Ecotoxicology and Environmental Safety 210 (2021) 111842

Contents lists available at ScienceDirect

Ecotoxicology and Environmental Safety

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

Sorption of tetrabromobisphenol A onto microplastics: Behavior, mechanisms, and the effects of sorbent and environmental factors

Shengsheng Li [a,b,1], Ruixue Ma [a,1], Xiaohui Zhu [a], Chang Liu [a], Liangzhong Li [a,*], Ziling Yu [a], Xichao Chen [a], Zongrui Li [a], Yan Yang [b,c,**]

[a] State Environmental Protection Key Laboratory of Environmental Pollution Health Risk Assessment, Center for Environmental Health Research, South China Institute of Environmental Sciences, The Ministry of Ecological and Environment of PR China, Guangzhou 510655, PR China
[b] School of Environmental & Safety Engineering, Changzhou University, Changzhou 213164, PR China
[c] Guangdong Key Laboratory of Environmental Catalysis and Health Risk Control, Guangzhou Key Laboratory of Environmental Catalysis and Pollution Control, School of Environmental Science and Engineering, Institute of Environmental Health and Pollution Control, Guangdong University of Technology, Guangzhou 510006, PR China

ARTICLE INFO

Edited by Professor Bing Yan

Keywords:
Microplastics
Tetrabromobisphenol A
Sorption
Ionic strength
Humic acid

ABSTRACT

Microplastics (MPs) and halogenated organic pollutants coexist in ambient water and MPs tend to sorb organic pollutants from surrounding environments. Herein, a study on the sorption behavior of tetrabromobisphenol-A (TBBPA) onto four different MPs, namely, polyethylene (PE), polypropylene (PP), polystyrene (PS), and polyvinyl chloride (PVC) was carried out. Effects of MPs properties and environmental factors, including the type, surface charge and pore volume as well as the ionic strength (Ca^{2+}) and humic acid (HA) on the sorption of TBBPA were discussed. Results showed that the sorption of TBBPA onto the MPs could reached an equilibrium within 24 h, and the sorption capacities decreased in the following order —PVC (101.85 mg kg^{-1}) >PS (78.95 mg kg^{-1}) >PP (58.57 mg kg^{-1}) >PE (49.43 mg kg^{-1}). Adsorption kinetics data fitted by intraparticle diffusion model revealed both surface sorption and intraparticle diffusion contributed, in the interfacial diffusion stage approximately 11–29% of TBBPA slowly diffused onto the surface of the MPs, and finally, in the intraparticle diffusion stage. The increase of Ca^{2+} concentration could promote the sorption of TBBPA by PE, PP, and PS, but no significant alteration for PVC. For all the four MPs, HA was found to exert a negative effect on TBBPA sorption. The adsorption was mainly driven by hydrophobic partition and electrostatic interactions.

1. Introduction

Small-sized (<5 mm in diameter) plastics, known as microplastics (MPs) are significantly abundant in the environment. In recent years, reports have increasingly demonstrated the occurrence of MPs in marine, inland, and freshwater environments (Di and Wang, 2018; Ghosal et al., 2018; Zhang et al., 2018, 2020; Rose and Webber, 2019) and even in remote and sparsely inhabited areas, such as the Siling Co Lake Basin (Zhang et al., 2016) and the polar regions (Kanhai et al., 2018). It is estimated that by 2025, over five trillion pieces of plastic will invade the oceans and MPs will account for 92% of that plastic contamination (Eriksen et al., 2014; Sebille et al., 2015). In aquatic environments, MPs, such as polyethylene (PE), polypropylene (PP), polystyrene (PS), and polyvinyl chloride (PVC) are predominantly present. In the deep Arctic seas, the predominant type of MP is PVC, which accounts for the largest proportion (38%) of MPs (Bergmann et al., 2017). About 2.9 trillion microbeads per year are released into aquatic habitats in the United States via WWTP effluents (Rochman et al., 2015). In China, an estimation of 39 tons of MPs were emitted into the environment based on the huge amount of personal care products usage (Lei et al., 2017). In the Three Gorges Reservoir, 89% of MPs are found to be composed of PE, PP, and PS (Di and Wang, 2018). The contaminant transfer effects of MPs can be more significant than larger plastic debris due to the minute particle size of MPs. Together with adsorbed contaminants, MPs can be easily ingested and accumulated by aquatic organisms in their bodies. In recent years, increasing microplastic pollution has attracted global attention (Wang and Wang, 2018; Wu et al., 2019; Zhang et al., 2020).

From surrounding environments, MPs can adsorb and accumulate

* Corresponding author.
** Corresponding author at: School of Environmental & Safety Engineering, Changzhou University, Changzhou 213164, PR China.
E-mail addresses: liliangzhong@scies.org (L. Li), yy129129@163.com (Y. Yang).
[1] Both the authors contributed equally to this work.

https://doi.org/10.1016/j.ecoenv.2020.111842
Received 21 July 2020; Received in revised form 14 December 2020; Accepted 19 December 2020
Available online 8 January 2021

hydrophobic organic contaminants (HOCs) and heavy metals (HMs) due to their strong hydrophobic properties and specifically, large surface areas (Lee et al., 2014; Wang et al., 2018a, 2018b). Not only the properties of MPs (type, particle size, and dose) but also environmental factors, such as the presence of ionic strength and dissolved organic matter (DOM) have been also suggested to influence sorption behavior (Seidensticker et al., 2017; Wang et al., 2018a). For instance, polyamide (PA) has been reported to sorb more antibiotics than the other types of MPs (Li et al., 2018a, 2018b). PS and PE could adsorb more lubricating oil with the maximum sorption capacities of 5.2 g g^{-1} and 6.8 g g^{-1} respectively (Hu et al., 2017). Results obtained on the sorption behavior of tylosin by the four MPs, namely PE, PP, PS, and PVC have suggested that tylosin exhibits higher sorbent accessibility on PVC than on PE, PP, and PS (Guo et al., 2018). Smaller particle size can facilitate the sorption of HOCs by MPs (Lin et al., 2019). Ionic strength and DOM also have been shown to change the partition coefficient of contaminants between MPs and water but no consensus reached on their effects on the sorption of various contaminants (Zhang et al., 2010; Seidensticker et al., 2017).

Tetrabromobisphenol A (TBBPA) is the most commonly used brominated flame retardant (BFR) in the world, accounting for about 60% of the total BFR market (Liu et al., 2016; Yu et al., 2019). As an additive flame retardant in plastic products, TBBPA has been widely employed because its phenolic hydroxyl group is not bonded to the polymer covalently and therefore, it could be released into the environment easily (He et al., 2010; Alexander et al., 2011; Covaci et al., 2011; NTP, 2014; Yu et al., 2019). Due to its huge production and application, TBBPA is ubiquitous in air, dust, soil, water, sediment and sewage sludge, and also frequently detected in various environmental matrix even in humans (Fijalkowski et al., 2017) with the concentration up to 4870 ng L^{-1} in lake water (Yang et al., 2012) and 9750 ng g^{-1} in sediment and sewage (Feng et al., 2012). A recent study reported the concentration of TBBPA was 520 ng L^{-1} of TBBPA in the surface water and 21.9–0.482 ng g^{-1} dw was measured in the sediments of Chao Lake, Anhui province, China and those in seawater in the coastal intertidal zone of Qingdao, China ranged from nd to 1800 ng L^{-1} (Gong et al., 2017). TBBPA exposure may lead to endocrine disorders and reproductive toxicity, and as a potential carcinogenic substance, it can increase the incidence of uterine tumors in female rats (NTP, 2014; Cope et al., 2015; Lai et al., 2015; Yu et al., 2018). Recently, TBBPA has been upgraded to Group 2A, probably carcinogenic to humans by the International Agency for Research on Cancer (IARC) on the basis of sufficient evidence of carcinogenicity in experimental animals (IARC, 2018). In aqueous environments, MPs, especially for their own additive properties have been proved to act as important carriers of BFRs readily (Kwon et al., 2017).

Currently, limited information on the interaction of TBBPA with MPs is available except for few studies on the sorption of hexabromocyclododecane (HBCDs), Polychlorinatedbiphenyls (PCBs), Polybrominateddiphenylethers (PBDEs) and Bisphenol A (BPA) investigated (Velzeboer et al., 2014; Zhan et al., 2016; Liu et al., 2018; Wu et al., 2019a, 2019b; Xu et al., 2019). In order to promote the understanding of the adsorption behavior, and possible mechanisms that influenced the sorption, the present study was conducted to (1) elucidate the adsorption behavior of TBBPA onto four commonly used of MPs, polyethylene (PE), polypropylene (PP), polystyrene (PS), and polyvinyl chloride (PVC); (2) investigate the mechanisms of interaction involved in sorption process; and (3) determine the influence of environmental factors, such as ionic strength and DOM, on the sorption of TBBPA. This may contribute to a better understanding of the environmental significance of these two co-existing emerging contaminants.

2. Materials and methods

2.1. Chemicals and materials

Standard TBBPA (CAS# 79-94-7, (>98% pure) was purchased from Sigma-Aldrich (St.Louis, MO, USA). In the present study, four types of the pristine MPs including polyethylene (PE, 3.2 mm i.d), polypropylene (PP, 3.2 mm i.d), polystyrene (PS, 3.2 mm i.d), and polyvinyl chloride (PVC, films) were purchased from Aladdin Industrial Corporation (Shanghai, China). Methanol of HPLC grade was supplied by AnPu Scientific Instruments, while $CaCl_2$ (>96% pure) and HA (˃90% pure) were purchased from J&K Scientific Ltd. (Beijing, China) and Sigma Aldrich (St. Louis, MO,USA), respectively. Ultrapure water (18.2 MΩ cm^{-1}) was produced by Milli-Q purification system (Millipore, Milford, MA, USA). Stock solution of TBBPA (100 mg L^{-1}) was prepared in methanol and stored at −20 ℃ in the dark. Working solutions for calibration curve was obtained (R^2 >0.999) by diluting to a series of different concentrations (5–100 μg L^{-1}) in ultrapure deionized water.

2.2. Microplastic preparations and characterization

The virgin MP pellets were crushed or cut into small pieces, then ground in an analytical mill (IKA Werke GmbH & Co.KG,. Staufen, Germany) before sieving through a mesh of 150 μm. After these, microplastics were washed with deionized water and methanol, and dried at 50 ℃ for 72 h and then stored in a desiccator.

The composition of MP microspheres was confirmed through Fourier transform infrared spectra (FT-IR) spectroscopy (Nicolet iN10 MX, Thermo-Fisher Scientific Inc., USA). Data were collected in the range of 4000–400 cm^{-1} at a resolution of 2 cm^{-1} with a 3 s collection time. To reflect the surface electric property of MPs under various conditions, zeta potential of the tested microplastics were determined on a Zetasizer Nano-ZS ZEN3500 ((Malvern Instruments Ltd, Malvern, UK) with water as a dispersant (Refractive Index =1.33). The measurements of hydrodynamic diameter was also carried out once for four replicates (n = 4, see Fig.S3). The surface morphology was observed by scanning electron microscopy SEM. The specific surface areas (SSA) as well as pore size distributions and total pore volumes (TPV) were used to describe the MPs properties by Brunauer-Emmett-Teller (BET) N_2 specific surface area and porosity analyzer (ASAP 2460, Micromeritics, USA). The physicochemical properties of tested MPs are provided in Table S1.

2.3. Batch adsorption experiments

Experiments on adsorption kinetics were carried out using 20 mg MPs and 100 μg L^{-1} of TBBPA in glass flask. The volumes of organic solvent for all samples was controlled below 0.1% (v/v). 0.01 M $CaCl_2$ and 0.02% (w/v) NaN_3 were added into the background solution to maintain the ionic strength of the suspension and to inhibit microbial degradation. After that, the initial pH was adjusted to 7.0 ± 0.2 by HCl and NaOH solution. The mixture solutions of batch experiments were then incubated at 25 ℃ in dark on a thermostat vibration shaker at 160 rpm. Samples were then withdrawn at specific time intervals (0 h, 1 h, 2 h, 4 h, 6 h, 12 h, 24 h, 36 h, and 48 h) based on preliminary experiment., and then filtered through 0.22 μm filters prior to instrumental analysis. Procedure blank control spiked with TBBPA but microplastic-free was set up under the same condition to evaluate the procedure loss during incubation. Another control of MP-spiked but TBBPA-free showed that no detectable TBBPA was released from the MPs during the sorption process. Each treatment was conducted in triplicate.

Sorption isotherm were conducted at initial concentrations of TBBPA from 5 to 100 μg L^{-1}. An incubation time of 48 h was set based on the kinetic results. Samples were collected at the end of the incubation in triplicate.

2.4. Factors influencing TBBPA sorption

In order to investigate the effects of adsorbent dose on adsorption, batch equilibrium approach were carried out using the doses of MPs from 5 to 50 mg with the initial TBBPA concentration of 100 μg L^{-1} in background solution. The effects of ionic strength on the sorption of

TBBPA were evaluated with a series of $CaCl_2$ ranging from 0.001 to 0.1 mol L^{-1}. Effects of dissolved organic matter (DOM) on the adsorption behavior were examined using humic acid (HA) as a representative material from 5 to 50 mg kg^{-1}. $CaCl_2$ solution (0.01 M) and 0.02% (w/v) of NaN_3 were also added into the mixture, as described in the adsorption kinetics study, then filtered before pH adjusted to 6.5 for further batch experiments. The vials were incubated on a reciprocal shaker for 72 h, then TBBPA in aqueous phase were quantified when the adsorption reached equilibrium.

2.5. Instrumental analysis

Analysis of aqueous TBBPA concentrations was performed on LC-MS/MS, using a triple quadrupole mass spectrometer (API 4000 LC/MS/MS, AB Sciex, USA) with a Poroshell 120 EC-C18 column (3.0 × 50 mm, 2.7 μm; Agilent Technologies, Santa Clara, CA, USA) as described in our previous study (Yu et al., 2020). Breifly, the mobile phase consisted of methanol and deionized water in a ratio of 9:1. The injection volume was 10 μL and the temperature of the column was set to 40 °C. The flow rate was kept at 200 μL min^{-1}. The retention time of TBBPA was 1.09 min

2.6. Data analysis

The adsorption kinetics were evaluated by measuring the adsorption capacity of TBBPA in solution at different time intervals (0–48 h). The nonlinear models of pseudo-first-order, pseudo-second-order and intra-particle diffusion model were used to fit the sorption kinetics. pseudo-first-order model represents that the rate-limiting step is a physical process affecting by analyte concentrations, while the pseudo-second-order model suggests the adsorption process involving the interaction affinity between adsorbents and adsorbates (Mohan et al., 2006). The pseudo-first-order, pseudo-second-order, and intra-particle diffusion models were used to describe the kinetics of TBBPA sorption onto the MPs:

$$\log(Q_e - Q_t) = \log Q_e - \frac{K_1 t}{2.303} \quad (1)$$

$$\frac{t}{Q_t} = \frac{1}{K_2 Q_e^2} + \frac{t}{Q_e} \quad (2)$$

$$Q_t = K_i t^{0.5} + \text{constant} \quad (3)$$

where Q_e and Q_t (mg kg^{-1}) are the amounts of TBBPA adsorption on the adsorbents at equilibrium and time t, respectively; K_1 (h^{-1}) and K_2 ($kg \cdot mg^{-1} \cdot h^{-1}$) are the rate constants for the pseudo-first-order and pseudo-second-order models of sorption reaction, respectively; and K_i is the rate constant for the intra-particle diffusion model.

The results from the isotherm experiment were fitted with the Linear, the Freundlich, and the Langmuir model as follows.

Linear model equation:

$$Q_e = K_d \times C_e \quad (4)$$

Freundlich model equation:

$$Q_e = K_f \times C_e^n \quad (5)$$

Langmuir model equation:

$$Q_e = \frac{Q_m \times K_L \times C_e}{1 + K_L \times C_e} \quad (6)$$

where C_e (mg L^{-1}) is the concentrations of TBBPA in the aqueous phase at equilibrium state; K_d ($L \cdot g^{-1}$) is the distribution coefficient of the solid (MPs) and aqueous phase; K_f ($\mu g^{1-1/n} \cdot L^{1/n} \cdot g^{-1}$) and n are the Freundlich constants; Q_m ($mg \cdot kg^{-1}$) and K_L ($L \cdot \mu g^{-1}$) are the Langmuir coefficients, represents the maximum sorption capacity and the sorption affinity between adsorbent and adsorbate, respectively.

3. Results and discussion

3.1. Characteristics of the MPs

Morphology of the four types of MPs by SEM showed irregular grain shape with wrinkles and pits (Fig. S1). The surface of PP particle was relatively smooth, while PE and PVC were more rough with many folds, exhibiting spherical bulges and micropores. Important absorption bands for FT-IR spectra were identified and band assignments were provided in Fig. S2 (Supporting Information). The spectrum of microplastic debris showed similar absorption characteristic as reported previously (Chen et al., 2019; Zhou et al., 2020). At the temperature of −196 ℃, the pore diameter, total pore volume and specific surface area (SSA) were quantitatively measured by nitrogen adsorption isotherm (Fig. S3). The particle sizes distribution of these polymers were given in the Fig.S4. The BET surface areas of the four microplastics as well as total pore volume were listed Table S1. Zeta potentials at different pH value were shown in Fig. S5.

3.2. Adsorption kinetics

The adsorption kinetics of TBBPA onto four microplastics were illustrated in Fig. 1. Adsorption of TBBPA onto microplastics showed an intense adsorption capacity at the initial time of incubation and subsequently achieved an equilibrium after 48 h. The sorption equilibrium time was about 24 h, 24 h, 12 h, and 6 h for PVC, PS, PP, and PE, respectively. The four different MPs were found to have distinct sorption affinities for TBBPA and it decreased in the following order—PVC >PS >PP >PE. As shown in Table S2, the parameters of two kinetic model indicated that the pseudo-second-order model fitted better than the first-order model with higher R^2 values, and the Qe values predicted by the pseudo-second-order model were in high agreement with the experimental values, indicating the pseudo-second-order model was more applicable to describe the sorption behavior of TBBPA. This may reflect that TBBPA can be adsorbed to different binding sites in the MPs. Our previous study showed that the adsorption of TBBPA onto PE particle yielded a better fit for pseudo-second-order model (Yu et al., 2020), similar findings were also reported for bisphenol analogs, musks, and antibiotics on PVC microplastics with the R^2 value > 0.99 (Guo et al., 2019; Wu et al., 2019a, 2019b).

The intraparticle diffusion model better illustrates the critical stages controlling the sorption process. In this study, the diffusion curves of the four MPs did not pass through the origin of the coordinate, indicating

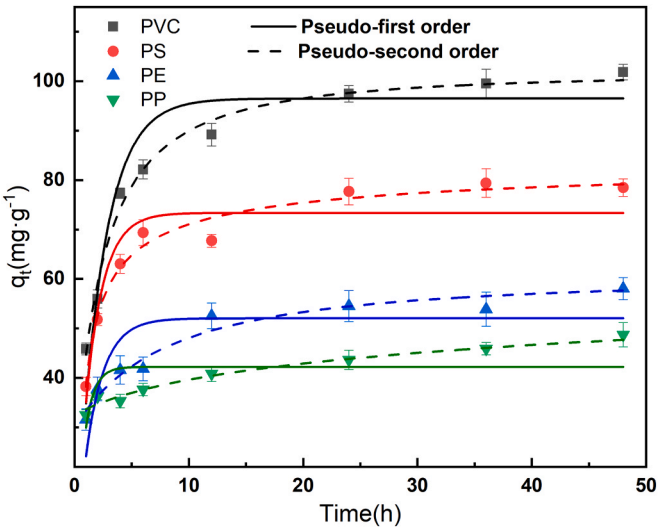

Fig. 1. Adsorption kinetics of TBBPA onto microplastics fitted by the pseudo-first-order model and the pseudo-second-order model.

that both surface sorption and intra-particle diffusion contributed to the actual sorption process of TBBPA on MPs (Fig. 2). The fitted sorption can be divided into three successive linear steps as follows: external mass transfer (Allen et al., 1989; Wu et al., 2019; Zhou et al., 2014a, 2014b), interfacial diffusion (Ai et al., 2011; Wu et al., 2019b) and intraparticle diffusion (Wu et al., 2019a, 2019b; Zhou et al., 2014a, 2014b). Approximately 56%−74% of TBBPA was adsorbed in the external mass transfer; 11%−29% of TBBPA was slowly diffused from the liquid phase to the surface of MPs in the interfacial diffusion phase. As the sorption rate of TBBPA slowed significantly, the sorption gradually stabilized and reached dynamic sorption equilibrium in the intraparticle diffusion stage.

The sorption characteristics of TBBPA onto different types of MPs could be closely related to the property of plastic particles, such as crystallinity, the polarity, and surface charge and functional groups of MPs (Guo et al., 2019; Wang et al., 2015). Previous studies revealed the crystallinity of MPs might be an important impact factor for the adsorption behavior of MPs. Liu et al. (2019) found a high crystallinity could lead to a high adsorption capacity, while an inverse correlation between the crystallinity and adsorption capacity was observed by Guo et al. (2012). Although rubbery plastics such as PE were reported to exhibit higher sorption affinities for many pollutants than glassier microplastics (e.g. PP, PVC, PS) (Li et al., 2018a, 2018b; Wang et al., 2015, 2018a; Wang and Wang, 2018), our study showed that PVC had the largest Q_m (101.85 mg kg^{-1}) among the four MPs but PE the lowest, indicating some other inherent factors of microplastics that can correlate with the adsorption intensity other than the degree of crystallinity. Wang et al. (2015) found the polar functional groups may negatively affect the sorption affinity of plastics. PVC and PS are more polar than PE and PP due to their substitution of one C-H by C-Cl and C-π for each unit (Chen et al., 2019). However, in this study, PVC exhibited larger sorption capacities than PE and PP, one possible reason could be that the sorption domains with chlorine atoms in PVC showed more affinity for TBBPA through polar-polar interaction.

3.3. Sorption isotherms

The Linear, Freundlich and Langmuir models were used to study the interaction behavior between TBBPA and MPs (Fig. 3). The calculated parameters of isotherm models were summarized in Table 1, from which, it can be seen that the Linear model and Freundlich model were both appropriate for PE, PP and PS, while PVC is better fitted by the Freundlich model with higher R^2, indicating the adsorption to

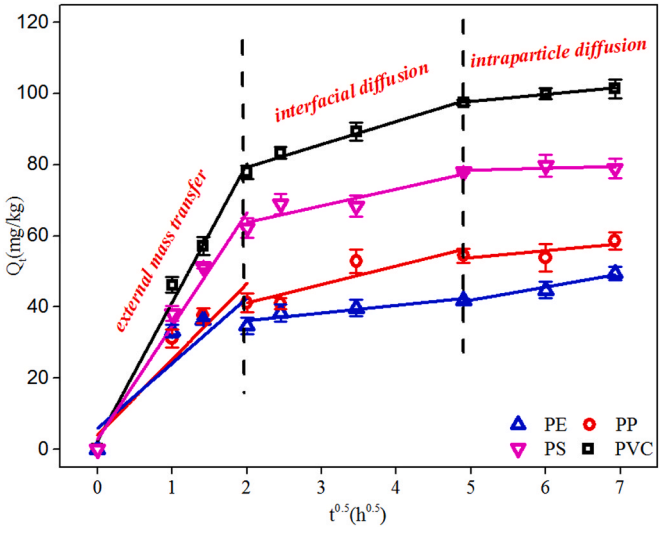

Fig. 2. The sorption kinetic of TBBPA on to MPs fitted by intraparticle diffusion kinetic model.

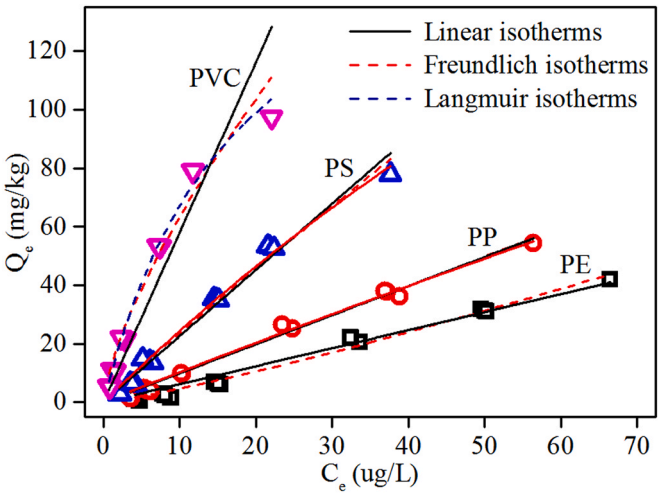

Fig. 3. The sorption isotherms of TBBPA to four microplastics (initial TBBPA concentration ranging from 5 to 100 μg L^{-1}).

heterogeneous surfaces or surfaces supporting sites of diverse affinities. Freundlich model reflects the adsorption occurring on the surface of the adsorbent with uneven distribution of binding site (Wang and Wang, 2018; Wu et al., 2019a, 2019b; Xu et al., 2019; Guo et al., 2019). As the maximum sorption capacities calculated by Langmuir model deviated from the experimental results for PE, the process may not mainly be the monolayer sorption driven by electrostatic force. Similar phenomena were also observed for the adsorption of organophosphate esters (Chen et al., 2019) and bisphenol analogs (Wu et al., 2019a, 2019b) on PVC microplastics. The nonlinearity index (n values) of Freundlich model indicates the sorption tendency under different initial concentrations. The *n* values > 1 suggested a favorable sorption with the increasing initial adsorbate concentrations (Guo et al., 2018; Xu et al., 2019). However, in present study, the *n* values were less than 1 for PS and PVC, which indicated a decreasing sorption tendency according to Guo et al. (2013) and Wu et al. (2019a, 2019b). The hydrophobic interaction was an adsorption mechanism reflected by the loading capacity (K_d) of the Linear model (Guo et al., 2018; Liu et al., 2019; Wu et al., 2019a, 2019b). Sorbent with higher affinity generally exhibited higher K_d values. TBBPA has a relatively higher hydrophobicity with the octanol-water partition coefficient ($logK_{ow}$) of 4.75 (pH 7.53). From Table 2, the K_d values of four MPs for TBBPA varied in the order of PVC (5.814 L g^{-1}) > PS (2.263 L g^{-1}) > PP (0.993 L g^{-1}) > PE (0.616 L g^{-1}), suggesting the hydrophobic partitioning was probably another mechanism for TBBPA adsorption onto PVC.

To further discuss the potential mechanism, zeta potential was determined in a series of background solution with pH values ranging from 3.0 to 11.0 to investigate the surface charge of MPs in aqueous phase. According to the zeta potentials (Fig. S5), the surface of all four microplastics was negatively charged at pH > 7 and became more negative with the increasing pH values. Previous studies have found electrostatic forces could be a critical mechanism (Guo et al., 2013; Wu et al., 2019a, 2019b; Li et al., 2018a, 2018b; Liu et al., 2019). TBBPA has two pKa values of 7.5 and 8.5 (Dam et al., 2012). At pH > 8.5, TBBPA will be dissociated and present essentially in the form of negatively charged ion, and between pH of 7.5 and 8.5, there is mainly monoanion form. Sorption isotherms were produced under weak acidity, in which the surface of PVC, PP and PS was almost negatively charged based on the zeta potential. This was in favor of sorption as TBBPA exists mostly in the protonated and molecular form, thus can be combined with MPs by electrostatic attraction. Although in this study, the *n* value of PVC was smaller, its K_f value was remarkably higher, suggesting a significant adsorption affinity than the other types of MPs. As the particle fraction process was significantly associated with both the surface charge of MPs

Table 1
Sorption isothermic parameters of TBBPA onto four microplastics.

MPs	Linear		Freundlich			Langmuir		
	K_d ($L \cdot g^{-1}$)	R^2	K_f ($ug^{1-1/n} \cdot L^{1/n} \cdot g^{-1}$)	n	R^2	Q_m ($mg \cdot kg^{-1}$)	K_L ($L \cdot ug^{-1}$)	R^2
PE	0.616	0.974	0.305	1.183	0.984	Can not be fitted by Langmuir directly		
PP	0.993	0.987	0.987	1.002	0.986	878.21	0.001	0.987
PS	2.263	0.982	2.658	0.949	0.982	494.94	0.005	0.986
PVC	5.814	0.881	12.447	0.708	0.96	187.48	0.056	0.988

and physicochemical property of TBBPA. The more negative charge on surface of PVC makes electrostatic repulsion be one of the advantages of keeping MPs well-dispersed to favor the adsorption, hence, electrostatic interactions might play important functions in the adsorption of TBBPA onto PVC.

To sum up, the sorption of TBBPA by four MPs are multi-layer sorption on a heterogeneous surface, which was probably simultaneously dominated by both hydrophobic partition and electrostatic forces.

3.4. The effect of dissolved organic matter

Humic acid (HA) is a common type of natural organic matter, usually exists with a negative charge, carries oxygen-functional groups, and can form a copolymer with MPs (Chen et al., 2018). This type of macromolecule performs various roles in the sorption process of MPs. The negatively charged HA molecules could offer new sorption sites for sorbates in aqueous phase, directivity leading to a competitive adsorption (Sun et al., 2019). As can be seen from Fig. 4, after 24 h incubation, the absorbed amounts of TBBPA onto the four test MPs were reduced by 5.4−42.8% with the HA concentrations increasing from 0 to 50 mg L^{-1}, indicating a negative effect on TBBPA sorption. The results were in accordance with the findings for non-polar compounds such as 17 α-ethinyl estradiol, BDE-47, which might be attributed to the competitive adsorption interactions in-between organic pollutants, DOM and microplastics.

Another influencing factor might be the surface coverage as the DOM molecule could preferentially cover the surface of the microplastics, thereby inhibiting the sorbate from entering the sorption site reported (Xu et al., 2019). In comparison to the adsorption levels in the absence of HA, a drastic decline in adsorption was observed even at a low concentration of HA for PVC and PE. As demonstrated by the micropore volume of the four MPs (Table S1), the micropore volume of PE and PVC was higher than that of PS and PP, the decreased sorption could be ascribed to the pore blockage that altered the partitioning of TBBPA between MPs and water. Recent studies, however, showed that the interactions between PE microplastics and DOM were negligible (Seidensticker et al., 2017). Seidensticker et al. (2017) provided direct evidence through fluorescence measurements that no DOM sorption occurred on different amounts of PE microplastics. In this study, pore blockage might be the main factors involved with HA present in the sorption process. Whether different types of MPs can interact with DOM containing abundant functional groups warrants further investigation.

3.5. Effect of ionic strength on the sorption of TBBPA

The effect of Ca^{2+} on the sorption of TBBPA on MPs might have a significant impact on their migration and transformation in an ecosystem. As shown in Fig. 5, as the ionic concentrations increased from 0 to 0.005 mol L^{-1} (equivalent to the corresponding salinity of 0–0.56%), the sorption of TBBPA on PE, PP and PS increased by 43−81%, and then subsequently remained relatively stable (ionic concentration increased from 0.005 to 0.1 mol L^{-1} (equivalent to the corresponding salinity of 0.56–11.1%). The salinity of brackish water systems was in range of 0.5−30% (Bakir et al., 2014; Xie et al., 1997). Therefore, the adsorption capacity of TBBPA on PE, PP and PS microplastics could be enhanced in brackish water, such as estuaries, inland salt lakes, and marine waters.

The sorption of organic pollutants (e.g., diethyl phthalate, dibutyl phthalate, and perfluorooctane sulphonate) on MPs (e.g., PVC, PE and PS) increased with increasing ion concentrations (NaCl and $CaCl_2$), as a result from the salting-out effect (Liu et al., 2019; Wang et al., 2015; Zhang et al., 2010). The salting-out effect of NaCl and $CaCl_2$ is of key in enhancing the sorption affinity of hydrophobic compounds by decreasing their solubility (Xie et al., 1997). Studies by Ni and Yalkowsky's showed that the solubility of phenanthrene, 2-phenylphenol, ketoprofen, carbamazepine and bisphenol A (BPA) reduced by 5–6% with NaCl concentration increased from 0 to 100 mmol L^{-1} (Ni and Yalkowsky, 2003). Based on the structural similarity between BPA and TBBPA, the solubility of TBBPA would decrease with the increase in

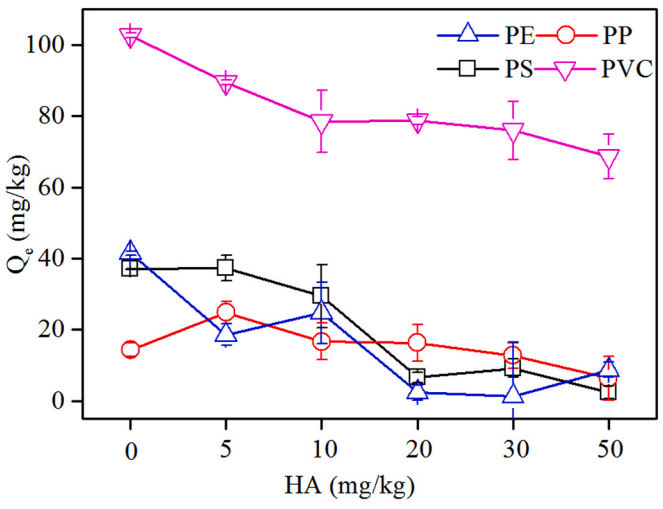

Fig. 4. Effect of the HA concentrations on the sorption.

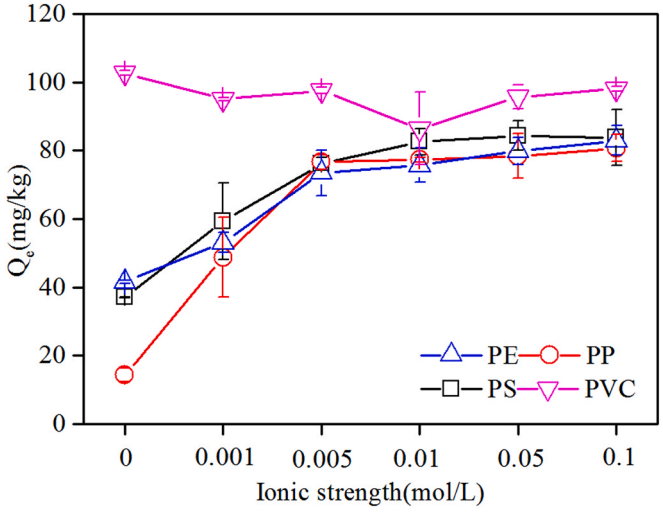

Fig. 5. Effect of the ionic strength ($CaCl_2$) on the sorption.

$CaCl_2$ concentration, thus subsequently facilitate the hydrophobic interaction with the MPs. However, as ionic strength increased to a certain degree, the sorption sites might be competitively occupied by the relatively abundant free Ca^{2+} due to electrostatic attraction, leading to a reduction of the sorption of TBBPA on the MPs. By contrast, the sorption capacities of TBBPA on PVC were barely affected and maintained a high sorption state. Similar phenomenon in PVC adsorption of synthetic musks and phenanthrene was also observed by Bakir et al. (2014), which implied an insignificant impact on sorption exerted by salting-out effect with the adsorbent of large sorption capacity. One possible mechanism was that ionic strength could influence the aggregation of plastic particles. Previous study with polystyrene nanoplastics found that the increase of NaCl concentration promotes the particle aggregation by compressing the electrical double layer, thus decreasing the repulsive forces between the particles (Wu et al., 2019a, 2019b). Similar behavior was observed by Li et al. (2018) for polystyrene microplastics, where the presence of $CaCl_2$ and $BaCl_2$ (divalent electrolytes) accelerated the aggregation. As a result, the adsorption sites on the surface of PVC microplastics might reduce as the particles become more compact. Moreover, the higher the electrolyte concentration, the more and the faster that surface charge could be neutralized.The results of PVC exhibited that adsorption enhancement of TBBPA due to the salting-out effect might be compensated by the fewer adsorption sites owing to particle aggregation. Therefore, the influence of ionic strength for the adsorption behavior may vary depending on the type of sorbent, sorbate, and the electrolyte.

4. Conclusions

The present study discussed the interaction between a widely used flame retardant TBBPA and four widely applied types of MPs including PP, PVC, PE, PS. Adsorption kinetics data fitted by intraparticle diffusion model revealed both surface sorption and intraparticle diffusion contributed to the actual sorption process of TBBPA on MPs. PVC had the largest adsorption capacity (101.85 mg kg^{-1}), followed by PS, PP and PE, and that changes in the ionic strength and content of humic acid considerably influenced the adsorption of TBBPA by MPs. Under the experimental conditions of ionic strength, the adsorption capacity of TBBPA on PE, PP and PS microplastics could be enhanced to a certain extent, while that of PVC was barely affected, indicating the influence of ionic strength for the adsorption behavior may vary depending on the type of sorbent, sorbate, and the electrolyte.The findings from the present work indicate that the adsorption of TBBPA on four microplastics was mainly driven by both hydrophobic and electrostatic interactions related to the polymeric properties of MPs (functional group, surface area and charge), and matrix effects (salinity and dissolved organic matter).

CRediT authorship contribution statement

Shengsheng Li: Methodology, Writing - original draft preparation. **Ruixue Ma:** Data curation, Writing - original draft preparation, Writing - review & editing. **Xiaohui Zhu:** Methodology, Investigation. **Chang Liu:** Formal analysis, Software. **Liangzhong Li:** Conceptualization, Project administration. **Ziling Yu:** Data Curation, Validation. **Xichao Chen:** Resources, Data Curation. **Zongrui Li:** Writing - review & editing. **Yan Yang:** Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This research was supported by the National Natural Science Foundation of China (42007390, 22006102, 41931298), the Natural Science Foundation of Guangdong Province (2018A030313945), Guangdong Basic and Applied Basic Research Foundation (2020A1515010532).

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.ecoenv.2020.111842.

References

Ai, L., Zhang, C., Chen, Z., 2011. Removal of methylene blue from aqueous solution by a solvothermal-synthesized graphene/magnetite composite. J. Hazard. Mater. 192, 1515–1524.
Alexander, J., Boobis, A., Domenico, Ad, Mutti, A., 2011. Scientific opinion on tetrabromobisphenol A (TBBPA) and its derivatives in food: TBBPA and its derivatives in food. EFSA J. 9 (12), 2477.
Allen, S.J., McKay, G., Khader, K.Y.H., 1989. Intraparticle diffusion of a basic dye during adsorption onto sphagnum peat. Environ. Pollut. 56, 39–50.
Bakir, A., Rowland, S.J., Thompson, R.C., 2014. Transport of persistent organic pollutants by microplastics in estuarine conditions. Estuar. Coast. Shelf Sci. 140, 14–21.
Bergmann, M., Wirzberger, V., Krumpen, T., Lorenz, C., Primpke, S., Tekman, M.B., Gerdts, G., 2017. High quantities of microplastic in arctic deep-sea sediments from the HAUSGARTEN observatory. Environ. Sci. Technol. 51, 11000–11010.
Chen, W., Ouyang, Z., Qian, C., Yu, H., 2018. Induced structural changes of humic acid by exposure of polystyrene microplastics: a spectroscopic insight. Environ. Pollut. 233, 0269–7491.
Chen, S., Tan, Z., Qi, Y., Ouyang, C., 2019. Sorption of tri-n-butyl phosphate and tris(2-chloroethyl) phosphate on polyethylene and polyvinyl chloride microplastics in seawater. Mar. Pollut. Bull. 149, 110490.
Cope, R.B., Kacew, S., Dourson, M., 2015. A reproductive, developmental and neurobehavioral study following oral exposure of tetrabromobisphenol A on Sprague-Dawley rats. Toxicology 329, 49–59.
Covaci, A., Harrad, S., Abdallah, M.A., Ali, N., Law, R.J., Herzke, D., de Wit, C.A., 2011. Novel brominated flame retardants: a review of their analysis, environmental fate and behaviour. Environ. Int. 37, 532–556.
Dam, G., Pardo, O., Traag, W., Lee, M., Peters, R., 2012. Simultaneous extraction and determination of HBCD isomers and TBBPA by ASE and LC–MSMS in fish. J. Chromatogr. B 898, 101–110.
Di, M.X., Wang, J., 2018. Microplastics in surface waters and sediments of the three gorges reservoir, China. Sci. Total Environ. 616–617, 1620–1627.
Eriksen, M., Lebreton, L.C., Carson, H.S., Thiel, M., Moore, C.J., Borerro, J.C., Galgani, F., Ryan, P.G., Reisser, J., 2014. Plastic pollution in the world's oceans: more than 5 trillion plastic pieces weighing over 250,000 tons afloat at sea. PLoS One 9, e111913.
Feng, A., Chen, S., Chen, M., He, M., Luo, X., Mai, B., 2012. Hexabromocyclododecane (HBCD) and tetrabromobisphenol A (TBBPA) in riverine and estuarine sediments of the pearl river delta in southern China, with emphasis on spatial variability in diastereoisomer-and enantiomer-specific distribution of HBCD. Mar. Pollut. Bull. 64, 919–925.
Fijalkowski, K., Rorat, A., Grobelak, A., Kacprzak, M.J., 2017. The presence of contaminations in sewage sludge–the current situation. J. Environ. Manag. 203, 1126–1136.
Ghosal, S., Chen, M., Wagner, J., Wang, Z.M., Wall, S., 2018. Molecular identification of polymers and anthropogenic particles extracted from oceanic water and fish stomach - a Raman micro-spectroscopy study. Environ. Pollut. 233, 1113–1124.
Gong, W., Zhu, L., Jiang, T., Han, C., 2017. The occurrence and spatial-temporal distribution of tetrabromobisphenol A in the coastal intertidal zone of Qingdao in China, with a focus on toxicity assessment by biological monitoring. Chemosphere 185, 462–467.
Guo, X., Chen, C., Wang, J.L., 2019. Sorption of sulfamethoxazole onto six types of microplastics. Chemosphere 228, 300–308.
Guo, X., Pang, J., Chen, S., Jia, H., 2018. Sorption properties of tylosin on four different microplastics. Chemosphere 209, 240–245.
Guo, X., Wang, X., Zhou, X., Kong, X., Tao, S., Xing, B., 2012. Sorption of four hydrophobic organic compounds by three chemically distinct polymers: role of chemical and physical composition. Environ. Sci. Technol. 46 (13), 7252–7259.
Guo, X., Yang, C., Dang, Z., Zhang, Q., Li, Y., Meng, Q., 2013. Sorption thermodynamics and kinetics properties of tylosin and sulfamethazine on goethite. Chem. Eng. J. 223, 59–67.
He, M.J., Luo, X.J., Yu, L.H., Liu, J., Zhang, X.L., Chen, S.J., Chen, D., Mai, B.X., 2010. Tetrabromobisphenol-A and hexabromocyclododecane in birds from an e-waste region in South China: influence of diet on diastereoisomer- and enantiomer-specific distribution and trophodynamics. Environ. Sci. Technol. 44, 5748–5754.
Hu, J., Yang, S., Guo, L., Xu, X., Yao, T., Xie, F., 2017. Microscopic investigation on the adsorption of lubrication oil on microplastics. J. Mol. Liq. 227, 351–355.
IARC, 2018. Some Industrial Chemicals IARC Monographs on the Evaluation of Carcinogenic Risks to Humans, 115. IARC Publications.

Kanhai, L., Gardfeldt, K., Lyashevska, O., Hassellov, M., Thompson, R.C., O'Connor, I., 2018. Microplastics in sub-surface waters of the arctic central basin. Mar. Pollut. Bull. 130, 8–18.
Kwon, J.H., Chang, S., Hong, S.H., Shim, W.J., 2017. Microplastics as a vector of hydrophobic contaminants: importance of hydrophobic additives. Integr. Environ. Assess. Manag. 13, 494–499.
Lai, D.Y., Kacew, S., Dekant, W., 2015. Tetrabromobisphenol A (TBBPA): possible modes of action of toxicity and carcinogenicity in rodents. Food Chem. Toxicol. 80, 206–214.
Lee, H., Shim, W.J., Kwon, J.-H., 2014. Sorption capacity of plastic debris for hydrophobic organic chemicals. Sci. Total Environ. 470–471, 1545–1552.
Lei, K., Qiao, F., Liu, Q., Wei, Z., Qi, H., Cui, S., Yue, X., Deng, Y., An, L., 2017. Microplastics releasing from personal care and cosmetic products in China. Mar. Pollut. Bull. 123, 122–126.
Lin, W., Jiang, R., Wu, J., Wei, S., Yin, L., Xiao, X., Hu, S., Shen, Y., Ouyang, G., 2019. Sorption properties of hydrophobic organic chemicals to micro-sized polystyrene particles. Sci. Total Environ. 690, 565–572.
Liu, F., Liu, G., Zhu, Z., Wang, S., Zhao, F., 2019. Interactions between microplastics and phthalate esters as affected by microplastics characteristics and solution chemistry. Chemosphere 214, 688–694.
Liu, K., Li, J., Yan, S., Zhang, W., Li, Y., Han, D., 2016. A review of status of tetrabromobisphenol A (TBBPA) in China. Chemosphere 148, 8–20.
Liu, X., Zheng, M., Wang, L., Ke, R., Lou, Y., Zhang, X., Dong, X., Zhang, Y., 2018. Sorption behaviors of tris-(2,3-dibromopropyl) isocyanurate and hexabromocyclododecanes on polypropylene microplastics. Mar. Pollut. Bull. 135, 581–586.
Li, S., Liu, H., Gao, R., Abdurahman, A., Dai, J., Zeng, F., 2018b. Aggregation kinetics of microplastics in aquatic environment: complex roles of electrolytes, pH and natural organic matter. Environ. Pollut. 237, 126–132.
Li, J., Zhang, K., Zhang, H., 2018a. Adsorption of antibiotics on microplastics. Environ. Pollut. 237, 460–467.
Mohan, D., Singh, K.P., Singh, V.K., 2006. Trivalent chromium removal from wastewater using low cost activated carbon derived from agricultural waste material and activated carbon fabric cloth. J. Hazard. Mater. 135 (1–3), 280–295.
Ni, N., Yalkowsky, S.H., 2003. Prediction of Setschenow constants. Int. J. Pharm. 254, 167–172.
NTP, 2014. Technical Report on the Toxicology Studies of Tetrabromobisphenol A (CASNO. 79–94-7) in F344/NTac Rats and B6C3F1/N Mice and Toxicology and Carcinogenesis Study of Tetrabromobisphenol A in Wistar Han [Crl: WI (Han)] Rats and B6C3F1/N Mice (Gavage Studies) National Toxicology Program. P.O. Box 12233, Research Triangle Park, NC 27709.
Rochman, C.M., Tahir, A., Williams, S.L., Baxa, D.V., Lam, R., Miller, J.T., Teh, F.-C., Werorilangi, S., Teh, S.J., 2015. Anthropogenic debris in seafood: Plastic debris and fibers from textiles in fish and bivalves sold for human consumption. Sci. Rep. 5, 14340.
Rose, D., Webber, M., 2019. Characterization of microplastics in the surface waters of Kingston harbour. Sci. Total. Environ. 664, 753–760.
Sebille, E., Wilcox, C., Lebreton, L., Maximenko, N., Hardesty, B., Franeker, J., Eriksen, M., Siegel, D., Galgani, F., Law, K., 2015. A global inventory of small floating plastic debris. Environ. Res. Lett. 10, 124006.
Seidensticker, S., Zarfl, C., Cirpka, O., Fellenberg, G., Grathwohl, P., 2017. Shift in mass transfer of wastewater contaminants from microplastics in presence of dissolved substances. Environ. Sci. Technol. 51, 12254–12263.
Sun, B., Hu, Y., Cheng, H., Tao, S., 2019. Releases of brominated flame retardants (BFRs) from microplastics in aqueous medium: kinetics and molecular-size dependence of diffusion. Water Res. 151, 215–225.
Velzeboer, I., Kwadijk, C., Koelmans, A., 2014. Strong sorption of PCBs to nanoplastics, microplastics, carbon nanotubes and fullerenes. Environ. Sci. Technol. 48, 4869–4876.
Wang, Z., Chen, M., Zhang, L., Wang, K., Yu, X., Zheng, Z., Zheng, R., 2018b. Sorption behaviors of phenanthrene on the microplastics identified in a mariculture farm in Xiangshan bay, southeastern China. Sci. Total Environ. 628–629, 1617–1626.
Wang, F., Shih, K., Li, X., 2015. The partition behavior of perfluorooctanesulfonate (PFOS) and perfluorooctanesulfonamide (FOSA) on microplastics. Chemosphere 119, 841–847.
Wang, W., Wang, J., 2018. Different partition of polycyclic aromatic hydrocarbon on environmental particulates in freshwater: microplastics in comparison to natural sediment. Ecotoxicol. Environ. Saf. 147, 648–655.
Wang, F., Wong, C., Chen, D., Lu, X., Wang, F., Zeng, E., 2018a. Interaction of toxic chemicals with microplastics: a critical review. Water Res. 139, 208–219.
Wu, P., Cai, Z., Jin, H., Tang, Y., 2019b. Adsorption mechanisms of five bisphenol analogues on PVC microplastics. Sci. Total Environ. 650, 671–678.
Wu, J., Jiang, R., Lin, W., Ouyang, G., 2019a. Effect of salinity and humic acid on the aggregation and toxicity of polystyrene nanoplastics with different functional groups and charges. Environ. Pollut. 245, 836–843.
Xie, W., Shiu, W., Mackay, D., 1997. A review of the effect of salts on the solubility of organic compounds in seawater. Mar. Environ. Res. 44, 429–444.
Xu, P., Ge, W., Chai, C., Zhang, Y., Jiang, T., Xia, B., 2019. Sorption of polybrominated diphenyl ethers by microplastics. Mar. Pollut. Bull. 145, 260–269.
Yang, S., Wang, S., Liu, H., Yan, Z., 2012. Tetrabromobisphenol A: tissue distribution in fish, and seasonal variation in water and sediment of Lake Chaohu, China. Environ. Sci. Pollut. Res. Int. 19, 4090–4096.
Yu, Y., Ma, R., Qu, H., Qu, H., Zuo, Y., Yu, Z., Hu, G., Li, Z., Chen, H., Lin, B., Wang, B., Yu, G., 2020. Enhanced adsorption of tetrabromobisphenol a (TBBPA) on cosmetic-derived plastic microbeads and combined effects on zebrafish. Chemosphere 248, 126067.
Yu, Y., Xiang, M., Gao, D., Ye, H., Wang, Q., Zhang, Y., Li, L., Li, H., 2018. Assimilation, distribution and toxicity of tetrabromobisphenol A to female Wistar rats through subchronic dermal exposure. Int. Biodeterior. Biodegad. 128, 171–176.
Yu, Y., Yu, Z., Chen, H., Han, Y., Xiang, M., Chen, X., Ma, R., Wang, Z., 2019. Tetrabromobisphenol A: disposition, kinetics and toxicity in animals and humans. Environ. Pollut. 253, 909–917.
Zhang, S., Shao, T., Bekaroglu, S.S., Karanfil, T., 2010. Adsorption of synthetic organic chemicals by carbon nanotubes: effects of background solution chemistry. Water Res. 44, 2067–2074.
Zhang, K., Su, J., Xiong, X., Wu, X., Wu, C., Liu, J., 2016. Microplastic pollution of lakeshore sediments from remote lakes in Tibet plateau, China. Environ. Pollut. 219, 450–455.
Zhang, Q., Xu, E.G., Li, J., Chen, Q., Ma, L., Zeng, E.Y., Shi, H., 2020. A review of microplastics in table salt, drinking water, and air: direct human exposure. Environ. Sci. Technol. 54, 3740–3751. https://doi.org/10.1021/acs.est.9b04535.
Zhang, H., Zhou, Q., Xie, Z., Zhou, Y., Tu, C., Fu, C., Mi, W., Ebinghaus, R., Christie, P., Luo, Y., 2018. Occurrences of organophosphorus esters and phthalates in the microplastics from the coastal beaches in north China. Sci. Total Environ. 616–617, 1505–1512.
Zhan, Z., Wang, J., Peng, J., Xie, Q., Huang, Y., Gao, Y., 2016. Sorption of 3,3',4,4'-tetrachlorobiphenyl by microplastics: a case study of polypropylene. Mar. Pollut. Bull. 110, 559–563.
Zhou, D., Chen, B., Wu, M., Liang, N., Zhang, D., Li, H., Pan, B., 2014a. Ofloxacin sorption in soils after long-term tillage: the contribution of organic and mineral compositions. Sci. Total Environ. 497–498, 665–670.
Zhou, X., Wei, J., Liu, K., Liu, N., Zhou, B., 2014b. Adsorption of bisphenol A based on synergy between hydrogen bonding and hydrophobic interaction. Langmuir 30, 13861–13868.
Zhou, Y., Yang, Y., Liu, G., He, G., Liu, W., 2020. Adsorption mechanism of cadmium on microplastics and their desorption behavior in sediment and gut environments: the roles of water pH, lead ions, natural organic matter and phenanthrene. Water Res. 184, 116209.