The sorption kinetics and isotherms of sulfamethoxazole with polyethylene microplastics

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ABSTRACT

Microplastics and sulfamethoxazole coexist ubiquitously in the marine environment, and microplastics tend to sorb organic pollutants from the surrounding environment. Here, the sorption kinetics and isotherms of sulfamethoxazole on polyethylene (PE) microplastics closely fitted a pseudo-second-order model ($R^2 = 0.98$) and linear model ($R^2 = 0.99$), respectively, indicating that the sorption process was partition-dominant interaction. The main binding mechanism was possibly the van der Waals interaction for hydrophilic sulfamethoxazole onto hydrophobic PE microplastics. The effects of pH, dissolved organic matter and salinity on sorption behavior were also studied. The sorption behavior of sulfamethoxazole on PE microplastics was not significantly influenced by pH and salinity, probably because the electrostatic repulsion played a minor role. In addition, the negligible effect of dissolved organic matter was attributed to the greater affinity of sulfamethoxazole to PE microplastics than to dissolved organic matter. Our results demonstrated that PE microplastics may serve as a carrier for sulfamethoxazole in the aquatic environment.

1. Introduction

Since being defined in 2004, microplastics smaller than 5 mm in diameter have been detected worldwide in coasts, estuaries, and seas, and consequently have become a global concern (Browne et al., 2011; Hirai et al., 2011; Law and Thompson, 2014; Yonkos et al., 2014; Zhao et al., 2014; Fok and Cheung, 2015). Much attention has been paid to microplastics, mainly due to their small sizes and hydrophobic surfaces. In the marine environment, microplastics are known to adsorb organic contaminants (Engler, 2012), especially persistent, bio-accumulative and toxic substances including polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and dichloro-diphenyl-trichloroethanes (DDTs), recently expanding to perfluoroalkyl substances and some pharmaceuticals and personal care products (PPCPs) (Wang et al., 2015; Wu et al., 2016). More importantly, when accidentally ingested by aquatic organisms, microplastics have the potential to accumulate in the food chain, release organic chemicals adsorbed on them or leach additives, such as phthalates and bisphenol A (Engler, 2012). Rochman et al. (2013a) demonstrated that chemical pollutants sorbed on polyethylene (PE) microplastics had the bioaccumulation and toxicity to fish by ingestion. Browne et al. (2013) reported organic pollutants and additive chemicals could be transferred by microplastics into gut tissues of lugworms, leading to the disruption of ecophysiological functions linked to health and biodiversity, although higher concentrations of pollutants were transferred by sand. Therefore, microplastics may act as a vector for organic contaminants in the marine environment and cause a threat to marine creatures, and even humans via the food web (Cole et al., 2013; Foekema et al., 2013).

For the sorption of organic pollutants on microplastics, previous studies were mainly concerned with hydrophobic organic pollutants (Teuten et al., 2007; Bakir et al., 2012; Rochman et al., 2013b; Bakir et al., 2014a, 2014b; Velzeboer et al., 2014; Hueffer and Hofmann, 2016), which are usually non-polar and non-ionizable, but few focused on polar and ionizable organic pollutants, such as antibiotics. The ocean has a great potential to hold many terrestrial pollutants including antibiotics residues (Zhang et al., 2013), which can enter into marine environments via riverine inputs (Yan et al., 2013; Shi et al., 2014), sewage treatment plants effluent (Minh et al., 2009) and application in mariculture (Chen et al., 2015). Sulfamethoxazole, a representative of antibiotics, has often been found in estuarine waters with the median concentration of 43.8 ng/L (Yan et al., 2013), and in offshore waters with the mean concentration of 1.0 ng/L (Zhang et al., 2013), where microplastics could encounter it.

In this study, the sorption kinetics and isotherms of sulfamethoxazole on PE microplastics, a common and typical microplastic, were investigated. Then, we examined the effects of pH, dissolved organic
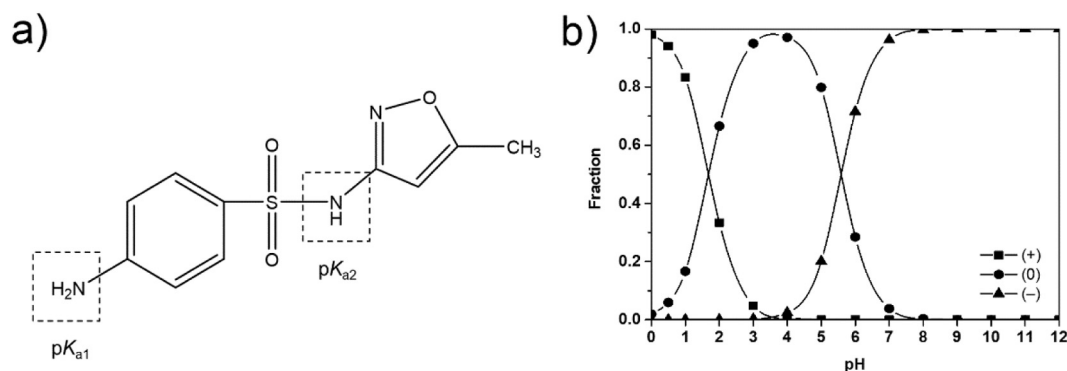

Fig. 1. a) The molecular structure of sulfamethoxazole. pK_a values were 1.7 and 5.7 determined by Yi et al. (2015); b) Speciation distribution of sulfamethoxazole at different pHs. (+, 0, −) represent its existing form as cation, zwitterion and anion, respectively. The isoelectric point of sulfamethoxazole is 4.06 calculated by ChemAxon.

matter and salinity on the sorption behavior. We hypothesized that 1) different species of sulfamethoxazole under various pHs may have different sorption behaviors via electrostatic interactions; 2) the change of salinity could model the environmental conditions from freshwater to marine and lead to different sorption behaviors; 3) the dissolved organic matter may increase or decrease the sorption capacity of sulfamethoxazole on microplastics due to possible interactions with PE microplastics or sulfamethoxazole.

2. Materials and methods

2.1. Chemicals

A PE microplastic sample (the mean size of 150 μm) was purchased from Goodfellow Company (Huntington, UK), and sulfamethoxazole (purity of 99%) was purchased from Dr. Ehrenstorfer GmbH (Germany). Sulfamethoxazole can exist as a cationic, zwitterionic or anionic form due to its ionizable functional groups (Wang et al., 2017). The molecular structure and speciation distribution are shown in Fig. 1. All chemicals used were analytical grade or higher purity and solvents were HPLC grade.

2.2. Sorption experiment

Sulfamethoxazole (100 mg/L) was dissolved in a basal solution consisting of 0.01 mol/L CaCl$_2$ and 200 mg/L NaN$_3$ (as a biocide). A sorption kinetics experiment of sulfamethoxazole on PE microplastics was then conducted. Briefly, 100 mg microplastics were placed in 40 mL amber glass vials which contained 20 mL basal solution. The initial concentration of sulfamethoxazole solution was 1 mg/L (Zhan et al., 2016). The experiments were performed in a temperature-controlled shaker at 25 °C and horizontally shaken at 200 rpm for given time intervals (0.5, 0.75, 1, 2, 4, 12, 24, 36, 48 and 72 h). Finally, 1 mL aliquots of solution were passed through 0.22 μm filters to remove microplastic particles, and sulfamethoxazole concentrations of the filtrates were quantified. For the sorption isotherms, the initial concentration of sulfamethoxazole was a gradient from 0.2 to 5 mg/L, and the shaking time was fixed at 24 h to reach sorption equilibrium. Other procedures were the same as with the sorption kinetics experiment. All experiments were conducted in triplicate.

To study the effects of pH, dissolved organic matter and salinity on the sorption of sulfamethoxazole on microplastics, the initial pH values of the background solution were adjusted to a range from 2 to 12 using NaOH or HCl. The fulvic acid solution was extracted from an Argiustoll soil in Heilongjiang Province, China, following the International Humic Substance Society procedures (Swift, 1996), and then diluted to give a dissolved organic carbon (DOC) content varying from 0 to 20 mg/L and NaCl solution was diluted to give a series of salinities. To guarantee the lowest NaCl concentration, NaN$_3$ was not added in these experiments. The initial concentration of sulfamethoxazole solution was 1 mg/L in the above experiments.

2.3. Sulfamethoxazole determination and microplastics characterization

The concentrations of sulfamethoxazole were determined with a UV detector at 270 nm by high-performance liquid chromatography (HPLC, Waters 2695, USA), Venusil C18 column (5 μm, 4.6 × 250 mm). The mobile phase was 30:70 (v:v) of acetonitrile: Milli-Q water (Millipore Co., USA) with 0.5% acetic acid and the flow rate was 1.0 mL/min.

The zeta potential of microplastics in the solid state was directly measured by an Electrokinetic Analyzer (SurPass 3, Anton Paar, Austria) coupled with the cylindrical cell, avoiding their uneven dispersion in solution. The Brunauer–Emmett–Teller (BET) surface area and porosity of PE microplastics were analyzed by the sorption-desorption isotherms of N$_2$ at 77 K (TriStar II, Micromeritics Co., USA). The morphology and microstructure of PE microplastics were characterized by field-emission scanning electron microscopy (SEM, SU-8010, Hitachi Ltd., Japan).

2.4. Data analysis

The pseudo-first-order model (PFOM) and pseudo-second-order model (PSOM) were used to describe the sorption kinetics (Zeng et al., 2014; Wang et al., 2015) using OriginLab 9.0. The PFOM and PSOM can be expressed as $Q_t = Q_e \times (1 - e^{-K_1 t})$ and $Q_t = K_2 Q_e^2 t/(1 + K_2 Q_e t)$, respectively, where Q_t (μg/g) and Q_e (μg/g) are the concentrations sorbed on microplastics at t time and equilibrium, and K_1 (/h) and K_2 [g/(μg h)] are the rate constants of PFOM and PSOM, respectively. Linear and Freundlich models were applied to fit the sorption isotherm (Wang and Chen, 2015). The form of a linear model can be represented by the following equation: $Q_e = K_d \times C_e$, where Q_e (μg/g) is the concentration on microplastics at equilibrium, C_e is the concentration in aqueous phase at equilibrium, and K_d (L/kg) is the linear sorption coefficient. The Freundlich equation is described as follows: $Q_e = K_f \times C_e^N$, where K_f [(μg/g) / (mg/L)^N] is the Freundlich sorption coefficient, and N is the exponential coefficient.

3. Results and discussion

3.1. Characterization of PE microplastics

The BET surface area of the PE microplastics used was 0.2341 m^2/g, similar to the previous study (0.308 m^2/g) (Hueffer and Hofmann, 2016). However, the surface areas and porosities of PE microplastics may be underestimated because these small pores are possibly not accessible to N$_2$ due to the capillary condensation, and N$_2$ may not able to