



Contribution of coated humic acids calculated through their surface coverage on nano iron oxides for ofloxacin and norfloxacin sorption



Hongbo Peng^a, Ni Liang^a, Hao Li^a, Fangyuan Chen^a, Di Zhang^a, Bo Pan^{a,*},
Baoshan Xing^b

^a Faculty of Environmental Science & Engineering, Kunming University of Science & Technology, Kunming, Yunnan 650500, China

^b Stockbridge School of Agriculture, University of Massachusetts, Amherst, MA 01003, USA

ARTICLE INFO

Article history:

Received 27 January 2015

Received in revised form

27 April 2015

Accepted 29 April 2015

Available online

Keywords:

Engineered nanoparticles
Ionic organic contaminants
Mineral particles
Organo-mineral complex
Pharmaceuticals

ABSTRACT

Sorption of organic contaminants on organo-mineral complexes has been investigated extensively, but the sorption contribution of mineral particles was not properly addressed before calculating K_{OC} , especially for ionic organic contaminants. We measured the surface coverage of a humic acid (HA) on nano iron oxides ($n\text{-Fe}_2\text{O}_3$) in a series of synthesized organo-mineral complexes. The contribution of the coated HA to ofloxacin (OFL) and norfloxacin (NOR) sorption in HA- $n\text{-Fe}_2\text{O}_3$ complexes was over 80% of the total sorption with the surface coverage of 36% and f_{OC} of 1.6%. All the coated HA showed higher sorption to NOR and OFL in comparison to the original HA, suggesting HA fractionation and/or physical re-conformation during organo-mineral complex formation. The decreased K_{OC} with multilayer coating may suggest the importance of site-specific interactions for OFL sorption, while the increased K_{OC} with multilayer coating may suggest the importance of partitioning in hydrophobic region for NOR sorption.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

The interactions between organic matter and mineral particles have attracted increasing research attention because of the unique roles of organo-mineral complexes in carbon stabilization, soil formation as well as element cycling (Kalbitz et al., 2005; Ransom et al., 1997). Previous studies also suggested that sorption of contaminants in organo-mineral complexes greatly alters their behavior and risks (Davis, 1982; Kretzschmar et al., 1997; Schlautman and Morgan, 1993). Considering the very special processes of organic matter fractionation and conformational rearrangement on mineral surfaces, organo-mineral complexes were considered as one of the most complicated environmental matrixes (Jones and Tiller, 1999; Yang et al., 2010).

Investigators have studied sorption of organic contaminants on organo-mineral complexes as affected by organic matter loading. It has been concluded that for hydrophobic organic contaminants (HOCs), the sorption was dominated by organic matter as long as organic carbon content was higher than 0.1% (Huang et al., 2003; Xiao et al., 2012), because of the high hydrophobicity of the

adsorbed organic matter and the changes of physical form of coated HA (Feng et al., 2006; Murphy et al., 1994; Wang and Xing, 2005; Wang et al., 2008). However, for ionizable organic contaminants (IOCs), various results were reported. Some researchers suggested that coated HA could significantly suppress IOC sorption because of the competition between coated organic matter and IOCs, or electrostatic repulsions between the coated organic matter and the negatively charged IOCs (Gu and Karthikeyan, 2008). However, the opposite results were also reported. The promoted sorption of IOCs on organo-mineral complexes in comparison to mineral particles was explained by the specific interactions (e.g., hydrogen bond) between IOC and organic functional groups (Gao and Pedersen, 2010). Hou et al. collected and analyzed the literature data, showing that sorption of sulfamathazole in soils was suppressed at low f_{OC} , and then promoted with increasing f_{OC} (Hou et al., 2010). A conceptual model for organic matter conformation change with f_{OC} in relation to IOC sorption was proposed. However, the turning point between positive and negative role that the coated organic matter plays in IOC sorption may be dependent on mineral types and chemical properties (Gao and Pedersen, 2010; Zhang et al., 2008).

Therefore, contradictory conclusions are found in the literature regarding IOC sorption as affected by organic matter loading on mineral particles. The environmental fate modeling and risk

* Corresponding author.

E-mail address: panbocai@gmail.com (B. Pan).

assessment of IOCs are thus hindered. Further investigation is thus needed. Different from HOCs, IOC sorption on mineral particles could not be ignored for organo-mineral complexes. Hence, it is important to separate the exact contribution of the coated organic matter and the exposed mineral surface (Zhang et al., 2008). Several concepts were previously applied for this purpose. Some investigators directly subtracted the sorption of pure mineral particles from the overall sorption of organo-mineral complexes (Zhang et al., 2008). This simple composite model did not consider the change of the sorption contribution of mineral particles in the organo-mineral complexes, and thus greatly underestimate the contribution of the coated organic matter. In the case of mineral particle sorption higher than organic matter (such as (Gu and Karthikeyan, 2008)), this method is not practical. Another group of researchers assumed that original organic matter and adsorbed organic matter have a similar surface area and thus they calculated the surface coverage through the surface area and organic carbon contents of both complexes and organic matter (Wang and Xing, 2005). However, this assumption is not always valid because the processes of dissolution and sorption fractionation were involved for organic matter during the formation of organo-mineral complexes (Salloum et al., 2001). Some other investigators calculated the surface coverage based on predicted adsorption maximum using Langmuir equation (Saha and Huang, 2010). The calculation assumed that the sorption properties of the adsorbed organic matter were the same as the bulk organic matter. Knowing that organic matter was fractionated (Jones and Tiller, 1999; Kang and Xing, 2008) or physically re-organized (Feng et al., 2006; Salloum et al., 2001; Yang et al., 2010) during the formation of organo-mineral complexes, this assumption was not valid either.

The above mentioned methods thus all have their limitations in estimating the sorption of the coated organic matter. An improved method is urgently needed. Because the diffusion of organic contaminants in mineral particles is unlikely, sorption of organic contaminants on the exposed mineral surface in organo-mineral complexes is proportionally related to the exposed surface area of the mineral particles. Therefore, based on the measurement of the exposed mineral surface, the sorption contributed by mineral particles could be easily deducted from the overall sorption of the organo-mineral complexes, which will provide a more accurate sorption estimate by the coated organic matter. In this study, homogeneous nano iron oxide particles ($n\text{-Fe}_2\text{O}_3$) with high surface area (nanoparticles to ensure high amount of organic matter loading) were used. Ofloxacin (OFL) and norfloxacin (NOR) are contaminants of emerging concern and have recently attracted a great deal of public concerns due to the evolution of antibiotic resistance in microorganisms and destruction of microbial communities in soil (Kim et al., 2007; Yu et al., 2009). They are now detected widely in natural surface waters, municipal wastewater treatment plant and soils (Kolpin et al., 2002; Picó and Andreu, 2007; Vieno et al., 2007). Thus, OFL and NOR are used as representative IOCs in this experiment. The primary objective of this study was to determine the actual contribution of the coated organic matter to OFL and NOR sorption in organo-mineral complexes.

2. Experimental section

2.1. Preparation and characterization of adsorbents

A soil sample was collected near Dianchi Lake, Yunnan province, China. The collected sample was freeze-dried, ground, and sieved. Plant residues were picked out manually. NaOH of 0.1 mol/L and $\text{Na}_4\text{P}_2\text{O}_7$ of 0.1 mol/L were mixed with the soil particles to extract humic (HA) and fulvic acids according to the conventional alkaline

extraction methods used by International Humic Substance Society (Swift, 1996). The mixture solution was adjusted to pH 1.0 using HCl, and heated in water bath in 40 °C for 2 h. After 12 h of equilibration, the mixture was centrifuged at 2000 g for 15 min. The precipitated HA was washed using HF three times followed by deionized water until the pH was 5–6, freeze-dried and ground into <500 nm particles.

An aliquot of 1 g HA was dissolved in 2 mL NaOH (0.5 mol/L) solutions and 200 mg/L NaN_3 solution was added until the volume was 100 mL. The dissolved HA solution filtered through a 0.45 μm membrane was used as a stock solution (TOC about 1 g/L). The pH of the stock solution was adjusted to 6.8 using HCl or NaOH. Organo-mineral complexes were prepared through adsorption. Briefly, nano iron oxides ($n\text{-Fe}_2\text{O}_3$, 30 nm, purity > 99.5%, Aladdin) were added into 1 g/L DOM with different solid:aqueous ratios varied in the range of 1:20 to 1:1000. All the samples were placed in dark and shaken in an air-bath shaker (150 rpm) at 25 °C for 3 d which were sufficient to reach apparent equilibrium. After the equilibration, all the organo-mineral complexes were centrifuged at 2500 g for 15 min, and the solids were washed using background solution for three times. All the solid particles were then freeze-dried. The organo-mineral complexes were noted as OM-1 to OM-8 following the increased organic carbon content (as measured by an elemental analyzer).

HA, $n\text{-Fe}_2\text{O}_3$ and their complexes were characterized for their organic elemental composition (MicroCube, Elementar, Germany) and surface area (N_2 Brunauer–Emmett–Teller method, Autosorb-1C, Quantachrome). All complexes and $n\text{-Fe}_2\text{O}_3$ were analyzed for their surface C, O, N and Fe content (X-ray photoelectron spectroscopy). The particle sizes of $n\text{-Fe}_2\text{O}_3$ and their HA complexes were measured by Zeta Potential Analyzer (Zeta PALS) according to dynamic light scattering principle. The aqueous:solid ratio was 800:1 and was consistent with the batch sorption experiments. The detection time was 0.5 min. The adsorbates used in this study were OFL and NOR, which were obtained from Bio Basic Inc. All the other chemicals were higher than analytical grade (purity > 99.5%). The chemical properties of OFL and NOR were listed in Table S1.

2.2. Batch sorption experiments

Batch sorption experiments were conducted for OFL and NOR separately on all the organo-mineral complexes, $n\text{-Fe}_2\text{O}_3$ and HA. OFL and NOR were separately dissolved in background solution containing 0.02 M NaCl (background electrolyte) and 200 mg/L NaN_3 (bio-inhibitor) to 64 mg/L as stock solutions. The stock solutions were diluted by the background solution spanning to 7 different concentrations in the range of 1–64 mg/L. The aqueous:solid ratio was 800:1 for the organo-mineral complexes and $n\text{-Fe}_2\text{O}_3$, and 10,000:1 for HA to ensure minimum headspace and 20–80% adsorption. The pH of the sorption system was 5.8 ± 0.2 by adding drops of HCl (1 M) and NaOH (1 M). Solutions of the adsorbates without any solid particles were kept in the same condition as in the sorption system and these samples were referred to as initial concentration references. The batch sorption experiments were conducted in 4–10 mL vials with Teflon-lined screw caps. All the vials were continuously shaken on an air-bath shaker in dark at 25 °C for 7 d to reach apparent equilibrium according to our preliminary study (Fig. S1). After 7 d equilibration, all the vials were centrifuged at 2000 g for 10 min and the supernatants were subjected to determination of solutes concentration. OFL and NOR were measured by HPLC (Agilent Technologies 1200) equipped with a reversed-phase C18 column (5 μm , 4.6×150 mm). The UV detector of HPLC was set at 286 nm and 280 nm for OFL and NOR, respectively. The mobile phase was 10:90 (v:v) of acetonitrile and deionized water with 0.8% acetic acid with a flow rate of 1 mL/min.

Download English Version:

<https://daneshyari.com/en/article/6317222>

Download Persian Version:

<https://daneshyari.com/article/6317222>

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