King Saud University

Journal of Saudi Chemical Society

www.ksu.edu.sa
www.sciencedirect.com

ORIGINAL ARTICLE

Properties of different natural organic matter influence the adsorption and aggregation behavior of TiO_2 nanoparticles

Muxi Luo [a,1], **Yuxiong Huang** [b,1], **Miao Zhu** [a], **Yue-ning Tang** [a], **Tongxuan Ren** [a], **Jie Ren** [a], **Hongtao Wang** [a,*], **Fengting Li** [a]

[a] *Key Laboratory of Yangtze River Water Environment, Ministry of Education, State Key Laboratory of Pollution Control and Resource Reuse, College of Environmental Science and Engineering, Tongji University, Shanghai 200092, China*
[b] *Bren School of Environmental Science and Management, University of California, Santa Barbara, CA 93106, United States*

Received 24 November 2015; revised 6 January 2016; accepted 27 January 2016

KEYWORDS

TiO_2 nanoparticles;
Humic acid;
Fulvic acid;
Entanglement;
Aggregation;
Interface interaction

Abstract Natural organic matter (NOM) has considerable influence on the aggregation and stability of titanium dioxide nanoparticles (TiO_2 NPs). However, the effect of chemical properties of NOM on the interface interaction and the aggregation process is still not clear. In this study, we investigated the effects of two typical types of NOM (fulvic acid (FA) and humic acid (HA)) on its adsorption onto TiO_2 nanoparticles and their aggregation behavior in aqueous phase. Nuclear Magnetic Resonance (NMR) was used to study their functional groups, indicating that HA has a stronger hydrophobicity than FA. The presence of HA or FA lowered the critical coagulation concentration (CCC) of TiO_2 NPs, while FA showed a more significant effect. HA promotes the aggregation of TiO_2 NPs when ionic strength (IS) > CCC, which was likely due to the bridging effect. Contact angle measurements indicate that HA has higher hydrophobic properties than FA, and it is easier to transfer from water to the surface of TiO_2 NPs. Transmission Electron Microscopy (TEM) was applied to investigate the aggregate formation and colloid interface morphology of NOM-coated-TiO_2 NPs and NOM entanglement. Different structures of HA and FA result in various behavior and their interface interaction mechanisms including IS-induced entanglement and NOM/IS bridging.

---

[*] Corresponding author. Tel.: +86 21 65980567; fax: +86 21 65985059.
E-mail addresses: luomuxi001@126.com (M. Luo), huangyx07@gmail.com (Y. Huang), zhumiao2013@163.com (M. Zhu), 1223278816@qq.com (Y.-n. Tang), 1269811997@qq.com (T. Ren), 1942124607@qq.com (J. Ren), hongtao@tongji.edu.cn (H. Wang), fengtingli@126.com (F. Li).
[1] These authors contributed equally to this work as first authors.

Peer review under responsibility of King Saud University.

Production and hosting by Elsevier

http://dx.doi.org/10.1016/j.jscs.2016.01.007
1319-6103 © 2016 King Saud University. Production and hosting by Elsevier B.V.

Please cite this article in press as: M. Luo et al., Properties of different natural organic matter influence the adsorption and aggregation behavior of TiO_2 nanoparticles, Journal of Saudi Chemical Society (2016), http://dx.doi.org/10.1016/j.jscs.2016.01.007

1. Introduction

TiO_2 nanoparticles (NPs) have been widely used in commercial applications, including cosmetic additives, environmental catalysts, solar cells, memory devices and food colorants [1,2]. Through various pathways, these NPs could be released into the aqueous environments [3], which would lead to the exposure of the organisms [4]. With the possible physical–chemical transformation and bioaccumulation in the environments, TiO_2 NPs further pose threats to human health and ecosystems [1,4,5]. Another study also indicated that large amounts of TiO_2 NPs (100–3000 μg/L) in the influent of sewage treatment plant would cause adverse impact on the urban sewage treatment system and sludge disposal [6].

Previous studies suggested that the aggregation process had a significant impact on NPs' physicochemical properties, such as the particle size, surface properties and their migration, transformation and toxicity in aqueous environments [7,8]. As reported [9], the presence of NOM as well as the IS and pH of solution has influence on the stability and aggregation of metal oxide NPs (TiO_2, CeO_2 and ZnO), with results showing that the aggregation and sedimentation of NPs were easily facilitated at pH values near the point of zero charge (pH_{pzc}), high IS and the presence of a low total organic carbon (TOC). In addition, these factors have effects on the removal of TiO_2 NPs by coagulation or porous media [10–12]. Particularly, the adsorption of NOM onto the surface of nanoparticles could lead to surface coating and modification, which would eventually change its properties such as hydrophobicity and surface charge [13]. Study indicated that the molecular weight (Mw) distribution and chemical properties of NOM significantly affect the aggregation of gold NPs [14]. Many studies focused on NOM adsorption onto the TiO_2 NPs' surface and the effects on the stability of TiO_2 NPs under different IS and pH [13,15–17]. Indeed, IS could compress electrical double layer of the TiO_2 NPs and form cationic bridges [18,19]. Some researchers have noticed the entanglement of NOM and its influence on the aggregation of NPs [14,20,21]. However, the influences of the structural properties of NOM on its entanglement mechanism were ignored.

In the aqueous environments, HA and FA are two common NOM with different Mws and functional groups. Recently, several studies investigated the adsorption of HA and FA onto the NPs' surface and its steric hindrance effect [22–25]. The types and amounts of HA and FA adsorbed onto the surface of TiO_2 NPs could affect the aggregation of TiO_2 NPs [16]. In addition, NOM adsorption onto the surface of TiO_2 NPs would change the hydrophilic–hydrophobic properties of the system [26,27]. However, the effects of the Mw and properties of NOM as well as the interface interaction mechanism on TiO_2 NPs aggregation process are not well understood.

In this study, the effects of HA and FA on the aggregation of TiO_2 NPs were systematically studied. It was found that the adsorption of NOM onto the surface of TiO_2 NPs was influenced by the hydrophilicity–hydrophobicity of the TiO_2-NOM system, which was measured by contact angle. In addition, the entanglement of NOM at different ionic strength (IS) was observed by Transmission Electron Microscopy (TEM). The mechanism of the interface interaction between TiO_2 NPs and HA or FA was proposed.

2. Materials and methods

2.1. TiO_2 NPs

TiO_2 NPs (rutile) were purchased from Sigma–Aldrich Trading Co., Ltd. (Shanghai, China). The BET surface area was determined to be 26.76 ± 0.16 m^2/g by N_2 adsorption (Table. S1). The size and shape of TiO_2 NPs were characterized by TEM (Fig. S1) to be diameter × length = 10 nm × 40 nm. We also measured the hydrated size of TiO_2 NPs by a Malvern Zetasizer (Nano ZS 90, UK). The average hydrodynamic diameter of the TiO_2 NPs was 195.4 nm (Fig. S2). TiO_2 NPs were added into Millipore water (Millipore, 18.2 MΩ cm, TOC < 2 ppb) to achieve 0.4 g/L stock suspension. The stock suspension of TiO_2 NPs was sonicated for 20 min [28] and the fresh stock was prepared daily.

2.2. Characterization of HA and FA

Suwannee River humic acid standard (Cat. No. 2S101H) and fulvic acid standard (Cat. No. 1S101F) were purchased from the International Humic Substances Society (IHSS). The HA and FA were added into Millipore water to achieve 400 mg/L and the pH was adjusted to 11 by adding 0.01 mol/L and 0.1 mol/L NaOH. The suspensions were stirred for 24 h to ensure complete dissolution and then centrifugated at 8000 rpm for 6 min and filtered by 0.22 μm filter membrane to remove the insoluble materials. The stock solutions were stored under 5 °C. The TOC of the HA and FA was measured by a Shimadzu TOC V-CPN. The TOC concentrations are about 4.19 ± 0.10 mg/L and 4.60 ± 0.10 mg/L for HA and FA respectively, whose mass concentrations are both 10 mg/L.

After adjusted to pH = 8.0 and filtered using 0.22 μm filter membrane, the average Mw and distribution of HA and FA were measured by gel permeation chromatography (GPC) method on a high performance liquid chromatography (HPSEC 2695 Waters, USA) system coupled with an UV/Vis Detector Waters (2489 Waters, USA) and Total organic carbon analyzer (Sievers 900 Turbo GE, USA), following the previous reported method [29]. Zeta potential was measured through Malvern Zetasizer (Nano ZS 90, UK). The structure and functional groups of HA and FA stock suspensions were characterized by Nuclear Magnetic Resonance (NMR, DMX 500) technique. Fourier transform infrared attenuated total reflectance (FTIR/ATR, Bruker-Vector 22) spectrometer equipped with a germanium crystal was used to determine the functional groups of HA and FA stock solutions. The background spectra were recorded in air.

2.3. Adsorption experiment

Generally, 10 mg/L of HA or FA solutions were added to 50 mL centrifuge tubes. To study the adsorption effect of HA or FA onto the surface of TiO_2 NPs, 100 mg/L TiO_2 NPs suspension was added to the HA/FA solution. To investigate the influence of IS on HA and FA, IS was provided by $CaCl_2$ stock solution (0–50 mmol/L) in the absence of TiO_2 NPs. 0.01 mol/L and 0.10 mol/L NaOH were used to adjust pH to 8 ± 0.05. The total volume was 20 mL