



Revealing the adsorption kinetics of microplastics towards hydrophobic antibiotic: New insights into the microplastics aging behavior and aquatic environmental factors

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ABSTRACT

Microplastics (MPs) present stronger adsorption performance towards hydrophobic antibiotic (like ofloxacin, OFX) after natural aging, however, the adsorption capacity of this alteration and the influence of multiple environmental factors on this adsorption behavior remain unknown. This study investigated the adsorption kinetics of polypropylene (PP) and polystyrene (PS), and their aged materials (aged PP and aged-PS) towards OFX, and compared the adsorption capacity of these four MPs under different aquatic environmental conditions, like pHs (3, 5, 7, 9 and 11), temperatures (5, 15, 25 and 35 °C), NaCl concentrations (10, 100, 1000, and 10,000 mg/L), and heavy metal ion types and concentrations (Cd^{2+} , Zn^{2+} , and Cu^{2+} : 1, 5, 25, 50, and 250 $\mu\text{mol}/\text{L}$). Results indicated that the aging behavior of PP and PS enhanced the OFX adsorption capacity by 1.4 and 1.5 times, respectively, which attributed to the increase in adsorption sites of aged-PP and aged-PS, and this result was confirmed by the extension of adsorption equilibrium time. Moreover, the adsorption behavior under different environmental factors indicated that the promoted adsorption performance caused by aging behavior of MPs might depend on the joint determination of multiple factors in actual aquatic environment. Mechanisms penetrated that the aging behavior and appropriate environmental factors could improve the van der Waals force and electrostatic interaction between MPs and OFX. Overall, this study provided novel insights for understanding the adsorption behavior of MPs towards hydrophobic antibiotics, and would contribute to the emerging contaminants control and ecological risk reduction in future work.

1. Introduction

The global production of plastic products reached 391 million tons in 2021 [1], resulting in a vast accumulation of recalcitrant plastics being discharged into the environment [2]. Plastic fragments with a diameter of less than 5 mm produced by natural weathering are defined as microplastics (MPs) [3], which are widely detected in aquatic environments (like oceans, rivers, lakes) [4–6] and other environmental media [7,8]. Several studies have also demonstrated that MPs can enter the food chain from nature ecosystem by biological adsorption, thus posing potential risks to human health [9,10]. Additionally, due to its hydrophobicity and high specific surface area, MPs are considered to serve as

carriers for other hydrophobic organic substances in aquatic environment, thereby affecting their bioavailability and ecological toxicity [11–14]. For example, previous studies have revealed that different types of MPs like polypropylene (PP) and polystyrene (PS) could adsorb multiple hydrophobic antibiotics (like ofloxacin, amoxicillin, and ciprofloxacin) to form microplastic-antibiotic complex, thus coexisting and accumulating in aquatic environment [15–17]. Unfortunately, antibiotic have also been widely detected in aquatic environments, recognizing the proliferation of antibiotic resistance genes triggered by antibiotic residues, antibiotics have received extensive attention [18]. Significantly, there is evidence to suggest that the persistent organic pollutants can be transferred from MPs to *Artemia nauplii* due to combined pollution [17].

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Therefore, considering the crucial role of MPs towards the migration, transformation, and distribution of antibiotics in natural aquatic environment [19–21], exploring the adsorption behavior of MPs towards antibiotics is significant for accurately understanding the environmental impact of emerging contaminants and controlling their ecological risks.

Previous studies have revealed that the adsorption capacity of MPs towards antibiotics was believed to be related to the type of MPs [22–24], antibiotics properties [17], and environmental factors [25]. Firstly, MPs as a type of polymer, consist of crystalline and amorphous regions, with the amorphous region further divided into rubber and glassy states [26]. Generally, amorphous region has better adsorption capacity than crystalline, and the glassy state has relatively poor affinity for pollutants [22–24]. For example, PP and polyethylene (PE) have lower crystallinity compared to PS, and the amorphous region of PS is in a glassy state, theoretically indicating stronger adsorption capacity of PP and PE [17]. Moreover, as a type of persistent organic substances, the hydrophobicity of antibiotics determines their adsorption affinity. Li et al. [17] have demonstrated that the adsorption affinity of five antibiotics (including ciprofloxacin, amoxicillin, trimethoprim, sulfamethoxazole, and tetracycline) on MPs decreases in sequence, which is almost consistent with their octanol water partition coefficients. Finally, environmental factors such as salinity, pH, and dissolved organic matter (DOM) are also considered to have different effects on the adsorption of MPs towards antibiotics [22,24,27]. For example, the salinity on the adsorption process is influenced by different adsorption mechanisms, including shielding the surface charge of MPs and increasing the solubility of antibiotics [22,24,25]. pH has been revealed to affect the adsorption capacity by influencing the form of antibiotics and the surface charge polarity of MPs. Shen et al. [27] have indicated that DOM competed for adsorption sites on MPs and altered the hydrophobicity and polarity of MPs. Obviously, the above research progress on the adsorption of MPs towards antibiotics provided a good theoretical basis for further exploration in this field.

Attentively, MPs generally were aged in aquatic environmental by biodegradation, physical abrasion, or chemical oxidation, and this aging behavior has been demonstrated to potentially alter the adsorption capacity of MPs [28]. Ju et al. [29] summarized that compared with fresh MPs, the biodegradable MPs after aging have increased functional groups (like carbonyl, alkoxy, aromatic rings), thus forming chemical bonds and promoting the adsorption capacity towards hydrophobic organic compounds. For example, Liu et al. [25] has revealed that the aging behavior could alter the crystallinity of MPs, thus promoting the co-adsorption of PS and ciprofloxacin. However, the alteration mechanism of this adsorption capacity of MPs towards antibiotics due to aging behavior are still not fully understood. On the one hand, although the influence of aging behavior on the microstructure and surface functional groups of MPs has been well investigated [30,31], the relationship between this influence and the adsorption kinetics alteration of MPs is still lacking in exploration. On the other hand, the alteration in adsorption capacity caused by this aging behavior is also influenced by multiple factors in actual aquatic environment [25]. Although the mechanism by which single factor on the adsorption of MPs towards antibiotics has been partially revealed [22,24,27], it is still unclear how multiple factors collectively affect the adsorption of antibiotics by MPs before and after aging. Therefore, we suggested that the alteration in adsorption capacity caused by aging behavior was not only related to the type of MPs, but also influenced by various environmental factors during the adsorption process, which collectively determined the improvement of adsorption capacity.

Overall, the aims of this study were to: 1) compare the adsorption capacity differences of PP and PS with different crystal structures and respective two aged MPs on OFX, a widely detected representative hydrophobic antibiotic with relatively higher level than other antibiotics in aquatic environments [32]; 2) reveal the relationship between adsorption kinetics alteration due to aging and microstructural changes of two MPs; 3) penetrate the joint mechanisms of multiple environmental

factors on promoting the adsorption capacity of MPs after aging. Collectively, this study is expected to provide more comprehensive insights into the adsorption process of MPs towards hydrophobic organic substances, which are important for comprehending the real behavior of MPs in aquatic environment.

2. Materials and methods

2.1. Fresh MPs, OFX, and aged MPs preparation

Both PP and PS were purchased from the manufacturer (Dongguan, China) with a diameter range of 50 ~ 100 μm , and the characters of two MPs were presented in Tab. S1. The OFX (98 %) was purchased from J&K Scientific (Beijing, China), and the properties were shown in Tab. S2. According to Guo et al. [33], the aging treatment of fresh MPs involved the following steps and details: firstly, appropriate amount of fresh PP and PS were respectively taken and washed with deionized water, and the clean PP and PS were evenly spread in a glass colorimetric dish after drying. Then, two MPs were continuously exposed to UV light (4 × 15 W, 254 nm) for 96 hours at a constant temperature (25 ± 1 °C) using cooling water circulation device (DC-2021, Naiai Instrument Co., Ltd, Shanghai), and the samples were flipped every 12 hours to ensure uniform illumination. Finally, the aged-PP and aged-PS samples were obtained after washing with deionized water and drying.

2.2. The adsorption kinetics experiment of four MPs towards OFX

The adsorption kinetics experiment was conducted on four MPs to reveal the effect of aging behavior on adsorption capacity. Referring to previous studies [34–36], 0.2 g of PP, aged-PP, PS, and aged-PS were respectively added into conical flask, and 50 mL of OFX solution (20 mg/L) were also added, then the conical flasks were shaken in a shaker at 150 rpm for 48 hours. The temperature was set at 25 °C, and the initial pH was 7.0. During this period, the samples were collected at 0, 1, 2, 4, 6, 8, 24, 36, and 48 hours respectively. Moreover, the blank group containing 50 mL of OFX solution was also operated simultaneously at same conditions. Similarly, the adsorption isotherm experiments were also conducted on four materials. Under 25 °C condition, 0.2 g of four materials and 50 mL of OFX solution (1, 5, 10, 20, and 50 mg/L) were respectively added into conical flask, all samples were shaken at 150 rpm for 24 h. During this period, the samples were collected after operation. Moreover, the blank groups containing 50 mL of OFX solution with different concentrations were respectively operated. The above experiments were conducted in three parallel groups, with samples collected using disposable syringes and filtered through 0.22 μm filter membrane [36].

2.3. The models of adsorption kinetics and isotherm

The adsorption kinetics of four MPs towards OFX were fitted using pseudo-first-order, pseudo-second-order, and intra-particle diffusion models, respectively [36]. The formulas were as follows:

$$\ln (q_e - q_t) = \ln q_e - K_1 t \quad (1)$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (2)$$

$$q_t = K_3 t^{1/2} + c \quad (3)$$

Where q_e (mg/g) is the equilibrium adsorption amount of OFX, and q_t (mg/g) is the OFX adsorption capacity of MPs at time t (h). K_1 (h^{-1}), K_2 (g/mg•h), and K_3 (mg/g• $\text{h}^{1/2}$) are the rate constants of the pseudo-first-order, pseudo-second-order, and intra-particle diffusion models, respectively, and c is the intraparticle diffusion model constant, which

indicates the thick-ness of the adsorption surface.

Moreover, the adsorption isotherm was respectively fitted using Langmuir and Freundlich isotherm models [36]:

Langmuir isotherm model:

$$q_e = \frac{q_{\max} K_L C_e}{1 + K_L C_e} \quad (4)$$

Freundlich isotherm model:

$$q_e = K_F C_e^{\frac{1}{n}} \quad (5)$$

Where q_{\max} (mg/g) is the maximum value of the OFX adsorption capacity of the four MPs. K_L (L/mg) and K_F [(mg/g) $(L/mg)^{1/n}$] are the Langmuir and Freundlich distribution coefficients, respectively. $1/n$ is the Freundlich model parameter that reflects the adsorption intensity and heterogeneity of the adsorbent.

2.4. The influence of environmental factors on the adsorption of four MPs towards OFX

Consistent with the above adsorption experiments, adsorption tests were conducted on four MPs at different environmental factors to simulated the different scenes. For example, according to previous studies [27,37,38], the different pHs (3, 5, 7, 9, and 11) were set to cover acidic, neutral, and alkaline aquatic conditions [27], the four temperatures (5, 15, 25, and 35°C) were simulated the different aquatic temperature conditions in different seasons in China [27], the salinity (NaCl concentrations: 10, 100, 1000, and 10,000 mg/L) were selected with freshwater, seawater, and saline wastewater conditions [27], and heavy metals ($CdCl_2/ZnCl_2/CuCl_2$ concentrations: 1, 5, 25, 50, and 250 μ mol/L) were set to simulate the environmental conditions of leachate from domestic waste landfills [37]. The pH was adjusted by 0.1 M NaOH or HCl solution, and the different temperatures were controlled by constant temperature shaker. Moreover, to investigate the adsorption behavior of four MPs on OFX under the combined interference of multiple factors, eight sets of interaction experiments were conducted based on above single factor adsorption results, including pH (5 and 7), temperature (15 and 25°C), salinity (NaCl concentration: 10 and 100 mg/L). More details about interaction experiments were presented in part 3.3. The above experiments were also conducted in three parallel groups, with samples collected using disposable syringes and filtered through 0.22 μ m filter membrane.

2.5. Detection of OFX

The OFX concentrations of all collected samples were detected by high-performance liquid chromatography (PerkinElmer, Shimadzu, Japan) [32]. The chromatographic column was a Hypersil GOLD C18 column (150 mm \times 4.6 mm, 5 μ m). The test condition was set as following: the column temperature was 30°C; the flow rate was 0.8 mL/min; the injection volume was 5 μ L. More details of mobile phases and detection wavelengths were presented in Table S3.

2.6. Characterization of four MPs

Referring to Babalar et al. [39], the specific surface area (SSA), pore diameter, and volume of four MPs were detected by BET (Autosorb iQ, Quantachrome, USA). The surface morphology changes of PP and PS before and after aging were observed by SEM (Regulus 8100, Hitachi, Japan). The crystal structures of four MPs were analyzed by X-ray diffractometer (SmartLab, Rigaku, Japan). The changes in surface functional groups of PP and PS before and after aging were characterized by FTIR (Nicolet iS20, Thermo Scicentic, USA).

2.7. Data analysis

The OFX concentration and error bar of all samples were determined by mean and standard deviation analysis (Excel, Microsoft, USA). The crystallinity of the four MPs was calculated by MDI JADE 6 (Materials Data, USA) based on XRD analysis compared to built-in PDF database. The carboxyl index was the ration of carbonyl characteristics peak area ($A_{C=O}$) near 1900 \sim 1650 cm $^{-1}$ wavenumbers to the methylene characteristics peak area (A_{C-H_2}) near 2960 \sim 2850 cm $^{-1}$ wavenumbers. The significant difference analysis was calculated by SPSS (IBM, USA), and p-value ≤ 0.05 was regarded as statistically significant.

3. Results and discussion

3.1. Adsorption kinetics of four MPs towards ofloxacin

The adsorption kinetics with three models of four MPs were presented in Fig. 1. Firstly, the adsorption processes of PP and PS towards OFX plotted the similar trend before and after aing, and the processes could be divided into three stages: (1) within 0 \sim 4 h, the adsorption affinity of the four MPs towards OFX gradually increased, and the adsorption capacities of PP, aged-PP, PS, and aged-PS towards OFX respectively reached 48.9 %, 54.6 %, 72.3 %, and 73.6 % of the adsorption equilibrium at 4 h; (2) within 4 \sim 8 h, althoght the adsorption capacity kept increase, the adsorption rate gradually slowed down; (3) with 8 \sim 24 h, the adsorption capacity had a slight increase until equilibrium. Eventually, the Q_e of OFX on the four MPs were 0.184 (aged-PS) $>$ 0.149 (aged-PP) $>$ 0.123 (PS) $>$ 0.106 (PP), indicating that the adsorption capacity of PS was stronger than PP, and the aging behavior improved the adsorption capacity (Fig. 1 A and B). Moreover, as shown in Fig. 1 (C), the intraparticle diffusion model further indicated that the adsorption process of OFX on the four MPs was divided into intraparticle diffusion, external diffusion, and interfacial adsorption equilibrium [13]. As the fitted curve did not pass through the original point, the intraparticle diffusion was not the only rate limiting step. Overall, the adsorption process of OFX on these four MPs was synergistically regulated by internal and external diffusion [40].

To further determine the alteration in adsorption capacity, Table 1 listed the parameters of the pseudo first and second order models of four MPs. Obviously, the R^2 value of pseudo-first-order model was higher than that of the pseudo-second-order model, and there was a considerable difference between the q_e obtained by the pseudo-second-order model and the experimental data. Thus, the pseudo-first-order model was more suitable for describing the adsorption process of four MPs towards OFX, indicating a liner relationship between the occupancy rate of adsorption sites and the number of non-adsorption sites [41]. Based on the fitted q_e value, the aging behavior has increased the adsorption capacity of PP and PS by 1.4 and 1.5 times, respectively. Moreover, the K_1 value determined that the adsorption rate of MPs slowed down and the adsorption equilibrium time was prolonged by aging behavior, which might be related to the number of adsorption sites of MPs was increased due to the surface structure damaging during aging process.

3.2. Adsorption isotherms of four MPs

Considering that all four MPs could reach adsorption equilibrium towards OFX within 24 h, the adsorption isotherms were analyzed at 24 h to further investigate the effect of aging behavior on the adsorption process. The Langmuir and Freundlich models were shown in Fig. 2, and the parameters of isotherm model fitting curves were listed in Table 2. Compared to Langmuir, due to the R^2 was closer to 1, the Freundlich model could better fit the isothermal adsorption process of the four MPs, indicating that the adsorption processes of these four MPs might all be nonuniform surface-two steps adsorption [42,43]. Moreover, the K_F values of aged-PP and aged-PS were respectively higher than PP and PS, revealing that aging behavior improved the adsorption capacity of two

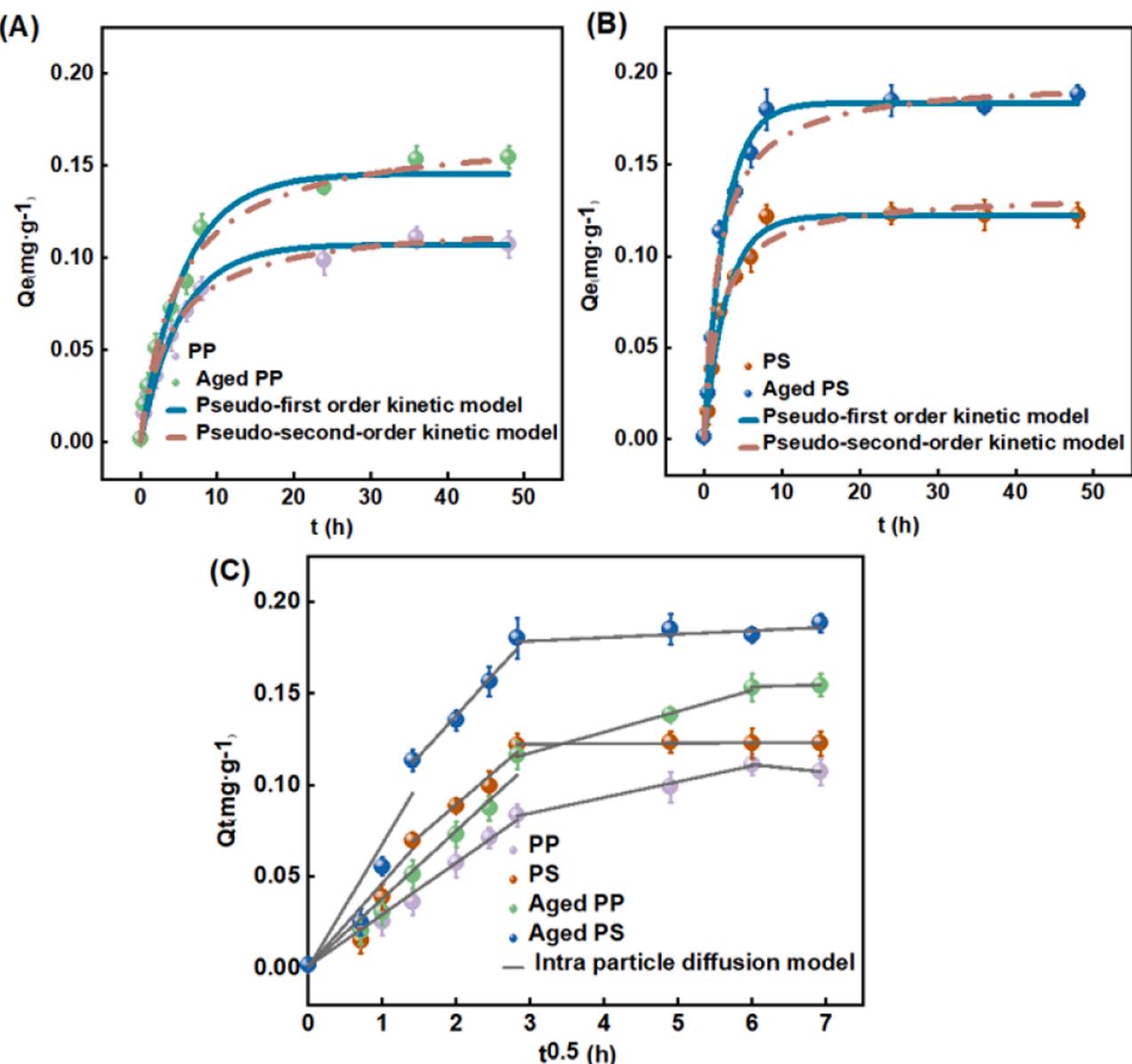


Fig. 1. (A) the adsorption kinetics of PP and aged PP on ofloxacin; (B) adsorption kinetics of PS and aged PS on ofloxacin; and (C) intra particle diffusion model of four materials on ofloxacin.

Table 1
Parameters of adsorption kinetics equation of four MPs adsorbing ofloxacin.

Materials	Pseudo-first-order model		Pseudo-second-order model			
	$q_e \text{ (mg/g)}$	$K_1 \text{ (h}^{-1}\text{)}$	R^2	$q_e \text{ (mg/g)}$	$K_2 \text{ (g/mg} \cdot \text{h)}$	R^2
PP	0.1056	0.1956	0.9944	0.1047	0.9734	0.9852
Aged-PP	0.1487	0.1782	0.9924	0.1504	1.3936	0.9864
PS	0.1225	0.3832	0.9973	0.1228	1.5120	0.9879
Aged-PS	0.1838	0.3502	0.9904	0.1884	5.8952	0.9839

MPs [24,35,44], which was consistent with the above adsorption kinetics results. Moreover, compared with the results revealed in previous reports, the adsorption difference between PP and aged PP in Fig. 2(A) was not distinct, which was speculated to be related to the differences in aging methods. For example, Feng et al. [45] respectively obtained two types of aged PP using $\text{Fe}^{2+}/\text{PMS}$ and alkaline aging methods, and the degree of variation in adsorption capacity between the two aged PP and fresh PP was also different.

Furthermore, as PP and PS are respectively aliphatic and aromatic polymers (Tab. S1), their differences in the physical and chemical properties inevitably affect their adsorption behavior. For example, PP have lower crystallinity compared to PS, and the amorphous region of PS is in a glassy state, theoretically indicating stronger adsorption capacity of PP [17]. Although previous study has demonstrated that the aging process could change the surface structure of MPs [34], the effect of this change on adsorption capacity should be further clarified. In this regard, the aging behavior and the adsorption differences between the two MPs towards OFX would be further discussed with more details in part 3.4.1.

3.3. The influence of aquatic environmental factors on adsorption capacity

In addition to differences in their own properties, the adsorption capacity of MPs was also determined by multiple factors in the aquatic environment. To further investigate the adsorption differences of four MPs towards OFX, the adsorption capacities of four MPs under single and multiple environmental factors were compared.

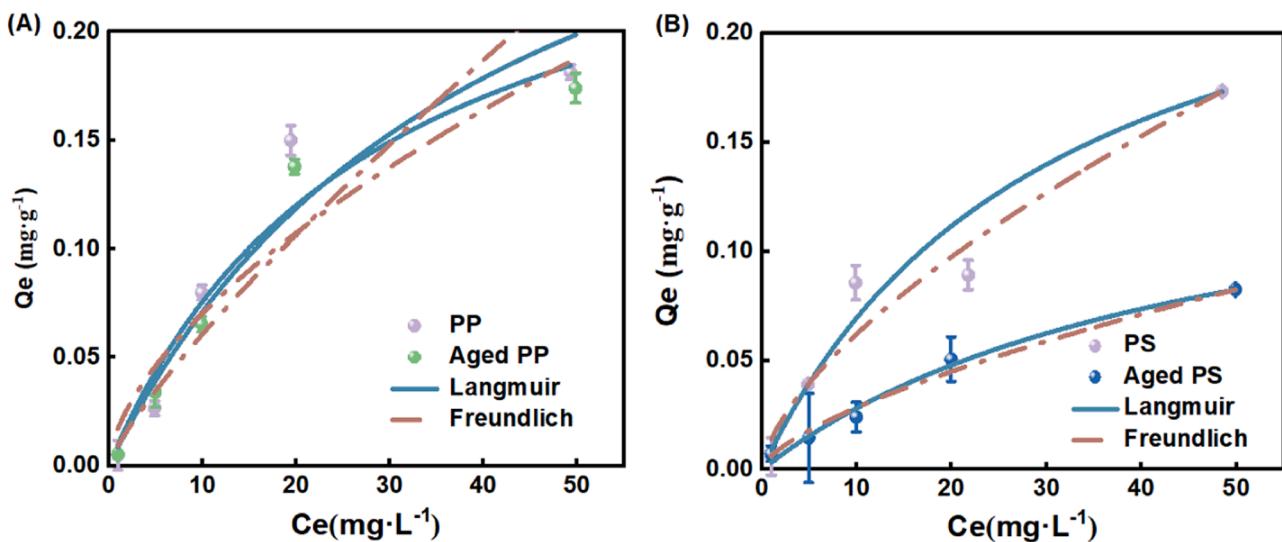


Fig. 2. Isotherm model fitting curves of four MPs adsorbing ofloxacin.

Table 2
Parameters of isotherm model fitting curves of four MPs adsorbing ofloxacin.

Materials	Langmuir model			Freundlich model		
	q_{\max} (mg/g)	K_L (L/ mg)	R^2	K_F [(mg/g) (L/mg) $^{1/n}$]	$1/n$	R^2
PP	0.2914	0.035	0.9635	0.0093	0.6118	0.9734
Aged-PP	0.3622	0.0243	0.9682	0.0172	0.8132	0.9821
PS	0.2822	0.0327	0.9723	0.0062	0.6485	0.9992
Aged-PS	0.1592	0.0215	0.9701	0.0140	0.6617	0.9985

As shown in Fig. 3, the different single environmental factors have varying effects on the adsorption capacity of the four MPs towards OFX. Firstly, within the pH range of 3 ~ 11, the adsorption capacity of all four MPs presented a trend of first increasing and then decreasing, and reached a maximum at pH= 5 condition (Fig. 3A). Due to the isoelectric points of PP and PS being 4.7 and 4.1, respectively, and OFX being a zwitterionic molecule with pK_{a1} of 5.77 and pK_{a2} of 8.44, these two MPs could exhibit electronegativity, and OFX mainly existed in the form of OFX^+ at pH= 5 condition [37]. Therefore, electrostatic interaction might be the main mechanism by which pH promoted adsorption capacity of two MPs towards OFX in mildly acidic aquatic environment.

Then, within the temperature range of 5 ~ 35°C, the adsorption capacity of the four MPs exhibited a trend of first increasing and then decreasing, and reached its maximum adsorption capacity at 15°C (Fig. 3B). Dong et al. [46] demonstrated that an increase in temperature could simultaneously enhance the migration rate and dissolution rate of adsorbed molecules, but also reduced the surface tension and van der Waals forces of organic matter, thereby promoting adsorption or desorption processes, respectively. Therefore, the effect of temperature on the adsorption capacity should be determined by the net adsorption capacity (NAC), which was the difference between the adsorption amount and the desorption amount. Obviously, the NAC of the two aged MPs for OFX was higher than that of fresh ones in the range of 5 ~ 25°C (Fig. 3B), which might be related to the change in material surface structure and properties caused by aging behavior, and this result would be discussed in detail in part 3.4.

As shown in Fig. 3 (C), the adsorption capacity of the four MPs towards OFX decreased continuously with increasing salinity, indicating that NaCl exhibited a adsorption inhibition. Pascall et al. [47] revealed that a reduction in free volume was detrimental to the adsorption of a potential migrating species. Wu et al. [48] also suggested that an increase in ion concentration could alter the viscosity and density of the

solution, thus inhibiting mass transfer from liquid to solid phase. Obviously, this result was consistent with these theoretical foundations, and indicated that freshwater was likely more conducive to MPs adsorption of OFX compared to seawater.

However, compared to NaCl, the three different heavy metal ions presented differential patterns of adsorption processes (Fig. 3D-F), indicating that there were other mechanisms underlying the effects of heavy metal ions. Zhao et al. [49] demonstrated that Cd^{2+} could form cation bridge in tetracycline molecules, thereby promoting the adsorption of tetracycline by PS. As shown in Fig. 3D, the adsorption capacity of OFX on the surfaces of the four MPs gradually promoted with the increase of Cd^{2+} concentration, while the aging behavior induced this promotion to be inferior to that of fresh MPs. Differently, an increase in the concentration of Cu^{2+} and Zn^{2+} inhibited the adsorption of OFX on the four MPs, and the aging behavior certainly alleviated this inhibition (Fig. 3E and F) [50]. The above differences might be related to the presence of carboxyl group in the OFX molecular structure, which have been shown to chelate heavy metal ions [51]. Moreover, this chelating properties of different heavy metals were related to the external electronic structure arrangement. In comparison, Cd atom has an average external electron configuration and presents non chemical reactivity, while Cu atom and Zn atom are more reactive, especially the latter. Therefore, due to the higher complexation of Cu^{2+} or Zn^{2+} with OFX, four MPs have a lower adsorption capacity towards OFX compared to the Cd^{2+} group at dosage of 25 ~ 250 $\mu\text{mol/L}$ (Fig. 3E and F).

To more accurately reflect the influence of complex factors on the adsorption of antibiotics by MPs in the actual aquatic environment, it was essential to conduct multi-factors interactive experiments to simulate this adsorption scenario. As shown in Tab. S4, the significant difference analysis of single factor adsorption experiments indicated that the changes of pH, temperature, and NaCl concentration within a certain range have a more significant impact on the adsorption capacity of four MPs. Therefore, the adsorption capacities of four MPs towards OFX under eight sets of multi-factors interactive experiments at different pHs (5.0 and 7.0), temperatures (15 and 25°C) and NaCl concentrations (10 and 100 mg/L) were compared (Table 3). Firstly, the adsorption capacity of OFX was higher at 15°C under the same pH and salinity conditions. Then, four MPs exhibited better adsorption capacity for OFX under pH= 5 condition. Moreover, at the same temperature and pH condition, the NaCl still presented concentration inhibitory effect. Overall, these results were consistent with the single factor results (Fig. 3), indicating that MPs have strong anti-interference ability in the adsorption process of OFX, and the adsorption capacity of aged PS was

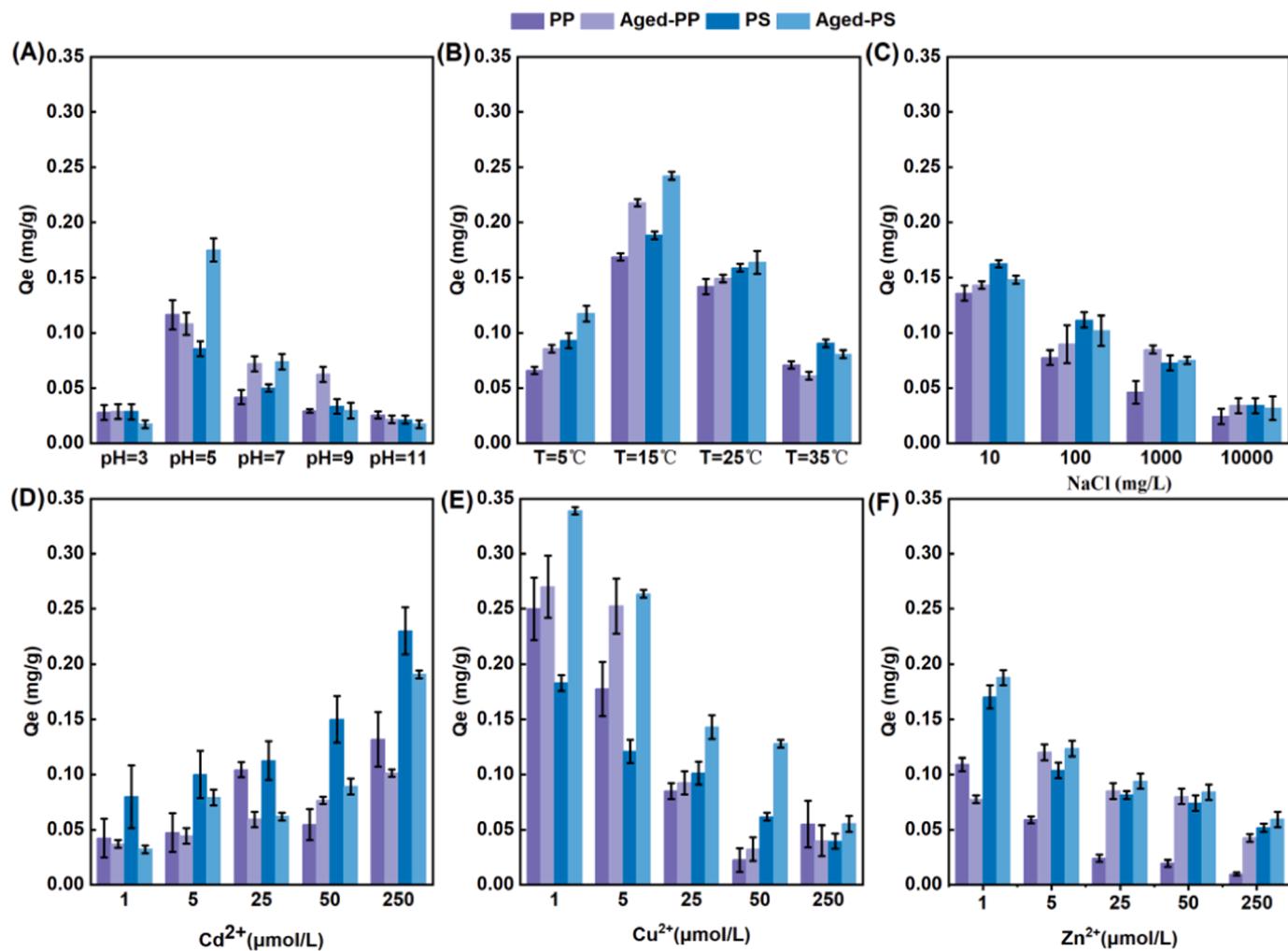


Fig. 3. Comparison of adsorption capacity of four MPs for ofloxacin among different (A) pH, (B) temperature conditions, and (C) NaCl, (D) Cd²⁺, (E) Zn²⁺, and (F) Cu²⁺ concentrations.

Table 3

Comparison of adsorption capacity of four MPs for ofloxacin under multi-factors interactive experiments.

pH	T (°C)	NaCl (mg/L)	Q_e (mg/g)			
			PP	Aged PP	PS	Aged-PS
5	15	10	0.12	0.17	0.18	0.27
5	25	10	0.09	0.15	0.12	0.17
5	15	100	0.06	0.12	0.06	0.13
5	25	100	0.02	0.04	0.02	0.11
7	15	10	0.05	0.07	0.08	0.15
7	25	10	0.02	0.03	0.06	0.15
7	15	100	0.07	0.05	0.06	0.09
7	25	100	0.01	0.02	0.02	0.09

better than that of aged-PP under almost conditions. Interestingly, the adsorption capacities of aged-PS under single conditions of pH=5 (0.18 mg/g), temperature= 15°C (0.24), and NaCl= 10 mg/L (0.16 mg/g) were all lower than that under multi-factors condition (0.27 mg/g), indicating that the interaction between various factors in the aquatic environment might induce adsorption synergy.

3.4. Mechanisms analysis of aging behavior and aquatic environmental factors

3.4.1. Characterization of microstructure and properties of four MPs

As shown in Fig. 4 and Fig. 5, the critical properties of four MPs were detected to penetrate the mechanisms of aging behavior and aquatic environmental factors on the adsorption kinetics. Firstly, it could be confirmed that the aging behavior changed the color of PS from white to yellow, while PP presented no change, indicating that the properties of PS were more susceptible to UV aging (Fig. 4). Bandow et al. [52] and Hu et al. [53] demonstrated that the inner layer of MPs could generate chromophores related to ultraviolet absorption, and the length of conjugated C=C-C bonds in polyene structures could also induce aged PS to turn yellow. The SEM characterization further confirmed that the surface microstructures of the four MPs were different each other. Among them, PP and PS were irregular particles, with the former having a smoother surface, while aged PP and aged PS have more rough surfaces, cracks, and pores, and were in the form of thin flakes falling off (Fig. 4A-D). The above results indicated that UV aging effectively changed the surface microstructures, which might be related to the alteration in MPs adsorption performance caused by aging behavior.

Then, BET characterization verified that the cracks and pores on the aged MPs surface increased their SSA (Fig. 4E), and the SSA of the four MPs were aged PS (0.941 m²/g), PS (0.841 m²/g), aged PP (0.810 m²/g), and PP (0.742 m²/g), respectively. The differences in pore diameter

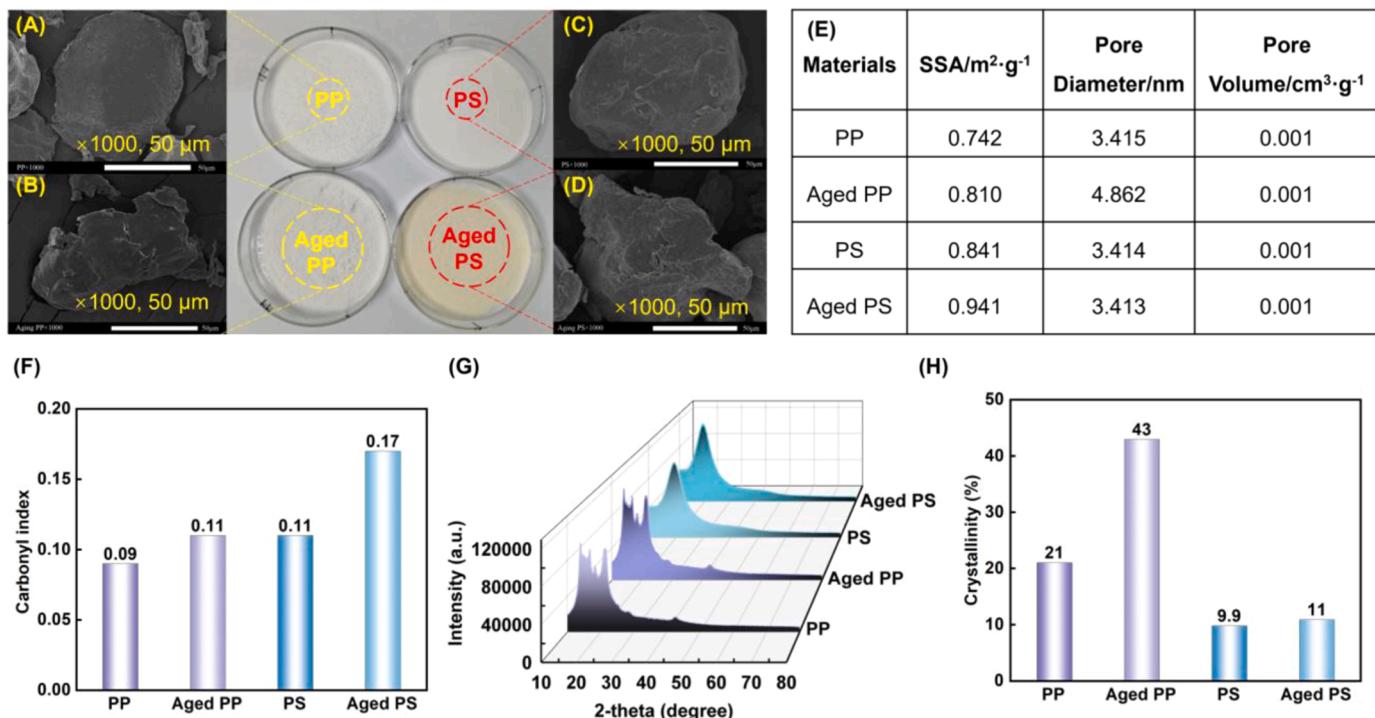


Fig. 4. The SEM images of PP (A), aged-PP (B), PS (C), and aged-PS (D) under 50 μm scale. The BET (E), the carbonyl index (F), XRD (G), and crystallinity (H) results of four MPs.

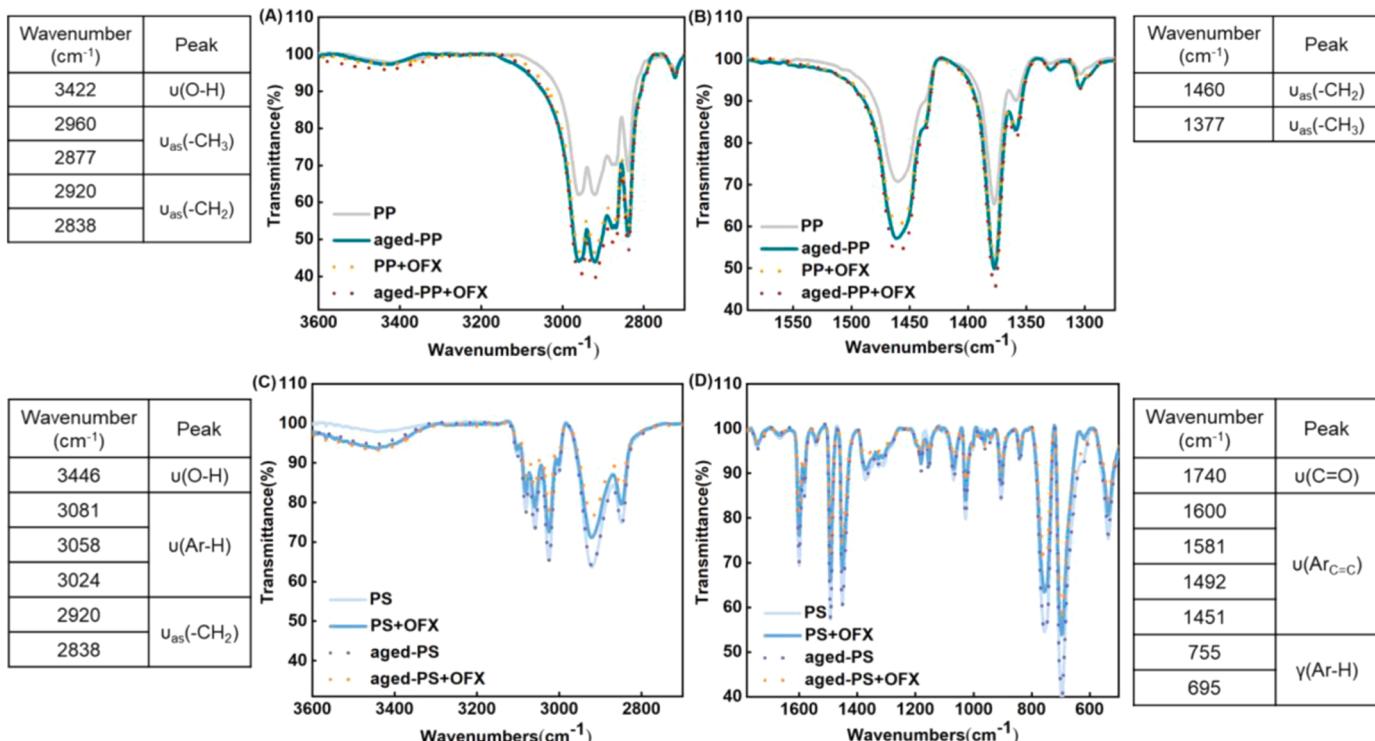


Fig. 5. The FTIR analyses of PP and aged-PP at 3600–2700 cm^{-1} (A) and 1589–1274 cm^{-1} (B) wavenumbers; the FTIR analyses of PS and aged-PS at 3750–2700 cm^{-1} (C) and 1800–500 cm^{-1} (D) wavenumbers.

and volume among the four MPs were not significant, indicating that aging behavior mainly altered the surface structure of MPs. The carbonyl index could evaluate the aging degree of PP and PS after UV exposure. Fig. 4(F) plotted that the carbonyl index of aged PP and aged PS increased by 22.2 % and 54.5 % respectively compared to fresh PP and

PS. Overall, these results indicated that PS was more susceptible to aging, and the aging behavior increased the content of oxygen-containing functional groups in MPs, which might be attributed to the content and types of additives (like antioxidant and UV absorber) contained in PS.

Moreover, the adsorption capacity differences among four MPs were further evaluated by XRD analysis (Fig. 4G). The results indicated that the peak patterns of PP and PS were different, but the aging behavior has not significantly changed the crystal structure of the two MPs. It is well known that PP is a rubbery polymer with a regular internal molecular chain structure, while PS is a glassy polymer with a benzene ring (Tab. S1). Obviously, the difference between the two types of microplastic materials determined the differential crystal structures. Previous study reported that the chains of MPs would be broken during aging process and formed short chain polymers, thus increasing crystallinity [54]. It is generally believed that the higher the crystallinity, the weaker the surface activity and adsorption capacity [22–24]. As shown in Fig. 4(H), the crystallinity of the four MPs was 21 % (PP), 43 % (aged-PP), 9.9 % (PS), and 11 % (aged-PS), respectively. Although the lower crystallinity of PS was consistent with the stronger adsorption capacity (Fig. 1), the promotion in crystallinity caused by aging behavior was not the determined factor affecting the adsorption capacity of MPs.

Finally, the FTIR spectra of the four MPs were presented in Fig. 5. For PP (Fig. 5A), the absorption peaks, like 1377 cm^{-1} , 2877 cm^{-1} , and 2960 cm^{-1} of $-\text{CH}_3$, 1460 cm^{-1} , 2838 cm^{-1} , and 2920 cm^{-1} of $-\text{CH}_2$, were consistent with the characteristic peaks of aged PP (Fig. 5B) [30]. Additionally, the characteristic peaks of aged-PP were increased compared to fresh PP, and this result could be attributed to the aging behavior inducing the increase of the oxygen-functional groups, like O-H (3422 cm^{-1}). Moreover, after the adsorption process of PP and aged PP, there was no new adsorption peaks observed in the spectrum. Obviously, considering the structural characteristics of PP, the adsorption mechanism of OFX by PP and aged PP was mainly hydrophobic. For PS (Fig. 5C), the absorption peaks, like $3000\text{--}3100\text{ cm}^{-1}$ of $=\text{CH}$, 1600 cm^{-1} , 1582 cm^{-1} , 1492 cm^{-1} and 1451 cm^{-1} of $\text{C}=\text{C}$, 697 cm^{-1} and 753 cm^{-1} of $=\text{CH}$, were consistent with the characteristic peaks of aged PS (Fig. 5D) [55]. Compared to PS, the characteristic peak of the benzene ring in aged PS decreased at a wavenumber of 1600 cm^{-1} , indicating that the aging behavior induced the ring opening reaction, which was consistent with the observed minimum peak of the benzene ring after aged PS absorbed OFX. This result also confirmed that $\pi\text{-}\pi$

interactions played vital role during adsorption process of PS. Additionally, Sun et al. [56] penetrated that the oxygen-containing functional groups formed on the surface of aged PS promoted electrostatic interactions and hydrogen bonding, which was also confirmed by the enhanced absorption peak of aged PS at 3446 cm^{-1} and 1744 cm^{-1} wavenumbers. Therefore, hydrogen bonds, electrostatic interactions, and $\pi\text{-}\pi$ interactions during adsorption processes could promote adsorption capacity of PS towards OFX after aging.

3.4.2. Relationship between adsorption capacity and aquatic environmental factors

As mentioned above, the adsorption kinetics of the four MPs towards OFX determined by the material properties and structure, and the main principle of aging behavior for improving the adsorption capacity was the increases of oxygen-containing functional groups and SSA on the material surface. However, the alteration of adsorption capacity before and after aging were not achieved overnight in actual aquatic environments [57]. As shown in Fig. 6, the critical factors in the aquatic environment have differential mechanisms affecting the adsorption capacity of MPs towards OFX. Firstly, under different pH conditions, the adsorption capacities of MPs were related to their isoelectric point (pH_{pzc}) and the dissociation constant (pK_a) of antibiotics. Therefore, electrostatic adsorption might dominate the adsorption process under appropriate pH conditions (Fig. 6A). Then, the promotion of adsorption capacity by temperature depended on the NAC between the adsorption and desorption processes. Within a certain range of temperature, it could simultaneously promote the entropy of the reaction process and accelerate the migration and dissolution of molecules. Once the NAC was greater than zero, the temperature exhibited a promoting effect on the adsorption of antibiotics by MPs (Fig. 6B). Moreover, the adsorption inhibitions of salinity were reflected in the competition of Na^+ for adsorption sites, the inhibition of Cl^- on pore diffusion, and the increase of solution viscosity and density due to the increased ion concentration (Fig. 6C). Finally, the different external electronic structure arrangement of different heavy metals determined their chemical properties, which could induce different mechanisms during the adsorption process.

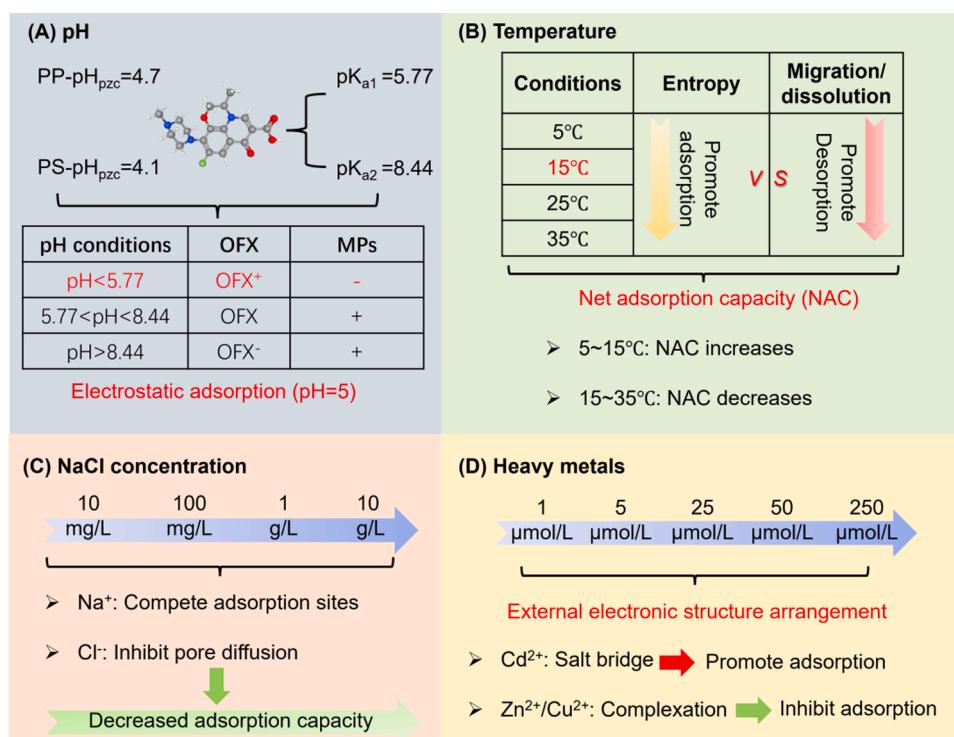


Fig. 6. The potential mechanisms of aquatic environmental factors on the adsorption kinetics of microplastics towards hydrophobic antibiotic.

For example, the relative stable Cd²⁺ could act as a salt bridge between MPs and OFX, thus promoting the adsorption process, while Zn²⁺ and Cu²⁺ easily chelated with OFX to form complexation, thereby inhibiting adsorption affinity (Fig. 6D).

3.5. Environmental implication

The widespread detection of MPs and antibiotics in the environment has raised global concerns. The aging of MPs leads to enhanced adsorption towards hydrophobic antibiotics, resulting in the aggregation of these two emerging contaminants. However, the mechanism behind this adsorption alteration and the impact of aquatic environmental factors on this adsorption behavior are not fully understood. This study demonstrated that the structure of MPs dominated the adsorption process, and aging behavior increased the oxygen-containing functional groups and specific surface area of MPs, thereby prolonging the adsorption equilibrium time. This study also revealed that multiple factors combined to affect the adsorption process of MPs towards antibiotics in actual aquatic environment, and these factors ultimately altered the adsorption capacity through synergistic or antagonistic mechanisms on the adsorption behavior. Hence, future studies on the development of elimination technologies for aggregates of various emerging contaminants are urgently required to reduce the risks of emerging contaminants in complex environmental conditions.

4. Conclusion

The innovative purposes of this study were to penetrate the mechanisms of enhanced adsorption of hydrophobic antibiotics by MPs after aging, and to reveal the influence mechanisms of aquatic environmental factors on this adsorption capacity alteration. Overall, this study provided novel insights for understanding the adsorption behavior of MPs towards hydrophobic antibiotics in aquatic environment. The main conclusions of this study include:

- The adsorption kinetics of two representative MPs (PP and PS) and their aged materials (aged PP and aged PS) towards OFX demonstrated that aging behavior prolonged the adsorption equilibrium time, and PS exhibited stronger adsorption capacity than PP.
- The microstructure and property characterizations of four MPs penetrated that aging behavior mainly increased the oxygen-containing functional groups and SSA on the material surface, and the structural differences between PP and PS determined their respective adsorption processes. PP was mainly based on physical adsorption, however, due to the presence of benzene ring, the hydrogen bonds, electrostatic interactions, and π-π interactions, these multiple mechanisms jointly determined the adsorption behavior of PS.
- This study compared the adsorption capacities of four MPs towards OFX under various key factors in aquatic environment (like pH, temperature, salinity, heavy metal types and concentrations), and clarified the synergistic or antagonistic effect on adsorption process was jointly induced by different potential mechanisms. However, considering the complexity of the actual aquatic environment (like the composition and occurrence content of MPs and antibiotics, and other environmental factors), the adsorption behavior between MPs and hydrophobic antibiotics deserves further exploration in future work.

CRediT authorship contribution statement

Xue-jian Li: Resources, Methodology, Data curation. **Lei-lei Lu:** Funding acquisition. **Hao Zhou:** Writing – review & editing, Supervision, Resources. **Sheng-hu Zhang:** Writing – review & editing, Supervision, Funding acquisition. **Yuan-qing Bu:** Supervision. **Hou-hu Zhang:** Writing – review & editing, Project administration, Funding

acquisition. **Ping Wu:** Writing – original draft, Investigation, Formal analysis, Data curation. **Guo-dong Kang:** Writing – original draft, Formal analysis.

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.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jece.2025.115444.

Data Availability

Data will be made available on request.

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