Marine Pollution Bulletin 136 (2018) 516–523

Contents lists available at ScienceDirect

Marine Pollution Bulletin

journal homepage: www.elsevier.com/locate/marpolbul

Sorption and desorption of selected pharmaceuticals by polyethylene microplastics

Roger Mamitiana Razanajatovo[a], Jiannan Ding[a,b], Shanshan Zhang[a], Hang Jiang[a], Hua Zou[a,b,*]

[a] School of Environmental and Civil Engineering, Jiangnan University, Wuxi 214122, China
[b] Jiangsu Collaborative Innovation Center of Technology and Material of Water Treatment, Suzhou 215009, China

ARTICLE INFO

Keywords:
Microplastics
Pharmaceuticals
Sorption
Desorption
Model

ABSTRACT

The aim of the present study was to evaluate the sorption and desorption of sulfamethoxazole (SMX), propranolol (PRP) and sertraline (SER) by polyethylene (PE) microplastics in water. After the 96 h mixture, the sorption percentages of pharmaceuticals on PE microplastics decreased according to the following order: SER (28.61%) > PRP (21.61%) > SMX (15.31%). The sorption kinetics were fitted well with the pseudo-second-order model. Both linear and Freundlich models were able to describe the sorption isotherm. The results suggest that the sorption process of the pharmaceuticals may be adequately described by their hydrophobicity and electrostatic interactions. The desorption results showed that 8% and 4% of PRP and SER, respectively, were released from the microplastics within 48 h, but the sorption of SMX was irreversible. The results indicate the potential risks of PRP and SER for bioaccumulation in aquatic organisms via ingestion of the microplastics in aquatic environments.

1. Introduction

Due to excessive use and improper disposal, large quantities of plastics are accumulating in aquatic environments via surface runoff, wind dispersal, and other routes (Horton et al., 2017). It is estimated that there will be over 250 metric tons of plastics accumulated in the ocean by 2025 (Jambeck et al., 2015). Due to weathering processes (e.g., photo-oxidative and thermo-oxidative) (Alimi et al., 2018), plastics are broken down into smaller pieces with a size < 5 mm, which are also known as microplastics (Thompson et al., 2004). The presence of microplastics in marine and freshwater environments has been widely documented (Barboza and Gimenez, 2015; Eerkes-Medrano et al., 2015; Li et al., 2016; Shim and Thomposon, 2015). Several works have reported that microplastics are the primary sources of a number of additive chemicals such as plastizers, flame retardants, and antioxidants in the aquatic environment (Gouin et al., 2011; Hahladakis et al., 2018; Hammer et al., 2012; UNEP, 2015). In addition, because microplastics possess a size similar to that of planktons, microplastics may be ingested by aquatic organisms and distributed in their tissues (Cole et al., 2013; Ding et al., 2018). The ingested microplastics would release the additive chemicals and may have effects on aquatics organisms (Koelmans et al., 2013).

Apart from the release of additive chemicals, recent studies have demonstrated the role of microplastics as a vector for other pollutants in aquatic environments (Ziccardi et al., 2016; Teuten et al., 2009). Once the pollutant-sorbed microplastics are ingested by aquatic organisms, the pollutants may be desorbed from the microplastics and accumulate in the tissues (Paul-Pont et al., 2016; Qu et al., 2018). Hence, sorption and desorption by microplastics may play important roles in the fate of organic pollutants in aquatic ecosystems. To better understand the environmental and ecological impacts of microplastics, there is an urgent need to study the sorption and desorption behaviors of organic pollutants and microplastics in the aquatic environment (Lee et al., 2014).

In the last few decades, the widespread accumulation of pharmaceuticals in aquatic environments has received growing attention (Boxall et al., 2012). Due to the extensive production and usage, pharmaceutical compounds are continuously being emitted into the aquatic environment (Kümmerer, 2009). Several pharmaceutical products, such as antibiotics, antidepressants, and beta-blockers, have been detected in surface waters (Khetan and Collins, 2007). Recently, a few studies have shown that some pharmaceutical agents present in water may be sorbed onto microplastics (Wu et al., 2016; Li et al., 2018; Xu et al., 2018). These results suggest that microplastics may affect the fate and transport of various pharmaceutical agents in aquatic environments. However, most of these studies only investigated the sorption of pharmaceuticals by microplastics. Information on the desorption behavior between pharmaceuticals and microplastics is limited.

* Corresponding author at: School of Environmental and Civil Engineering, Jiangnan University, Wuxi 214122, China.
E-mail address: zouhua@jiangnan.edu.cn (H. Zou).

https://doi.org/10.1016/j.marpolbul.2018.09.048
Received 13 August 2018; Received in revised form 26 September 2018; Accepted 26 September 2018

The aim of this study was to examine the sorption and desorption processes of pharmaceutical compounds relative to microplastics in water. In the present study, the antibiotic sulfamethoxazole (SMX), the beta-blocker propranolol (PRP), and the antidepressant sertraline (SER) were selected as the sorbates. Ultra-high molecular weight polyethylene (UHMW-PE) microplastics were selected as sorbents. The three target pharmaceuticals and PE microplastics were chosen due to their widespread presence in aquatic environments, as reported by previous studies (Yan et al., 2018; Xie et al., 2017; Aus Der Beek et al., 2016; Godoy et al., 2015; Schultz et al., 2010; Duis and Coors, 2016). Batch experiments were conducted to study the sorption and desorption behaviors of SMX, PRP, and SER by PE microplastics. The sorption/desorption kinetics and sorption isotherms for the three different pharmaceutical compounds were determined. Through these experiments, we hope to broaden our understanding of the environmental behavior of pharmaceuticals affected by microplastics.

2. Materials and methods

2.1. Materials and chemicals

Three target pharmaceuticals (SMX, PRP, and SER) were obtained from Shanghai Send Pharm Co., Ltd. (Shanghai, China) and had a declared purity > 98%. The different physicochemical properties of the three pharmaceuticals are presented in Table S1. A stock solution of each pharmaceutical agent was obtained by dissolving 0.01 g of each pharmaceutical in 1 mL of methanol (HPLC Grade). Working standard solutions of SMX, PRP, and SER (60 μg L^{-1}) were prepared from the stock solutions by serial dilution. This initial concentration was chosen based on the solubility of each pharmaceutical compound (OECD, 2000). UHMW-PE powder with a size ranging from 45 to 48 μm was purchased from Sigma Aldrich (St. Louis, MO, USA) as a representative of PE microplastics. The shape and surface characteristics of the used PE microplastics are shown in Fig. 2. Sodium taurocholate was purchased from Shanghai Macklin Biochemical Co., Ltd. (Shanghai, China). Ultrapure water (DI water, 18.2 MΩ-cm) was taken from a laboratory water purification system (Master - Q15). GF/D glass fiber filters were purchased from Whatman (Maidstone, UK).

2.2. Batch experiments

2.2.1. Sorption kinetics and isotherm experiments

The kinetic studies involved two steps. First, a preliminary experiment was performed to identify the equilibrium time and relevant sorbent:solution ratio (OECD, 2000). A definitive study was then conducted to develop the sorption kinetics and isotherms of the three pharmaceutical compounds to PE microplastics.

In the preliminary experiment, different amounts of PE microplastics were added to 50 mL glass centrifuge tubes containing 40 mL of ultra-pure water. The obtained concentrations of PE microplastics were 50, 200, and 500 mg L^{-1}. In addition, 0.01 M $CaCl_2$ and 0.02% (w/v) NaN_3 were added to the tubes to maintain the ionic strength of the suspension and to prevent microbial degradation, respectively. Then, PRP was spiked at an initial concentration of 100 μg L^{-1}. Each test was conducted in triplicate. Tubes were capped and wrapped with aluminum foil to prevent potential photochemical reactions during mixing and were agitated horizontally at 150 rpm at 24 °C for 144 h. The samples were then withdrawn with glass syringes at specific time intervals (3, 6, 12, 24, 32, 48, 72, 96, 120, and 144 h) and filtered through glass fiber filters with a pore size of 2 μm to remove the microplastic particles. Finally, the filtering mediums were stored in the dark at −20 °C until further analysis. Control samples without microplastics were set up under the same testing conditions to determine the possible degradation or the sorption of PRP to the glass receptacle.

In the kinetics study, all of the initial concentrations of PRP, SER, and SMX were 60 μg L^{-1}. Based on the results of the preliminary experiment, a microplastics to solution ratio of 1:5 (*w:v*) was used. The experiment duration was 96 h in the kinetics study (Fig. S2). The sample was withdrawn at specific time intervals (3, 6, 12, 24, 48, 72, and 96 h). All of the other procedures were the same as those used in the preliminary experiment and each test was conducted in triplicate.

The sorption isotherm study also followed the procedures mentioned above, but five different concentrations (1, 10, 20, 50, and 100 μg L^{-1}) were used for each pharmaceutical agent. The samples were taken at 96 h when the equilibrium was reached for the three pharmaceutical agents as determined by the sorption kinetic studies.

2.2.2. Desorption experiment

After the sorption isotherm experiment, the suspension was filtered through a 2 μm glass fiber filter. The filters containing the PE microplastics were then dried in a vacuum desiccator for 2 d. The vacuum desiccator was wrapped with aluminum foil to avoid any possible photodegradation of the pharmaceutical agents. Then, the dried glass fiber filter with PE microplastics was added to a 50 mL centrifuge tube. The tube was filled with 40 mL of ultrapure water containing 0.01 M $CaCl_2$, 0.02% (w/v) NaN_3, and 15.5 mM sodium taurocholate to simulate the internal environment of the digestive tract for some aquatic organisms, to determine the role of gut surfactant in desorption of pharmaceuticals from microplastics (Bakir et al., 2014a; Bakir et al., 2016). Afterward, the tube was wrapped with aluminum foil and shaken at 24 °C in the dark. Each test was conducted in triplicate. Then, 1 mL of the sample was withdrawn at each given time interval (3, 6, 12, 24, and 48 h) and filtered through a 2 μm glass fiber filter. All of the obtained samples were stored at −20 °C until the following analyses.

2.3. Analysis of the pharmaceutical agents and microplasics surface properties

All samples of the pharmaceutical agents were analyzed with an ultra-high-performance liquid chromatography-tandem mass spectrometer (UPLC/MS/MS). The UPLC/MS/MS instrument was Waters ACQUITY UPLC Xevo TQ with electrospray source (Milford, OH, USA) containing an Acquity BEH C18 column (100 mm × 2.1 mm, 1.7 μm). Chromatographic separation was performed with acetonitrile and 0.1% formic acid. During the mass spectrometric detection, the electrospray ionization source (ESI) for the three pharmaceuticals was set to the positive mode. Detailed protocols of the analysis are available in the Supplemental Material (Table S2 and S3). The areas of the peaks of the target compounds were plotted against the standard concentrations resulting in a linear correlation with $R^2 > 0.99$ (Fig. S1). The microplastics surface properties were analyzed with Scanning Electron Microscope (SEM, FEI Quanta 200, Eindhoven, Netherlands).

2.4. Statistical analyses

The statistical analysis and data fitting were performed with Microsoft Office Excel 2016 and Sigma Plot 12.5.

The mass difference between the initial and residual concentration was used to determine the amount of pharmaceuticals sorbed to the PE microplastics at a given time (*t*).

$$q_t = \frac{(C_0 - C_t) \times V_W}{m_{PE}} \quad (1)$$

where q_t (μg g^{-1}) is the concentration of pharmaceuticals sorbed to the microplastics at a given time; C_0 and C_t (μg L^{-1}) are the initial concentration and residual concentration of a pharmaceutical at given time (*t*) in liquid phase, respectively; V_w (L) is the solute volume; and m_{PE} (g) is the mass of PE microplastics.

The percentage sorbed was calculated according to Eq. (2):

$$\%\text{Sorbed} = \left(\frac{C_0 - C_t}{C_0}\right) \times 100 \quad (2)$$