Sorption mechanisms of sulfamethazine to soil humin and its subfractions after sequential treatments☆

Xiaoying Guo [a, b], Xiaofang Shen [a], Meng Zhang [a], Haiyun Zhang [a], Weixiao Chen [a], Hui Wang [a], A.A. Koelmans [c], Gerard Cornelissen [d], Shu Tao [a], Xilong Wang [a, *]

[a] Laboratory for Earth Surface Processes, College of Urban and Environmental Sciences, Peking University, Beijing 100871, China
[b] School of Chemical Engineering and Energy, Zhengzhou University, Zhengzhou 450001, Henan province, China
[c] Aquatic Ecology and Water Quality Management Group, Wageningen University, P.O. Box 47, 6700 AA Wageningen, The Netherlands
[d] Department of Environmental Engineer, Norwegian Geotechnical Institute, POB 3930, Ulleval Stadion, N-0806 Oslo, Norway

ARTICLE INFO

ABSTRACT

Sorption mechanisms of an antibiotic sulfamethazine (SMT) to humin (HM) isolated from a peat soil and its subfractions after sequential treatments were examined. The treatments of HM included removal of ash, O-alkyl carbon, lipid, and lignin components. The HF/HCl de-ashing treatment removed a large amount of minerals (mainly silicates), releasing a fraction of hydrophobic carbon sorption domains that previously were blocked, increasing the sorption of SMT by 33.3%. The de-O-alkyl carbon treatment through acid hydrolysis greatly reduced polarity of HM samples, thus weakening the interaction between sorbents with water at the interfaces via H-bonding, leaving more effective sorption sites. Sorption of SMT via mechanisms such as van der Waals forces and π-π interactions was enhanced by factors of 2.04 −2.50. After removing the lipid/lignin component with the improved Soxhlet extraction/acid hydrolysis, the organic carbon content-normalized sorption enhancement index E_{oc} was calculated. The results demonstrated that the $E_{oc-lipid}$ for SMT (16.9%) was higher than $E_{oc-lignin}$ (10.1%), implying that removal of unit organic carbon mass of lipid led to a higher increase in sorption strength than that of lignin. As each component was progressively removed from HM, the sorption strength and isotherm nonlinearity of the residual HM samples for SMT were gradually enhanced. The K_{oc} values of SMT by HM samples were positively correlated with their aromatic carbon contents, implying that π-π electron donor-acceptor interactions between the benzene ring of sorbate and the aromatic domains in HM played a significant role in their interactions.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

In recent years, the occurrence, fate and transport of pharmaceutical antibiotics in soil and the aquatic environment is of growing concern due to the potential health effects and ecological environmental risks. Sulfonamides are an important class of antibiotics extensively used as veterinary drugs in animal husbandry both for prophylactic and therapeutic purposes (Lopes et al., 2012). Although the use of sulfonamides in agriculture has been withdrawn in EU countries since 2006 (Baran et al., 2011), they are still widely and illegally used as feed supplements to increase feed efficiency and weight gain in food-producing animals in many places (Kantiani et al., 2010), due to low cost and relatively high efficiency against many common bacterial infections. As reported, the concentrations of sulfonamides detected in liquid manure and dung samples have reached up to 20 and 91 mg/kg, respectively (Martinez-Carballo et al., 2007) and at parts per billion levels in the soil environment (Kemper, 2008). Since the sulfonamide antibiotics given to livestock are poorly metabolized and absorbed, a large fraction is released into the soil environment (Tolls, 2001). They may lead to the proliferation of antimicrobial-resistant pathogens, further affecting aquatic organisms and eventually human health through the food chain and drinking water (Heuer et al., 2011; Jesus Garcia-Galan et al., 2011; Luo et al., 2011; Schmitt et al., 2004). Sorption of sulfonamide antibiotics to SOM is a critical process that controls their transport, bioavailability, exposure and reactivity in soils. Their sorption by the whole soil, minerals, dissolved organic

---

☆ This paper has been recommended for acceptance by Klaus Kummerer.
* Corresponding author.
 E-mail address: xilong@pku.edu.cn (X. Wang).

matter, humic acid (HA), biochar and black carbon was studied (Gao and Pedersen, 2005; Haham et al., 2012; Ji et al., 2011; Kahle and Stamm, 2007; Srinivasan et al., 2014; Teixido et al., 2011, 2013; Zheng et al., 2013), but reports on sorption of sulfonamides on humin (HM) are still lacking.

Humin is known as a strongly associated organo-mineral complex formed by strong interactions between natural organic matter and minerals in soils (Malekani et al., 1997). It is a fraction of humic substances (HS) insoluble at any pH (Rice, 2001). Traditionally, humic substances are divided into humic acid (HA), fulvic acid (FA) and humin (HM) fractions in terms of their solubility. Until now, roles of HA and FA as sorbents for organic compounds have been extensively studied (Han et al., 2014; Wang et al., 2011a; Yang et al., 2011). In contrast, research activities concentrating on the sorptive properties of HM remain incomplete, even though it typically represents over 50% of organic carbon in soil and more than 70% in sediment (Hedges and Keil, 1995; Mayer, 1994).

Thus far, work on HM is warranted for understanding the transport and fate of organic compounds entering into soils and sediments, as well as into ground water. Several investigators have documented stronger sorption of organic contaminants to HM than to other SOM fractions. For instance, Chiou et al. (2000) reported that sorption of diuron and 3,5-dichlorophenol to HM from a peat soil was three times stronger than that to the whole peat soil, or HA isolated from it. This was explained by the much larger surface area of HM (4.5 m^2/g) than that of the whole peat soil (1.4 m^2/g) or HA (0.16 m^2/g). Drori et al. (2008) found that HM exhibited higher sorption (K_{oc}) for phenanthrene, atrazine and chlorotoluron than the bulk soils. Zhang et al. (2009) demonstrated that HM had higher aromatic carbon content measured by CP/MAS ^{13}C NMR and gave higher K_{oc} value for benzo[α]pyrene relative to HA. Yang et al. (2011) also observed stronger sorption of phenanthrene to the original- and de-ashed HMs than HAs extracted from the same peat soil. Given that HM has a very strong sorption affinity for organic chemicals, their interaction mechanisms need to be further explored and better understood. Among those limited studies on HM, the sorbates mainly included polycyclic aromatic hydrocarbons (PAHs) and herbicides. The work regarding sorption behaviors of antibiotics to HM has rarely been reported, with two literature available mainly focusing on the interactions of tetracycline with sludge-derived humin (Tenenbaum et al., 2014) and peat humin (Souza et al., 2016).

As a typical organo-mineral complex, HM consists of complex components including the organic part (e.g., carbohydrates, lipids, lignins, and black carbon) and the inorganic part (e.g., diverse minerals). To the best of our knowledge, no published studies have concentrated on sorption changes of antibiotics to HM as induced by removing each intrinsic component (minerals, O-alkyl carbon, lipid and lignin). To better understand the underlying interaction mechanisms between organic compounds and HM, roles of different components in their sorption should be further investigated in addition to the bulk composition. Since organic matter in HM is tightly bound to minerals, it is extremely difficult to separate HM into sub-fractions directly using the common chemical methods. Here, we sequentially removed individual constituents in HM with varying procedures to probe their possible spatial arrangement and the associated impact on sorption of antibiotics, from the aim to better understand their interaction mechanisms.

To achieve our research aim, sulfamethazine (SMT) was chosen as sorbate. Four chemical methods were used to selectively remove ash (mainly silicates), O-alkyl carbon, lipid, and lignin. Overall, the aims of the present study were to investigate the structure and composition of the original and treated HM by different methods; and to examine the sorption behaviors of SMT on HM and its various subfractions, trying to unveil the underlying mechanisms

and provide basic data for predicting the environmental fate of sulfonamide antibiotics once they are released into soils and sediments.

2. Materials and methods

2.1. Fractionation of humin samples

The peat soil was collected from Sanjiang Plain, Jilin Province in China. The original humin sample (ORH) was the residue of 17-fold extraction of the abovementioned peat soil with alkaline solution (0.1 M $Na_4P_2O_7$ + 0.1 M NaOH for the first 10 extractions and 0.2 M NaOH for the last 7 ones). All other humin-origin samples were obtained after different treatments of ORH (Fig. 1). HM consists of complex components including an organic part (e.g., carbohydrates, lipids, and lignins) and an inorganic part (mainly minerals). The minerals in HM may reduce the accessibility of some interior sorption domains for organic chemicals (Yang et al., 2011). Therefore, they were removed at the first step in the series of treatments (Fig. 1) to probe the effect of minerals in HM on organic compound sorption, and also to better understand the roles of diverse organic components of HM with respect to organic compound sorption, while excluding the influence of minerals. The detailed methods of de-ashing, de-O-alkyl carbon, de-lipid and de-lignin treatments of HM samples are provided in the Supplementary Data (SD).

2.2. Characterization of the HM fractions

The carbon, hydrogen, and nitrogen contents of all samples were determined using a Vario EL CHN Elemental Analyzer (Germany). Ash contents were measured by heating in a muffle furnace at 900 °C for 4 h. The oxygen content of all samples was calculated by mass balance. Aside from the bulk elemental composition of the samples, their surface elemental composition and the abundance of carbon-based functionalities were determined using an AXIS-Ultra X-ray Imaging Photoelectron Spectrometer (Kratos Analytical Ltd., UK) with a monochro-mastic Al Kα radiation source operated at 225 W, 15 mA and 15 kV.

To obtain information regarding the structure and abundance of various functional groups of HMs, solid-state cross-polarization magic angle-spinning and total-sideband-suppression ^{13}C NMR spectra of all samples were obtained with a Bruker AV 300 MHz NMR Spectrometer (Bruker Corporation, Germany) operated at a ^{13}C frequency of 75 MHz. The NMR running parameters and chemical shift assignment are described elsewhere (Wang et al., 2011b).

Surface area (SA) and porosity of sorbents were determined for all HM samples using an Autosorb-1-MP Surface Area Analyzer (Quantachrome Instruments, USA) after outgassing at 105 °C for 16 h. Surface area of samples was derived from N_2 sorption isotherms at 77 K using a multipoint BET method with relative pressure P/P_0 from 0.05 to 0.3. The meso- and macro-pore volumes (1.5–200 nm in diameter) were calculated from the N_2 desorption isotherms employing the Barrett-Joyner-Halenda (BJH) model. Due to diffusion limitations at a temperature of 77 K, N_2 molecules could fail to access a fraction of ultra-micro pores within instrumentally acceptable equilibration times, resulting in underestimation and inaccuracy of the porosity of samples by Dubinin-Radushkevich (DR) method. This was solved by using CO_2 as sorbate. The micropore volumes ($\leq$1.5 nm) of all samples were calculated from CO_2 sorption isotherms at 273 K using Density Functional Theory (DFT) with relative pressure P/P_0 ranging from 10^{-4} to 0.1. Therefore, the total pore volume was taken as a sum of meso- and macro-pore volume (1.5–200 nm) by N_2 isotherms, and micropore volume (0.4–1.5 nm) calculated from the CO_2 isotherms.