



Comparative evaluation of sorption kinetics and isotherms of pyrene onto microplastics

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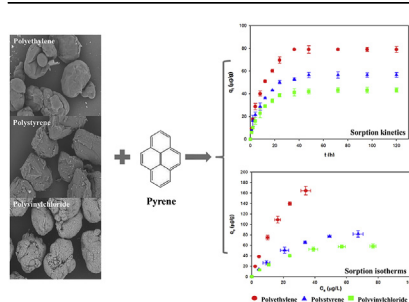
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HIGHLIGHTS

- Sorption kinetics and isotherms of pyrene onto microplastics were studied.
- Sorption of pyrene followed the order of PE > PS > PVC.
- Pseudo-second-order model was appropriate to describe the sorption kinetics.
- Sorption equilibrium data were best fitted to the Langmuir model.

GRAPHICAL ABSTRACT



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ABSTRACT

Concerns regarding microplastics pollution and their potential to concentrate and transport organic contaminants in aquatic environments are growing in recent years. Sorption of organic chemicals by microplastics may affect the distribution and bioavailability of the chemicals. Here sorption process of pyrene (Pyr), a frequently encountered polycyclic aromatic hydrocarbon in aquatic environments, on three types of mass-produced plastic particles (high-density polyethylene (PE), polystyrene (PS) and polyvinylchloride (PVC)), was investigated by comparative analysis of different sorption kinetic and isotherm models. Optimum kinetic and isotherm models were predicted by the linear least-squares regression method. The pseudo-second-order kinetic model was more appropriate in describing the entire sorption process ($R^2 > 0.99$). Sorption rates of Pyr onto microplastics were mainly controlled by intraparticle diffusion. PE exhibited the highest affinity for Pyr, followed by PS and PVC. The sorption equilibrium data were best fitted to the Langmuir isotherm ($R^2 > 0.99$), indicating monolayer coverage of Pyr onto the microplastics.

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1. Introduction

Microplastics (<5 mm) pollution occurs in aquatic environments worldwide and has been increasingly recognized as a global concern (Cole et al., 2011; Dris et al., 2015). Sources of microplastics include scrubbers in cosmetic and cleaning products, manufactured pellets used in plastic production or as abrasives for sandblasting,

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plastic fibers from machine washing of clothes, and degradation of larger plastic debris (Barnes et al., 2009; Fendall and Sewell, 2009; Cole et al., 2011; Eerkes-Medrano et al., 2015). Due to the great surface-to-volume ratio and fugacity capacity, microplastics can sorb and concentrate various types of environmental chemicals, including hydrophobic organic compounds (HOCs) and heavy metals, from the external phases (e.g., ambient water) (Ashton et al., 2010; Rochman et al., 2013; Anderson et al., 2016). Increasing studies have demonstrated that plastic debris recovered throughout the world's oceans, coastlines, freshwater lakes and rivers contained measurable organic pollutants, such as polycyclic aromatic hydrocarbons (PAHs), organochlorine pesticides (OCPs), polybrominated diphenyl ethers (PBDEs), polychlorinated biphenyls (PCBs), environmental estrogens, and so on (Rios et al., 2007; Teuten et al., 2009; Hirai et al., 2011; Engler, 2012; Heskett et al., 2012; Fisner et al., 2013). Concentrations of organic chemicals loaded on the contaminated plastics can be many orders of magnitude higher than the ambient water (Engler, 2012; Wang et al., 2016). Microplastics, as well as the sorbed toxic chemicals, can enter into the bodies of aquatic biota by accidental ingestion (Ryan, 2016). Desorption of the sorbed chemicals from contaminated microplastics may be enhanced in the gut of aquatic organisms (Bakir et al., 2014; Seltnerich, 2015), which would increase the bioavailability of these chemicals (Besseling et al., 2013; Avio et al., 2015; Wang et al., 2016). The partitioning behavior of organic contaminants within microplastics has attracted increasing attention in recent years.

PAHs are an important class of HOCs, which widely consist in emissions from forest fires, volcanic activities, industrial processes, and combustion of fossil fuels or other organic substances like tobacco and garbage. Based on the potential of PAHs in mutagenicity and carcinogenicity, Environmental Protection Agency of United States has listed 16 kinds of PAHs as priority pollutants. PAHs are ubiquitously distributed in aquatic ecosystems and inclined to associate with solid particles, such as plastic debris, because of their hydrophobic nature (O'Connor et al., 2016). A better knowledge of interactions between PAHs and microplastics is of vital importance for evaluating the possible influence of microplastics on the moving dynamics of these organic chemicals in aquatic environments.

Much work has been done to investigate the sorptive behavior of PAHs or other organic pollutants within microplastics in the laboratory or under a field condition (Teuten et al., 2007; Bakir et al., 2012; Guo et al., 2012; Rochman et al., 2013; Huffer and Hofmann, 2016; Wu et al., 2016). However, most of these previous studies tended to conduct one or two of the most commonly used sorption models to elucidate the sorption process. The possible applicability of other solid-water sorption models, which might be helpful in giving insight into the potential mechanisms involved in the sorption of organic chemicals by microplastics, is largely ignored. The objective of the present study was to achieve a deep understanding of the interactions between microplastics and organic pollutants by comparative analysis of different sorption models. Three mass-produced plastics, polyethylene, polystyrene and polyvinylchloride, which are also the predominant polymer types of plastic debris present in aquatic ecosystems (Moore, 2008; Dris et al., 2015), were selected as the model sorbents, and pyrene, a ubiquitous PAH in contaminated sites which has been proved to cause toxicity in aquatic organisms and human (Clément et al., 2007; Han and Currell, 2017), was selected as the model sorbate in the sorption experiments. The experimental data were measured and fitted into different sorption kinetic and isotherm models with linear least-squares method to evaluate the fitness of each model.

2. Materials and methods

2.1. Materials and chemicals

Three kinds of mass-produced plastic particles: high-density polyethylene (PE), polystyrene (PS), polyvinylchloride (PVC), used as the sorbents, were purchased from Shanghai Youngling Technology Ltd. (China). The microplastics were sieved to the size range of 100–150 μm . The Brunauer, Emmett, and Teller (BET) surface areas of microplastics were determined from N_2 sorption data collected at 77 K with the Autosorb 1-MP Surface Area Analyzer (Quantachrome Corp., USA). Their surface characteristics were also examined using a scanning electron microscopy (SEM) (TM3030, Hitachi, Japan) (Fig. A1). Basic properties of microplastics used in this study are shown in Table A1.

Pyrene (Pyr, solid powder, purity > 98%) used as the model sorbate and *m*-terphenyl used as the internal standard were purchased from AccuStandard (USA). Methanol (HPLC grade) and *n*-hexane (HPLC grade) were purchased from Fisher Scientific (USA). Sodium azide (NaN_3) anhydrous sodium sulfate (Na_2SO_4), calcium chloride dihydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$), sodium hydrogen carbonate (NaHCO_3), potassium chloride (KCl), magnesium sulfate heptahydrate ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$), potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$), sodium hydroxide (NaOH), nitric acid (HNO_3) and sulfuric acid (H_2SO_4) (all analytical grade) were from Shanghai Sinopharm Group (China).

The Pyr stock solution was prepared in methanol and kept in the dark at 4 °C. The artificial freshwater (AFW) was used as the background solution and prepared as deionized water with KCl (1.2 mg/L), $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (58.5 mg/L), NaHCO_3 (13.0 mg/L), and $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (24.7 mg/L) (Akkanen and Kukkonen, 2003). The initial pH of AFW was adjusted to 7 by adding either 0.1 M HNO_3 or 0.1 M NaOH.

2.2. Sorption experiments

The sorption experiments were carried out in the 60-mL glass bottles. 10 mg of microplastics (PE, PS, or PVC) were added into each bottle containing 50 mL of AFW, and 25 mg/L of NaN_3 as bio-inhibitor. Each bottle was spiked with the methanol solution containing a predesigned amount of Pyr. The volumes of methanol (spiking solvent) for all the samples were same and less than 0.2% (v/v). The bottles were sealed using Teflon caps and horizontally shaken on a TS-200B orbital shaker (200 rpm) (Shanghai Tensuc Ltd., China) in the dark at room temperature (25 °C). All sorption experiments were performed in triplicate. In the kinetics experiment, each test bottle was spiked with 50 $\mu\text{g/L}$ of Pyr and agitated continuously in the shaker. Samples were collected at specified time intervals and passed through the 0.45 μm Whatman GF/C glass fiber filters, and aqueous concentrations of Pyr were analyzed. The kinetics data indicated that sorption equilibriums of Pyr onto the three microplastics were achieved within 48 h (Fig. 1A). Sorption isotherm experiment was conducted using seven initial aqueous concentrations of Pyr in the range of 0–100 $\mu\text{g/L}$. After being continuously agitated for 48 h, samples were collected to quantify the equilibrium concentrations of Pyr in aqueous phase. Detailed information regarding chemical analysis of Pyr and quality assurance and quality control measures is given in the Appendices.

2.3. Statistical analysis

The amount of Pyr sorbed per unit mass of microplastics upon equilibrium, q_e ($\mu\text{g/g}$), was estimated by the mass balance equation as follows:

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