The role of crystallinity and particle morphology on the sorption of dibutyl phthalate on polyethylene microplastics: Implications for the behavior of phthalate plastic additives☆

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A R T I C L E   I N F O

A B S T R A C T

The sorption behavior of phthalate additives in plastic and microplastic litter is an important process controlling the exposure, net health risk and ecotoxicity of these co-occurring pollutants. Plastic crystallinity and particle morphology are hypothesized to be important variables for microplastics sorption behavior, but to date there have been few direct studies to explicitly test for the influence of these parameters. To address this, in this study we explored the sorption of dibutyl phthalate (DBP) as a probe molecule to diverse polyethylene microplastics including irregularly-shaped pure polyethylene microplastics (IPPM), black plastic film microplastics (BPFM), white plastic film microplastics (WPFM), and commercial microspheres (CM), which had crystallinities ranging from 17 to 99%. Sorption kinetics for all materials could be well represented with both a pseudo-first-order (R^2 = 0.87–0.93) and pseudo-second-order model (R^2 = 0.87–0.93). Further, sorption was highly linear in the concentration range of 0.5–10 mg L^{-1}, with no greater performance from a linear sorption model (R^2 = 0.96–0.99) than the non-linear Freundlich or Temkin sorption models. The partition coefficient (K_d) of DBP sorption onto IPPM, BPFM, WPFM and CMs were 1974.55 L kg^{-1}, 1483.85 L kg^{-1}, 1477.45 L kg^{-1} and 509.37 L kg^{-1}, respectively, showing a significant decrease with increasing crystallinity (r^2 = 0.98). The particle size of microplastics (27–1000 μm) is, however, an indecisive factor affecting their sorption behavior for DBP in this study. This study provides new insight that crystallinity plays a governing role on the sorption of phthalate from microplastic. This should be considered in future exposure studies and assessments of phthalates from plastics and microplastics.

1. Introduction

The ubiquity of plastic in daily life has led to some to call this age the "Plastic-age" (Shen et al., 2019). The world's annual production of plastic increased 200 times in 2018 compared with 1950, reaching to 359 million tons (Feng et al., 2020). There is a current focus on how the plastic-age has led to ecological and environmental threats to the earth, such as from emissions of microplastics (Thompson et al., 2004) or

harmful plastic additives (Gong and Xie, 2020). In recent years, microplastics have been defined as 1 μm–5 mm primary or secondary plastic particles (Frias and Nash, 2019). It is estimated that about 900,000 tons of microplastics enter the terrestrial environment each year (Horton et al., 2017). Microplastics have been widely distributed due to their small size and fast migration (Gong and Xie, 2020). Marine, fresh water, air and soil environments all contain quantifiable levels of microplastic, with commonly occurring plastic types being polyethylene (PE),

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polypropylene (PP), polystyrene (PS) and polyvinyl chloride (PVC) (Akdogan and Guven, 2019).

Plastic mulching to improve crop yield and quality has become a global agricultural practice for diverse purposes like reducing weeds, retaining moisture and increasing soil temperature (Steinmetz et al., 2016). Plastic mulches from PE are popular, but they do break down over their deployment, from processes such as photodegradation (Chamas et al., 2020), often leading them to need replacement by the end of the season and remaining in the soil in the form of microplastics (Krueger et al., 2015; Steinmetz et al., 2016). Meanwhile, the residues of PE microplastics from mulches or other sources, such as biosolids (Crossman et al., 2020), could cause leaching out of the plasticizers, especially the commonly used phthalic acid esters (PAEs), which are considered endocrine disruptors (Magdouli et al., 2013). Therefore, the coexistence of PE microplastics and PAEs occurs in agricultural soil environments (Song et al., 2018). In China, this is considered to be a major potential exposure route to PAEs, with cereal crops considered responsible for up to 45% of the exposure to adults and 40% for children (Sui et al., 2014). However, the exposure of PAEs from microplastics in soil and other media to humans and ecosystems is poorly understood, due to a lack of attention on PAE-plastic sorption behavior. Clarifying the sorption mechanism of PAEs on PE microplastics has great significance to understand the relationship between microplastics and plasticizers in the environment regarding their exposure and ultimately risk.

One driver of this sorption mechanism is the crystallinity of the plastic (Hale et al., 2010; Endo et al., 2011). For a completely crystalline polymer, only adsorption on the surface occurs. For semi-crystalline microplastics, like PE, both adsorption on the surface and absorptive partitioning into the amorphous domains could occur (Haider and Karlsson, 2001). Generally, the crystalline fraction of the polymers would be changed when the polymers degraded in the environment (Andrady, 2017; Garvey et al., 2020). Even though PAEs is a common co-existing pollutant with microplastics, and as a plasticizer is added to increase the amount of amorphous regions in the plastic, research on the sorption mechanism of PAEs to PE microplastics is lacking.

In addition to crystallinity, the influence of microplastics' particle size and shape on sorption behavior cannot be neglected (Liu et al., 2018; Yu et al., 2020). Yu et al. (2020) investigated the sorption process of tetracycline onto PE and found that the sorption capacity increased with the decrease of particle size. Size related sorption can be due to surface-adsorptive processes dominating (increased surface area to volume ratio with a decreasing size). However, Liu et al. (2019) found that particle size had no effect on the sorption capacities of 17β-Estradiol onto different microplastics, indicating dominance of absorptive interactions into amorphous bulk volumes.

Recently, several sorption studies on to different microplastic materials, including commercial microspheres (CM), plastic raw materials, and microplastics made from broken plastic products (Lee et al., 2014; Alimi et al., 2018; Besson et al., 2020; Li et al., 2020), were reported. Wang et al. (2020a) used PE raw materials to study the interaction between microplastics and pesticides, and found that the sorption efficiencies of atrazine onto PE raw materials were about 60–70%. However, Ateia et al. (2020) found that the sorption efficiencies of atrazine onto PE commercial microspheres were only 30–40%, while PE microplastics formed by crushing actual plastic products were about 60%. A hypothesis that could account for this is the differences in available amorphous volumes/adsorptive surfaces for sorption (Guo et al., 2012). Tourinho et al. (2019) and Kutralam-Muniasamy et al. (2020) concluded from several previous studies that the properties of microplastics and environmental conditions would affect the sorption process, and raised questions about the differences between laboratory studies and field studies. For example, the degradation of microplastics may generate free radicals which can promote the sorption efficiency of pollutants onto microplastics (Wang et al., 2020b). However, the influence of particle size and different morphology of microplastics on sorption behavior of PAEs onto PE microplastics remains unclear.

We hypothesize that the mechanism of sorption of PAEs on PE microplastics are dominated by accessibility to amorphous subdomains, which is governed by crystallinity, and this would explain differences in sorption to different microplastics. To test this hypothesis, the sorption kinetics and isotherms of dibutyl phthalate (DBP), a common PAE plasticizer, to microplastics of various particle size, shape and crystallinity were explored. Characterization and model fitting were used to elucidate the potential sorption mechanism, and the relevance of this environmental exposure and risk assessment are discussed.

2. Materials and methods

2.1. Chemicals and materials

CM made of PE were purchased from Cospheric (USA), with diameter of 850–1000 μm (CM1), 425–500 μm (CM2), 106–125 μm (CM3), 27–45 μm (CM4). Irregularly-shaped pure polyethylene materials (IPP) used for producing actual plastic products were sourced from Sigma Aldrich (China). Black plastic film (BPF) and white plastic film (WPF), representative of those used for mulching, were sourced from Min Feng Company (Shandong, China). The three materials above were ground and sieved to a particle size of 250–600 μm to obtain the IPP microplastics (IPPM), BPF microplastics (BPFM), and WPF microplastics (WPFM), respectively. The CMs, IPPM, BPFM and WPFM are collectively referred to as PE microplastics. DBP (≥99%) and methanol (chromatographic purity) were obtained from Ehrenstorfer GmbH (Augsburg, Germany) and Accustandard Inc. (New Haven, CT, USA), respectively. Anhydrous calcium chloride ($CaCl_2$) and sodium azide (NaN_3) were obtained from Sigma Aldrich.

2.2. Characterization analysis

The pore structure was analyzed using a Micromeritics ASAP 2020 Sorptometer, based on nitrogen adsorption and desorption. Scanning electron microscopy (SEM, ZEISS EVO18) was used to observe the surface morphology. Fourier transform infrared spectrometer (FTIR, Nexus 870 FTIR) was used to study the change of microplastic surface functional groups in transmittance mode. The crystallinity calculated from differential scanning calorimeter (DSC, NETZSCH DSC 200F3 240-20-0687-L) data, which is considered an index to describe the characteristics of microplastics crystal domain (Bungu et al., 2018). The crystallinity of microplastics were determined by DSC under the condition of N_2 as a purge gas, with a temperature increase from 30 °C to 180 °C at the heating rate of 10 °C min^{-1}, followed by a decrease to 60 °C at 10 °C min^{-1} after 5 min of constant temperature. The crystallinity calculation formula used is as follow:

$$W_{ch} = \Delta H_m / \Delta H_m^0 \tag{1}$$

where ΔH_m represents the melting enthalpy of semi-crystalline polymers and ΔH_m^0 represents the melting enthalpy of fully crystalline polymers. The ΔH_m^0 of polyethylene used was 288 J g^{-1} (Bungu et al., 2018).

2.3. Sorption experiments

Sorption kinetic and isotherm experiments were set up as follows, using 20 mL amber glass vials. The 0.01 mol L^{-1} $CaCl_2$ was used as a background solution, in which 0.2% NaN_3 were added as a biocide. In the sorption kinetic experiments, 0.4 mL of 100 mg L^{-1} DBP standard solution were added to 19.6 mL background solution to obtain a DBP concentration of 2 mg L^{-1} in the vials. Then 10 mg of microplastics (i.e. IPPM, WPFM, BPFM or CMs) were added to each vial. The vials were oscillated in a rotating oscillator at 50 r min^{-1} under dark conditions at 25 °C. The sampling time was set as 0, 1, 2, 4, 8, 12, 24, 48 72 and 96 h. The liquid solutions were sampled and centrifuged at a high speed at 10,000 r min^{-1} for 3 min, and the supernatant was analyzed by high
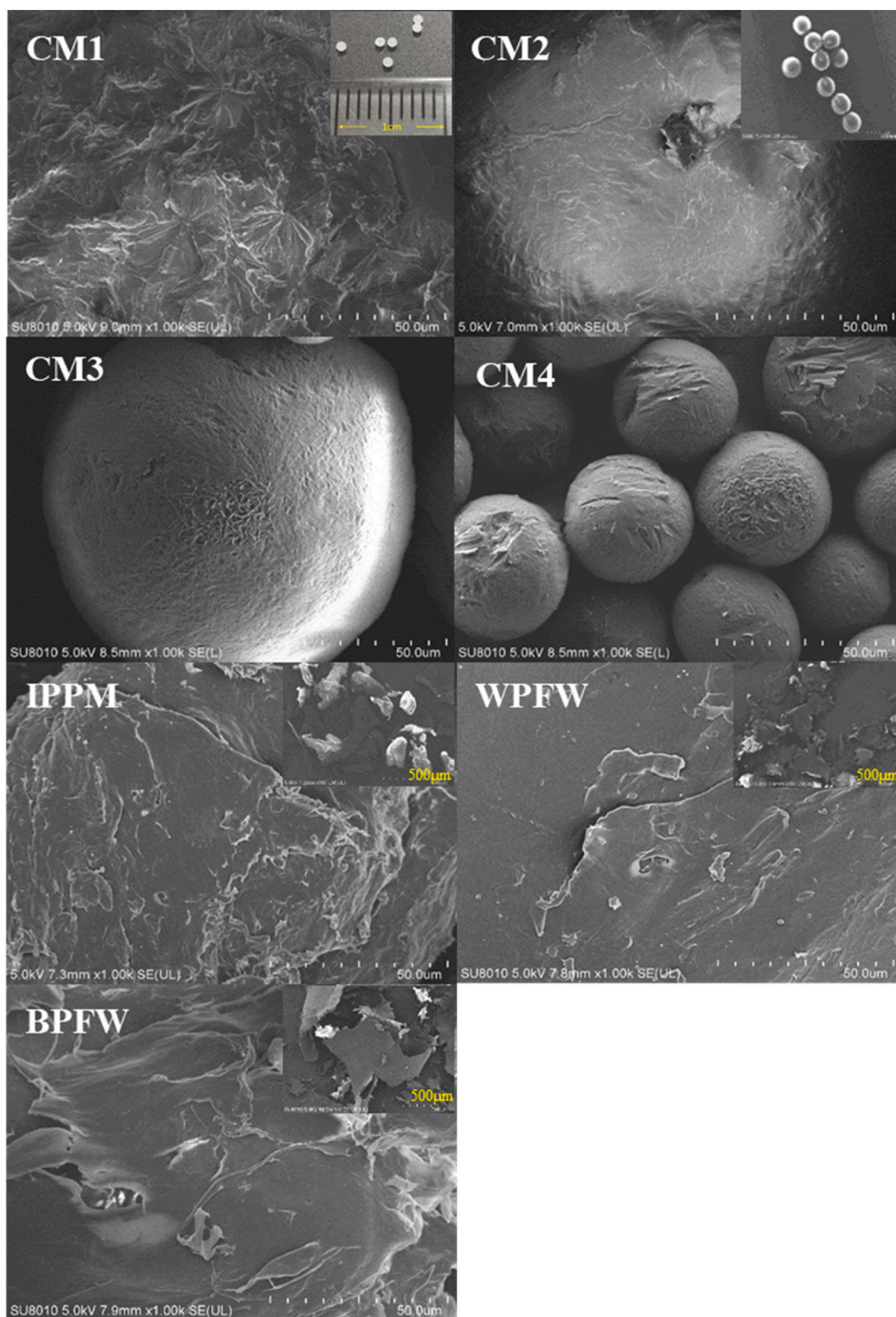
Fig. 1. Scanning electron microscopy images of microplastics, including commercial microspheres with diameter sizes of 850–1000 μm (CM1), 425–500 μm (CM2), 106–125 μm (CM3) and 27–45 μm (CM4), irregularly-shaped pure polyethylene microplastics (IPPM), black plastic film microplastics (BPFM) and white plastic film microplastics (WPFM).

performance liquid chromatography (HPLC) to determine the concentrations of DBP.

In the sorption isotherms experiments, 0.4 mL of 25, 50, 75, 100, 175, 250, 375 and 500 mg L^{-1} DBP standard solution were add so that the DBP concentrations in the vials were 0.5, 1.0, 1.5, 2.0, 3.5, 5.0, 7.5

and 10 mg L^{-1}, respectively. Then 10 mg microplastics (i.e. IPPM, WPFM, BPFM or CMs) were added to each vial. The shaking conditions were the same as the sorption kinetic experiment mentioned above. After 96 h, the samples were centrifuged at a high speed at 10,000 r min^{-1} for 3 min, and the supernatant was analyzed by HPLC.

2.4. Determination of DBP concentrations

The concentration of DBP in solution was determined by HPLC (Agilent 1260 InfinityII) with ultraviolet detector and a C18 column (4.6 × 250 mm). Methanol/ultra-pure water (9/1, v/v) was used as the mobile phase. Twenty μL samples were injected into a C18 separation column at a flow rate of 1 mL min^{-1} and column temperature of 35 °C, and ultraviolet detection wavelength of 275 nm.

2.5. Data analysis

Pseudo-first-order, pseudo-second-order and two-compartment models were used to fit the kinetic experimental results (Rudzinski and Plazinski, 2006; Chen et al., 2012). Linear, Freundlich and Temkin sorption isothermal models were used to describe the equilibrium sorption processes (Ayawei et al., 2017; Guo et al., 2019; Velzeboer et al., 2014).

$$\text{Pseudo} - \text{first} - \text{order:} \ Q_t = Q_e \left[1 - \exp\left(-k_1 t\right)\right] \quad (2)$$

$$\text{Pseudo} - \text{second} - \text{order:} \ Q_t = (k_2 Q_e^2 t)/(1 + k_2 Q_e t) \quad (3)$$

$$\text{Two} - \text{compartment:} \ Q_t = Q_e\{1 - [F_{fast} \exp\left(-k_{fast} t\right) + F_{slow} \exp\left(-k_{slow} t\right)]\} \quad (4)$$

$$\text{Linear:} \ Q_e = K_d C_e \quad (5)$$

$$\text{Freundlich:} \ Q_e = K_F C_e^n \quad (6)$$

$$\text{Temkin:} \ Q_e = (R T \ /b)\ln\left(a C_e\right) \quad (7)$$

where Q_t and Q_e are the sorption capacity at time t and sorption equilibrium, respectively (mg kg^{-1}); t (min) is the sorption time; k_1 (min^{-1}) and k_2 (kg mg^{-1} min^{-1}) are the pseudo-first-order and pseudo-second-order rate constants, respectively; F_{fast} is the proportion of components in fast sorption reaction and F_{slow} is the proportion of components in slow sorption reaction; k_{fast} and k_{slow} are the rate constants (h^{-1}) of fast and slow reactions; C_e (mg L^{-1}) refers to the equilibrium concentration of solution; K_d (L kg^{-1}) is the linear partition coefficient; K_F is the Freundlich constant (mg kg^{-1})(mg L^{-1})^n; n is the unitless sorption affinity constant; a and b are the Temkin constants; and $R T/b$ is related to the enthalpy of sorption (J mol^{-1}) ($R = 8.314$ J mol^{-1} K^{-1}, $T = 298.15$ K).

Origin Pro (Version 8.5) was used for data analysis and model fitting of sorption experiment data. One-way ANOVA of Statistical Product and Service Solutions (V20.0.) was adopted, and the significant difference Duncan comparison was tested at the $p < 0.05$ level.

2.6. Quality control

The blank experiments with either no DBP or just DBP added in the solutions were conducted. All experiments were performed in triplicate. Preliminary tests were done to confirm that the PE microplastics would not release PAEs during the experiment, and the recovery rate of DBP was 85–98%.

3. Results and discussion

3.1. Characterization of microplastics

As evident from the SEM photographs (Fig. 1), the surface morphologies of IPPM, WPFM, BPFM and CM were substantially different from each other. IPPM, WPFM and BPFM showed irregularly-shaped granules or film shapes, while CMs with four diameter sizes (850–1000 μm, 425–500 μm, 106–125 μm, 27–45 μm) all exhibited regular sphericity. The surfaces of the CMs were relatively smooth compared with the IPPM, WPFM and BPFM samples. There was no pore
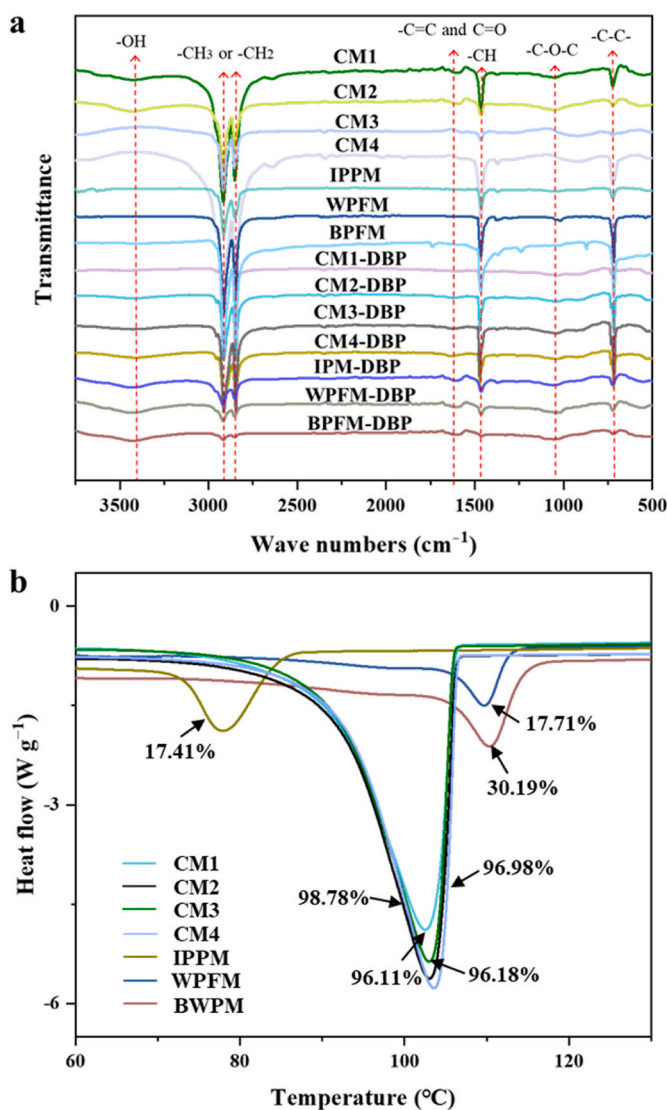

Fig. 2. Fourier transform infrared spectrometer results of microplastics before and after sorption of dibutyl phthalate (DBP)(**a**) and differential scanning calorimeter spectra of microplastics (**b**). Microplastics include commercial microspheres with diameter sizes of 850–1000 μm (CM1), 425–500 μm (CM2), 106–125 μm (CM3) and 27–45 μm (CM4), irregularly-shaped pure polyethylene microplastics (IPPM), black plastic film microplastics (BPFM) and white plastic film microplastics (WPFM).

structure visible on the surface of the selected microplastic samples. There was also no significant difference in surface areas among IPPM (1.045 m^2 g^{-1}), CM1 (1.063 m^2 g^{-1}), CM2 (1.032 m^2 g^{-1}), CM3 (1.141 m^2 g^{-1}) and CM4 (1.205 m^2 g^{-1}). However, the surface areas of WPFM (4.532 m^2 g^{-1}) and BPFM (4.238 m^2 g^{-1}) were significantly higher than IPPM and CMs ($p < 0.05$). The specific surface area of the sphere (per volume) is lower than that of any other three-dimensional shape, in the absence of pores and other surface irregularities (Wang et al., 2019).

Although the surface morphology of the microplastics were different, the surface functional groups observed by FTIR were consistent among all microplastics (Fig. 2a). The surface functional groups mainly include –CH, C=O or C=C, –CH$_3$ and –CH$_2$, C–O–C and C–C. The peaks at 2910–2840 cm^{-1} and 1480–1460 cm^{-1} are derived from the expansion of aliphatic or alkanes –CH$_3$, –CH$_2$ and –CH– (Wu et al., 2018). The positions of 1630–1610 cm^{-1} are C=O or C=C stretching vibration, 1060–1020 cm^{-1} and 730–710 cm^{-1} are aliphatic C–O–C and C–C stretching vibration, respectively (Mayakaduwa et al., 2016; Wu et al., 2018). The slight presence of carbonyls C=O is attributable to

Fig. 3. Sorption kinetics of dibutyl phthalate (DBP) onto commercial microspheres with diameter sizes of 850–1000 μm (CM1), 425–500 μm (CM2), 106–125 μm (CM3) and 27–45 μm (CM4), irregularly-shaped pure polyethylene microplastics (IPPM), black plastic film microplastics (BPFM) and white plastic film microplastics (WPFM). Pseudo-first-order model (green dashed curves), pseudo-second-order model (blue solid curves) and two-compartment model (red dotted curves). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)
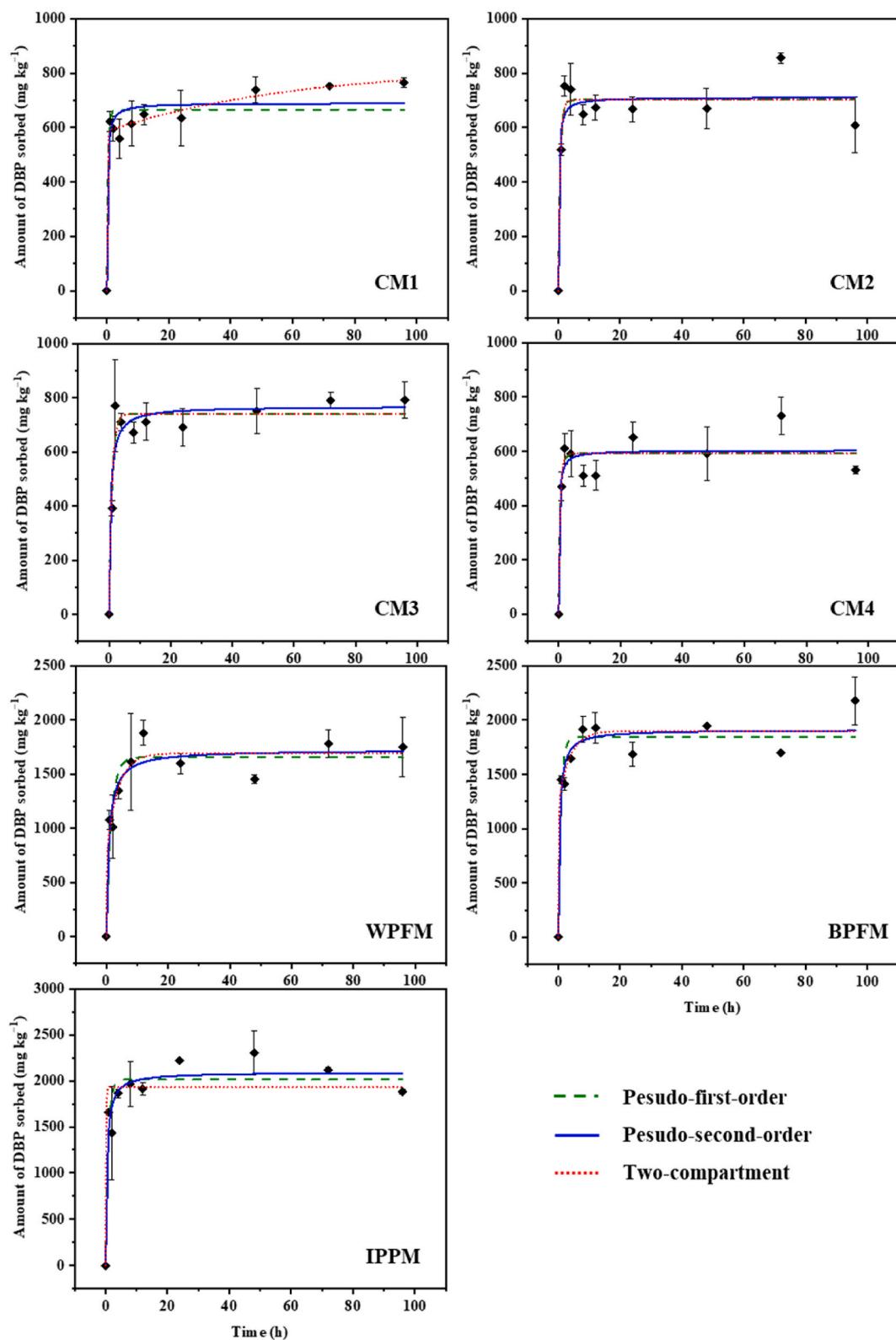
Table 1
Sorption kinetics parameters of dibutyl phthalate onto commercial microspheres with diameter sizes of 850–1000 μm (CM1), 425–500 μm (CM2), 106–125 μm (CM3) and 27–45 μm (CM4), irregularly-shaped pure polyethylene microplastics (IPPM), black plastic film microplastics (BPFM) and white plastic film microplastics (WPFM).

	Pseudo-first-order			Pseudo-second-order			Two-compartment model					
	k_1	Q_e	R^2	k_2	Q_e	R^2	q_e	F_{fast}	F_{slow}	k_{fast}	k_{slow}	R^2
CM1	2.51 a	665.68 de	0.89	0.007 a	689.68 de	0.92	823.03 c	0.71 a	0.29 b	6.93 a	0.02 e	0.98
CM2	1.56 ab	702.15 d	0.89	0.007 a	711.03 d	0.87	702.15 cd	0.70 a	0.30 b	1.56 e	1.56 b	0.83
CM3	1.03 b	739.95 d	0.93	0.002 a	767.77 d	0.90	739.98 cd	0.67 ab	0.33 b	1.03 f	1.03 c	0.88
CM4	1.71 ab	591.62 e	0.87	0.008 a	603.07 e	0.87	591.63 d	0.70 a	0.30 b	1.71 d	1.71 b	0.79
IPPM	1.19 b	2013.96 a	0.88	0.001 a	2092.49 a	0.93	1928.66 a	0.72 a	0.28 b	6.93 a	6.90 a	0.73
WPFM	0.64 b	1654.03 c	0.89	0.001 a	1721.22 c	0.91	1690.29 b	0.44 b	0.56 a	6.90 b	0.28 f	0.90
BPFM	1.17 b	1844.25 b	0.89	0.001 a	1910.62 b	0.93	1898.74 a	0.64 ab	0.36 ab	6.90 c	0.28 f	0.90

The lower case letters in each column represent the significance of the difference at $p < 0.05$.

photooxidation of the polyethylene surface (Albertsson et al., 1987). It appears, IPPM, WPFM, BPFM and CMs have the same surface functional groups, but the absorption intensity of characteristic peaks increases for the CMs.

The crystallinity of microplastics were in the order of CM2 (98.78%) > CM3 (96.98%) > CM4 (96.18%) > CM1 (96.11%) > WPFM (30.19%) > BPFM (17.79%) > IPPM (17.41%) (Fig. 2b). There was no significant difference in the crystallinities among CMs with different particle sizes, but they were substantially higher than those of IPPM, WPFM and BPFM.

3.2. Sorption kinetics

As shown in Fig. 3, in the first 60 min, kinetic sorption of PAEs into the PE microplastics was quite rapid, and then slowed down until sorption equilibrium was reached within 48 h. The pseudo-first-order, pseudo-second-order and two-compartment models were used to fit the kinetic experimental results of DBP sorption onto PE microplastics, respectively (Fig. 3). Specific parameters of kinetic model fitting are shown in Table 1. The pseudo-first-order ($R^2 = 0.87$–0.93), pseudo-second-order ($R^2 = 0.87$–0.93) and two-compartment ($R^2 = 0.73$–0.98) models can all fit the kinetic process well, of which the pseudo-first-order and pseudo-second-order models performed similarly, and the more complicated two-compartment model did not perform worse.

Both pseudo-first-order and pseudo-second-order models fitting the data well, indicates that kinetics is dependent on the concentration of the sorbent (pseudo-first-order) and in addition the available sorption domains of the PE (pseudo-second-order). Wang and Wang (2018) also found that the sorption process of hydrophobic organic compounds onto PE, PVC and PS microplastics could be well fitted into the pseudo-first-order or pseudo-second-order kinetic models. In both the first and second order models, the sorption reaction rates of DBP onto CMs (with the exception of CM3) were generally higher, but not significantly, than those of IPPM, WFPM and BPFM. These measurements are consistent with CMs being more crystalline, as adsorption (a surface process) would be dominating, and this is generally a more rapid process than absorption into the amorphous domains, such as within IPPM, WFPM and BPFM (Seidensticker et al., 2019).

3.3. Sorption isotherm

The linear, Freundlich and Temkin isotherm models were established to further clarify the sorption mechanism of DBP onto microplastics, respectively (Fig. 4), and the model fitting parameters are summarized in Table 2. Both linear and Freundlich isothermal models fit the sorption data of DBP onto PE microplastics well ($R^2 > 0.95$), indicating that accounting for sorption non-linearity with this system is not statistically necessary.

The Freundlich isotherm model is usually used to empirically describe the non-linear sorption to heterogenous systems such as surfaces (Razanajatovo et al., 2018). Of the fitting parameters of Freundlich

model, n and K_F represent surface non-uniformity measurement and sorption capacity, respectively (Tang et al., 2020). The $0 < n \ll 1$ means that the chemical sorption process is non-linear/heterogeneous, while an n of approximately 1 represents homogenous, linear-partitioning (Schwarzenbach et al., 2005). The fitting of the Freundlich model shows linearity, with all sorption coefficients being similar to 1, and also the K_d are similar to the K_F with sorption of DBP to the IPPM being approximately a factor 5 greater than the CMs. The sorption ability of PE microplastics in this study (with K_F ranging from 0.29 to 2.24 (mg g^{-1}) (mg L^{-1})^n) was significantly higher than those onto soil (with K_F ranging from 0.02 to 0.07 (mg g^{-1})(mg L^{-1})^n) or sand, silts and clays (with K_F ranging from 0.05 to 0.14) (mg g^{-1})(mg L^{-1})^n) (Wu et al., 2018; Xiang et al., 2019; Xue et al., 2020) (Table S1). In this study, the R^2 of DBP sorption onto PE microplastics fitted by Temkin model was lower than that of Linear and Freundlich models, and the correlation was poor. Therefore, the extra complexity brought in by Temkin models can be considered unnecessary. The values of the partition coefficient (K_d) were in the order of IPPM > BPFM > WFPM > CMs. The good fit of the linear isotherm model showed that the interaction between PE microplastics and DBP was consistent over the concentration range studied.

3.4. Influence of particle size and morphology of microplastics

As described in the Introduction, the effects of particle size on the sorption behavior of microplastics still remains unclear. In this study, therefore, CMs with different particle sizes were used to sorb DBP to determine the impact of particle size (Table 2). When the particle size is over 100 μm, there is no significant difference in the sorption of DBP onto CMs. However, when the particle size was less than 100 μm, the sorption capacity of CM was significantly lower than those with particle size higher than 100 μm. This was an unexpected result, there was no correlation between the sorption capacity of DBP onto CMs and particle size, and it did not increase with decreasing of particle size. The explanation of this results should be that i) the specific surface area and crystallinity of CMs with different particle size do not show significant differences in this study, and ii) surface agglomerations may occur with smaller microplastics due to electrostatic attraction, which would cause some of the surface to be inaccessible or substantially kinetically limited (Summers et al., 2018). A previous study also reported that the sorption capacity of 17β-Estradiol onto PE microplastics is not affected by microplastics particle size (Liu et al., 2019).

The sorption capacity of the least crystalline material, IPPM was significantly higher than WPFM and BPFM ($p < 0.05$) in all cases. Similarly, even with the similar particle sizes, the sorption capacities of DBP onto the WPFM and BPFM were also significantly higher than those the most crystalline material, the CMs of different particle sizes ($p < 0.05$) (Table 2). These results are consistent with the hypothesis that sorption increases with decreasing polymer crystallinity (Endo et al., 2011; Guo et al., 2012; Arp et al., 2015).
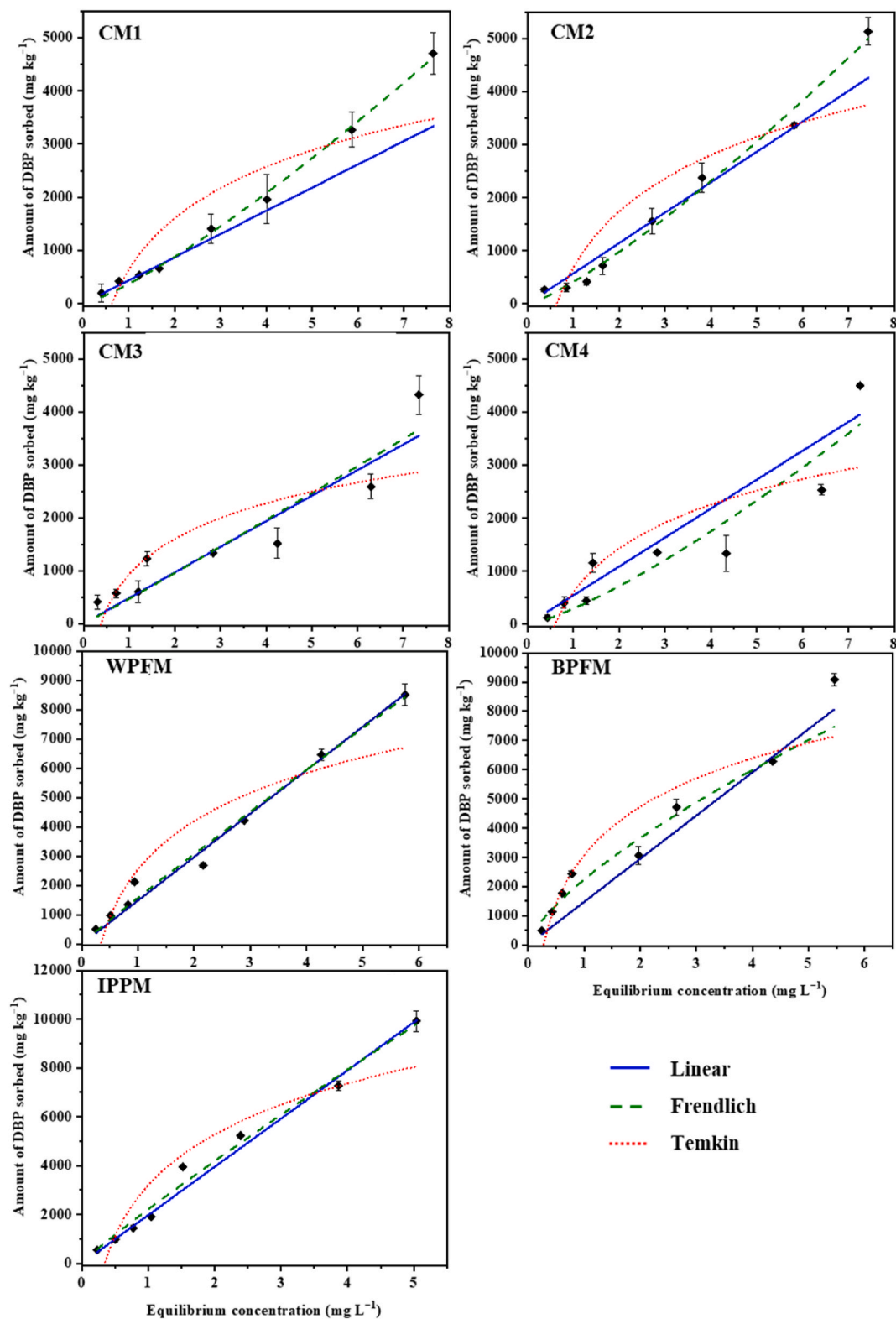
Fig. 4. Sorption isotherms of dibutyl phthalate (DBP) onto commercial microspheres with diameter sizes of 850–1000 μm (CM1), 425–500 μm (CM2), 106–125 μm (CM3) and 27–45 μm (CM4), irregularly-shaped pure polyethylene microplastics (IPPM), black plastic film microplastics (BPFM) and white plastic film microplastics (WPFM). Linear model (bule solid lines), Freundlich model (green dashed curves) and Temkin model (red dotted curves). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Table 2
Sorption isotherm parameters of dibutyl phthalate onto commercial microspheres with diameter sizes of 850–1000 μm (CM1), 425–500 μm (CM2), 106–125 μm (CM3) and 27–45 μm (CM4), irregularly-shaped pure polyethylene microplastics (IPPM), black plastic film microplastics (BPFM) and white plastic film microplastics (WPFM).

	Linear		Freundlich			Temkin		
	K_d	R^2	K_F	n	R^2	a	b	R^2
CM1	436.53 d	0.98	373.89 c	1.24 ab	0.99	1.58 b	1.78 bc	0.76
CM2	572.82 c	0.99	414.28 c	1.24 ab	0.99	1.56 b	1.62 bc	0.75
CM3	483.11 cd	0.96	468.37 c	1.03 abc	0.86	2.61 ab	2.56 a	0.63
CM4	545.03 c	0.97	294.73 c	1.29 a	0.84	1.66 b	2.08 ab	0.66
IPPM	1974.55 a	0.98	2208.70 a	0.92 cd	0.98	2.89 ab	0.82 d	0.85
WPFM	1483.85 b	0.97	1578.75 b	0.96 bcd	0.98	2.91 ab	1.04 cd	0.81
BPFM	1477.45 b	0.98	2242.30 a	0.71 d	0.98	3.60 a	1.03 cd	0.85

The lower case letters in each column represent the significance of the difference at $p < 0.05$.

3.5. Sorption mechanism

In general, the sorption of organic contaminants onto polymers could be divided into two overarching mechanisms, i.e., adsorption onto the surfaces and absorptive partitioning into the amorphous phase (Xing and Pignatello, 1997). The CMs, with lower surface area and higher crystallinity than those of IPPM, BPFM, and WPFM, showed the fastest sorption equilibrium rate and lowest sorption capacity for DBP. This firstly indicates that a fast sorption rate does not necessarily mean a high sorption capacity of the microplastics. In fact, surface adsorption often occurs more quickly than the absorptive partitioning of organic compounds onto sorbents (Sun et al., 2012). In the crystalline phase, the adsorption mechanism includes concurrent dissolution, hole–filling and so on (Vieth, 1991; Haider and Karlsson, 2001). In the case of the studied microplastics, there are no pores, no cracks, and the CMs are nearly 100% crystalline. Therefore, it could be inferred that the main sorption of DBP on CMs occurs by surface adsorption to the spheres. But it should be noted that the absorptive partitioning into rubbery subdomains should not be completely ignored for CMs, nor should aggregation of smaller CMs, preventing complete access to the CM surface area, which both need further study.

The higher sorption capacities of DBP onto the IPPM, WFPM and BPFM than those for CMs can therefore be explained both by their higher surface areas and by their lower crystallinities than those of CMs. High specific surface areas could generally enhance the sorption site of the sorbent. But, importantly, lower crystallinity results in the increased amounts of amorphous, absorbing phases in the IPPM, WFPM and BPFM, which can enhance the amount sorbed per volume. There was a significant negative correlation between the sorption capacities and crystallinity of the microplastics used in this study ($r^2 = 0.98$) (Fig. S1). The fitting results of linear model demonstrated that DBP sorption onto PE microplastics was absorptive partitioning dominated. Moreover, the FTIR analysis showed that the peaks of surface functional groups of the PE microplastics did not shift after sorption of DBP, which indicated the DBP molecules do not bind to the surface functional groups of microplastics. Thus, absorptive partitioning plays a key role in the sorption of organic pollutants by PE-film based microplastics in the environment, consistent with findings elsewhere for thin plastic, semi-crystalline films (Endo et al., 2011; Arp et al., 2015). Previous studies have also indicated that absorption of the inner amorphous phase is significantly stronger than that of the crystalline phase (Xing and Pignatello, 1997; Arp et al., 2015).

The commercial microspheres showed different morphology and crystallinity from those of the film based microplastics, even though they were made of the same original material (PE) and have the same particle size. Consequently, the commercial microspheres showed significant different sorption capacities for DBP from those of the film based microplastics. To mimic the environmental behavior of PE film based microplastics, commercial microspheres are likely not the most representative ones, since they show different morphology and crystallinity. It is important to select the appropriate morphology and crystallinity of microplastics when simulating environmental behaviors of

microplastics in the laboratory, as well in terms of how such work is taken into exposure and risk studies.

4. Conclusion

The particle size of PE microplastics is an indecisive factor affecting their sorption for DBP, but the morphology and the crystallinity of PE microplastics is important in determining their sorption capacities. The sorption capacities of DBP onto CMs were significantly lower than those onto IPPM, WPFM and BPFM. Therefore, this study suggests that commercial microspheres do not reflect the sorption behavior of secondary PE microplastics. It further suggests that studies on PAEs and plastics in the environment should account for the crystallinity of PAE-containing plastic, as this will have an important impact on exposure and risk assessments. As PAEs are generally added as plasticizers to PE, to make it more rubbery and therefore more amorphous, future work should look at how the desorption of additive PAEs affects the crystallinity and sorption behavior. Future work could also be done on the effect of crystallinity of other polymer types, as well as additional morphologies of commonly occurring microplastics, such as fibers.

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.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2021.117393.

Credit author contribution statement

Shi Yao: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Writing – original draft. **Huihui Cao:** Data curation, Formal analysis. **Hans Peter H. Arp:** Conceptualization, Formal Analysis, Writing – review & editing, Funding acquisition. **Jia Li:** Investigation, Writing – review & editing, Funding acquisition. **Yongrong Bian:** Methodology. **Zubin Xie:** Writing – review & editing. **Francesco Cherubini:** Writing – review & editing. **Xin Jiang:** Funding acquisition, Resources, Project administration, Supervision. **Yang Song:** Investigation, Visualization, Writing – review & editing, Funding

acquisition, Resources, Supervision.

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