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Influence of microplastics on the photodegradation of perfluorooctane sulfonamide (FOSA)

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ABSTRACT

PFAS (per- and polyfluoroalkyl substances) are omnipresent in the environment and their transportation and transformation have attracted increased attention. Microplastics are another potential risk substances that can serve as a carrier for ubiquitous pollutants, thus affecting the presence of PFAS in the environment. In this study, the adsorption of perfluorooctane sulfonamide (FOSA) and perfluorooctanoic acid (PFOA) on four microplastics (PE, PVC, PS, and PTFE) and their effect on the photodegradation of FOSA were studied. The adsorption capacity of FOSA by PS was the highest, in similar, PS displayed the highest adsorption capacity in the presence of PFOA. Different effects of pH and salinity on the adsorption of FOSA and PFOA were observed among different microplastics indicating inconsistent interaction mechanisms. Furthermore, FOSA could be photodegraded, with PFOA as the main product, while the presence of microplastics had a negligible effect on the degradation of this contaminant. The results indicated that microplastics could act as PFAS concentrators. Moreover, their photochemical inertias make the pollutants enriched on microplastics more resistant to degradation.

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Introduction

Per- and polyfluoroalkyl substances (PFAS) are alkyl-based materials with all or partial hydrogen atoms substituted by fluorine atoms. They have been widely used in manufactured goods and various industries, including food packaging, fire-fighting foam, surfactants, metal plating, textiles, and non-stick cookware, due to their hydrophobic and oleophobic properties and high stability (Lu et al., 2020; Zabaleta et al., 2015). In these compounds, perfluoroalkane sulfonic acids (PFASs)

and perfluoroalkyl carboxylic acids (PFCAs) have attracted an increased interest due to their toxicity, persistence, and bioaccumulation (Lindstrom et al., 2011). PFASs and PFCAs have been widely detected in various environment matrixes, including water, soil, air, wildlife, and humans (Dauchy et al., 2019; Gao et al., 2015; Liu et al., 2019; Ma et al., 2018; Pan et al., 2018; Zhao et al., 2020). Direct emission and transformation of precursors are two major ways to release PFASs and PFCAs into the environment (Ahrens and Bundschuh, 2014; Prevedouros et al., 2006). Increased efforts have been taken to limit the usage of PFAS by international and government organisations including the Stockholm Convention (United Nations Environment Program, 2009). However, there are several challenges in the control of precursors because studies and

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data about the transformation of PFAS precursor compounds are limited.

Perfluorooctanesulfonate precursors (PreFOS), known as precursors and derivatives of PFOS (Martin et al., 2010), can potentially degrade to PFOS. Perfluorooctane sulfonamide (FOSA) is a typical PreFOS and is also an intermediate formed during the transformation of other PFOS-precursors (Fu et al., 2015). It was confirmed that FOSA could transform into perfluorooctanesulfonate acid (PFOS), perfluorooctanoic acid (PFOA), and shorter chain PFCAs (Fu et al., 2015; Martin et al., 2006; Zhang et al., 2017). Our previous work described that FOSA could be degraded to PFOA and shorter PFCAs in water under visible irradiation (Lv et al., 2020). Homoionic cation montmorillonites can promote this progress by stabilising the generation of superoxide anion and hydroxyl radicals, which will participate in the degradation of FOSA (Lv et al., 2020).

Microplastics (≤ 5 mm) are ubiquitous in the environment and have attracted much attention recently (Farady, 2019; Tien et al., 2020). They could appear in the environment using two main pathways: the decomposition of large plastic and release from products for a particular use (such as personal care products, drug delivery vehicles, and electronics), called primary and secondary microplastics, respectively (Egessa et al., 2020; Tien et al., 2020). Millions of tons of plastics are produced yearly, and a large proportion of them are used as packages (Wright and Kelly, 2017). Only a small part of plastic can be recycled after being used for the first time, while a considerable part of plastic will be abandoned and lost in the environment (Ouyang et al., 2020; Tiwari et al., 2020). After that, large plastics could be decomposed into smaller ones under sunlight, wind, wave, and biodegradation (Lam et al., 2020). Due to the widespread presence of microplastics, encountering some pollutants and microplastics is inevitable (Benson and Fred-Ahmadu, 2020). It was also shown that microplastics could adsorb and concentrate organic pollutants (Hüffer et al., 2019) and metals (Brennecke et al., 2016; Prunier et al., 2019) due to the hydrophobicity of plastic waste (Alimi et al., 2018). This indicates that microplastics can affect the migration and transformation of organic pollutants. Microplastics can be consumed by biota and then enter the food chain, which can be particularly serious in seafood (Avio et al., 2020; Farady, 2019; Savoca et al., 2020). Thus, the bioavailability and persistence of pollutants in the presence of microplastics could be different from those without microplastics (Grigorakis and Drouillard, 2018). Furthermore, the density of plastics is generally lower than or similar to that of water (Grigorakis and Drouillard, 2018). Thus, the plastic debris often prefers to enrich on the surface microlayer (Eriksen et al., 2014). Therefore, they can absorb more sunlight, which may further influence the photodegradation of pollutants in these environments (Lv et al., 2020; Russell et al., 2010; Styler et al., 2013). Considering these aspects, the influence of microplastics on the photodegradation of organic pollutants needs to be elucidated.

This study aimed to investigate the influences of microplastics on the adsorption and photo-transformation of PFAS. Four types of plastics, including polyethylene (PE), polyvinyl chloride (PVC), polystyrene (PS), and polytetrafluoroethylene (PTFE), were investigated because they are the most produced plastics and widely distributed in the environment. Adsorption isotherms of FOSA and PFOA on

microplastics were applied to measure the adsorption capacity. The influence of pH and salinity on adsorption was also investigated. The adsorption energies of FOSA and PFOA on PS were calculated to clarify the differences in the adsorption behaviour of plastics. The results are beneficial to understanding the coupled environmental behaviour of PFAS and microplastics in the water environment.

1. Materials and methods

1.1. Materials and instrumental analysis

PFAS standards used for analysis were perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluoro-*n*-[$^{13}\text{C}_8$]octanoic acid (M8PFOA), sodium perfluoro-1-[$^{13}\text{C}_8$]octanesulfonate (M8PFOS), all acquired from Wellington Laboratories. Perfluorooctanesulfonamide (FOSA, 90%) was obtained from J&K (Shanghai, China). HPLC grade acetonitrile and methanol were purchased from Fisher Chemical (Thermo Fisher Scientific, USA). Perfluorooctanoic acid (high grade, $>98.0\%$) was obtained from TCI (Tokyo chemical industry, Shanghai, China). Ultra-pure grade water used in this study was prepared using a Milli-Q instrument (Millipore, Billerica, MA, USA).

Microplastic powder of different materials including polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), polystyrene (PS), polytetrafluoroethylene (PTFE) was purchased from Shanghai Yiji Industrial Co. Ltd. (Shanghai, China). Sodium chloride (guaranteed reagent), hydrochloric acid (analytical reagent), and sodium hydroxide (analytical reagent) were purchased from SCR (Shanghai, China). HPLC grade Ammonium acetate was purchased from Dikma Technologies Inc. (USA).

All samples were analysed to quantify FOSA and PFAS with an LC-MS/MS system using an Agilent 1290 Infinity HPLC system coupled to a 6460A mass spectrometer (Agilent Technologies, Santa Clara, CA, USA). A Waters ACQUITY UPLC® BEH C18 column (2.1×100 mm, $1.7 \mu\text{m}$) coupled with a Waters ACQUITY UPLC® Protein BEH C18 VanGuard™ pre-column column (2.1×5 mm, $1.7 \mu\text{m}$) separated the target analytes. The temperature of the columns was maintained at 40°C . The injection volume was $10 \mu\text{L}$ and the flow rate was 0.2 mL/min . The mobile phases were 2 mmol ammonium acetate water (A) and acetonitrile (B), and the initial proportion was $10\% \text{ B}$.

The ion spray source of the mass spectrometer was operated in the negative electrospray ionisation (ESI-) mode. The analytes were qualified and quantified with multiple reaction monitoring mode. More details about the analysis are provided in Appendix A.

1.2. Batch adsorption experiments

Batch adsorption experiments were conducted in 15 mL PP tubes. The preliminary adsorption investigations showed that the PP tube has no obvious adsorption on PFOA and FOSA and thus can be used as a reaction vessel. Sorption of PFOA and FOSA (initial concentration from 5 ng/mL to 500 ng/mL) by four kinds of microplastics, including PE, PVC, PS, and PTFE

(2 g/L), was studied. Each tube was covered with aluminium foil to avoid illumination and shaken at 150 r/min (25°C) for 7 days. Then, the tube was centrifuged at 4,500 r/min for 15 min, and the supernatant was collected for treatment and analysis. The influence of pH (5, 6, 7, 8, and 9) and NaCl (concentrations of 0.001, 0.005, 0.01, 0.05, and 0.1 mol/L) on the adsorption were examined with the initial concentration of FOSA and PFOA 100 ng/mL. Other experimental conditions are consistent with the adsorption experiments described in the previous paragraph. All adsorption experiments were performed three times.

1.3. Sample pretreatment extraction and analysis

For the investigations dealing with FOSA, the mixture of 0.1 mL of water sample and 0.9 mL methanol was vortexed for 1 min. Then 0.1 mL of the mixture was transferred to another vial and combined with 0.5 ng M8PFOS. The solution was evaporated to dryness under a gentle stream of N₂ at 40°C and then resolubilised to precisely 0.5 mL of methanol. A similar procedure was performed to analyse other PFAS with some modifications, where 1 ng M8PFOS and 1 ng M8PFOA were added to a 0.5 mL water sample. The mixture was evaporated to dryness after being vortexed for 1 min and was reconstituted with 0.5 mL methanol. All samples were centrifuged at 10,000 r/min to remove particles. The supernatant was transferred into a 2 mL glass vial and then stored at 4°C before instrumental analysis. Appendix A offers detailed information about the instrumental parameters and conditions.

1.4. Interface computations

The CASTEP module in Materials Studio was used to model the adsorption of FOSA and PFOA on PS due to the highest adsorption capability of PS. The model of PS was built and optimised as adsorbents. The simulation of PS was conducted using two chains with five monomers in each chain. The visual molecular model of PS constructed by CASTEP is shown in Appendix A Fig. S6.

The molecules of FOSA and PFOA were also built and optimised by CASTEP. The energy of each state was obtained to evaluate the adsorption energy.

The adsorption energy was calculated as follows:

$$E_{\text{adsorption}} = E_{\text{adsorbate/adsorbent}} - (E_{\text{adsorbate}} + E_{\text{adsorbent}})$$

where $E_{\text{adsorption}}$ is the adsorption energy, $E_{\text{adsorbate/adsorbent}}$ is the total energy of the adsorbent (PS) with the adsorbed PFOA or FOSA. $E_{\text{adsorbate}}$ is the total energy of PS. $E_{\text{adsorbent}}$ is the total energy of adsorbate (PFOA or FOSA).

1.5. Photodegradation experiments

The illumination experiments were performed in a photochemical reactor (XPA-7 model, Xujiang Electromechanical Inc., Nanjing, China) equipped with a 1000 W xenon lamp (Philipps) to simulate natural light. The light intensity on the surface of the tube was 58 mW/cm². Quartz tubes (10 mL) were used as containers and the temperature was maintained at 25°C. 50 mL of an aqueous solution containing 500 µg/L FOSA

and 5 mg/L microplastics was added to each tube, and the solution was stirred continuously by a magnetic stirrer at a speed of 500 r/min during the experiment. At specific time intervals, 1 mL of the reaction solution was collected to analyse PFAS.

2. Results and discussion

2.1. Adsorption isotherms of FOSA and PFOA on microplastics

The adsorption isotherms of FOSA and PFOA (main photodegradation products of FOSA) on microplastics (Fig. 1) were investigated in the first instance. Results showed that the adsorption of PFOA and FOSA on microplastics were fitted relatively with the linear equation ($R^2 > 0.88$, Table 1), indicating a partition-dominated sorption mechanism. The relatively lower R^2 values for the PFOA adsorption on PTFE indicated the existence of other mechanisms (such as electrostatic interaction, porous structure, and hydrogen bonding) (Wang et al., 2015). The specific surface area normalised partition coefficient (K_n) of FOSA on all adsorbents followed the order: PS > PTFE > PVC > PE. The K_n values of PFOA on all adsorbents followed a similar order. This result indicates that PS showed higher adsorption capacity than the other microplastics investigated in this study. This is mainly because PS has a positive zeta potential and the other three microplastics have a negative zeta potential (Table 2). A positively charged PS surface has a strong electrostatic attraction to the negatively charged PFAS. For PTFE, the main monomer structure is C-F, which has a similar structure to PFAS, so PTFE has a higher adsorption capacity than PVC and PE.

The results displayed that FOSA could be more readily adsorbed on microplastics, including PE, PS, PVC, and PTFE, than PFOA. Previous studies (Wang et al., 2015) indicated that FOSA exists in water in the form of molecules and not ions due to the sulfonamide functional group at the end of the molecule. The pK_a value of PFOA is 2.8 (Goss, 2008), meaning that PFOA was mainly in anionic forms in this study (pH 5–9). The surface of the microplastics was charged negatively after PFOA was adsorbed on the surface. Thus, the surface of microplastics charged negatively repulsed the adsorption of more PFOA. The adsorption of FOSA and PFOA on PS was high (Fig. 1). It is supposed that the reason for this phenomenon is its relatively high hydrophobicity.

It was shown in Table 1 that PS had higher adsorption capability than PTFE both for FOSA and PFOA. This might be because of the different groups on the surface of these two adsorbents. The C-F bonds on the surface of PTFE lead to the surface being negatively charged because of fluorine's high electronegativity (O'hagan, 2008). Thus, the electrostatic repulsion between the surface of PTFE and negative PFAS leads to the lower adsorption capability of PTFE for PFAS. In contrast, the benzene rings and hydrogens on the surface of PS which are unsaturated groups (also electron-donating groups) made the surface of PS positively charged. Therefore, the electrostatic attraction between the PS and PFAS increased the adsorption capacity of PFAS on PS. As for PE and PVC, they have a lower

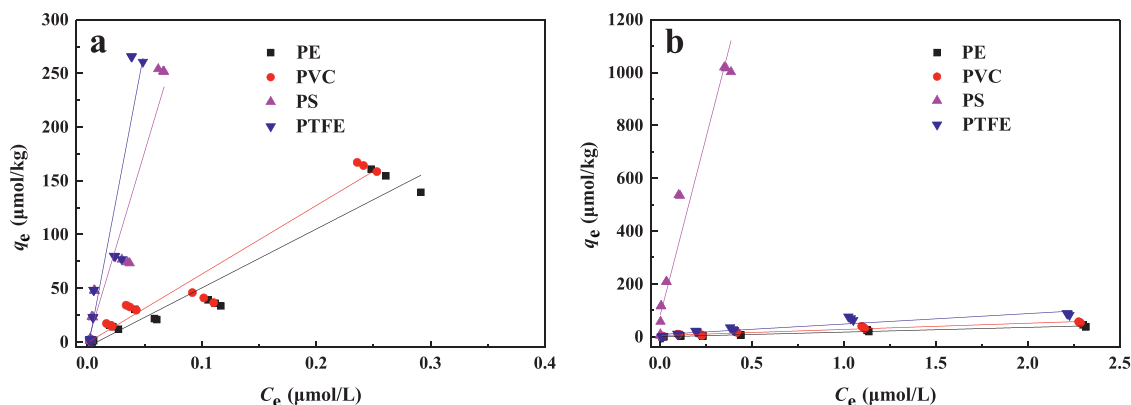


Fig. 1 – The adsorption isotherms of FOSA and PFOA on PE, PVC, PS, and PTFE (a for FOSA, b for PFOA).

Table 1 – Correlation parameters of the adsorption of FOSA and PFOA on adsorbents and $\text{Log}\Delta E$ derived from Materials studio.

	FOSA			PFOA		
	K_d (L/kg)	R^2	K_n (L/m ²)	K_d (L/kg)	R^2	K_n (L/m ²)
PE	688	0.955	0.72	17.9	0.979	0.02
PVC	924.9	0.927	1.25	23.4	0.948	0.03
PS	3766	0.976	16.09	2698	0.94	11.52
PTFE	7100.1	0.931	6.92	39.6	0.893	0.04

K_n : Specific surface area normalised K_d .

Table 2 – Parameters of specific surface area, partial size, Zeta potential hydrophilic-hydrophobic property, and $\text{log}k_{ow}$ of microplastics.

	BET (m ² /g)	Partical size (µm)	Zeta potential (mV)	$\text{log}k_{ow}$ of monomer
PE	0.9576 ± 0.0077	110.6 ± 60.2	-14.0 ± 3.7	1.13
PVC	0.7370 ± 0.0096	5.0 ± 0.3	-5.4 ± 2.8	1.46
PS	0.2341 ± 0.0042	31.8 ± 5.0	21.0 ± 3.4	3.0
PTFE	1.0265 ± 0.0200	63.2 ± 32.2	-16.7 ± 0.4	1.21

adsorption capacity than PS and PTFE, which may be due to their inert groups

2.2. Effect of pH and salinity on the adsorption of FOSA and PFOA on microplastics

The effect of pH on the adsorption capacity of microplastics was also investigated in this study (Fig. 2). For the adsorption of FOSA, pH had a negligible effect on the adsorption efficiency of PTFE because of its high adsorption capacity. PE, PVC, and PS adsorption efficiency decreased as pH increased. The reason could be that the protonation of PE, PVC, and PS interface was inhibited when the pH increased (Wang et al., 2015). In other words, the acidity of the surface decreased. Meanwhile, the influence of pH on FOSA was low as FOSA molecules are generally neutral with low alkalinity. As a result, the adsorption efficiency decreased because of the decrease of attraction between the surface and FOSA molecules.

The influence of pH on the adsorption of PFOA on microplastics was generally weak, except for PS. Because of the

decrease in pH, the PS surface was protonated and charged positively. The electrostatic attraction between the positive surface and the negatively charged molecules of PFOA raised the adsorption efficiency. This result corresponded well with previous investigations (Wang et al., 2015). However, pH had a low/negligible impact on the adsorption of PFOA on PE, PVC, and PTFE. As for the adsorption of PFOA on PTFE, the protonation of the surface was suppressed as the bond energy of C-F is very high compared to C-H. When PE was used, the adsorption sites of these two microplastics were few because of their large diameters, resulting in a low specific surface area (Table 2). Therefore, its adsorption capacity was low, and the effect of pH was not noticeable.

The effect of NaCl on the adsorption of FOSA and PFOA on microplastics is detailed in Fig. 2. The adsorption efficiency of FOSA on PS decreased with the NaCl increase, while the change of NaCl had a negligible influence on the adsorption of FOSA on PE, PVC, and PTFE (Fig. 2c). The reason for the low influence of NaCl on the adsorption of FOSA on PE, PVC, and PTFE could be that FOSA molecules are neutrally charged,

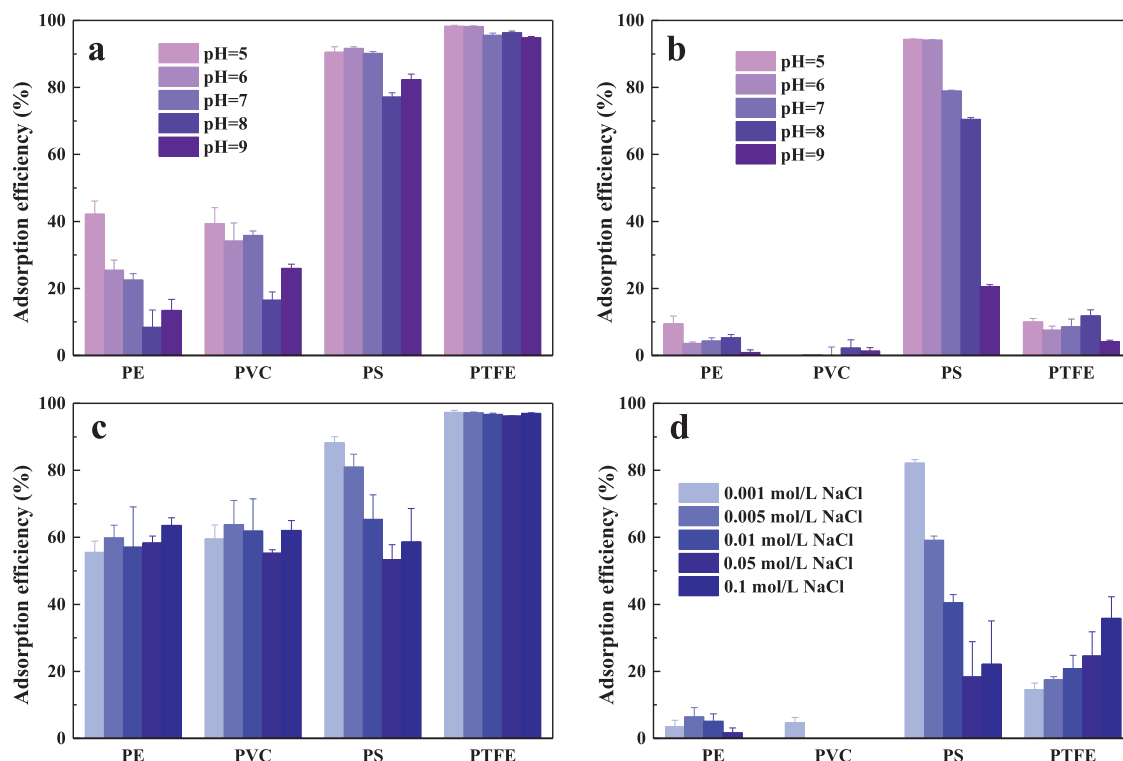


Fig. 2 – The effect of the concentration of pH and NaCl on the adsorption capacity of different microplastics (a, c for FOSA, b, d for PFOA).

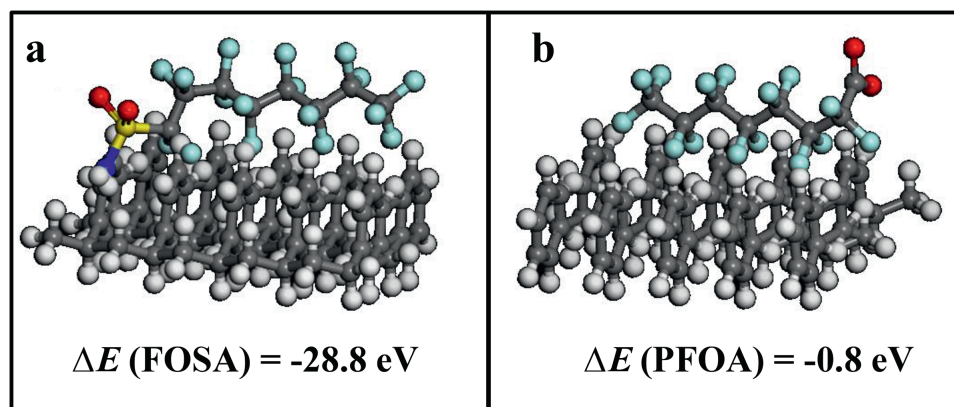


Fig. 3 – The 3D image of FOSA and PFOA adsorbed on PS.

which was scarcely influenced by inorganic salts. For PS, the increase of NaCl concentration leads to the decrease of the zeta potential of the PS surface which could further cause the aggregation of PS particles and reduce the adsorption of FOSA on PS. Fig. 2d indicated that NaCl had a low effect on the adsorption of PFOA on PE and PVC. The adsorption efficiency of PFOA on PTFE increased with the increase of NaCl, whereas the adsorption efficiency of PFOA on PS decreased with the increase of NaCl. An electrical double layer model could in-

terpret this phenomenon (Wang et al., 2015). The surface of PTFE was charged positively in an aqueous solution due to the presence of fluorine atoms on the surface. The change of concentration of NaCl influenced the adsorption by changing the ionic strength. The electrical double layer was compressed as the ionic strength increased. As a result, the attraction between the positive surface and PFOA charged negatively was weakened. On the other hand, repulsion between the negatively charged PS surface and PFOA increased because of the

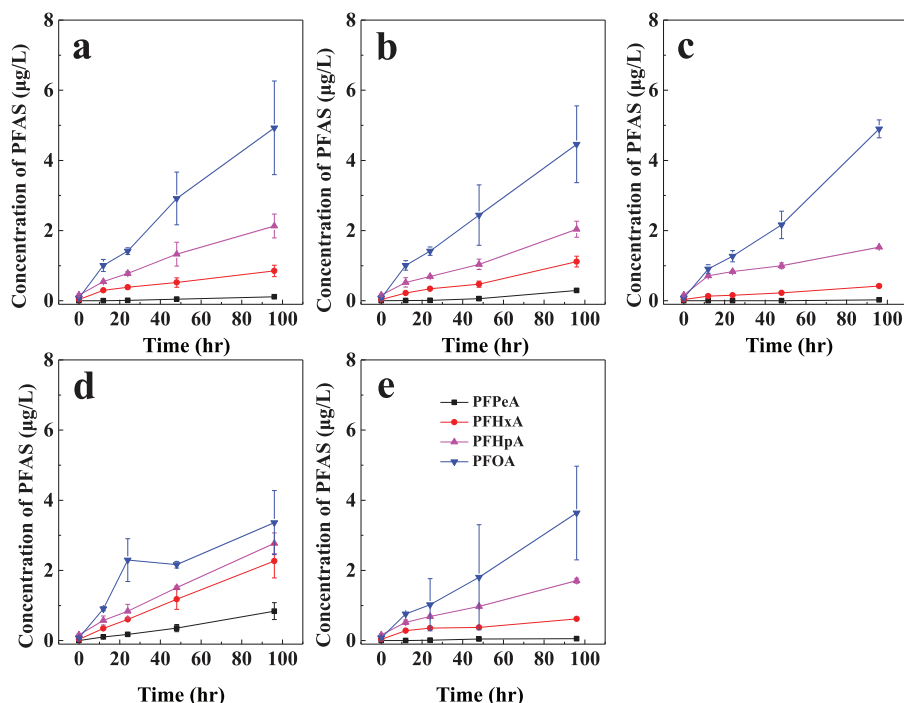


Fig. 4 – The concentrations of PFCAs increased with the passage of time in photodegradation of FOSA (a for PE; b for PVC; c for PS; d for PTFE; e for control).

compression of the electrical double layer. Related mechanism diagrams are provided in Appendix A Figs. S3 and S4.

The pH of seawater is approximately 7.5–8.5 in most cases (Marion et al., 2011), which is slightly more alkaline than fresh waters, including rivers, lakes, streams, and rainwater. Thus, we can suppose that when some microplastics carrying anionic pollutants such as PFOA reach the sea from the freshwater bodies/rivers through the estuary, the less polluted seawater will dilute the river, and then the pollutants could be desorbed from adsorbents into the water because of the lower concentration of pollutants in mixed water. At the same time, the rise of pH could accelerate the desorption of PFOA into the water, according to our results. The salinity in different waters varies in the environment because of their complicated components. Moreover, the salinity could influence the microplastics carrying pollutants in the transformation process. To our best knowledge, the salinity of seawater is universally higher than that of rivers. So the inflow of microplastics from the river to the ocean could change the adsorption of PFAS on the adsorbents. According to our results, we could suppose that the anionic organic compounds (such as PFOA) adsorbed on PS may desorb from the surface to aqueous media. As for PTFE, PFOA might not be desorbed. Moreover, PTFE could adsorb more PFOA, because the adsorption efficiency of PFOA on PTFE increased with the increase of NaCl. However, the concentration of pollutants in the ocean is usually lower than that in rivers. This is because most pollution sources are usually near the regions with high human/industrial activity, especially in land and rivers carrying pollutants washed from land or inundated from wastewaters. This means that rivers become the carriers of pollutants from sources to the ocean (Chen et al.,

2017). Thus, the dilution of seawater could promote the desorption of PFOA from the surface of PTFE. Hence, the influence of salinity on the partition of PFOA on PTFE should be weakened or counteracted.

2.3. Simulative interactions between FOSA and PFOA on microplastics

The adsorption energy of FOSA or PFOA on microplastics was calculated by CASTEP mode in Materials Studio. PS was selected as an example due to its remarkable adsorption capacity (part 3.1). Before the calculation of adsorption energy, the model of PS was built. The microplastic polymer model of PS was constructed and optimised by two chains with five monomers in every chain. The CASTEP module in the Materials Studio was used to calculate the adsorption energy of adsorbate on adsorbents according to optimisation of the conformation with the lowest binding free energy. The optimised 3D conformations are shown in Fig. 3, demonstrating that FOSA and PFOA were recumbently adsorbed on adsorbents.

The calculated adsorption energy ($E_{\text{adsorption}}$) of FOSA and PFOA adsorbed on PS, experimental partition coefficients (K_d), and specific surface area normalised K_d (K_n) were displayed in Fig. 3 and Table 1. The absolute adsorption energy value of FOSA adsorbed on PS was higher than that of PFOA, which is consistent with the higher K_n values of FOSA adsorbed on PS than that of PFOA. The specific surface area normalised adsorption constant K_n of FOSA and PFOA on PS were both the highest due to the highest zeta potential (positive) of PS. This might be because C–F bonds were the primary units of the FOSA and PFOA molecules. The fluorine atoms are electron-

withdrawing groups, leading to the negative charge of the surface of FOSA and PFOA. Especially for PFOA, in an aqueous solution, the molecules of PFOA were in the negative ion forms, leading to the surface of PS adsorbed with PFOA charged negatively. Thus, the electrostatic repulsion between the surface of PS and PFOA leads to the lower adsorption capability of PS for PFOA. The efficiency of simulation construction of microplastics was relatively low as they are polymers with complicated and indefinite structures. Therefore, the spatial structure of microplastics might be complex with multiple branched chains not only a single chain. Thus, they could capture chemicals in other ways. In addition, the computation and simulation are idealised. In actual cases, the pressure of the environment, the presence of water molecules, particle size, and volume of adsorbents could influence micro-interfaces' adsorption capacity.

2.4. Effects of microplastics on the photodegradation of FOSA

Our previous study showed that FOSA can be degraded to PFOA and shorter PFCAs in water under irradiation with visible light, and the degradation was enhanced by montmorillonite (Lv et al., 2020). Here, the influence of four kinds of microplastics (PE, PVC, PS, and PTFE) on the photodegradation of FOSA in water was investigated. As shown in Fig. 4, the concentrations of short-chain PFCAs increased, and their yields decreased as their carbon chain decreased during photodegradation. This result was consistent with our previous study and indicated that FOSA could be photodegraded to shorter carbon chain PFCAs (Lv et al., 2020).

As shown in Fig. 4, PFOA was the main degradation product in all systems. There were no apparent differences between PFOA concentrations in the systems of pure water and four kinds of microplastics. This indicates that microplastics were photochemically inactive and had no effect on the photodegradation of FOSA. The organic pollutants adsorbed by microplastics could concentrate on the surface of the water and absorb more sunlight, but due to the non-photochemical activity of microplastics, the degradation of the pollutants can not be accelerated. This indicates that the presence of microplastics may extend the half-life of FOSA.

3. Conclusions

In this work, adsorption isotherms were investigated to compare the adsorption of FOSA and PFOA on four kinds of microplastics. The results indicated that PS has higher adsorption capacity than PTFE, PVC, and PE. The illumination experiment showed that FOSA could be degraded to shorter-chain PFCAs under natural light irradiation, with PFOA as the main product. Unlike our previous findings that clay minerals can accelerate the photodegradation of FOSA, microplastics do not influence the photodegradation of FOSA, likely due to the photochemical inertness and high affinity of microplastics to FOSA. The role of microplastics as carriers or vectors of inorganic and organic pollutants has been widely reported. However, little is known about the role of microplastics in the photochemical behaviour of pollutants. This study provided

new insight into understanding the impact of microplastics on the fate of PFAS.

Declaration of Competing Interest

We declare that we do not have any commercial or associative interest that represents a conflict of interest in connection with the work submitted.

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Appendix A Supplementary data

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jes.2022.07.004.

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