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Adsorption of antibiotics on microplastics☆

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ABSTRACT

Microplastics and antibiotics are two classes of emerging contaminants with proposed negative impacts to aqueous ecosystems. Adsorption of antibiotics on microplastics may result in their long-range transport and may cause compound combination effects. In this study, we investigated the adsorption of 5 antibiotics [sulfadiazine (SDZ), amoxicillin (AMX), tetracycline (TC), ciprofloxacin (CIP), and trimethoprim (TMP)] on 5 types of microplastics [polyethylene (PE), polystyrene (PS), polypropylene (PP), polyamide (PA), and polyvinyl chloride (PVC)] in the freshwater and seawater systems. Scanning Electron Microscope (SEM) and X-ray diffractometer (XRD) analysis revealed that microplastics have different surface characterizes and various degrees of crystalline. Adsorption isotherms demonstrated that PA had the strongest adsorption capacity for antibiotics with distribution coefficient (K_d) values ranged from 7.36 ± 0.257 to 756 ± 48.0 L kg^{-1} in the freshwater system, which can be attributed to its porous structure and hydrogen bonding. Relatively low adsorption capacity was observed on other four microplastics. The adsorption amounts of 5 antibiotics on PS, PE, PP, and PVC decreased in the order of CIP > AMX > TMP > SDZ > TC with K_f correlated positively with octanol-water partition coefficients (Log K_{ow}). Comparing to freshwater system, adsorption capacity in seawater decreased significantly and no adsorption was observed for CIP and AMX. Our results indicated that commonly observed polyamide particles can serve as a carrier of antibiotics in the aquatic environment.

1. Introduction

During the last 60 years, plastic production increased considerably from around 0.5 million tonnes in 1950 to 311 million tonnes in 2014 (Thompson et al., 2009; Plastics, 2015), which accompanied by increasing release of plastic waste to the environment. It is estimated that 4.8–12.7 million tonnes of plastic waste washed offshore in 2010 alone (Jambeck et al., 2015). Recently, microplastics (MPs) with particle size in the micrometer range have become the focus of study due to their potential toxic impact to aquatic ecosystems. MPs have been detected in surface water (Zhao et al., 2015), water column (Nel and Froneman, 2015), and bottom sediments (Browne et al., 2011). Previous studies have showed that polyethylene (PE), polystyrene (PS), polypropylene (PP), polyamide (PA), and polyvinyl chloride (PVC) are the most frequently detected MPs in the aquatic environment (Hidalgo-Ruz et al., 2012; Fok et al., 2017). It is believed that MPs can accumulate various toxins and chemical pollutants and serve as a carrier for long-range transport (Guo et al., 2012; Turner and Holmes, 2015; Hueffer and Hofmann, 2016).

Studies have been conducted on the adsorption behaviors of organic pollutants or heavy metals onto different types of MPs (Bakir et al., 2014a, 2014b, Velzeboer et al., 2014; Wang et al., 2015; Hueffer and Hofmann, 2016; Wu et al., 2016) as well as the effects of plastic types and environmental factors (e.g., ionic strength and pH) on pollutants adsorption processes (Wang et al., 2015). Both the sorbent and the sorbate properties can influence the adsorption extent significantly. For instance, properties of MPs such as polarity, abundance of rubbery, and degree of crystalline have great impacts on adsorption capacities of pollutants (Guo et al., 2012; Wang et al., 2015; Brennecke et al., 2016). The hydrophobicity of organic contaminants is also important in determining their adsorption on MPs (Hueffer and Hofmann, 2016). Furthermore, adsorption of organic pollutants on MPs varied in the seawater and the freshwater (Velzeboer et al., 2014), which may be due to the impacts of salinity.

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As reported by Wang et al. (2015), perfluorooctanesulfonate (PFOS) adsorption on PE and PS increased with increasing of ionic strength, while ionic strength had no effect on perfluorooctanesulfonamide (FOSA) adsorption.

As a class of emerging contaminants, antibiotics have received increasing attention due to their impacts on the microbial community as well as the generation of resistance genes (Le et al., 2005; Yang et al., 2017). A large number of antibiotics are released into the environment every year. As evaluated by Zhang et al. (2015), only in China, 53,800 tonnes of antibiotics discharged into the receiving environment in 2013. Studies reported that tetracyclines, macrolides, fluoroquinolones, and sulfonamides are the frequently detected antibiotics in the aquatic environment worldwide (Kolpin et al., 2002; Watkinson et al., 2009; Jiang et al., 2011; Li et al., 2012). Antibiotics such as trimethoprim, fluoroquinolones, and sulfonamides were found to be stable in surface water (Lunestad et al., 1995; Lin et al., 2010). More importantly, the residual antibiotics may pose relatively high ecological risk to the relevant aquatic organisms (Xu et al., 2013). If antibiotics can be absorbed by MPs, both could have higher toxic effects on aquatic life due to the combined pollution. There is evidence that persistent organic pollutants (POPs) can transfer from MPs to Artemia nauplii and further to zebrafish via a trophic food web (Batel et al., 2016). Thus, understanding the possible reactions between different kinds of antibiotics and MPs is warranted for the evaluation of their environmental risks.

The physicochemical properties such as specific surface area, degree of crystallinity, and pore size distribution vary substantially among different types of microplastic particles and may dominate their antibiotics adsorption capacities. To verify this hypothesis, experiments were conducted 1) to describe the structures and properties of 5 MPs using analytical techniques such as Scanning Electron Microscope (SEM) and X-ray diffractometer (XRD); 2) to evaluate the adsorption capacities of 5 types of commonly used antibiotics in the freshwater and seawater systems.

2. Materials and method

2.1. Chemicals

Sulfadiazine (SDZ), amoxicillin (AMX), tetracycline (TC), ciprofloxacin (CIP), and trimethoprim (TMP) were purchased from Sigma-Aldrich (USA), with >99% purity. The physicochemical properties of antibiotics was shown in Table S1. Acetonitrile were high-performance liquid chromatography (HPLC) grade and were obtained from Anaqua Chemicals Supply (ACS, USA). Ultrapure water (MQ) was obtained from a Milli-Q water purification system (Millipore, Billerica, MA, USA). The other reagents were analytical grade or higher. Seawater was filtered through 0.45 μm membranes and irradiated with ultraviolet light to eliminate the influences of dissolved organic matter as much as possible. TC, AMX, and TMP were dissolved in the background solutions (i.e. ultrapure water and filtered seawater) directly to prepare the stock solutions. For SDZ and CIP, methanol was added to enhance their solubility in background solutions. All the stock solutions were kept in the dark at 4 °C for no long than one week. Stock solutions were diluted to the desired concentrations before use.

2.2. Microplastic particles and analytical methods

Polyethylene (PE), polystyrene (PS), polypropylene (PP), polyamide (PA), and polyvinyl chloride (PVC) were purchased as powders from Youngling Electromechanical Technology Co., Ltd. (Shanghai, China). The physicochemical properties of 5 MPs were shown in Table S2. The particle sizes distribution of these polymers were shown in Fig. S1. For any kinds of MPs, more than 90% of polymers fell into the 75–180 μm size classes. Their point of zero charge (PZC) were analyzed based on the method described by Ferro-Garcia et al. (1998). The polymers microscopic morphological characteristics were analyzed by a Scanning Electron Microscope (SEM) (S-4800, Hitachi, Japan). The crystalline compositions of MPs were measured using X-ray diffractometer (XRD) (XRD-7000, SHIMADZU, Japan) with a Cu-Kα as the radiation source (λ = 1.5406 Å). The samples were scanned over the range of 5–90° of 2θ at a rate of 1° min^{-1}.

2.3. Batch adsorption experiments

Batch adsorption experiments for 5 antibiotics were undertaken with 5 concentration gradients (i.e. 0.5, 1, 5, 10, and 15 mg L^{-1}) at room temperature (25 °C). Specifically, 0.02 g of each plastic particle was added into the glass vials. Different volumes of background solution (ultrapure water or filtered seawater) were added according to the concentration gradient. Then, antibiotic stock solution with a concentration of 50 mg L^{-1} was added to make up the suspension volume of 5 mL in each glass vial capped with a Teflon gasket. To minimize the effects of cosolvent, the volume ratio of methanol in the test solution was controlled below 0.1%. The glass vials were shaken in a temperature-controlled shaking incubator (HZS-HA, Harbin, China) at a shaking speed of 180 rpm at 25 °C for 4 d. After equilibrium, the sample was filtered through a 0.22 μm syringe filter before analysis. All the adsorption experiments were conducted in triplicate. The blank sorption experiments with the reactor system containing antibiotics without MPs were carried out. The loss of antibiotics during sorption test was calculated and subtracted from the blank loss. To improve calculation accuracy, the amounts of antibiotics adsorbed on MPs were calculated using the following equation:

$$q_e = \frac{\frac{m_2-m_1}{\rho_2}(c_0 - c_e) - \frac{m_1-m_0}{\rho_1}c_e - \alpha}{m} \quad (1)$$

where q_e (mg·g^{-1}) is the equilibrium adsorption amount; c_0 and c_e (mg·L^{-1}) are the initial concentration and the equilibrium concentration; ρ_1 and ρ_2 (g mL^{-1}) are density of the background solution and the antibiotic stock solution, respectively; m (g) is the mass of adsorbent; m_0 (g) is the mass of the adsorbent and the vial; m_1 (g) is the mass after adding the background solution; m_2 (g) is the mass after adding the antibiotic stock solution; α (mg) is blank loss.

2.4. Adsorption model

Linear, Freundlich, and Langmuir adsorption models were used to fit the adsorption isotherms of antibiotics. Briefly, the Linear model can be described as:

$$q = K_d C_e \quad (2)$$

where q (mg g^{-1}) is the absorbed amount of antibiotic; C_e (mg L^{-1}) is antibiotic mass in the aqueous phase at equilibrium the equilibrium; and K_d (L g^{-1}) is the partition coefficient. The Freundlich model is given by:

$$q = K_f C_e^n \quad (3)$$

where K_f (L g^{-1}) is the Freundlich adsorption coefficient which indicates adsorption capacity; n is the Freundlich isotherm exponent that determines the non-linearity. The Langmuir isotherm model can be expressed as follow: