nano-TiO_2 relative to solutions of NaCl of the same pH and ionic strength. Adsorption constant values (K_{ads}) for HAs varied in the order SLHA > FSDHA (freshwater sedimentary HA) > ESDHA (estuarine sedimentary HA). SSF results suggested that the more highly conjugated fractions of HA, which are more prevalent in SLHAs versus SDHAs, were preferentially adsorbed. In order to better understand the relationship between adsorption and aggregation, sedimentation studies were conducted and it was found that the percentage of nano-TiO_2 sedimentation was preferentially enhanced in the order of the presence of SLHA > FSDHA > ESDHA. The extent of nano-TiO_2 sedimentation was decreased with increasing HA concentration. TEM imaging of nano-TiO_2 confirmed that nano-TiO_2 was aggregated in the presence of HAs. The findings in this study suggest that HAs from different sources influence the fate and transport of nano-TiO_2 in the environment differently.

1. Introduction

The distribution of metal oxide nanoparticles (NPs) such as CuO, ZnO, Al_2O_3 and TiO_2 in commercial products such as industrial filters, ceramics, coatings, catalysts, semiconductors, and microelectronics has rapidly increased in recent years (Robichaud et al., 2009). In particular, titanium dioxide nanoparticles (nano-TiO_2) are one of the most widely produced nanoparticles because of their excellent dielectric and chemical properties (Schmidt and Vogelsberger, 2009). Some uses include stabilizing agents in sunscreens, cosmetics and paints (Aitken et al., 2006; Chen and Mao, 2007; Robichaud et al., 2009; Domingos et al., 2010) and in water treatment plants and pollution remediation due to its high specific surface area and sorption capacity for ionic and nonionic species (French et al., 2009). This huge demand for nano-TiO_2 has increased the extent of its possible entry into the environment and several studies have shown that nano-TiO_2 is toxic to plants and animals (Aruoja et al., 2009; Singh et al., 2010; Gao et al., 2012). Yang et al. (2013) described the enhanced toxicity of nano-TiO_2 to developing zebra fish (*Danio rerio*) in the presence of Suwannee River humic acid, while Lin et al. (2012) found that both adsorbed and dissolved humic acid reduced the toxicity of nano-TiO_2 to *Chlorella* species. Therefore, an understanding of the effect of humic acid on the fate and transport of nano-TiO_2 in environments is crucial.

The environmental partitioning of nano-TiO_2 in the environment depends on processes such as dispersion and agglomeration which are affected by environmental factors such as the presence of natural

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organic matter (NOM), including humic acid (HA) and solution chemistry (Wang et al., 2012; Chowdhury et al., 2012). Humic acid has been found to inhibit the aggregation of NPs associated with its adsorption onto NPs (Kilduff et al., 1996; Vermeer and Koopal, 1998; Vermeer et al., 1998; Thio et al., 2011). Chen et al. (2012) reported enhanced mobility of nano-TiO_2 in sand columns at an acidic pH but lower mobility at a basic pH due to variation in humic acid adsorption onto nano-TiO_2, as well as significant variation in nano-TiO_2 deposition as a factor of humic acid concentration and pH. Humic acids are formed from the microbial decomposition of animal and plant residues and are widely distributed on the planet in soils, sediments, and natural waters (Rezacova and Gryndler, 2006; Pospisilova and Fasurova, 2009). The variability of HA structure is based on its source and environmental exposure. Therefore, studies on how humic acids from different sources affect nano-TiO_2 fate and transport are extremely important.

The relative abundance of HA functional groups such as carboxylic acid and phenol, as well as aromatic rings and free radicals has a direct effect on HA properties (Chen et al., 2000; Pospisilova and Fasurova, 2009; Kwiatkowska-Malina, 2011; Lishtvan et al., 2012). Some studies have shown that slow microbial decomposition of lignin, which contains benzene carboxylic and phenolic components, is a major contributor to soil humic acids (SLHAs), while sedimentary humic acids (SDHAs) are derived primarily from algal or bacterial residues (Malcolm, 1990). HAs extracted from different environments have different characteristics which can be correlated to the abundance of various functional groups (McDonald et al., 2004; Rezacova and Gryndler, 2006). These differences in HA characteristics may have a significant effect on the extent of HA adsorption onto NPs and ultimately affect the extent of NP aggregation and deposition. Humic acids are frequently used in studies that look at the effect of naturally occurring organic matter on the fate and transport of NPs. The effect of HA characteristics and sources on HA adsorption onto nano-TiO_2 has not been evaluated when studying the fate and transport of NPs. The main objective of this work was to expand our understanding of the effect of HA source on the environmental fate and transport of nano-TiO_2.

2. Experimental methods

2.1. Materials

Titanium dioxide nanoparticles (nano-TiO_2) (CAS-Reg. No: 13463-67-7) were purchased from Degussa (nominal primary diameter of about 21 nm reported by manufacturer). In order to study the effect of HA extracted from different sources on HA adsorption onto nano-TiO_2, HAs which had previously been extracted from soils, freshwater sediments, and estuarine sediments from the state of Florida (Fig. S-1 and Table S-1) were utilized in this study. Soil humic acid samples included Florida Institute of Technology Jungle (SL1HA) and West Melbourne (SL2HA). A freshwater sedimentary humic acid (FSDHA) sample was derived from the Sebastian River (SD1HA) while estuarine sedimentary humic acids (ESDHAs) were derived from Kings Bay (SD2HA and SD3HA) and Mullet Creek (SD4HA). The extraction and purification procedures for HA samples were identical to those described in Cameron and Sohn (1992), however, an additional pre-extraction acidification step was undertaken to dissolve $CaCO_3$ and then wash Ca^{2+} from the carbonate-rich Florida samples, because not doing so would have hindered the extraction processes by forming insoluble HA-calcium salts in alkaline solutions. These samples were stored in desiccators until use. All chemicals were purchased from Sigma-Aldrich or Fischer Scientific and used without further purification. All aqueous solutions were prepared using Milli-Q water purified by an 18.2 MΩ Milli-Q purification system (Billerica, MA, USA). The pH of solutions was adjusted with NaOH and HCl using an Orion pH/ISEmeter (model 710A, Thermo Fisher Scientific, Waltham, MA). All experiments were performed at room temperature (22 ± 1 °C).

2.2. Preparation of HA stock solutions

Humic acid stock solutions were prepared by dissolving the dry powders (80 to 100 mg) of HA samples in either 100 mmol L^{-1} NaH_2PO_4 or 100 mmol L^{-1} NaCl. The solution pH was adjusted using concentrated HCl or NaOH as required. To dissolve the HAs, the solutions were gently stirred overnight at room temperature and any undissolved HA was removed by a previously weighed 0.45 μm filter (MF Membrane Filter, Cat No.: HAWP04700); HA concentrations were adjusted for the weight of the undissolved HA. The HA stock solutions were stored in the dark and their concentrations were routinely checked by measuring the absorbance at 254 nm. The solution pH was also checked routinely. For each experiment, solutions of HAs were prepared by diluting the prepared stock solution in either 100 mmol L^{-1} NaH_2PO_4 or 100 mmol L^{-1} NaCl to produce 10 mg L^{-1} HA (final solution pH adjusted to 7.8 ± 0.2).

2.3. Instruments

An Agilent Technology 8453 spectrophotometer was used to perform all UV–vis absorbance measurements using a 1 cm optical path length quartz cuvette. A FluoroMax-3 (J-Y/Horiba SPEX Fluorolog spectrophotometer) was used for synchronous scan fluorescence (SSF) measurements. The HA solutions were placed in a single 1 cm (4 mL) quartz cuvette and analyzed by SSF spectrophotometry. As was reported in a previous study in this laboratory (Horst et al., 2013), the synchronous scan fluorescence spectra were measured over a range of 240 to 650 nm at a constant wavelength difference ($\lambda_{em} - \lambda_{ex}$) of 55 nm. The slit widths for both the excitation and emission monochromators were held at 7 nm band pass and increments of 1.0 nm and an integration time of 0.3 s were used. The TEM images for selected HA-coated and uncoated nano-TiO_2 were captured using a low resolution (0.5 nm) Zeiss EM-900 instrument with an accelerating voltage of 80 kV using 400-mesh Carbon/Formvar TEM grids (Electron Microscopy Sciences).

2.4. Time study

In order to determine the time at which the equilibrium of HA-nano-TiO_2 suspensions was attained, 5 mg of nano-TiO_2 was added to 10 mL of 50 mg L^{-1} of each HA solution (pH adjusted to 7.8 ± 0.2 and ionic strength adjusted to 100 mmol L^{-1}). The HA-nano-TiO_2 suspensions were placed on a stirring plate for 96 h. During the experimental time period, 2 mL aliquots of the suspensions were filtered at 0, 4, 8, 12, 24, 48, 72, and 96 h using a 0.45 μm syringe filter (Nylon Syringe Filters, Pore: 0.45 μm, diameter: 13 mm). Filtered solutions were analyzed by UV–vis absorbance measurements at 254 nm. HA concentrations were determined from calibration curves.

2.5. Adsorption study

In order to evaluate adsorption isotherms, nano-TiO_2 was added in increments of 5 mg for a total of 0–25 mg to 10 mL of 10 mg L^{-1} of the various HA solutions. The HA-nano-TiO_2 suspensions were placed on a stirring plate for 48 h (based on time study). The suspensions were then filtered using 0.45 μm syringe filters. Samples were analyzed using UV–vis absorbance measurements at 254 nm. The mass of HA that was adsorbed onto nano-TiO_2 was determined from the difference in the absorbance before and after equilibration with nano-TiO_2. After completion of the adsorption measurements, synchronous scan fluorescence spectroscopy was used as a complementary technique, to provide more information about HA adsorption onto nano-TiO_2. Finally, the nano-TiO_2 suspended in HA solutions and their controls were subsequently utilized for further studies such as sedimentation measurements and TEM imaging.