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The effects of environmental conditions on the enrichment of antibiotics on microplastics in simulated natural water column

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ABSTRACT

Concerns regarding the release of microplastics (MPs) into the environment led us to explore the relationship between the different environmental factors and physicochemical properties of MPs, as well as the change of interaction between MPs and organic pollutants. In this study, the effects of environmental factors (ageing conditions), such as pH, temperature, ionic strength, ageing time, and humic acid (HA) concentration, on the characteristics of MPs and their adsorption toward tetracycline (TC) were systematically investigated. The results showed that ageing factors such as pH, ionic strength, and temperature were found to have little impact on the adsorptive capacity of MPs for TC. However, MPs aged in HA solution exhibited a significant decreased adsorptive capacity for TC. HA, which has numerous functional groups, can cover the surface of MPs and change their hydrophobicity, thereby reducing the adsorption affinity to TC. The electrostatic repulsion between adsorbed HA and TC molecules may also decrease the adsorption of TC. In addition, the competing effect of HA for adsorption sites on the surface of MPs further reduces the adsorption of TC. The data presented in this work provide useful information for understanding the transfer of antibiotics by aged MPs, which is of fundamental importance to assess the environmental impact of MPs.

1. Introduction

The production of synthetic polymers, so-called plastics, has increased rapidly since the introduction of plastic materials in the 1950s due to their light weight and high durability (Barnes et al., 2009; Cózar et al., 2014). Currently, more than 320 MT/year of plastics are produced and the production will continue to increase in the coming decades (Plastic Europe, 2016). The Large quantity of plastic debris that are resistant to biodegradation accumulated in the environments by various kinds of routes of discharge, such as inadequate waste management, improper waste disposal, and urban runoffs (Cole et al., 2011 ; Cózar et al., 2014;). Many studies have reported the extensive accumulation of plastic debris in natural habitats around our planet, such as in the soil, rivers, wastewater treatment plants, as well as in marine habitats (Barnes et al., 2009; Boerger et al., 2010; Huerta Lwanga et al., 2016). Plastics in the environment differ in shape and size and range from meters to micrometers.

Microplastics (MPs) are defined as plastic debris less than 1 mm in diameter, which pose substantial threat to aquatic lives and cause increasing concerns (Browne et al., 2011). Particularly, MPs are widespread in the marine environment and broadly migrated due to their floating behavior. MPs in the ocean are known to be colonized by microbial groups, increasing the risk of being ingested (Zettler et al., 2013; McCormick et al., 2014). MPs ingestion has been found from zooplankton to large mammals and the negative influence on organisms, such as Zooplankton, Lugworm, and fish, has been documented by many researchers (Besseling et al., 2012; Cole et al., 2013; Vandermeersch et al., 2015; Huerta Lwanga et al., 2016; Alomar et al., 2017). Even the fresh MPs without microflora can also be ingested by organisms since they look like food debris (Browne et al., 2008; Murray and Cowie, 2011; Cole et al., 2013). MPs can also absorb organic pollutant and may transport them from the surface water to the sediment, and thus leading to the exposure of benthic organisms to organic pollutant (Mato et al., 2001). These studies provide the evidence that contaminants on the surface of MPs can accumulate in the organisms through MPs digestion, which may enter the food chain and pose risks for human health (Teuten et al., 2009; Rainieri et al., 2018).

Because of the complexity of the marine environment, MPs in the open ocean not only change in physical properties, such as hydrophobicity, specific surface area, and particle size, but also probably have chemical changes, such as corrosion degradation and surface modification. The physical and chemical changes of MPs may affect their adsorption behavior for organic pollutants, and consequently affect the transfer, release, and risk associated with pollutants. Therefore,

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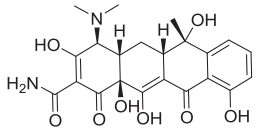
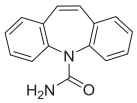
Table 1
Sorbate water solubility (S_W), n-octanol-water partition coefficient ($logK_{OW}$), and sequential acid dissociation constants (pK_as).

	Molecular structure	Molecular weight (g mol^{-1})	S_W (mg L^{-1})	logK_{OW}	pK_as
TC		444.43	1690[a]	−1.19[a]	3.30, 7.68, 9.69[a]
CBZ		236.27	170[b]	2.45[c]	2.3, 13.9[c]

[a] Tolls (2001).
[b] Ncibi and Sillanpää (2017).
[c] Shanmuganathan et al. (2015).

it is of great significance to investigate the effect of water environment on the adsorption behavior of MPs for pollutants.

Antibiotics are a representative kind of pollutants with high biotoxicity and proved to be easily enriched by MPs (Christou et al., 2017). Among which, tetracycline (TC) is one of the most commonly used, and widely concerned due to its high hydrophilicity, large solubility, rich functional groups, and high biotoxicity, as shown in Table 1 (Sarmah et al., 2006; Ji et al., 2009). Hence, we chose TC as the representative pollutant to explore the interaction between aged MPs and organic pollutant. In addition, we use medium hydrophilic carbamazepine (CBZ) as a comparison, as Table S1 shows, which has fewer functional groups.

The main objective of this study is to systematically examine the effects of different environmental factors on the physicochemical properties of MPs and determine the correlation between the change of MPs with the adsorption behavior of TC. To this end, MPs were first aged at different temperatures, pH, electrolyte concentrations, humic acid (HA) concentrations, and ageing times. Then, the adsorption capacity of the aged MPs for TC were investigated. Finally, we explained the possible correlation between the ageing condition and adsorption capacity of MPs by multiple characterizations.

2. Experimental section

2.1. Materials

Polyethylene plastic purchased from an plastic company was selected as the source of MPs. Polyethylene plastic was smashed and then sieved to obtain the MPs with the size range of 150–250 μm. These MPs were aged under different conditions, such as pH, temperature, ionic strength, HA concentration, and time. All the reagents used in this experiment were of analytical grade and used without further purification.

The ionic strength was adjusted by 0.01, 0.1, and 1 M of NaCl solutions. HA stock solution was prepared by adding HA powder to purity water to get a 100 mg L^{-1} bulk solution, and 2, 10 and 50 mg L^{-1} of HA solutions were prepared by diluting proportionately the stock solution, respectively. 0.01 M HCl or 0.01 M NaOH solutions were used to adjust the pH of ageing solution. The temperature was set as 5, 20, 30 °C to represent different seasons. In ageing experiment, 30 g MPs were soaked in different ageing solutions with the volume of solution of 600 mL and the ageing processes were done at 20 °C except the study of the effect of temperature. After 5, 30, and 90 days, the corresponding MPs were filtered, thoroughly washed with distilled water and dried at room temperature (19 ± 2 °C), and then stored in clean storage bags for further use.

2.2. Characterization of MPs

In order to determine the specific chemical groups in MPs, Fourier transform infrared (FTIR) spectra of the materials were collected on a Bruker FTIR EQUINOX 55 spectrometer (Bruker Corp., Ettlingen, Germany) with KBr pellets in the optical range of 4000–500 cm^{-1}. The Raman analysis of MPs was performed on a laser Raman spectrometer (LabRamHR, HORIBA Jobin Yvon. Co., Paris, France) with the laser radiation source operating at a power of 25 mW and a wavelength of 514 nm. The morphology of the MPs was analyzed by scanning electron microscopy (SEM, Sirion 200, FEI electron optics company, Hillsboro, OR, USA).

2.3. Batch sorption experiments

In the adsorption experiments, 2 g of MPs were added into each 250 mL conical flask containing 200 mL of 10 mg L^{-1} TC solution. The flask with the mixture was placed on an orbital shaker (180 rpm) at 20 °C until equilibration was reached within 10 days, which has been confirmed to be sufficient to reach sorption equilibrium by preliminary experiment. The concentration of TC in the aqueous solution was determined by a UV–Vis spectrophotometer (UV–1800; Shimadzu, Kyoto, Japan). To measure the aqueous TC concentrations, 4.5 mL of TC solution was filtered through 0.25 μm water filter membrane. Then, 0.05 mL of 0.01 M HCl was added to 4 mL of filtrate to acidify the TC solution and the concentration of TC was determined using the UV–Vis spectrophotometer at a wavelength of 270 nm. Calibration curves were prepared in the same way. The adsorbed amounts were calculated according to the mass balance.

2.4. Data analysis and quality control

In order to minimize the experimental errors, all the sorption experiments were performed in triplicate and each data point were the average of measurements. The adsorption experiment was conducted in the dark to prevent possible photodegradation of TC. The concentration of TC was determined as soon as the experiment was completed, and 4.5 mL of the same concentration of TC solution in the conical flask was immediately replenished. To avoid the effect of the self-degradation of TC on the experiment, we have also set up a pure TC solution as a comparison in the experiment, and the concentration of pure TC solution was almost unchanged during the experiment period (Fig. S1).

2.5. Contact angle measurements

The water droplet method was used to determine the contact angle of MPs using a goniometer (Combe et al., 1999). Prior to measurement, double–sided adhesive was cut into 20 mm × 1.5 mm strips and attached to a glass chamber. MPs were then evenly adhered to the