



Hydrophobic sorption behaviors of 17 β -Estradiol on environmental microplastics

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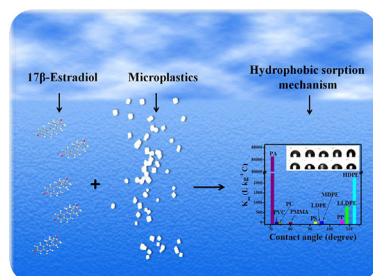
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HIGHLIGHTS

- The sorption ability of E2 on MPs followed the order of PA > HD/LLD-PE > PP > LD/MD-PE > PS > PC > PMMA > PVC.
- Hydrophobic partition of E2 on MPs was dominant sorption mechanism.
- The E2 sorption capacity on MPs was positively correlated with the crystallinity of MPs.
- The flexible rubbery state of amorphous domain of MPs is more favorable for E2 sorption.

GRAPHICAL ABSTRACT



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ABSTRACT

Microplastics (MPs) have been regarded as a vector for contaminants and greatly affect the migration and fate of hydrophobic organic compounds (HOCs) in marine water. In this study, the sorption behavior of 17 β -estradiol (E2) on MPs was investigated in marine water system. The sorption capacity of E2 varied greatly with the chemical structures of MPs. The adsorption or partition contribution of E2 sorption on MPs was well quantified with adsorption-partition dual-mode model mechanism. The hydrophobic partition dominantly regulates the sorption of E2 due to the high crystallinity of MPs and high accessibility of amorphous domain of rubbery MPs. Smaller particle size benefits the sorption of E2 on same kind of MPs. The salinity and dissolved organic matter (DOM) have minor effect on E2 sorption by MPs in real marine water. The result shows that the MPs greatly influence the transportation of E2 and cause potential environmental risk to marine ecosystem.

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1. Introduction

Plastic debris has been regarded as a global environmental threat because of their ubiquity and persistence. Of recent concern is microplastics (MPs, < 5 mm) which are exist in personal care product as exfoliants (plastic beads) or derived from the degradation of large plastic pieces. Accidental and deliberate

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environmental release has resulted in the accumulation of MPs in almost all marine habitats from beaches to the open oceans and deep-sea sediments (Bergmann et al., 2017; Feng et al., 2018; Lusher et al., 2015; Yonkos et al., 2014; Zhao et al., 2015). The ubiquity and persistence of MPs have raised concerns over indirect detrimental effects on marine organisms. Owing to their tiny particle size, strong hydrophobicity, high stability and mobility, MPs show strong sorption and enrichment tendency towards hydrophobic organic compounds (HOCs) (Alimi et al., 2018). The HOCs monitored on the MPs samples on beaches or in seawater can reach up to the level of ng g^{-1} to $\mu\text{g g}^{-1}$ with enrichment factors up to several orders of magnitude (Hirai et al., 2011; Mato et al., 2001; Rochman et al., 2013a, 2013c). Meanwhile, the hazardous additives (e.g., nonylphenol, phthalate, bisphenol A, etc.) (Lithner et al., 2011; Mato et al., 2001; Rochman et al., 2013b) and monomers can be released from MPs into the environment (Browne et al., 2008; Li et al., 2016; Tanaka and Takada, 2016; Ziajahromi et al., 2017). Hence, ingestion of MPs can result in uptake and bioaccumulation of HOCs and additives in marine organisms (Teuten et al., 2009; Thompson et al., 2009) ultimately causing more serious environmental risks (Desforjes et al., 2014; Engler, 2012). Therefore, a comprehensive understanding of the interactions between HOCs and MPs is of great importance for elucidating the fate and transport of HOCs with MPs.

Many possible reasons related with the sorption mechanisms were proposed to explain the various interactions between plastics and HOCs. Zhan et al. proposed a chemical sorption mechanism between polypropylene (PP) and PCB77 in their previous study (Zhan et al., 2016). However, as nonpolar plastics with no specific functional groups, it seems difficult for PP to enrich PCB77 through chemical interactions. Therefore, more reasonable sorption mechanisms related with the physicochemical properties of MPs should be explored. Zhan et al. suggested that the smaller PP particles would sorb more PCB77 than the bigger ones owing to their larger surface area (Andrady, 2017; Wang and Wang, 2018; Zhan et al., 2016). However, Huffer et al. observed that the sorption order of nonpolar organic compounds (e.g., *n*-hexane, cyclohexane, benzene, etc.) on polyethylene (PE) and polystyrene (PS) was not related to the particle size (Huffer and Hofmann, 2016). It can be concluded that factors other than particle size and surface area should also be taken into account in explaining the differences in sorption capacity among MPs. Crystallinity of sorption domains was reported to influence the partitioning of HOCs to MPs in a previous study of Guo et al. in which they compared the sorption of phenanthrene, naphthalene and lindane by seven types of PEs, and suggested that the alignment of MPs crystalline domains might affect the availability of amorphous sorption domains for HOCs accessibility (Guo et al., 2012). Similar results also confirmed the importance of the amorphous domain of MPs on the sorption (Endo et al., 2011b; Saquing et al., 2010). However, the result of Wang et al. showed that high crystalline PE possessed higher sorption capacity for perfluorooctanesulfonamide (FOSA) than the low crystalline polyvinylchloride (PVC), indicating that aggregation state of amorphous domains could also be used to interpret the sorption behavior of HOCs (Wang et al., 2015). All the aforementioned inconsistent findings indicate that additional work is required to further elucidate the mechanisms on how the physicochemical properties of MPs affect the sorption of HOCs.

The existence of endocrine disrupting chemicals (EDCs) in aqueous environments is becoming a serious environmental and health problem, because they were proved to have potential link with diseases involving the reproductive, immune and neurological systems (Kabir et al., 2015). 17 β -Estradiol (E2), one of the most potent EDCs, was reported to cause great harm at very low concentration ($\sim 1 \text{ ng L}^{-1}$) (Fan et al., 2013; Hansen et al., 1998; Pan

et al., 2009; Zhang and Zhou, 2005) and was frequently detected in aqueous system (Nie et al., 2015; Pojana et al., 2007). Moreover, E2 and MPs have been detected in the Chinese Yangtze Estuary (Nie et al., 2015; Peng et al., 2017), indicating that E2 have potential to interact with MPs in the environment. E2 was chosen as the model pollutant in the present study. Beside, existing data on the sorption of organic contaminants to plastic pellets are limited to 3–5 most commonly produced plastics (i.e. low-density polyethylene (LDPE), high-density polyethylene (HDPE), PP, PVC and PS) (Karapanagioti and Klontza, 2008; PlasticsEurope, 2016; Teuten et al., 2007), more types of MPs should be taken into account. From above point of view, the sorption experiments of E2 on ten types of MPs were conducted in this work to (a) figure out whether MPs can be vectors of E2; (b) investigate the sorption mechanism of E2 on MPs by innovating apply the dual-mode model; and (c) clarify how the physicochemical structural properties of MPs affect the sorption ability of E2 on different MPs.

2. Material and methods

2.1. Materials

The analytical virgin MPs (i.e., LDPE, linear low-density polyethylene (LLDPE), HDPE, PP, PS, polycarbonate (PC), PVC, polyamide (PA) and polymethyl methacrylate (PMMA)) were purchased from Youngling Electromechanical Technology Ltd. (Shanghai, China). Medium-density polyethylene (MDPE) was obtained from Alfa Aesar (Shanghai, China). 17 β -Estradiol (E2, molecular formula $\text{C}_{18}\text{H}_{24}\text{O}_2$, molecular weight 272.4, Log K_{ow} of 4.0, pKa of 10.6, and water solubility of 3.9–13.3 mg L^{-1} , at >99% purity) was purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). Stock solution of E2 (500 mg L^{-1}) was prepared in methanol (high performance liquid chromatography grade, Aladdin Industrial Corp., Shanghai, China) and kept in the dark at 4 °C. Ultrapure water (18.2 M Ω cm, Merck Millipore, Germany) was used throughout experiments.

2.2. Characterization of MPs

The shape of MPs was fragment-type except PMMA was microsphere. The microscopic images of morphology and particle size distribution of MPs were obtained by a Motic stereo microscope (MOTIC group Co. LTD., China). The X-ray diffraction (XRD) patterns of MPs were obtained using an Ultima IV X-ray diffractometer (XRD, D/Max-2500, Rigaku, Japan) employing a Cu $K\alpha$ source ($\lambda = 1.5406 \text{ \AA}$) at 40 kV and 100 mA in the 2θ range from 5° to 80° with a scan rate of 10° min^{-1} . The surface area and pore size distribution were measured by nitrogen adsorption with an ASAP2020 specific surface area analyzer (Micromeritics Instrument Corp., USA) using the Brunauer-Emmett-Teller (BET) method and the Barrett-Joyner-Halenda (BJH) technique, respectively. Differential scanning calorimetric analysis (DSC 204 F1, Netzsch, Germany) was used to determine the crystallinity (X_c) of MPs with a heating rate of 10 °C min^{-1} and N_2 as a purge gas. The crystallinity of material was calculated as follows: $X_c = \Delta H_m / \Delta H_m^0 \times 100\%$, where ΔH_m and ΔH_m^0 represent the fusion enthalpy of MPs measured versus that of purely crystalline polymers, respectively. The wetting behaviors of the MPs were obtained by measuring static water contact angles using the sessile water drop method on a DSA30 contact angle measuring device (Kruss, Germany) under ambient condition.

2.3. Sorption experiments

Sorption kinetics was carried out using 0.5 g of MPs and 20 mL E2 solution of 100 $\mu\text{g L}^{-1}$ in glass conical flask. Samples were

shaken at 160 rpm at 25 ± 1 °C on an air bath thermostatic oscillator. 0.5 mL of samples was taken out and centrifuged after 10, 30 min, 1, 3, 7, 12, 34, 72, 96 and 120 h. The E2 concentration was analyzed with Waters Acquity™ ultrahigh performance liquid chromatography-tandem mass spectrometer (UHPLC-MS/MS) system with an HSS T3 (2.1 mm × 100 mm, 1.7 μm particle sizes) column. Kinetic experiments suggested that the sorption reached equilibrium within 72 h, and therefore this experimental duration was used for further sorption experiments. Sorption isotherms were performed using 0.5 g MP in 20 mL E2 solution with concentration ranged from 500 ng L⁻¹ to 500 μg L⁻¹. Other procedures were the same as that of kinetics studies. The effects of particle size and water matrices on E2 sorption by MPs were also investigated according to sorption isotherm experiments. Owing to different size distribution of purchased MPs, five kinds of MPs were selected and sifted to study the particle size effects, namely LLDPE, MDPE, PP, PMMA (with particle size <150 μm, between 150 and 250 μm, and >250 μm) and PVC (with particle size <75 μm and between 75 and 150 μm). Three kinds of E2 matrices, namely MilliQ water, simulated seawater and real sea water were used to study the water matrix effects. The simulated seawater consisted of 24.7 g L⁻¹ NaCl, 3.0 g L⁻¹ MgCl₂·6H₂O and 3.97 g L⁻¹ Na₂SO₄·10H₂O (Zhao et al., 2011). Real seawater was sampled from Shengsi Islands which are part of the Zhoushan Archipelago at east Hangzhou Bay in China. The seawater was immediately filtered with 0.45 μm membrane to remove suspended particulate matters. All the experiments were conducted in triplicate.

2.4. Data analysis

The equilibrium sorption capacity of E2 on MPs was calculated as:

$$Q_e = (C_0 - C_e) \times V/m \quad (1)$$

where Q_e (μg g⁻¹) is the equilibrium sorption capacity of E2; C_0 and C_e (μg L⁻¹) are initial and equilibrium E2 concentrations, respectively; V (L) is the volume of the E2 solution, and m (g) is the mass of MPs.

The distribution coefficient (K_d) of E2 on MPs was calculated using equilibrium concentrations on the MPs and in water, respectively:

$$K_d = Q_e/C_e \quad (2)$$

Organic-carbon normalized sorption coefficient (K_{oc}) can be expressed as:

$$K_{oc} = K_d/f_{oc} \quad (3)$$

where f_{oc} is the organic carbon fraction of MPs.

The Freundlich model showing in Equation (4) describes sorption taking place on the heterogeneous surface (Foo and Hameed, 2010) of monolayer or multilayer sorption (Yang, 1998).

$$Q_e = K_f C_e^{nf} \quad (4)$$

where K_f is the Freundlich adsorption coefficient. nf is the nonlinearity factor and a measure of the sorption intensity or surface heterogeneity.

2.4.1. Dual-mode model

Sorption isotherms can be fitted with Freundlich isotherm model, so the total sorption amount Q_T can be approximately described as:

$$Q_T = aC_e^n \quad (5)$$

where a and n are constants, and C_e (μg L⁻¹) is sorption equilibrium concentration of E2.

In this dual-mode model interaction mechanism, the total sorption amount Q_T is the sum of adsorption capacity Q_A and partition capacity Q_P , it can also be represent as:

$$Q_T = Q_A + Q_P \quad (6)$$

The contribution of adsorption can reach saturation rapidly and the contribution of partition can linearly increase with increasing of E2 concentration. Thus, the isotherms of E2 on MPs at high concentration should be linearity and the total sorption amount Q_T' can be described as:

$$Q_T' = MC_e + N \quad (\text{only can be used at high E2 concentration}) \quad (7)$$

where M and N are constants. The constant N represents the saturated adsorption capacity of E2 on MPs, and MC_e is the sorption contribution through partition (Q_P). Considering the contribution of partition was linear over the entire concentration range, the adsorption capacity (Q_A) can be calculated as:

$$Q_A = Q_T - Q_P = aC_e^n - MC_e \quad (8)$$

Therefore, the contribution of adsorption and partition to the total sorption capacity can be obtained from this dual-mode model.

2.5. Statistical analysis

SPSS 23 software (SPSS Inc., USA) was applied to compare differences of sorption coefficients of E2 on MPs. A correlation was considered significant at $p < 0.05$.

3. Results and discussion

3.1. Sorption mechanism of MPs as sorbents for E2

The physicochemical properties of MPs selected in this work were characterized as shown in Table 1. The sorption isotherms of E2 on MPs can be seen in Fig. 1. The sorption capacity of E2 varied with the type of MPs following the order of PA > HDPE ≈ LLDPE > PP > LDPE ≈ MDPE > PS > PC > PMMA > PVC. The enrichment factor of E2 on MPs could reach up to 10¹-10⁴. And it was comparable with a previous report of Mato et al., in which the enrichment factor of PCBs and DDE on plastic pellets could reach up to 10⁵-10⁶ (Mato et al., 2001). Sorption capacity of E2 was intimately associated with the structure makeup of MPs. The plastic can be regarded as three-dimensional macromolecular entanglement in which HOCs can penetrate and intermingle with the strands of MPs. Generally, the plastic's structure can be understood through two structural levels: 1) macromolecular chain structure; and 2) aggregation structure formed through macromolecular chains' arrangement and stacking. The chain structure mainly describes the chemical composition and conformation of a polymer chain, while aggregation structure mainly refers to crystalline and amorphous structures. The plastic's structure can contribute to various E2 sorption capacities on different types of MPs (Rochman et al., 2013a). Moreover, even for MPs with the same chemical composition or primary structure (i.e., the four kinds of PEs), obviously different sorption capacity of E2 was found in this study. Even though the PEs in this study share the same chain structure, under the conditions of different processing molding, the produced

Table 1
The physicochemical properties of selected MPs.

Type	Molecular formula	Density (g cm ⁻³)	Particle size (μm)	Mean particle size (μm)	Surface area (m ² g ⁻¹)	Pore volume (10 ⁻³ cm ³ g ⁻¹)	Melting Point T _m (°C)	Glassy temperature (°C)	f _{oc} (%)	Contact Angle (°)	Crystallinity (%)	Structural formula
LDPE	(C ₂ H ₄) _n	0.92	2–20	9.5	0.843	0.727	102	-125.0	85.7	95.6 ± 3.2	35.0	
LLDPE		0.94	450–600	510.9	0.428	1.295	125	(Carraher, 2011)		104.8 ± 2.5	44.9	
MDPE		0.93	20–250	150.0	0.257	0.143	113			96.0 ± 3.4	52.6	
HDPE		0.955	20–120	54.4	0.415	0.393	135			108.8 ± 3.8	61.5	
PP	(C ₃ H ₆) _n	0.91	20–250	144.4	0.964	0.498	170	-10.0 (Carraher, 2011)	85.7	106.3 ± 2.3	38.4	
PS	(C ₈ H ₈) _n	1.05	10–130	59.0	0.343	0.695	103	97.2	92.3	95.7 ± 1.4	3.7	
PC	(C ₁₆ H ₁₄ O ₃) _n	1.20	10–40	21.4	0.319	0.548	241	148.9	75.6	74.4 ± 2.0	16.2	
VC	(C ₂ H ₃ Cl) _n	1.40	50–120	80.0	1.030	1.237	92	86.3	38.4	73.0 ± 4.5	1.5	
PA	(C ₆ H ₁₁ NO) _n	1.04–1.14	10–60	29.7	0.544	0.460	103	55.0	63.7	70.9 ± 6.6	36.6	
PMMA	(C ₅ H ₈ O ₂) _n	1.18	250–500	350.0	0.164	0.514	101	96.7	59.9	80.1 ± 1.9	6.1	

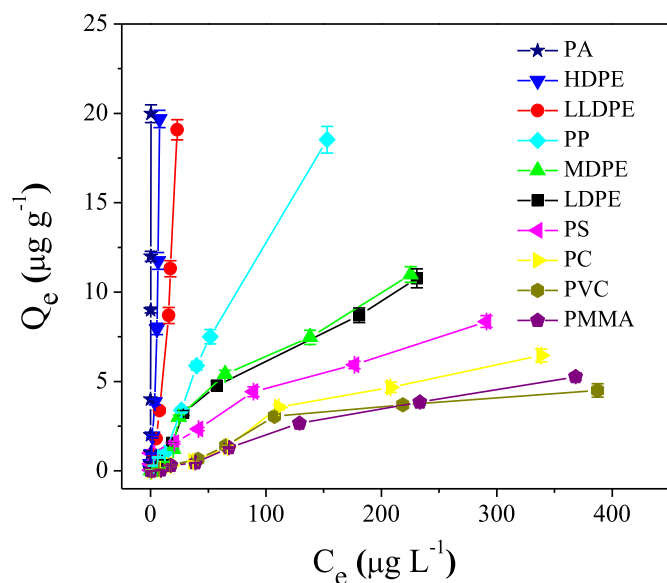


Fig. 1. The sorption isotherms of E2 on MPs.

plastics can show different aggregation structures with distinct sorption properties. Thus, compared with chain structure, the aggregation structure of polymers has a more important and direct influence on sorption performance though the influence of chain structure still cannot be neglected (Guo et al., 2012).

Based on the dual-mode model of polymer sorption theory, the sorption includes concurrent solid-phase dissolution and pore-filling mechanisms. The sorption of HOCs in rubbery polymers was recognized as undergoing solid-phase dissolution mechanism abiding by partition model. Pore-filling mechanism undergoes adsorption-like interaction between HOCs and polymers and usually occurs in glassy polymers. The total sorption is the sum of sorption in solid-phase dissolution phases and pore-filling phases, i.e. partition and adsorption interactions (Zhu and Chen, 2000; Zhu

et al., 2000). Generally speaking, the adsorption of HOCs on polymers is nonlinear which is dependent on the surface area of the sorbent and has a saturated sorption capacity; however, the partition process is linear and governed by the organic matter content of the sorbent (Zhu and Chen, 2000; Zhu et al., 2000). Compared with adsorption, the partition has lower enthalpy with linearized and noncompetitive property and a completely different mechanism. Previous studies have illustrated that the sorption isotherms of HOCs on rubbery PEs were highly linear compared to those for glassy plastics whose isotherms were generally nonlinear (Guo et al., 2012; Wu et al., 2016). It indicates that the predominant sorption mode of HOCs on rubbery PE and PP is governed by partitioning into the bulk (Guo et al., 2012; Velzeboer et al., 2014) rather than by adsorption onto the surfaces of the plastics. As Fig. 1 shows, sorption isotherms for E2 sorption on LLDPE and HDPE were highly linear, suggesting a complete partitioning mechanism. However, the sorption processes of E2 on the other MPs were not absolutely linear which indicates the sorption is controlled through combined partition and adsorption dual-mode mechanisms (Paul, 2016). The partition and adsorption also have different contributions to the total sorption amount of E2 on MPs. The total sorption amount (Q_T) of E2 on MPs is contributed by adsorption amount (Q_A) and partition amount (Q_P) which can be quantitatively described (Zhu and Chen, 2000; Zhu et al., 2000).

The Q_T , Q_P and Q_A of E2 on MPs were derived from Equations (5)–(7) according to the dual-mode model theory, with the results shown in Table S1 and Fig. 2. It can be seen from Fig. 2 that partition of E2 on MPs linearly increased with increasing E2 equilibrium concentration, while adsorption increased nonlinearly and reached saturation rapidly depending on the E2 equilibrium concentration and the type of MPs. Additionally, the partition was more powerful than the adsorption, suggesting the interaction mechanism regulating E2 sorption on MPs was a partition-dominating dual-mode sorption mechanism.

3.2. Hydrophobic partition nature of E2 sorption on MPs

The sorption of HOCs to soil organic matter (SOM) is

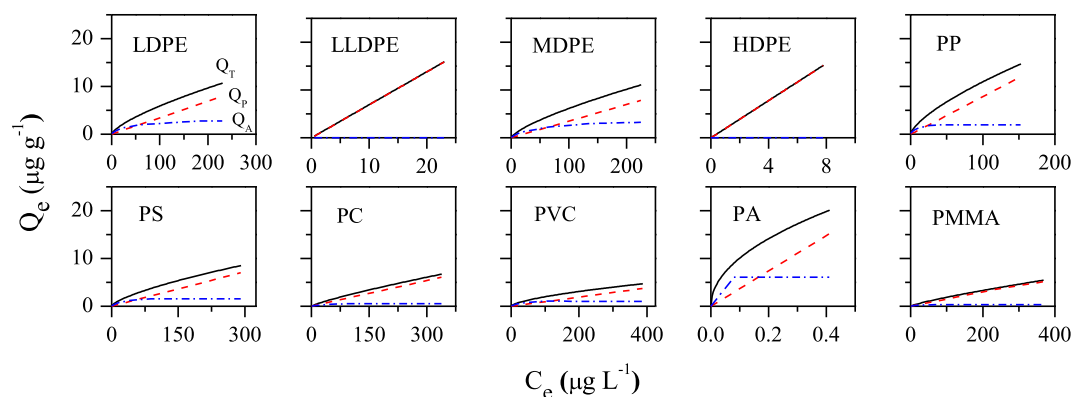


Fig. 2. The relevant models of Q_T (black lines), Q_P (red dotted lines) and Q_A (blue dotted lines) of E2 sorption on MPs. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

thermodynamically driven through the hydrophobic effect (Pignatello, 1998b). Polymers, i.e. plastics, can be simplified as the analogy of SOM to study the MPs-HOCs interactions (Feng et al., 2017; Guo et al., 2012; LeBoeuf and Weber, 1997). Studies have illustrated that the sorption amount of HOCs on plastics is positively correlated with the hydrophobicity of MPs (Lee et al., 2014; Wu et al., 2016). The static contact angle widely used for describing the external surface hydrophobicity of a plastic was analyzed and shown in Fig. 3 (inset) and Table 1. The relation between the organic carbon content-normalized sorption coefficient (K_{oc}) of E2 and the water contact angle of corresponding MPs is shown in Fig. 3. There is a significant positive correlation between K_{oc} of E2 and the water contact angle of MPs (** $p < 0.01$, $r = 0.834$). The sorption capacity of E2 was strongly dependent on the hydrophobicity of MPs. That is, the greater the contact angle, the stronger the hydrophobicity of MPs or the higher sorption capacity of E2 on MPs. It reconfirmed that the sorption of E2 on MPs should be a hydrophobic partition-dominating dual-mode sorption.

The surfaces of most MPs, such as nonpolar PEs and PP and weakly polar PS, are structurally homogeneous, inert, non-wetting and strongly hydrophobic, leading to accumulation of more E2. Polar PA, PC, PMMA with hydrophilic groups such as $-C(O)NH-$ or $-COO-$, and the strongly polar PVC, will increase the accessibility of

water on the material surface, hence decreasing the hydrophobicity and reducing the enrichment of E2. PA is a special case with the highest E2 sorption capacity and lowest hydrophobicity due to the presence of hydrogen bonding (N'Diaye et al., 2012). Hydrophobic E2 is present as neutral molecule below pH of 10.6 (pKa of 10.6), indicating that the electrostatic interactions involved in the sorption can be excluded in this work. While PA still has the highest sorption for binding E2, the hydrogen bonding interaction between E2 and the amide functional groups of PA should be considered (Ng and Elimelech, 2004; Nghiem et al., 2002, 2004; Schafer et al., 2003) besides hydrophobic dominating interaction (Yoon et al., 2004). Our result is consistent with Endo et al.'s report which showed that PA had higher sorption for diverse H-bond-donating compounds (e.g., hormones, pharmaceuticals, biocides and DDTs) than PE due to the H-bond accepting properties of PA (Endo et al., 2011a). It is clear that PS and PVC are different from PE due to their substitution of one hydrogen atom by benzene ring or chlorine atom which may make PS and PVC more polar than PE. The slightly higher sorption capacity of E2 on PS compared with that of PVC may be attributed to the $\pi-\pi$ interaction of benzene ring between them (Terzyk et al., 2010)[58]. The presence of chlorine in PVC increases in cohesive density and creates attractive forces between the individual PVC chains, resulting in a reduction of its free volume and ultimately inhibiting a potential migrating species to diffuse through it (Sangaj and Malshe, 2004).

3.3. Structural properties of MPs related to the sorption behaviors of E2

3.3.1. Crystallinity of MPs

The aggregation structure of MPs embodied with amorphous and crystalline domains has more important influence on the sorption process (Guo et al., 2012; Wang et al., 2015). The crystallinity has been quantitatively used for measuring the abundance of crystalline domains of MPs. The crystallinity of MPs was determined by the heat flow curve of DSC shown in Fig. 4a–b and Table 1. XRD shown in Fig. 4(c) was further applied to confirm the degree of crystallinity of MPs. All diffraction peaks of LDPE, LLDPE, MDPE, and HDPE could be indexed to polyethylene (PDF #054–1982) and the peaks of PP coincided well with polypropylene (PDF #054–1936), whereas the other five kinds of MPs (PC, PS, PVC, PA, PMMA) did not show obvious characteristic peaks. PEs and PP are demonstrated to possess relatively high crystallinity due to the regularity in chain structure, i.e. both of them with lower quantity of amorphous domain in this study, which is consistent with previous research (Wang et al., 2015). Reduction of crystallinity may occur when

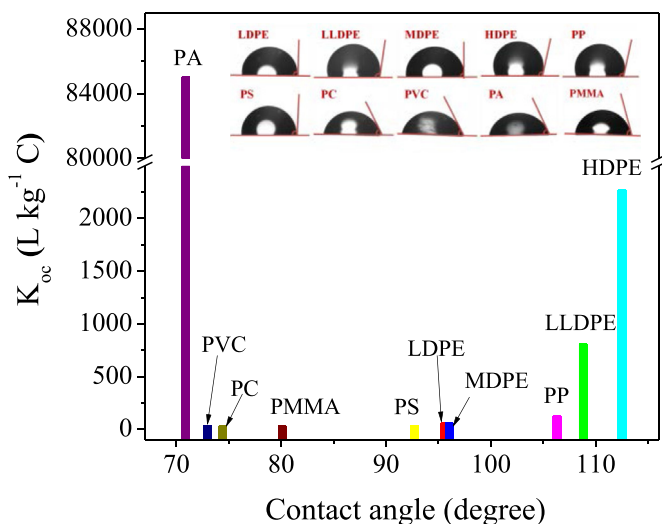


Fig. 3. Relation between K_{oc} of E2 on MPs with water contact angles of MPs (** $p < 0.01$, $r = 0.834$) with inset of contact angle images of MPs.

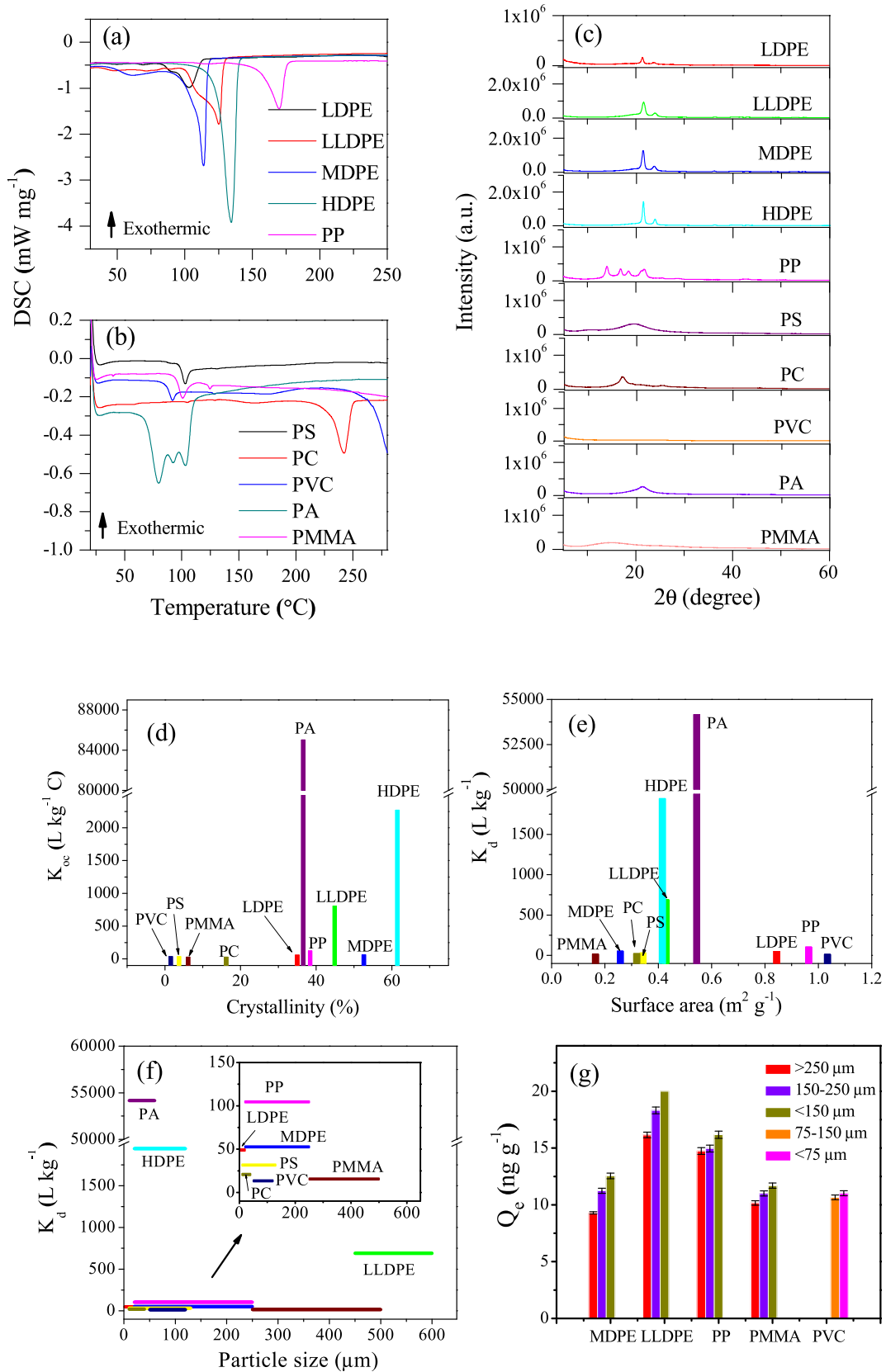


Fig. 4. DSC spectra (a and b), XRD patterns (c) of MPs; and relation between $K_{\infty c}$ of E2 with crystallinity (* $P < 0.05$, $r = 0.781$) (d), surface areas of MPs ($P > 0.05$) (e), particle sizes ($P > 0.05$) (f); and the sorption capacity of E2 on different size MPs (g).

introducing polar or chiral groups in the polymeric chains of MPs as observed in PC, PS, PVC, PA and PMMA. The boundary of crystalline versus amorphous domain of plastic is not clear due to the different degrees of order in the polymers. The degree of crystallinity varies considerably even for plastics with the same primary structure or chemical composition due to the chain branching, aligning and stacking, and the processing (Carragher, 2011). For example, in this study PE is classified into LDPE, LLDPE, MDPE and HDPE based mostly on its density and branching.

Previous studies have reported that the crystalline domains of MPs will have important impact on the partitioning of HOCs within MPs (Guo et al., 2012; Hale et al., 2011). The relation between K_{oc} of E2 with the crystallinity of MPs is shown in Fig. 4(d). The higher crystalline MPs (such as PEs, PP and PA) show higher K_{oc} values of E2 compared with amorphous MPs (such as PC, PS, PVC and PMMA). The significant positive correlation between K_{oc} and the crystallinity of MPs (* $P < 0.05$, $r = 0.781$) indicates that the crystalline domain greatly influences the accessibility of E2 to MPs. Wang et al. observed that the crystallinity didn't have a correlation with K_d values of perfluorooctane sulfonamide (FOSA) on three MPs (PE, PS and PVC) (Wang et al., 2015); whereas Guo et al. reported that the sorption capacity of phenanthrene, naphthalene, lindane and 1-naphthol on different PEs decreased with increasing crystallinity (Guo et al., 2012). The structural difference of contaminants sorbed on plastics may be responsible for these inconsistencies. In our study, K_{oc} values of E2 on MPs shows a significant positive correlation with hydrophobicity or crystallinity. As seen in Fig. S1, the crystallinity showed a significant positive correlation with hydrophobicity of MPs (** $P < 0.01$, $r = 0.823$). Overall, the higher crystallinity of MPs will connect with the higher hydrophobicity, thus leading to the higher E2 sorption capacity on MPs. Generally, the crystalline domains present alignment that could affect the availability of amorphous domains of MPs for HOCs sorption (Guo et al., 2012; Hale et al., 2011). Therefore, the influence of amorphous domain of rubbery and glassy MPs on E2 sorption should be addressed besides crystallinity.

3.3.2. Rubbery or glassy phase of MPs

Amorphous domains of plastics undergo a transition from a rubbery to a glassy phase upon cooling below the glass transition temperature (T_g). Plastics with T_g below ambient temperature are called rubbery plastics (e.g., PE and PP); while plastics with T_g above ambient temperature are called glassy plastics (e.g., PS, PC, PVC, PA and PMMA). T_g of MPs shown in Fig. 4(a)–4(b) could be monitored by the heat flow curve of DSC. The T_g of PEs and PP could not be detected from DSC analysis because their T_g are below ambient temperature as shown in Table 1. Owing to the low T_g , the separated chain segments of rubbery PEs and PP can move freely to form a more flexible status. However, the chains of glassy PS, PC, PVC, PA and PMMA are “frozen” and the flexibility of amorphous domain is reduced drastically at room temperature. Rubbery PEs and PP sorb greater amounts of E2 than the other five kinds of glassy MPs in this study due to varying diffusivity and sorption capacity within rubbery or glassy polymers (Pignatello, 1998a). Amorphous regions in rubbery MPs may have higher mobility, diffusivity and accessibility for E2 than that of glassy MPs. Similar research showed that higher concentrations of PAHs and PCBs were accumulated on rubbery PEs and PP with higher free volume of the internal cavities than on PET and PVC (Pascall et al., 2005). Therefore, the flexible rubbery or freezing glassy state of amorphous domain of MPs also influences the sorption of E2.

3.3.3. Surface area of MPs

Specific surface area was reported to be an important factor influencing HOCs sorption on MPs (Wang and Wang, 2018). The N_2

adsorption-desorption isotherms of various MPs used in this study are illustrated in Fig. S2 and Table 1. The N_2 adsorption-desorption isotherms of MPs showed a typical Type-II curve at higher relative pressure according to the IUPAC classification, indicating typical physical sorption (Thommes et al., 2016). The specific surface areas of all plastics are relatively small with values around $0.3\text{--}1.0\text{ m}^2\text{ g}^{-1}$. MPs with the larger surface area did not inevitably mean the higher uptake capacity for E2, and vice versa. The relation between the surface areas of corresponding MPs with K_d of E2 is shown in Fig. 4(e). It can be seen that the surface areas of corresponding MPs didn't have obvious correlation with the K_d values of E2. For example, PVC had the largest surface area of $1.034\text{ m}^2\text{ g}^{-1}$ but had the lowest sorption capacity for E2; while PA, HDPE and LLDPE had medium surface areas around $0.4\text{--}0.5\text{ m}^2\text{ g}^{-1}$ but had the highest sorption capacity for E2. Therefore, the surface adsorption of E2 on MPs or the pore-filling mechanism should not be the dominant sorption mechanism. Nevertheless, the role of the surface area of MPs on E2 sorption cannot be ignored especially at lower E2 concentrations proved in Fig. 2.

3.3.4. Particle size of MPs

The size of MPs particles will constantly decrease as a consequence of environmental physical, chemical and biological degradation and other external forces. It is generally believed that small micro-plastics may be more dangerous to marine organisms than the larger pieces due to their larger surface areas which can concentrate more toxic chemicals than those of the larger ones (Zhan et al., 2016) and can be more easily confused with natural food. The particle size distribution of MPs is shown in Fig. S3 and Table 1, and the relation between particle size of MPs and sorption capacity of E2 is shown in Fig. 4(f). It can be observed that the particle size of MPs didn't correlate with the sorption capacity of E2. For example, LLDPE had the largest mean particle size but exhibited larger sorption capacity for E2 than MDPE, LDPE, PP, PC, PVC and PMMA, and lower than PA and HDPE. The effect of particle size on the sorption capacity of chemicals on MPs was also mentioned in previous studies. Xu and his coworkers observed a great difference in sorption capacity of tetracycline on different types of MPs with the same particle size ($<280\text{ }\mu\text{m}$) (Xu et al., 2018). The particle sizes of poly (butylene adipate co-terephthalate) (PBAT) and PEc (made from plastic bags) were in the same range and were larger than those of PEv (purchased) and PS, showing the sorption capacity did not correlated with particle sizes of plastics (Zuo et al., 2019). Our study is consistent with above report confirming that the particle size was not the major factor affecting the sorption process of E2. However, the influence of MPs particles sizes on the intra-MPs diffusion pathway length of E2 or the E2 sorption kinetics still can't be neglected.

Five kinds of MPs, i.e. MDPE, LLDPE, PP, PMMA and PVC were sifted to obtain different size fractions. The sorption capacity of E2 on different sizes of MPs is shown in Fig. 4(g). The sorption capacity of E2 on MPs with the same chemical composition significantly increased with decreasing particle size because the effective sorption surface area of corresponding MP fraction was enhanced. For example, the surface areas of different LLDPE fractions were 0.478 , 0.418 and $0.336\text{ m}^2\text{ g}^{-1}$ corresponding to the particle sizes in the ranges of $<150\text{ }\mu\text{m}$, $150\text{--}250\text{ }\mu\text{m}$, and $>250\text{ }\mu\text{m}$, respectively; the resulted sorption capacity of E2 increased from 16.2 to 20 ng g^{-1} . Zhan et al. also reported similar result that the sorption capacity of PCB77 significantly increased with decreasing particle size of PP (Zhan et al., 2016). It is expected that the number of plastic particles in the ocean increases exponentially with decreasing sizes because of the fragmentation of larger plastics (Cozar et al., 2014), leading to greatly increased potential environmental risks.

3.4. The sorption kinetics of E2 on MPs

Temporal patterns of E2 sorption on MPs were examined to better understand the equilibrium interaction between MPs and E2 and the results are shown in Fig. 5. Fast sorption kinetics of E2 on HDPE and PA were observed compared with other eight kinds of MPs. Apparent sorption of E2 on HDPE and PA could reach equilibrium in 24 h due to their high affinity for E2. The uptake capacities of E2 by other eight kinds of MPs gradually increased with time until the achievement of sorption equilibrium in 3 days. Sorption of HOCs to MPs is reported to be kinetically controlled by diffusive transfer within the plastic matrix. In previous research, chemicals may exhibit a relatively rapid sorption onto the surface of glassy MPs due to relatively faster diffusion into the polymeric matrix, as is expected for rubbery MPs. Long-term field measurements by Rochman and co-authors at five locations in San Diego Bay (CA, USA) has suggested that faster saturation of PCBs and PAHs on PET and PVC was reached based upon their glassy polymeric structure, compared with HDPE, LDPE, and PP (Rochman et al., 2013a). In this study, no obvious differences were observed in sorption rate of E2 on glassy or rubbery MPs. It indicates that hydrophobicity may play a more important role in sorption rate of E2 on MPs. The stronger hydrophobicity may mean the faster sorption rate. PC was observed to reach equilibrium quickly due to its smaller particle size besides the role of its hydrophobicity. It is generally true that larger pellet requires a longer time than a smaller pellet for reaching sorption equilibrium due to shorter intra-polymer diffusion path lengths (Endo et al., 2013). In the case of assessing HOCs in aquatic environments with 20 μm thickness plastics, it took a few days to reach equilibrium (Adams et al., 2007). Pellets of a few mm took ~200 days to reach equilibrium (Karapanagioti et al., 2010). The sorption equilibrium of HOCs on MPs will be more complex under real environmental conditions. Rochman et al. reported that PCBs and PAHs required at least 6 months to reach sorption equilibrium within HDPE, LDPE and PP in the field, which was much longer than that estimated in laboratory (Rochman et al., 2013a). This might be mainly attributed to polymer weathering that would increase the effective diffusivity and the additional sorption sites (Mato et al., 2001; Wang et al., 2016).

3.5. Sorption potential of E2 on MPs in different water matrices

Plastic debris from land sources will transport long distances before entering into the sea through river networks (Gruber and Galloway, 2008; Ludwig et al., 1996). Therefore, the impact of salinity on E2 sorption by MPs in different water matrices was assessed and the results are shown in Fig. S6. The main properties and compositions of tested water matrices are presented in Table S2. It seems that the sorption capacity of E2 on rubbery phase PE and PP in seawater slightly decreased compared with that in Milli-Q water. It was evident that salinity had an inhibition effect on sorption ability of E2 on PEs and PP; while the salinity enhanced the sorption ability of E2 on PS, PC, PVC and PMMA due to different structural properties of MPs. The increase of salinity will reduce the solubility of E2 (known as the “salting-out” effect), which enhances the hydrophobic interaction between E2 and certain type of MPs indirectly. Similar salinity effect on hydrophobic interaction was also observed in marine sediments (Yang and Zheng, 2010) and protein sorption in hydrophobic interaction chromatography (Lin et al., 2001). In a previous study, increased salinity showed no significant effect on the sorption of phenanthrene on PE and PVC but decreased the sorption of DDT (Bakir et al., 2014). Xu et al. investigated the effect of salinity in sorption of tetracycline to microplastics (PE, PP and PS) and found no significant effect of sorption within a wide range of salinity from 0.05% to 3.5% (Xu et al., 2018). Increase of salinity enhanced the sorption of triclosan but showed minor influence on 4-methylbenzylidene camphor, carbamazepine and 17 α -ethinyl estradiol (Wu et al., 2016). In addition, dissolved organic matter (DOM) contained in filtered seawater may also have effect on sorption of E2. Previous studies have demonstrated that sorption capacity of chemicals dramatically decreased with the increase of DOM concentration (Xu et al., 2018). And it might be explained by increased dissolution of chemicals in the presence of DOM in solution. No obvious effect of DOM on E2 sorption was found in this experiment, probably because of the low concentration of DOM. Besides, the effect of salinity and DOM on the sorption of HOCs to MPs may vary among compounds and plastic types. In short, the effect of salinity and DOM of in environmental water on E2 sorption on MPs is minor in this hydrophobic partitioning-dominating sorption system.

4. Conclusions

This study suggested that MPs can be potentially served as a transport medium for E2 in marine water. The sorption ability of E2 on various MPs followed the order of PA > HD/LLD-PE > PP > LD/MD-PE > PS > PC > PMMA > PVC. Partition-dominating sorption mechanism of E2 on MPs was obtained through applying the dual-mode model. The difference in E2 sorption capacities among ten types of MPs mainly caused by the diverse crystallinity, the aggregation structure, and rubbery or glassy phase in the amorphous domains of MPs. Notably, the sorption PA has the highest sorption for binding E2 due to the great contribution of hydrogen bonding. However, the potential environmental risk of smaller MPs particles should also be stressed, because smaller particle size/larger the specific surface area will obviously strengthen the sorption ability and facilitate the sorption rate of E2 on the same type of MPs. This study will provide foundation for predicting the fate, transport and risk of MPs associated HOCs in the marine environment.

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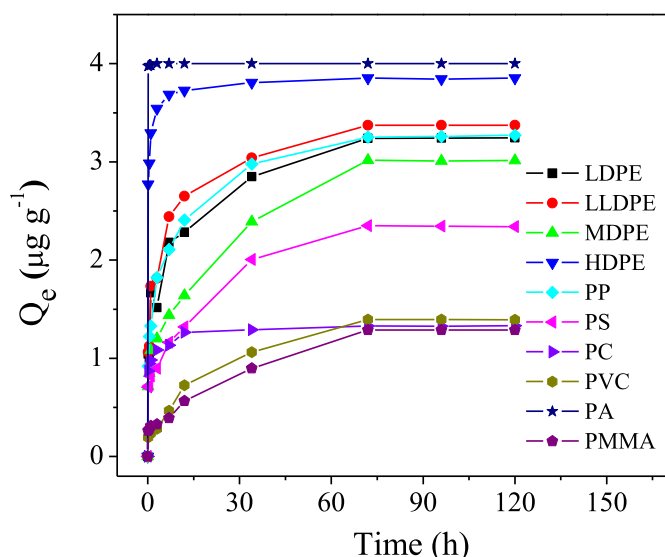


Fig. 5. The sorption kinetics of E2 on MPs.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemosphere.2019.03.162>.

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