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### Adsorption of phenanthrene and its monohydroxy derivatives on polyvinyl chloride microplastics in aqueous solution: Model fitting and mechanism analysis

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#### HIGHLIGHTS

- Adsorption of OHPs on PVC was first investigated compared to PHE.
- The adsorption efficiency of PHE on PVC was higher than that of either of OHPs.
- Kinetics, isotherm and thermodynamics were clarified for PHE/OHPs adsorption on PVC.
- Hydrophobic interaction could be critical for PHE/OHPs adsorption on PVC.

#### GRAPHICAL ABSTRACT



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#### ABSTRACT

The pervasiveness of microplastics, which can absorb pollutants, has a certain impact on pollutant migration in natural waters. Differences in functional groups, such as the hydroxyl group, of pollutants will affect their adsorption on microplastics. In this study, the adsorption of phenanthrene (PHE) or its monohydroxy derivatives, including 1-hydroxyphenanthrene (1-OHP), 2-hydroxyphenanthrene (2-OHP), 4-hydroxyphenanthrene (4-OHP), and 9-hydroxyphenanthrene (9-OHP), on polyvinyl chloride (PVC, measured mean particle size = 134  $\mu$ m) microplastics was studied. The adsorption efficiency of PHE was shown to be higher than that of either of OHPs. A better fit for pseudo-second-order and Freundlich isotherm models was obtained, indicating different binding sites on the surface of PVC microplastics. The adsorption processes of PHE and OHPs on PVC microplastics were demonstrated to be exothermic and spontaneous. Combined with FT-IR analysis, theoretical calculation, and comparative adsorption of PHE/OHPs on PVC microplastics. These findings indicate the influence of the hydroxyl group on adsorption and improve the understanding of interactions between PVC microplastics and PHE/OHPs.

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#### 1. Introduction

In recent years, plastic production has increased dramatically worldwide, with an annual production of more than 320 million metric tons (Plastics Europe, 2019). A previous study showed that plastic waste was generated up to 275 million metric tons in 192 coastal countries in 2010, with 4.8 to 12.7 million metric tons reaching the marine environment (Jambeck et al., 2015). Under natural effects such as solar radiation and wave slap (Wu et al., 2019), large plastics are fragmented into small plastic debris, which will be defined as microplastics if the diameter is less than 5 mm (Arthur et al., 2009). In addition, disposal of microplastics from personal care products to the aquatic environment is another pollutant source, accounting for 0.1% of the overall emissions in Denmark (Duis and Coors, 2016). Microplastics have been detected in surface water from the eight major river outlets of the Pearl River Delta, with the number and mass concentrations of 0.005-0.7 particles m<sup>-3</sup> and 0.004–1.28 mg m<sup>-3</sup> (Mai et al., 2019). Under laboratory experiments, microplastics were reported to cause adverse effects on organisms (e.g., Daphnia magna) via ingestion (Rist et al., 2017). Therefore, microplastic pollution has become an urgent environmental problem in the world.

Due to their hydrophobic surface, microplastics can adsorb a variety of pollutants (Alimi et al., 2018), such as polycyclic aromatic hydrocarbons (PAHs) (Tang et al., 2018), polychlorinated biphenyls (PCBs) (Pascall et al., 2005), organochlorine pesticides (OCPs) (Mizukawa et al., 2013), and heavy metals (Holmes et al., 2012). Microplastics are thus considered a vector for transporting pollutants into the environment (Brennecke et al., 2016). Under laboratory conditions, the impacts of environmental variables, including salinity, pH, humic acid, and fulvic acid, on the adsorption behaviors of pollutants on microplastics have been documented (Dong et al., 2019; Guo et al., 2019; Xu et al., 2018). For example, the adsorption capacity of sulfamethoxazole on polyvinyl chloride (PVC) microplastics decreased with the increasing pH and salinity in the solution (Guo et al., 2019). Wu et al. (2019) indicated a positive effect of hydrophobic interactions on bisphenols adsorption on PVC microplastics (Wu et al., 2019); however, the report regarding the interaction mechanisms in the PVC-pollutant system by theoretical calculation techniques, such as density functional theory (DFT), is quite limited (Liu et al., 2019a).

PAHs are one of the persistent organic pollutants (POPs) and have received global attention during the past half-century. In China, the concentrations of PAHs in the dissolved phase were  $15.1-72,400 \text{ ng L}^{-1}$  for surface water and 19.8–10,984 ng  $L^{-1}$  for seawater, respectively (Han and Currell, 2017). Hydroxylated polycyclic aromatic hydrocarbons (OH-PAHs) are generated by the chemical or biological conversion of PAHs in the seawater, atmosphere, and soil (Eriksson et al., 2000; Halsall et al., 2001; Yao et al., 1998). OH-PAHs were detected in seawater from the Tokyo Bay and Kashima Bay of Japan, with the maximum concentrations of up to ng  $L^{-1}$  levels (Itoh et al., 2005). The coexistence of PAH (or OH-PAH) and microplastics in the aquatic environment will cause the generation of adsorption complexes, resulting in the increasing migration capacity (Teuten et al., 2007) and toxicity (Oliveira et al., 2013). A trophic food chain experiment showed that food-borne microplastic-associated benzo[a]pyrene may transfer to Artemia nauplii and further to zebrafish (Batel et al., 2016). PAHs were reported to be adsorbed by microplastics (Teuten et al., 2007), while there is no research about the adsorption of OH-PAHs on microplastics. The effect of functional groups such as hydroxyl groups on the adsorption capacity is poorly understood.

PVC is one of the most commonly used plastics and thereby was frequently found in the aquatic environment. Munier and Bendell (2018) identified PVC as the most abundant plastic debris, accounting for 27% of all samples collected from urban intertidal regions in Canada (Munier and Bendell, 2018); this suggests that PVC may have a great impact on the aquatic environment. Based on the commercial availability and environmental persistence, phenanthrene (PHE) and its monohydroxy derivatives, including 1-hydroxyphenanthrene (1-OHP), 2-hydroxyphenanthrene (2-OHP), 4-hydroxyphenanthrene (4-OHP), and 9-hydroxyphenanthrene (9-OHP), were chosen as the target compounds. Therefore, the aims of this study were to (1) investigate the adsorption behaviors of PHE and its monohydroxy derivatives on PVC by the traditional models of adsorption kinetics, isotherms and thermo-dynamics and (2) clarify the interaction mechanisms between PVC and PHE or its monohydroxy derivatives by the experimental and theoretical studies.

#### 2. Material and methods

#### 2.1. Chemicals and reagents

Polyvinyl chloride (PVC) particles were purchased from Aladdin (Shanghai, China), with a labeled particle size of 140 µm in diameter. Phenanthrene (PHE, 99%) and its monohydroxy derivatives (OHPs), including 1-hydroxyphenanthrene (1-OHP, 98%), 2-hydroxyphenanthrene (2-OHP, 98%), 4-hydroxyphenanthrene (4-OHP, 99.5%), 9-hydroxyphenanthrene (9-OHP, 98%), were obtained from Dr. Ehrenstorfer (Augsburg, Germany). Individual stock solutions of PHE and OHPs were prepared in methanol or acetone at a concentration of 50 mg L<sup>-1</sup>, kept at 4 °C, and diluted to the required concentrations in ultrapure water prior to the adsorption experiment. The basic information of PVC and target analytes is given in Table S1. Methanol and dichloromethane with HPLC grade were supplied by CNW Technologies (Dusseldorf, Germany), while other chemicals and reagents were analytical grades. Ultrapure water ( $\geq$ 18.25 MΩ•cm) was acquired from a NIKO water purification system (Chongqing, China).

#### 2.2. Characterization of PVC microplastics

The morphology and particle size of commercial PVC particles were measured by a Hitachi S-4800 field emission scanning electron microscopy (SEM) (Hitachi Ltd., Japan) with 1- and 5-kV accelerating voltage and 7400- and 9800-nA emission current. The XRD pattern was characterized by a Bruker D8 advance X-ray diffractometer (Bruker Daltonics, Germany) with a tube voltage of 40 kV, a current of 40 mA, and a scanned angle range of  $10^{\circ}$ - $80^{\circ}$  ( $2\theta$ ) at room temperature. Brunner-Emmet-Teller (BET) specific surface area was determined by nitrogen physisorption on a Quantachrome Instruments Quadrasorb SI surface area and pore size analyzer (ASAP2460), after degassing at 110 °C for 12 h. Fourier transform infrared spectra (FT-IR) were recorded on a Thermo Fisher Nicolet 6700 spectrometer (Thermo Fisher Scientific Inc., USA) to analyze the functional groups of PVC microplastics before and after batch adsorption experiments.

#### 2.3. Batch adsorption experiments

Batch adsorption experiments of PHE or OHPs on PVC were conducted in 250 mL amber glass conical flasks with screw caps to avoid solution evaporation. The flask containing 100 mL solution was placed on a thermostatic oscillator with a shaking speed of 150 rpm at 25 °C for 60 h to reach an adsorption equilibrium. The dosages of PVC (0.25, 0.5, 1, 1.5, and 2 g), the initial levels of PHE or OHPs (0.2, 0.5, 1, 1.5, and 2.5 mg  $L^{-1}$ ), and the adsorption equilibrium time were optimized. Since our study focused on the adsorption mechanism between microplastics and hydrophobic pollutants, we set a higher initial level of target analytes, which is in keeping with a previous study (Liu et al., 2020), than the environmentally relevant concentration for more precise determination. Adsorption kinetic experiments were carried out by collecting samples at 0, 0.5, 1, 3, 6, 12, 24, 36, 48, and 60 h. Adsorption isotherm experiments were investigated under the solution temperatures of 25 °C (298.15 K), 35 °C (308.15 K), and 45 °C (318.15 K) with PHE (or OHPs) concentrations ranging from 0.2 to 2.5 mg  $L^{-1}$  (0.2, 0.5, 1, 1.5, 2.5 mg  $L^{-1}$ ). To study the effect of pH, the aqueous pH values

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were adjusted to 3, 7, and 11. To investigate the effect of natural water, the simulated seawater was prepared as the background solution based on a previous standard (ASTM, 2003). To verify the positive effect of hydrophobic interaction, adsorption of PHE on polystyrene (PS, ca. 140 µm in diameter) was conducted under the same experimental conditions to those of PVC. For the analysis of PHE (or OHPs) at a certain time, 3 mL of suspension was sampled, passed through a 0.22 µm syringe filter, and measured at the maximum absorption wavelength of each analyte (Table S2) by a MAPADA UV-3200 Spectrophotometer (Shanghai Mapada Instruments Co. Ltd., China). The UV absorbance spectra and the calibration curve of each analyte are shown in Figs. S1a-1b and Table S2. UV and high performance liquid chromatography equipped with a diode array detector (HPLC-DAD) have been reported to determine PHE or OHPs (Wang et al., 2019; Wu et al., 2020). In this study, we used UV as the analysis tool because it is readily available in the laboratory and good at accurately quantitating an individual chemical. A comparative study was conducted and found that the results from UV were comparable to those of HPLC-DAD (Fig. S1c), indicating the UV method was robust. All adsorption experiments were conducted in triplicate and with microplastic-free controls to clarify whether the degradation of PHE/OHPs occurs or not. Each target analyte, including PHE or OHPs, was found to be stable in the microplastic-free controls (Fig. S2a), indicating no significant influence of hydrolysis or biodegradation on the adsorption of PHE or OHPs on PVC microplastics. The measured data were fitted with the models of adsorption kinetics, isotherms, and thermodynamics. Detailed information on model fitting can be referred to Text S1. All data analysis was performed using Origin software for windows.

#### 2.4. Theoretical calculations

Density functional theory (DFT) as a powerful tool was applied to explore the interaction between PVC and PHE (or OHPs) in this study (Liu et al., 2019a; Wan et al., 2019). Based on the plane-wave basis and periodic boundary conditions, the theoretical calculation was performed on a Vienna Ab-initio Simulation Package (VASP) (Kresse and Furthmüller, 1996). The geometry and energy of PVC and adsorbates (PHE or OHPs) were optimized in a single box. Detailed procedures of theoretical calculations are provided in Text S2. In brief, PVC and each adsorbate were optimized and calculated individually (Table S3), after which the optimized PVC and each adsorbate were assembled as an adsorbent: adsorbate complex according to the optimum combination condition. The complex was then optimized and calculated (Table S4). Finally, the binding energy ( $\Delta E$ ) can be calculated by Eq. 1:

$$\Delta E = E_{Complex} - E_{PVC} - E_{Adsorbate} \tag{1}$$

where  $E_{Complex}$ ,  $E_{PVC}$ , and  $E_{Adsorbate}$  are the total DFT-D energies of the complex between PVC and adsorbates (PHE or OHPs), PVC, and adsorbates (PHE or OHPs), respectively. The lower values of binding energy indicate the stronger interaction force between PVC and adsorbates (Table S5).

#### 3. Results and discussion

#### 3.1. Characterization of PVC microplastics

The characterization of PVC was tested by SEM, XRD, BET, and FT-IR. PVC microplastics were found to have an irregular grain shape, rough surface morphology, porous internal structure with many folds (Figs. 1a-b), which is similar to the results of Dong et al. (2019) (Dong et al., 2019). The particle sizes of PVC were confirmed in the range of  $80-210 \mu$ m, with a mean value of  $134 \mu$ m (Fig. 1c). The measured mean particle size was almost equal to the labeled value of  $140 \mu$ m, indicating their microscale diameters. Based on the XRD pattern (Fig. 1d), the poor crystallinity of PVC microplastics can be seen following a

previous study (Wang et al., 2015). At the temperature of -196 °C (77.15 K), the pore diameter distribution and specific surface area of PVC were quantitatively measured by nitrogen adsorption isotherm (Fig. 1e). The nitrogen adsorption isotherm of PVC exhibited type III isotherm, which was the typical characteristics of weak adsorbateadsorbent interactions and porous adsorbents (Sangwichien et al., 2002). A type H3 hysteresis loop can be found between adsorption and desorption branches (Fig. 1e), indicating that the PVC microplastics were the typical mesoporous material consisting of slit-shaped capillaries. Based on the Brunauer-Emmett-Teller (BET) (Brunauer et al., 1938) and Barrett-Joyner-Halenda (BJH) (Barrett et al., 1951) methods, the specific surface area of PVC was 0.595  $m^2 g^{-1}$ , and the pore size had a wide distribution range between 2 and 50 nm. The leading adsorption bands of PVC microplastics in the FT-IR spectrum are shown in Fig. 1f. The characteristic peaks were assigned to the stretching vibration of O—H of water at  $3405 \text{ cm}^{-1}$ , symmetric stretching vibration of  $-CH_2$ at 2844 cm<sup>-1</sup>, deformation vibration of Cl–CH<sub>2</sub> at 1434 cm<sup>-1</sup>, out-ofplane deformation vibration of Cl-CH at 1254 cm<sup>-1</sup>, and stretching vibration of C—Cl at 691  $\text{cm}^{-1}$  (Table S6). These bands are mostly similar to the data from a previous literature for PVC (Coltro et al., 2013).

#### 3.2. Adsorption models of PHE or OHPs on PVC microplastics

It is well known that the adsorbent amount has great impacts on adsorption capacities towards organic chemicals (Wang et al., 2019). Before the investigation of adsorption models, a preliminary experiment about the adsorption efficiency of PHE or OHPs on different dosages of PVC microplastics should be conducted to establish an optimum PVC dosage. The adsorption efficiencies of all chemicals raised with the increasing PVC dosages from 0 to 1.5 g and almost reached equilibrium when the PVC dosage was higher than 1.5 g (Fig. S2b). The increasing trend can be explained by the supplementation of adsorption sites from the substantial addition of PVC microplastics, while the equilibrium occurred after 1.5 g of PVC dosages due to enough adsorption sites for the certain amounts of adsorbates (Wu et al., 2019). We also optimized the initial concentration of OHPs. The adsorption efficiencies were similar from 0.2 to 1.5 mg  $L^{-1}$  so that 1.5 mg  $\bar{L}^{-1}$  was chosen (Fig. S2c) since the absorbance values of all target analytes were within the sensitive detection range from 0.2 to 0.6. At last, the equilibrium time was optimized. The adsorption curve raised from 0 to 24 h and then almost flattened (Fig. S2d). Accordingly, the optimum PVC dosage, initial analyte concentration, and equilibrium time were set to 1.5 g, 1.5 mg  $L^{-1}$ , and 24 h, and then used for subsequent adsorption experiments.

#### 3.2.1. Adsorption kinetics models

Adsorption kinetic models can be used to describe the chemical adsorption rate and mechanism during adsorption processes by pseudofirst-order and pseudo-second-order mathematical models (Balouch et al., 2013; Ho and McKay, 1999). If the pseudo-first-order and pseudo-second-order mathematical models are not enough to explain the complicated adsorption mechanism, the dynamic models, including intraparticle diffusion and liquid film diffusion, can be used for supplementary interpretation (Zhou et al., 2017).

As shown in Fig. 2 and Table S7, the adsorption kinetics were better fitted by pseudo-second-order models ( $R^2 = 0.996-0.999$ ) than pseudo-first-order models ( $R^2 = 0.852-0.963$ ). As we know, the 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  $R^2$  values of each analyte by pseudo-second-order models were quite close to 1.000, indicating that PHE or OHPs can be adsorbed to different binding sites in PVC microplastics, while the calculated maximum adsorption capacity ( $q_{e,cal}$ ) values of each analyte from pseudo-second-order models were closer to the experimental

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Fig. 1. SEM images of PVC microplastics at different scales (a and b); the particle size distribution plot of PVC microplastics (c); the XRD pattern of PVC microplastics (d); the nitrogen adsorption-desorption isotherm and pore size distribution curve (the insert) of PVC microplastics (e); the FT-IR spectrum of PVC microplastics (f).

maximum adsorption capacity ( $q_{e,exp}$ ) values than those fitting by pseudo-first-order models. Previous studies showed that the adsorption of organic pollutants, including bisphenol analogs, musks, and antibiotics, on PVC microplastics yielded a better fit for pseudo-secondorder models, with the R<sup>2</sup> value >0.99 (Dong et al., 2019; Guo et al., 2019; Wu et al., 2019). In addition, the R<sup>2</sup> values of each analyte from intraparticle diffusion and liquid film diffusion models were lower than those of the pseudo-second-order model (Table S7), suggesting that the rate-limiting process was not completely controlled but probably affected by intraparticle diffusion. The three-stage linear plots in Fig. 2c also reveal the importance of external mass transfer between the solid and liquid phase and adsorption/desorption dynamic equilibrium processes for the adsorption of PHE or OHPs on PVC microplastics (Olu-Owolabi et al., 2014).

#### 3.2.2. Adsorption isotherm models

Adsorption isotherm models are generally used to describe the interaction behavior between adsorbents and adsorbates when the adsorption equilibrium occurs. Fig. 3 shows the fitting curves of five analyte adsorption by PVC microplastics based on Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich isotherm models, while Table S8 summaries the calculated parameters of isotherm models. The Langmuir and Freundlich isotherm models represent that the adsorption occurs on the surface of the adsorbent with uniform and uneven



**Fig. 2.** Adsorption kinetics of PHE/OHPs on PVC microplastics fitted by the (a) pseudo-first-order, (b) pseudo-second-order, (c) intraparticle diffusion, and (d) film diffusion models. Adsorption experiments were performed on a thermostatic oscillator with a shaking speed of 150 rpm at 25 °C, with the conditions of [PVC] = 1.5 g and [Adsorbate]<sub>initial</sub> = 1.5 mg L<sup>-1</sup>.



**Fig. 3.** Adsorption isotherm of PHE/OHPs on PVC microplastics fitted by the (a) Langmuir, (b) Freundlich, (c) Temkin, and (d) Dubinin-Radushkevich models. Adsorption experiments were performed on a thermostatic oscillator with a shaking speed of 150 rpm at 25 °C, with the conditions of [PVC] = 1.5 g, [Adsorbate]<sub>initial</sub> = 0.2, 0.5, 1, 1.5, and 2.5 mg L<sup>-1</sup>, and  $t_{equilibrium} = 24$  h.

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distribution of binding sites, respectively (Xu and Li, 2010). Most adsorption studies preferred to use both of the above isotherm models for data fitting. For example, Huffer and Hofmann (2016) demonstrated that, based on the R<sup>2</sup> values, Freundlich models were more suitable than Langmuir models for the fitting of adsorption isotherms of seven nonpolar organic compounds (e.g., alkanes, benzene, and its derivatives) on PVC microplastics(Huffer and Hofmann, 2016). In this study, the R<sup>2</sup> values of most analytes for Freundlich models (0.904-0.988) were higher than those of Langmuir models (0.791-0.929), indicating the adsorption to heterogeneous surfaces or surfaces supporting sites of diverse affinities (Vijayaraghavan et al., 2006). A similar phenomenon was also observed for the adsorption of organophosphate esters (Chen et al., 2019) and bisphenol analogs (Wu et al., 2019) on PVC microplastics. The slope of the Freundlich model (1/n) is used to determine whether the adsorption is favorable for adsorbates or not (McKay et al., 1982). The obtained *n* values were higher than one (n > 1) (Table S8), suggesting that increasing PHE or OHP amounts in the solution will enhance the adsorption. However, both the Langmuir and Freundlich models were unable to describe the data well for PHE, when compared to the other models, including Temkin and Dubinin-Radushkevich isotherm models (Table S8). These findings suggest that (1) the adsorption heat may decrease linearly with coverage, and (2) the PVC microplastics have a porous structure (Vijayaraghavan et al., 2006), which is in accordance with the results of nitrogen adsorption/desorption isotherms in this study.

#### 3.2.3. Adsorption thermodynamic models

Three different temperatures, including 25, 35, and 45 °C (298.15, 308.15, and 318.15 K), were set to clarify the effect of temperatures on adsorption capacities. A thermodynamic model was further used to explore whether the adsorption process was exothermic/automatic or not. As shown in Table 1, the obtained  $\Delta H$  values ranged from -10.472 to -8.455 kJ mol<sup>-1</sup>. The  $\Delta H$  values lower than zero indicate the exothermic nature of PHE or OHPs on PVC microplastics. In addition, all analytes had negative  $\Delta G$  values, suggesting the adsorption process was spontaneous without external energy when the temperatures were in the range of 25-45 °C (298.15-318.15 K). The results also show that the adsorption capacities of PHE monohydroxy derivatives decreased with the increasing temperature (Fig. S3). A similar trend was observed for the adsorption of most organic pollutants on microplastics under different temperatures (Chen et al., 2019; Dong et al., 2019). It may be attributed to the fracture of hydrogen bond (Li et al., 2013) or the reduction of van der Waals force (Gusso and Burnham, 2016) when the temperature increased. On the contrary, the adsorption capacity of PHE increased with the increasing temperature (Fig. S3). It is well known that the temperature increases, the more potent hydrophobic force occurs, implying that hydrophobic interaction played an essential role in the PHE adsorption on PVC microplastics.

#### 3.3. Adsorption mechanisms of PHE or OHPs on PVC microplastics

The interaction mechanism of PHE/OHPs and PVC microplastics was investigated by FT-IR analysis, theoretical calculation, and adsorption experiments by different pH, background solution, and microplastics.

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As shown by the FT-IR spectra in Fig. S4, no apparent change in the bands of PVC microplastics after PHE or OHPs adsorption can be seen. These findings indicate that the adsorption of PHE/OHPs on PVC microplastics did not rely on chemical adsorption such as covalent, ionic, and metallic bonding, but the impacts of hydrophobic interaction (Pan et al., 2008), electrostatic force (Sun et al., 2017), hydrogen bonding (Li et al., 2012) or halogen bonding (Wang et al., 2007) should be concerned.

Based on the Log K<sub>ow</sub> values (Table S1), PHE is shown to be more hydrophobic than OHPs. Combined with the results of higher adsorption efficiencies of PHE on PVC microplastics, we can conclude that the hydrophobic interaction played a vital role during the adsorption process between PHE/OHPs and PVC microplastics. For the hydrophobic pollutants such as tylosin, the adsorption procedure on polyethylene (PE), polypropylene (PP), polystyrene (PS), or PVC microplastics was proven to be dominated by hydrophobic interaction (Guo et al., 2018). The electrostatic force is another interaction based on the physicochemical property of pollutants. The difference of chemical structure between PHE and OHPs is the hydroxyl group, leading to their different  $pK_a$ value (Table S1). The chemicals are mostly found in the neutral form when the solution pH is lower than its  $pK_a$ ; otherwise, the deprotonated form of chemicals will dominate in the solution. The solution pH values of adsorption experiments maintained at about 7.8, which were lower than the pK<sub>a</sub> of PHE (> 15) and OHPs (9.40–9.77), suggesting the neutral form was the dominant species in the solution. Since the  $pK_a$  values of OHPs were close to the solution pH value, it can be expected that OHPs will be partially deprotonated and existed as anions. As reported by Wu et al. (2019), the point of zero charge of PVC microplastics was reported to be 3.41 (Wu et al., 2019), revealing positive or negative charges on the surface of PVC microplastics under the condition of pH < 3.41 or > 3.41, respectively. In this case, electrostatic repulsion should be considered and could be one of the mechanisms that suppressed the adsorption of OHPs on PVC microplastics. Besides, the effects of pH values were evaluated. The adsorption efficiency of PHE was similar in different aqueous pH values (pH = 3, 7, and 11), while that of 4-OHP was lower in pH = 11 than pH = 3 or 7 (Fig. S5). The difference can be attributed to electrostatic repulsion (Guo et al., 2019), which is associated with the hydroxyl group, between the negative charges on the surface of PVC microplastics and the dominant deprotonated form of 4-OHP under the condition of pH = 11. To investigate the real environmental situation, the simulated seawater was used as the background solution. Guo et al. (2019) indicated that the salinity of background solutions inhibited sulfamethoxazole adsorption on PVC (Guo et al., 2019). In keeping with this earlier report, the absorption efficiency of PHE or 4-OHP seemed to decrease in simulate seawater compared to ultrapure water (Fig. S5). Since the surface of PVC microplastics is negatively charged, in simulated seawater, the more cation will bind to the surface of microplastics by electrostatic attraction (Liu et al., 2020); this competition for adsorption sites will lead to the reduction in the adsorption of PHE or 4-OHP on PVC microplastics. These results are beneficial to understand the environmental behavior of PVC microplastics, which could increase the accumulation of a chemical in fish tissues (Sheng et al., 2021) and slow down the degradation of a chemical in natural waters (Chen et al., 2020).

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The measured parameters of The and oth s by adoorption diethodynamic models
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	$\ln k_{\rm c}$ (µg L <sup>-1</sup> )			$\Delta G$ (kJ mol <sup>-1</sup> )		$\Delta H$ (kJ mol <sup>-1</sup> )	$\Delta S$ (kJ mol <sup>-1</sup> )		
	25 °C	35 °C	45 °C	25 °C	35 °C	45 °C			
1-OHP	4.270	4.460	4.516	-10.579	-11.421	-11.939	-9.953	-0.680	
2-OHP	4.430	4.402	5.636	-10.975	-11.272	-14.903	-8.455	-1.964	
4-OHP	3.975	4.245	4.247	-9.849	-10.872	-11.228	-9.290	-0.690	
9-OHP	4.332	4.400	4.515	-10.735	-11.267	-11.939	-10.109	-0.602	
PHE	4.250	4.223	4.070	-10.530	-10.814	-10.760	-10.472	-0.115	
PHE	4.250	4.223	4.070	-10.530	-10.814	-10.760	-10.472	-0.115	

<sup>a</sup> Adsorption experiments were performed on a thermostatic oscillator with a shaking speed of 150 rpm at different solution temperatures, with the conditions of [PVC] = 1.5 g, [Adsorbate]<sub>initial</sub> = 1.5 mg L<sup>-1</sup>, and  $t_{equilibrium} = 24$  h.

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#### Table 2

The calculated total DFT-D energy of different interaction models between PHE/1-OHP and PVC.



A calculation study based on density functional theory (DFT) was used to explore the interaction, including hydrogen bonding and halogen bonding, between PHE/OHPs and PVC microplastics. Table 2 shows the total DFT-D energy of the complex of PVC and PHE or 1-OHP with different interaction modes. As we know, the lower the interaction energy is, the more stable affinity can be obtained. For the combination of PHE and PVC, model-III was the most stable interaction mode, indicating that CH/ $\pi$  interaction is a weak hydrogen bonding that the alkyl group (-CH) donates its protons to the delocalized aromatic rings (Li et al., 2012). In addition, the interaction energy of model-II or -IV. These findings suggest that halogen bonding was generated between the halogen atoms and delocalized aromatic rings (Wang et al., 2007). However, halogen bonding may only play a minor role in the adsorption due to the higher interaction energy of model-I between PVC and 1-OHP (Table 2). Likewise, the lower interaction energy of model-III or -IV reveals the affinity of the hydroxyl group of OHPs to the alkyl group or chlorine atom. Based on the optimization of combination calculation, the optimized PVC and PHE or OHPs were assembled as a complex according to the optimum combination condition. As can be seen from Fig. 4, the binding energy between PVC and PHE/OHPs followed the order as PHE < 4-OHP < 9-OHP < 1-OHP < 2-OHP, which is in accordance with the result of adsorption efficiency experiments (Fig. S2d), implying that the theoretical calculation used in this study was reliable. These findings reveal that the hydroxyl-substituted



Fig. 4. Total DFT-D energy of each PHE/OHPs (Left side) and binding energy of interaction complexes of PVC: PHE/OHPs (Right side).

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position on phenanthrene would lead to different adsorption efficiencies. However, the mechanism of hydroxyl substituent effects is ambiguous and needs to be clarified in the future.

In order to further verify that hydrophobic interaction was the most crucial factor affecting the adsorption of PHE/OHPs on PVC microplastics, a comparative study regarding the adsorption efficiency of PHE on PVC or PS microplastics was conducted under the same experimental conditions. The results reveal that the PS microplastics had a higher adsorption capacity for PHE than the PVC microplastics (Fig. S6). It is consistent with the results of an earlier report (Wang and Wang, 2018) and can be explained by the benzene ring of PS, facilitating PHE adsorption on microplastics. Another study showed that the adsorption ability of 17<sup>β</sup>-estradiol on microplastics followed the order of PS > PVC, and hydrophobic partition was the dominant adsorption mechanism (Liu et al., 2019b). Our findings not only prove the significant impact of hydrophobic interaction on the adsorption process but also suggest that  $\pi$ - $\pi$  stacking interaction should be considered for benzene-containing microplastics, which could cause higher adsorption of hydrophobic pollutants.

#### 4. Conclusions and perspectives

The present study investigated the adsorption behavior and mechanism of phenanthrene (PHE) and its monohydroxy derivatives (OHPs) on polyvinyl chloride (PVC) microplastics. PHE was shown to have a better adsorption efficiency than OHPs, suggesting that the hydroxyl group could inhibit the adsorption of a chemical on PVC microplastics. The adsorption of most target analytes on PVC microplastics was well fitted with pseudo-second-order and Freundlich isotherm models and proved to be exothermic and spontaneous. Through FT-IR analysis, theoretical calculation, and comparative adsorption experiments, hydrophobic interaction played a vital role during the adsorption process. In contrast, electrostatic repulsion,  $CH/\pi$  interaction, and halogen bonding were the other mechanisms, to a certain extent, affecting the adsorption of PHE/OHPs on PVC microplastics. Our results have implications on the influence of PVC microplastics in natural waters, which will increase the complexity of the environmental behavior of organic pollutants. Further investigations regarding how hydrophobic pollutants release from microplastics under different environmental conditions should be concerned.

#### **CRediT** authorship contribution statement

ZZ Bao, ZF Chen and ZW Cai designed the experiments. ZZ Bao and YH Zhong performed the characterizations. ZZ Bao and GZ Wang performed the density functional theory calculations. ZZ Bao performed the adsorption experiments. ZZ Bao and ZH Qi analyzed all data. ZZ Bao, ZF Chen and ZW Cai wrote the paper. All authors discussed and commented on the manuscript.

#### **Declaration of competing interest**

The authors declare no competing financial interest.

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#### Appendix A. Supplementary data

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#### References

- Alimi, O.S., Farner Budarz, J., Hernandez, L.M., Tufenkji, N., 2018. Microplastics and nanoplastics in aquatic environments: aggregation, deposition, and enhanced contaminant transport. Environ. Sci. Technol. 52 (4), 1704–1724.
- Arthur, C., Baker, J., Bamford, H., 2009. Proceedings of the international research workshop on the occurrence, effects and fate of microplastic marine debris. NOAA. NOAA Technical Memorandum NOS-OR & R-30. Silver Spring, p. 530 (September 9–11,2008).
- ASTM, 2003. ASTM D1141–1998: Standard Practice for the Preparation of Substitute Ocean Water. ASTM International, West Conshohocken, PA, USA https://www.astm. org/DATABASE.CART/HISTORICAL/D1141-98R03.htm.
- Balouch, A., Kolachi, M., Talpur, F.N., Khan, H., Bhanger, M.I., 2013. Sorption kinetics, isotherm and thermodynamic modeling of defluoridation of ground water using natural adsorbents. Am. J. Anal. Chem. 04 (05), 221–228.
- Barrett, E.P., Joyner, L.G., Halenda, P.P., 1951. The determination of pore volume and area distributions in porous substances. I. Computations from nitrogen isotherms. J. Am. Chem. Soc. 73 (1), 373–380.
- Batel, A., Linti, F., Scherer, M., Erdinger, L., Braunbeck, T., 2016. Transfer of benzo[a]pyrene from microplastics to Artemia nauplii and further to zebrafish via a trophic food web experiment: CYP1A induction and visual tracking of persistent organic pollutants. Environ. Toxicol. Chem. 35 (7), 1656–1666.
- Brennecke, D.B., Duarte, B., Paiva, F., Cacador, I., Canning-Clode, J., 2016. Microplastics as vector for heavy metal contamination from the marine environment. Estuar. Coast. Shelf S. 178, 189–195.
- Brunauer, S., Emmett, P.H., Teller, E., 1938. Adsorption of gases in multimolecular layers. J. Am. Chem. Soc. 60 (2), 309–319.
- Chen, S., Tan, Z., Qi, Y., Ouyang, C., 2019. Sorption of tri-n-butyl phosphate and tris(2chloroethyl) phosphate on polyethylene and polyvinyl chloride microplastics in seawater. Mar. Pollut. Bull. 149, 110490.
- Chen, C., Chen, L., Li, Y., Fu, W., Shi, X., Duan, J., Zhang, W., 2020. Impacts of microplastics on organotins' photodegradation in aquatic environments. Environ. Pollut. 267, 115686.
- Coltro, L., Pitta, J.B., Madaleno, E., 2013. Performance evaluation of new plasticizers for stretch PVC films. Polym. Test. 32 (2), 272–278.
- Dong, X., Zheng, M., Qu, L., Shi, L., Wang, L., Zhang, Y., Liu, X., Qiu, Y., Zhu, H., 2019. Sorption of tonalide, musk xylene, galaxolide, and musk ketone by microplastics of polyethylene and polyvinyl chloride. Mar. Pollut. Bull. 144, 129–133.
- Duis, K., Coors, A., 2016. Microplastics in the aquatic and terrestrial environment: sources (with a specific focus on personal care products), fate and effects. Environ. Sci. Eur. 28, 2.
- Eriksson, M., Dalhammar, G., Borg-Karlson, A.-K., 2000. Biological degradation of selected hydrocarbons in an old PAH/creosote contaminated soil from a gas work site. Appl. Microbiol. Biotechnol. 53, 619–628.
- Guo, X., Pang, J., Chen, S., Jia, H., 2018. Sorption properties of tylosin on four different microplastics. Chemosphere 209, 240–245.
- Guo, X., Chen, C., Wang, J., 2019. Sorption of sulfamethoxazole onto six types of microplastics. Chemosphere 228, 300–308.
- Gusso, A., Burnham, N.A. 2016. Investigation of the range of validity of the pairwise summation method applied to the calculation of the surface roughness correction to the van der Waals force. Surf. Sci. 651, 28–40.
- Halsall, C.J., Sweetman, A.J., Barrie, L.A., Jones, K.C., 2001. Modelling the behaviour of PAHs during atmospheric transport from the UK to the Arctic. Atmos. Environ. 35 (2), 255–267.
- Han, D., Currell, M.J., 2017. Persistent organic pollutants in China's surface water systems. Sci. Total Environ. 580, 602–625.
- Ho, Y.S., McKay, G., 1999. Pseudo-second order model for sorption processes. Process Biochem. 34 (5), 451–465.
- Holmes, L.A., Turner, A., Thompson, R.C., 2012. Adsorption of trace metals to plastic resin pellets in the marine environment. Environ. Pollut. 160, 42–48.
- Huffer, T., Hofmann, T., 2016. Sorption of non-polar organic compounds by micro-sized plastic particles in aqueous solution. Environ. Pollut. 214, 194–201.
- Itoh, N., Tao, H., Ibusuki, T., 2005. Optimization of aqueous acetylation for determination of hydroxy polycyclic aromatic hydrocarbons in water by stir bar sorptive extraction and thermal desorption–gas chromatography–mass spectrometry. Anal. Chim. Acta 535 (1–2), 243–250.
- Jambeck, J.R., Geyer, R., Wilcox, C., Siegler, T.R., Perryman, M., Andrady, A., Narayan, R., Law, K.L., 2015. Plastic waste inputs from land into the ocean. Science 347 (6223), 768–771.
- Kresse, G., Furthmüller, J., 1996. Efficient iterative schemes for *ab initio* total-energy calculations using a plane-wave basis set. Phys. Rev. B 54 (16), 11169–11186.
- Li, Q., Han, C., Horton, S.R., Fuentes-Cabrera, M., Sumpter, B.G., Lu, W., Bernholc, J., Maksymovych, P., Pan, M., 2012. Supramolecular self-assembly of  $\pi$ -conjugated hydrocarbons via 2D cooperative CH/ $\pi$  interaction. ACS Nano 6 (1), 566–572.
- Li, H., Huang, G., An, C., Hu, J., Yang, S., 2013. Removal of tannin from aqueous solution by adsorption onto treated coal fly ash: kinetic, equilibrium, and thermodynamic studies. Ind. Eng. Chem. Res. 52 (45), 15923–15931.
- Liu, Y., Liu, Y., Liu, Z., Du, F., Qin, G., Li, G., Hu, X., Xu, Z., Cai, Z., 2019a. Supramolecularly imprinted polymeric solid phase microextraction coatings for synergetic recognition nitrophenols and bisphenol a. J. Hazard. Mater. 368, 358–364.
- Liu, X., Xu, J., Zhao, Y., Shi, H., Huang, C.H., 2019b. Hydrophobic sorption behaviors of 17βestradiol on environmental microplastics. Chemosphere 226, 726–735.
- Liu, Z., Qin, Q., Hu, Z., Yan, L., Ieong, U.I., Xu, Y., 2020. Adsorption of chlorophenols on polyethylene terephthalate microplastics from aqueous environments: kinetics, mechanisms and influencing factors. Environ. Pollut. 265, 114926.

#### Z.-Z. Bao, Z.-F. Chen, Y. Zhong et al.

Mai, L., You, S.N., He, H., Bao, L.J., Liu, L.Y., Zeng, E.Y., 2019. Riverine microplastic pollution in the Pearl River delta, China: are modeled estimates accurate? Environ. Sci. Technol. 53 (20), 11810–11817.

- McKay, G., Blair, H.S., Gardner, J.R., 1982. Adsorption of dyes on chitin. I. Equilibrium studies. J. Appl. Polym. Sci. 27, 3043–3057.
- Mizukawa, K., Takada, H., Ito, M., Geok, Y.B., Hosoda, J., Yamashita, R., Saha, M., Suzuki, S., Miguez, C., Frias, J., Antunes, J.C., Sobral, P., Santos, I., Micaelo, C., Ferreira, A.M., 2013. Monitoring of a wide range of organic micropollutants on the Portuguese coast using plastic resin pellets. Mar. Pollut. Bull. 70 (1), 296–302.
- 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.

Munier, B., Bendell, L.I., 2018. Macro and micro plastics sorb and desorb metals and act as a point source of trace metals to coastal ecosystems. PLoS One 13 (2), e0191759.

- Oliveira, M., Ribeiro, A., Hylland, K., Guilhermino, L., 2013. Single and combined effects of microplastics and pyrene on juveniles (0+ group) of the common goby *Pomatoschistus microps* (Teleostei, Gobiidae). Ecol. Indic. 34, 641–647.
- Olu-Owolabi, B.I., Diagboya, P.N., Adebowale, K.O., 2014. Evaluation of pyrene sorptiondesorption on tropical soils. J. Environ. Manag. 137, 1–9.
- Pan, B., Ning, P., Xing, B., 2008. Part IV-sorption of hydrophobic organic contaminants. Environ. Sci. Pollut. Res. Int. 15 (7), 554–564.
- Pascall, M.A., Zabik, M.E., Zabik, M.J., Hernandez, R.J., 2005. Uptake of polychlorinated biphenyls (PCBs) from an aqueous medium by polyethylene, polyvinyl chloride, and polystyrene films. J. Agric. Food Chem. 53 (1), 164–169.
- Plastics Europe, 2019. Plastics The Facts 2019. Plastics Europe, Brussels, Belgium https:// www.plasticseurope.org/en/newsroom/events/2019/identiplast-2019.
- Rist, S., Baun, A., Hartmann, N.B., 2017. Ingestion of micro- and nanoplastics in Daphnia magna - quantification of body burdens and assessment of feeding rates and reproduction. Environ. Pollut. 228, 398–407.
- Sangwichien, C., Aranovich, G.L., Donohue, M.D., 2002. Density functional theory predictions of adsorption isotherms with hysteresis loops. Colloid. Surface A 206 (1), 313–320.
- Sheng, C., Zhang, S., Zhang, Y., 2021. The influence of different polymer types of microplastics on adsorption, accumulation, and toxicity of triclosan in zebrafish. J. Hazard. Mater. 402, 123733.
- Sun, W., Wang, C., Pan, W., Li, S., Chen, B., 2017. Effects of natural minerals on the adsorption of 17β-estradiol and bisphenol a on graphene oxide and reduced graphene oxide. Environ. Sci. Nano 4 (6), 1377–1388.
- Tang, G., Liu, M., Zhou, Q., He, H., Chen, K., Zhang, H., Hu, J., Huang, Q., Luo, Y., Ke, H., Chen, B., Xu, X., Cai, M., 2018. Microplastics and polycyclic aromatic hydrocarbons (PAHs) in

#### Science of the Total Environment xxx (xxxx) xxx

Xiamen coastal areas: implications for anthropogenic impacts. Sci. Total Environ. 634, 811–820.

- Teuten, E.L., Rowland, S.J., Galloway, T.S., Thompson, R.C., 2007. Potential for plastics to transport hydrophobic contaminants. Environ. Sci. Technol. 41 (22), 7759–7764.
- Vijayaraghavan, K., Padmesh, T.V., Palanivelu, K., Velan, M., 2006. Biosorption of nickel(II) ions onto Sargassum wightii: application of two-parameter and three-parameter isotherm models. J. Hazard. Mater. 133 (1–3), 304–308.
- Wan, T., Lu, S., Cheng, W., Ren, J., Wang, M., Hu, B., Jia, Z., Li, Y., Sun, Y., 2019. A spectroscopic and theoretical investigation of interaction mechanisms of tetracycline and polystyrene nanospheres under different conditions. Environ. Pollut. 249, 398–405.
- 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., Ma, N., Chen, Q., Wang, W., Wang, L., 2007. Halogen bonding as a new driving force for layer-by-layer assembly. Langmuir 23 (19), 9540–9542.
- Wang, F., Shih, K.M., Li, X.Y., 2015. The partition behavior of perfluorooctanesulfonate (PFOS) and perfluorooctanesulfonamide (FOSA) on microplastics. Chemosphere 119, 841–847.
- Wang, J., Liu, X., Liu, G., Zhang, Z., Wu, H., Cui, B., Bai, J., Zhang, W., 2019. Size effect of polystyrene microplastics on sorption of phenanthrene and nitrobenzene. Ecotoxicol. Environ. Saf. 173, 331–338.
- Wu, P., Cai, Z., Jin, H., Tang, Y., 2019. Adsorption mechanisms of five bisphenol analogues on PVC microplastics. Sci. Total Environ. 650, 671–678.
- Wu, Z., Sun, Z., Liu, P., Li, Q., Yang, R., Yang, X., 2020. Competitive adsorption of naphthalene and phenanthrene on walnut shell based activated carbon and the verification via theoretical calculation. RSC Adv. 10, 10703.
- Xu, X.R., Li, X.Y., 2010. Sorption and desorption of antibiotic tetracycline on marine sediments. Chemosphere 78 (4), 430–436.
- Xu, B., Liu, F., Brookes, P.C., Xu, J., 2018. Microplastics play a minor role in tetracycline sorption in the presence of dissolved organic matter. Environ. Pollut. 240, 87–94.
- Yao, J.-J., Huang, Z.-H., Masten, S.J., 1998. The ozonation of pyrene: pathway and product identification. Water Res. 32 (10), 3001–3012.
- Zhou, Y., Liu, X., Xiang, Y., Wang, P., Zhang, J., Zhang, F., Wei, J., Luo, L., Lei, M., Tang, L., 2017. Modification of biochar derived from sawdust and its application in removal of tetracycline and copper from aqueous solution: adsorption mechanism and modelling. Bioresour. Technol. 245, 266–273.