

## Article

# Microplastics Meet Metoprolol in Natural Water: Sorption Behavior and Mechanism

Tao Peng<sup>1</sup>, Zhuo Yang<sup>1</sup>, Danni Chen<sup>1</sup>, Hongyu Cao<sup>1</sup>, Yuehua Deng<sup>1,\*</sup> and Wei Zhao<sup>2,\*</sup>

<sup>1</sup> College of Geology and Environment, Xi'an University of Science and Technology, Xi'an 710054, China; pengtao@xust.edu.cn (T.P.); yangzhuo0816@163.com (Z.Y.); 23209226073@stu.xust.edu.cn (D.C.); 23209226100@stu.xust.edu.cn (H.C.)

<sup>2</sup> School of Materials Engineering, Changshu Institute of Technology, Changshu 215500, China

\* Correspondence: yhdeng2018@xust.edu.cn (Y.D.); lmjzhaowei@foxmail.com (W.Z.)

**Abstract:** As an ideal carrier for the spread of pollutants in the aquatic environment, microplastics (MPs) can adsorb pharmaceutical  $\beta$ -blockers, which can affect their migration and lead to some unpredictable adverse consequences. In this paper, the sorption behaviors and mechanism of MPs (polyvinyl chloride (PVC) and polypropylene (PP)) for typical  $\beta$ -blocker metoprolol (MTL) were investigated. The effects of pH, salinity and humic acids (HAs) on the sorption were studied, which proved that the sorption behavior was different under different environmental conditions. Both low pH and high salinity inhibited the sorption of MTL by the MPs. Specifically, the sorption capacity of MTL increased, with pH increase from 3 to 10. When pH = 10, the sorption capacities of MTL on PVC (1.75 mg/g) and PP (3.34 mg/g) reached the maximum. After pH > 10, the amount of MTL adsorbed on PVC was slightly decreased, while that on PP was essentially the same. The addition of salt ions inhibited the sorption in the concentration range of 5–250 mg/g for both NaCl and CaCl<sub>2</sub>, with the inhibitory effect of Ca<sup>2+</sup> being stronger than that of Na<sup>+</sup>. Moreover, the presence of HAs promoted the sorption of MPs for MTL. In the absence of HAs, the sorption capacities of PP and PVC for MTL were 0.34 mg/g and 0.79 mg/g, respectively. When HA concentration was 100 mg/L, the highest sorption capacities of PP and PVC reached 0.79 mg/g and 1.37 mg/g, respectively. This indicated that the promoting effect of HAs on PP was stronger than that on PVC. In general, based on the study of the sorption behavior of MTL and the characterization of the MPs, the sorption mechanism was speculated to consist mainly of electrostatic interactions, cation exchange, hydrophobic interaction and halogen bonding. The sorption kinetics of MTL on the two MPs were well-fitted by the pseudo-second-order model with  $R^2 > 0.99$ . The sorption isotherms both fitted the Freundlich model, which substantiated that the sorption of MTL on the MPs (PVC and PP) was multilayered and heterogeneous. Collectively, these findings provided a theoretical basis for revealing the complex interactions between MPs and MTL in natural water and a new insight into the fate and migration of MPs and  $\beta$ -blockers in the environment.

**Keywords:** microplastics; sorption;  $\beta$ -blockers; metoprolol; environmental conditions



**Citation:** Peng, T.; Yang, Z.; Chen, D.; Cao, H.; Deng, Y.; Zhao, W. Microplastics Meet Metoprolol in Natural Water: Sorption Behavior and Mechanism. *Water* **2024**, *16*, 3278. <https://doi.org/10.3390/w16223278>

Academic Editor: Grzegorz Nałęcz-Jawecki

Received: 10 October 2024

Revised: 6 November 2024

Accepted: 13 November 2024

Published: 14 November 2024



**Copyright:** © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

## 1. Introduction

Recently, emerging pollutant microplastics (MPs) have constituted a global concern [1]. Due to their large specific surface area and high hydrophobicity and fluidity, MPs can interact with chemical pollutants and act as micropollutant carriers [2,3]. It is reported that MPs can adsorb a variety of pollutants, such as heavy metals and organic pollutants (e.g., antibiotics, personal care products, and some pesticides), etc. [4–7]. Once MPs enter the aquatic environment, they will adsorb other pollutants owing to their properties, and then affect the migration of those pollutants differently [8]. In view of this, it is necessary to research the sorption behavior of MPs for different coexisting pollutants to understand their environmental fate and assess their potential risk.

The sorption of contaminants on MPs plays a crucial role in their environmental behavior, affecting their distribution, bioavailability, and toxicity [9,10]. Sorption processes involve the physical or chemical interaction between contaminants and MP surfaces, which is influenced by their characteristics [11]. For example, the sorption behaviors of most nonpolar compounds are dominated by hydrophobic interactions, whereas polar compounds are more susceptible to other sorption interactions [12]. Besides the characteristics of different pollutants, the polymer type affects sorption behavior. The main types of MPs commonly detected in the environment are polyvinyl chloride (PVC), polypropylene (PP), polyethylene (PE), polystyrene (PS), and polyamide (PA) [10]. In a previous experiment, their sorption behaviors for other coexisting pollutants were significantly different. Guo et al. revealed the sorption capacity of different MPs for  $\text{Sr}^{2+}$  is  $\text{PP} > \text{PS} > \text{PA}$ , because PP and PS had higher sorption affinity for  $\text{Sr}^{2+}$  than PA [13]. In addition, the sorption of MPs for pollutants can be statistically affected by a series of environmental factors, especially pH, salinity, and coexisting substances, like humic acids (HAs) [14–16]. For instance, the sorption ability of  $\text{Cd}^{2+}$  on MPs is raised with increasing pH, since it makes a more negative charge on MP surfaces, which leads to more electrostatic attraction taking place between  $\text{Cd}^{2+}$  and MPs [14]. Moreover, when investigating the sorption of nonsteroidal anti-inflammatory drugs (NSAIDs) on MPs, it was suggested that, at the condition of  $\text{pH} = 2$ , the sorption capacities were highest for three types of NSAIDs at  $\text{pH} < 5$ , because they existed mainly in their non-ionized form [15]. Furthermore, the presence of soil irons was found to decrease the sorption of MPs. The experiment documented that the sorption ability of PVC for levofloxacin (OFL) decreased with the increase in salinity, which may be actuated by the aggregation of PVC MPs, reducing the number of activated sorption sites [16]. Additionally, when HAs are present, sorption increases with increasing HA concentration, since HAs form complexes with metals that bring  $\text{Cd}^{2+}$  to the MP surface [14]. Thus, when investigating the environmental fate of MPs, it is indispensable to assess the effects of environmental conditions (e.g., pH, salinity, HAs) on their sorption behavior.

Aside from the environmental factors that will impact the sorption of MPs, the influence of the sorption mechanisms of MPs on pollutants is also complex. Different kinds of MPs have different sorption mechanisms for the same pollutants. Research indicates that the main sorption mechanism of methylene blue (MB) on all three MPs, including PS, PVC, and Polymethyl methacrylate (PMMA), has a  $\text{CH}/\pi$  interaction, the sorption on PS also includes hydrogen bond and  $\pi$ – $\pi$  conjugated interaction and the halogen bond on PVC, and there are electrostatic interaction and a polarity effect, both on PVC and PMMA [17]. These confirm that the sorption mechanism of MB for different types of MPs is not exactly the same. Moreover, when the specific polymer adsorbs different pollutants, the sorption mechanism is also different. It is demonstrated that the sorption mechanism of norfloxacin (NOR) on PS MPs is dominated by chemical sorption, which mainly includes  $\pi$ – $\pi$  conjugation and intermolecular hydrogen bonding, but the sorption mechanism of TYL on PS MPs is closely related to electrostatic interactions, surface complexation and hydrophobic interactions [18,19]. Therefore, the sorption of organic pollutants by MPs is sophisticated and usually involves multiple mechanisms [20]. To sum up, further studies on the sorption of contaminants on MPs are needed.

Beta-blockers ( $\beta$ -blockers) are a class of emerging pollutants that have been detected in wastewater treatment plants, surface water and even groundwater [21]. Their presence may affect the natural life of aquatic organisms, which has raised concerns about their fate and potential ecological consequences [22]. Reports of interactions between MPs and  $\beta$ -blockers reported in the literature are limited and scarce [23,24]. Puckowski et al. evaluated the sorption capacity of nine pharmaceuticals, including two  $\beta$ -blockers (propranolol (PRO) and nadolol (NAD)), on PP, PE and PVC, and the effect of  $\text{CaCl}_2$  addition and pH on the sorption process were also examined. The results showed that the sorption capacity varied depending on the pharmaceuticals selected, the type of MPs and the environmental conditions [23]. McDougall et al. studied a range of pharmaceuticals with different speciation (cationic, anionic and neutral) and hydrophobicity for sorption on

PE MPs, including two  $\beta$ -blockers (PRO and atenolol (ATL)). A particular focus has been given to the different sorption mechanisms of pharmaceuticals with different speciation and hydrophobicity on PE, as well as the effects of changing wastewater composition (pH and NaCl addition) on PE sorption behavior. The outcome showed that ATL had no detectable sorption on PE, whereas PRO reached the greatest sorption at pH 7 and 8, and NaCl addition inhibited the sorption of PRO on PE [24]. However, since this research focused on analyzing differences in sorption behaviors of different kinds of pharmaceuticals on MPs, environmental factors affecting the sorption behaviors, such as different salts (NaCl and CaCl<sub>2</sub>), were not considered in these studies. Last but not least, HAs exist widely in natural water, and available literature has manifested that HAs play an important role in the sorption of MPs [25]. Thus, fully understanding the impact of environmental factors on the sorption of  $\beta$ -blockers by MPs is critical for understanding their behavior in the environment.

Metoprolol (MTL) is one of the most commonly detected  $\beta$ -blockers in natural water [22]. Titov et al. extracted MPs (low-density PE, polyethylene terephthalate (PET) and PVC) environmental samples from river water and detected 27 types of drugs (including MTL) on MPs, indicating that MPs have the potential to serve as carriers for MTL. However, it is not clear how MTL adsorbed onto MPs and what influenced the sorption process in natural waters [26]. Therefore, in the present study, the sorption behaviors and mechanisms of MTL on two different MPs (PVC and PP) were investigated. The objectives of this study were (i) to examine the effects of pH, salinity (NaCl and CaCl<sub>2</sub> addition) and HAs on the sorption of MTL on MPs, (ii) to investigate the kinetic characteristics and isothermal sorption of MTL on the two MPs, and (iii) to discuss the possible sorption mechanisms of MTL on the MPs, in order to better understand the fate and potential risks of MPs and  $\beta$ -blockers in aquatic environments.

## 2. Materials and Methods

### 2.1. Materials and Reagents

MTL was acquired from Shanghai Jiuding Chemical Technology Co., Ltd. (Shanghai, China). The purity of the above agents was greater than 98%. MP pellets (PVC and PP) were bought from Zhongxin Plastic Material Co., Ltd. (Jieyang, China), and the average particle diameter of PVC and PP was approximately 13  $\mu$ m. Sodium humic acid was acquired from Shanghai Aladdin Biochemical Technology Co., Ltd. (Shanghai, China). NaCl and CaCl<sub>2</sub> were obtained from the Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China), and were used to control the salinity of aqueous solutions. The pH of aqueous solutions was adjusted using 0.1 mg/L HCl and NaOH. Methanol and acetonitrile (Tedia, Fairfield, OH, USA) were of HPLC grade. All other chemicals were of analytical grade.

### 2.2. MP Characterization and $\beta$ -Blocker Determination

Scanning electron microscopy (SEM, JSM-7610F, JEOL, Anichuan, Japan) was used to observe the microscopic morphology and surface structure of MP particles, which provided a reference for studying the sorption mechanism of MTL onto the MPs. The Fourier transform infrared spectrometer (FTIR, TensorII, Bruker, Saarbrücken, Germany) spectrum was recorded in the 4000–400  $\text{cm}^{-1}$  region with a resolution of 4  $\text{cm}^{-1}$ . X-ray diffraction (XRD, XD-3, General Instrument Co., Ltd., Beijing, China) was used to evaluate the crystallinity of the MPs, employing a Cu-K $\alpha$  as the radiation source ( $\lambda = 1.54056 \text{ \AA}$ ), and samples were scanned over the range of 5–90° of  $2\theta$  at a scan rate of 0.02° per 0.8 s. A micromeritics-specific surface and porosity analyzer was used to determine the specific surface area, pore volume and size of MPs by the Brunauer–Emmett–Teller (BET, ASAP 2020, Norcross, GA, USA) nitrogen sorption–desorption method at 77.35 K [23].

The concentration of MTL was analyzed by HPLC with a 4.6  $\times$  150 mm SB-C18 column (Agilent, Santa Clara, CA, USA). The analytical wavelength of MTL was 245 nm, 20  $\mu$ L samples were injected into the HPLC system, and the mobile phase was 77:23 (*v/v*)

buffer salt and methyl alcohol. The flow rate was always  $1 \text{ mL}\cdot\text{min}^{-1}$ , and the column temperature was  $30 \text{ }^\circ\text{C}$ .

### 2.3. Batch Sorption Experiments

Two kinds of batch sorption experiments were carried out in this study: sorption model experiments and environmental factor influence experiments.

For sorption model experiments, 0.15 g MPs (PP or PVC) were introduced into MTL solution with different concentrations. In the kinetic sorption experiments, 1 mL MTL stock solution with a concentration of  $25 \text{ mg}\cdot\text{L}^{-1}$  was added to 40 mL glass vials, then PP or PVC was added. The pH of solution was adjusted to 6 by  $0.1 \text{ mg/L}$  NaOH and HCl. Finally, it was necessary to dilute the solution to 20 mL using ultrapure water. The samples were shaken on an oscillator (ZD-85, Guohua, Beijing, China) at 150 rpm and analyzed at specific time intervals (10, 20, 30, 60, 120, 240, 480, 720, 1440 and 2880 min). In experiments for the sorption isotherms, the initial concentration of MTL in 40 mL glass vials was set as 5, 10, 15, 20, 25, 50, 100, 150, 200, 250  $\text{mg}\cdot\text{L}^{-1}$  by adding different amounts of MTL mother liquor. After 24 h of sorption, 1 mL sample was extracted for analysis. The other reaction conditions are the same as for the kinetic experiments. Each group of experiments was repeated three times.

The sorption experiments on environmental factors included pH, salinity and HAs. To evaluate the impact of pH on the sorption of MTL, 0.15 g MPs were first added to a centrifuge tube containing the  $25 \text{ mg}\cdot\text{L}^{-1}$  MTL solution, and then the pH of the solution was adjusted to 3–11 using  $0.1 \text{ mol/L}$  NaOH and HCl. After the pH is stable, the volume is fixed to 20 mL with ultrapure water. Similarly, the MTL solution with different concentrations of HAs ( $0\text{--}200 \text{ mg}\cdot\text{L}^{-1}$ ) and salinity ( $0\text{--}250 \text{ mg}\cdot\text{L}^{-1}$ ) was prepared. All experiments oscillated at  $25 \text{ }^\circ\text{C}$ . After 24 h, the sample solution was filtered through a  $0.22 \text{ }\mu\text{m}$  filter and finally measured using HPLC as mentioned above. All experiments were performed in triplicate.

### 2.4. Analysis Methods

The number of MTL adsorbed per unit mass of MPs at equilibrium,  $q_e$  ( $\text{mg}\cdot\text{g}^{-1}$ ) was estimated using [Equation (1)]:

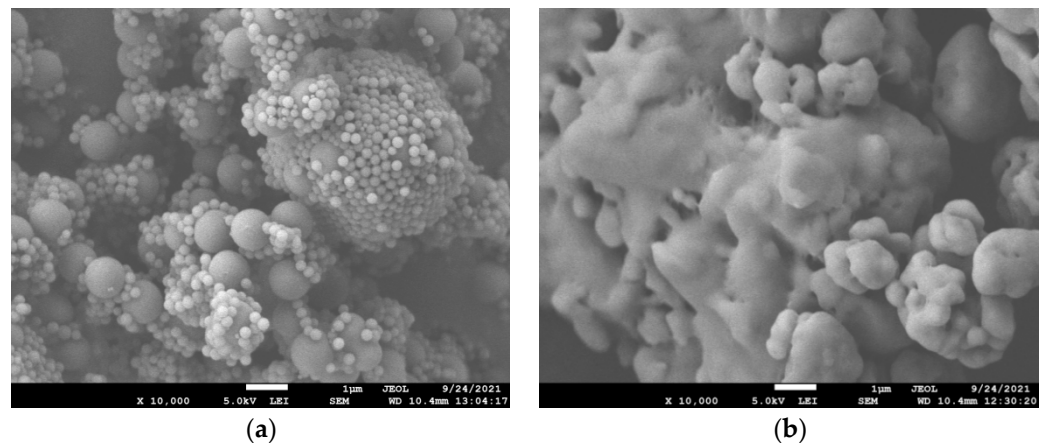
$$q_e = \frac{(C_0 - C_e)v}{m} \quad (1)$$

where  $q_e$  ( $\text{mg}\cdot\text{g}^{-1}$ ) is the equilibrium sorption capacity of MTL,  $C_0$  ( $\text{mg}\cdot\text{L}^{-1}$ ) and  $C_e$  ( $\text{mg}\cdot\text{L}^{-1}$ ) represent the initial and equilibrium MTL concentration, respectively,  $v$  (L) indicates the added volume of the MTL solution, and  $m$  (g) refers to the mass of the added MPs.

## 3. Results and Discussion

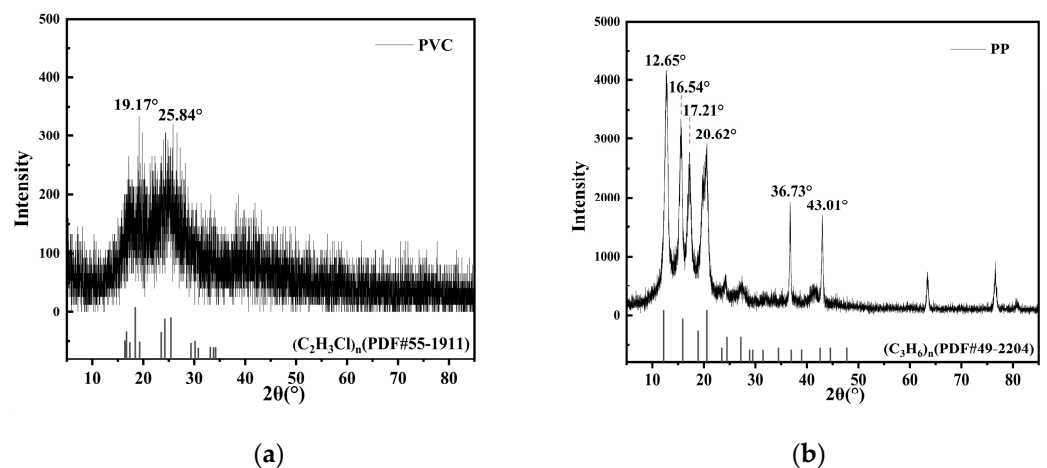
### 3.1. Characterizations of the MPs

The sorption capacity of MPs is related to their physical properties [18]. The surface and the morphology of the MPs are shown in Figure 1. SEM micrographs explained that the surface of both PVC and PE MPs was relatively smooth. The shape of the PVC was regular spherical, but PP was irregular and had several pores. The BET calculation results revealed that PVC had a larger specific surface area and pore volume, with values of  $3.1434 \text{ m}^2\cdot\text{g}^{-1}$  and  $0.006067 \text{ cm}^3\cdot\text{g}^{-1}$ . The specific surface areas and the pore volume of PP were  $2.6252 \text{ m}^2\cdot\text{g}^{-1}$  and  $0.003911 \text{ cm}^3\cdot\text{g}^{-1}$ , respectively. Therefore, the specific surface area and pore volume of MPs was  $\text{PVC} > \text{PP}$ . Due to these properties, PVC has a greater probability of contact with MTL, which can be attributed to surface sorption and pore-filling action. Therefore, the sorption amount of MTL on PVC was higher than that of PP.



**Figure 1.** SEM images of (a) PVC and (b) PP.

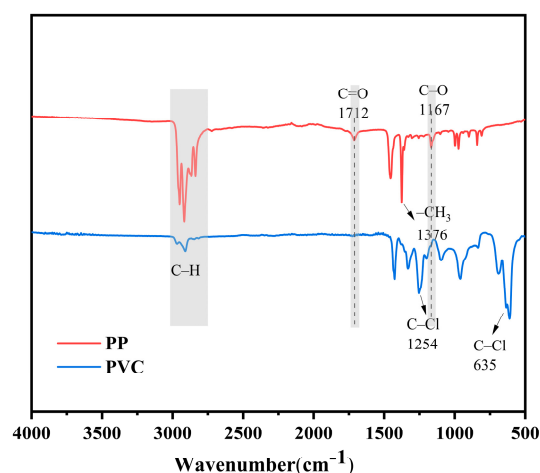
To illustrate the chemical sorption mechanism of MTL sorption by the two MPs, XRD analysis and the corresponding standard diffraction file card (PDF#55-1911 and PDF#49-2204) are shown in Figure 2. XRD patterns are commonly used to characterize the crystallinity of plastic materials. The diffraction peak of PVC was not obvious; however, PP had six distinct characteristic diffraction peaks with different characteristics at  $12.65^\circ$ ,  $16.54^\circ$ ,  $17.21^\circ$ ,  $20.62^\circ$ ,  $36.73^\circ$ , and  $43.01^\circ$ . This phenomenon proved that PP had a semi-crystalline structure, while PVC had an amorphous structure. Thus, the crystallinity of the MPs was  $PP > PVC$ , which was consistent with the research conducted by Wang et al. [27]. Generally, a lower degree of crystallinity results in a more disordered polymeric chain with greater proportions of amorphous regions where the atoms can move more freely, promoting the sorption of MPs [10]. Therefore, the sorption capacity of MPs should be  $PVC > PP$ , which is consistent with the experimental results we obtained later.



**Figure 2.** XRD patterns of MPs before and after sorption of MTL (a) PVC and (b) PP.

The FTIR spectra of MPs are depicted in Figure 3. The characteristic peaks of the stretching vibration of C-H bonds are observed on both PP and PVC (shaded area). In addition to the C-H bond, the peaks at  $1167\text{ cm}^{-1}$  and  $1712\text{ cm}^{-1}$  of PP indicated the existence of C-O and C=O [28]. The C-Cl bending vibration peaks of PVC are observed at  $635\text{ cm}^{-1}$  and  $1254\text{ cm}^{-1}$  [29]. Studies have shown that halogen bonds are formed between the chlorine atoms on PVC and the  $\pi$  electrons on the benzene ring, suggesting that these special functional groups can affect the sorption of pollutants on its surface [17].



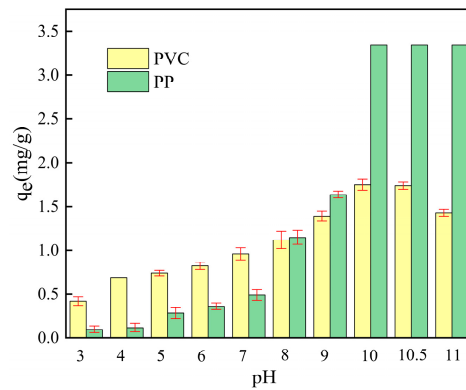


**Figure 3.** FTIR patterns of PP and PVC.

### 3.2. Effects of Environmental Factors on Sorption

#### 3.2.1. pH

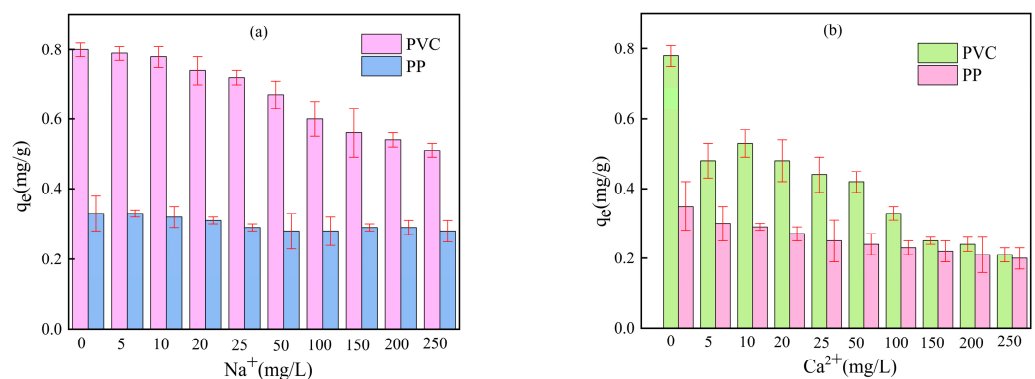
Literature shows that pH is a basic variable in natural water that affects the surface charge of MPs and drug morphology [30,31]. Therefore, pH plays an important role in affecting  $\beta$ -blocker sorption of MPs. We calculated the significant correlation indices between the sorption of MPs and pH, and the results showed that the correlation coefficients between pH and the sorption of PVC and PP were 0.9545 and 0.9217, respectively (Figure S2). This indicated that the sorption of MPs was significantly correlated with pH. Figure 4 describes the effect of different pH (3–11) conditions on the sorption of MTL by the MPs. The sorption capacity of MTL on PVC and PP was increased with a pH increase in the range of 3 to 10. Previous research demonstrated that MPs were always negatively charged in alkaline solutions to adsorb positively charged species through electrostatic interactions [19,32]. Thus, we suggest that elevated  $H^+$  may compete with MTL for sorption sites, resulting in less sorption of MTL on negative MPs under acid conditions. The competitive effect of  $H^+$  diminished as the pH increased, thereby the sorption of MTL increased. However, the amount adsorbed by PVC was slightly decreased, while PP was essentially the same at pH = 10–11. It was noteworthy that the maximum sorption of MTL on PP and PVC was achieved at pH = 10, with sorption amounts of 3.34 mg/g and 1.75 mg/g, respectively. This may be related to the pKa (9.7) of MTL [22]. In previous studies, speciation fractions for PRO are described: the pKa of PRO was 9.53, when the pH was less than 9.53, and PRO primarily existed in cationic form; when the pH value was higher than 9.53, PRO existed mainly in molecular form [33]. Hence, we can speculate that other  $\beta$ -blockers may show a similar speciation change with PRO under different pH. Therefore, after pH > 10, the sorption capacity of MTL on PVC is reduced, which may be connected with the weakening of electrostatic interaction. Nevertheless, the sorption capacity of MPs for MTL was higher at pH 10–11 compared to acidic and neutral conditions, which may be attributed to the large proportion of neutral molecules in MTL, so that the hydrophobic interaction dominated the sorption process [12]. Therefore, alkaline waters are more conducive to increasing the ability of MPs to act as carriers. This finding was in line with Puckowski et al., who found that another  $\beta$ -blocker, propranolol (PRO), adsorbed more strongly on the surface of the tested MPs under alkaline pH conditions [23]. In addition, we evaluated the difference in sorption capacity between PVC and PP through *t*-test. However,  $p = 0.522$  was obtained, indicating that there was no significant difference in sorption capacity between PVC and PP under the influence of pH (Figure S1). However, when pH = 10–11, the sorption capacity of PP for MTL was significantly greater than that of PVC (*t*-test,  $p < 0.01$ ), which was consistent with the study by Puckowski et al. This was due to the fact that the  $K_d$  of PP was greater than that of PVC, resulting in a stronger hydrophobic effect [23].



**Figure 4.** The effect of pH on the sorption of MTL by the MPs.

### 3.2.2. Salinity

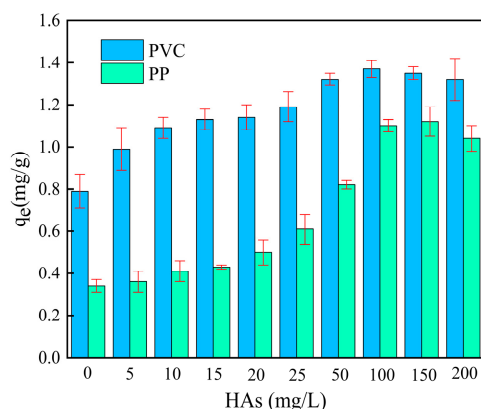
The effects of salinity on the sorption of MTL on the MPs are summarized in Figure 5. We found that, for two MPs studied, salinity influenced MTL sorption processes differently. With the rise in NaCl and CaCl<sub>2</sub> salinity, the sorption capacities of PVC for MTL exhibited an obvious decreasing trend (*t*-test,  $p < 0.01$ ). This may be explained by the competition of Ca<sup>2+</sup> and Na<sup>+</sup> for cationic exchange sites on the PVC surfaces [34]. It is also possible that an increase in salinity reduces the thickness of the electric double layer, neutralizes the surface charge of PVC, and weakens the electrostatic interaction between MTL and MPs [35]. According to Puckowski et al. and Wagstaff et al., the sorption capacity of PVC for MTL declined with the increase in Na<sup>+</sup> and Ca<sup>2+</sup> concentrations in the solution, which was in agreement with our experimental result [23,36]. There was little impact of NaCl salinity on the sorption on PP, demonstrating that NaCl has a negligible effect on pharmaceutical sorption to PP [24]. However, after the addition of 5 mg·L<sup>-1</sup> CaCl<sub>2</sub>, the sorption capacity of PP to MTL decreased. Combining our results with those of Wagstaff et al., Ca<sup>2+</sup> can produce a charge shielding effect on the surface of the MPs and reduce the electrostatic interaction between the MPs and positively charged MTL [36]. Generally, the inhibition effect of salinity on the sorption of PVC is stronger than that on PP, which may be related to the specific surface area, functional group and crystallinity of the MPs. Meanwhile, compared with Na<sup>+</sup>, this suppression was considerably more obvious at Ca<sup>2+</sup> concentrations, which may be related to the radius of cations and the number of charges. These results suggest that ions are not beneficial to the sorption of MTL on the MPs, in line with other studies [23]. It was anticipated that the interaction between MPs and MTL would be weaker in natural waters with higher salinity than with lower salinity because electrostatic interaction and cation exchange are involved in the sorption mechanism. Moreover, we calculated the significant correlation index between MP sorption and salinity (Table S1) and evaluated the difference in sorption capacity between PVC and PP through *t*-test (Figure S1).



**Figure 5.** The effect of salinity on MTL sorption on MPs (a) Na<sup>+</sup>; (b) Ca<sup>2+</sup>.

### 3.2.3. HAs

Dissolved organic matter (DOM) plays a crucial role in the sorption interaction of drugs and MPs in aquatic environments, which will change with its concentration [32]. As a ubiquitous DOM in aquatic environments, HAs contain a variety of functional groups, and thus can affect the behavior of MPs [16,37]. In this study, the significant correlation indices between the sorption of the MPs and HAs were calculated (Figure S2), indicating that the sorption of MPs was correlated with HAs. The influence of different HA concentrations is depicted in Figure 6. Obviously, the sorption capacity of MTL on the MPs increases as the HAs concentration increases at 0–100 mg·L<sup>-1</sup>, indicating that the presence of HAs has a promoting effect on the sorption of MTL. This result may be due to the following reasons: (1) the adsorbed HAs can act as a bridge between MTL and MP; (2) HAs may be sorbed on the surface of MPs and increase their hydrophobicity; (3) HAs had some negatively charged groups, e.g., hydroxyl and carbonyl functional groups, which may improve the electronegativity of the MPs [37]. After adding HAs, the sorption capacity of PP increased from 0.34 mg/g to 1.1 mg/g and the sorption capacity of PVC increased from 0.79 mg/g to 1.37 mg/g, indicating that the promotion effect of HAs on the sorption of PP was more obvious than that of PVC. This may be attributed to the fact that the presence of chloride ions in PVC makes it more electronegative, which facilitates stronger electrostatic interactions with HAs [16]. However, when HAs concentration exceeds 100 mg·L<sup>-1</sup>, the sorption capacity of MTL on MPs decreases slightly. A possible explanation is that HAs can be adsorbed onto MPs, competing with MTL for the available sorption sites. Moreover, owing to the large number of aromatic and carboxylic groups on HAs, the formation of  $\pi$ - $\pi$  and hydrogen bonds with MTL is favored, hence reducing the hydrophobic interactions between MTL on the MPs [38]. It is worth noting that PVC has a higher sorption capacity for MTL than PP, which may be attributed to the formation of halogen bonds between the chlorine atoms on PVC and the  $\pi$  electrons on the benzene ring of MTL [17]. Furthermore, we evaluated the difference in sorption capacity between PVC and PP through *t*-test. The calculation showed that  $p = 0.00073$  was obtained, indicating that there was significant difference in sorption capacity between PVC and PP under the influence of HAs (Figure S1).



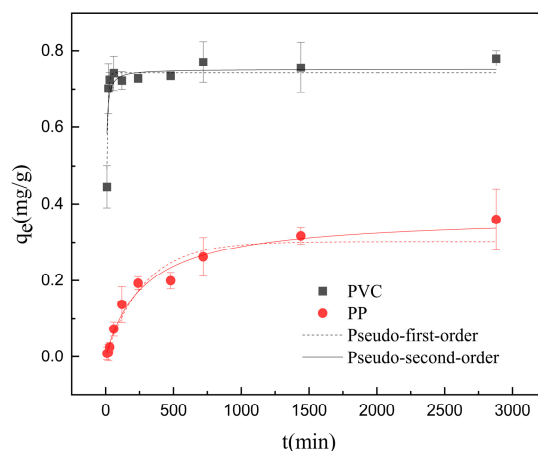
**Figure 6.** The effect of HAs on MTL sorption on MPs.

### 3.3. Sorption Kinetics

The curves of MTL adsorbed onto MPs are presented in Figure 7. The sorption of MTL increased rapidly in the early stage for the studied conditions, and the sorption rate gradually slowed down with the increase in contact time. PVC showed faster initial sorption of MTL than PP, reaching more than 80% of sorption equilibrium for ATL and more than 90% for MTL within 1 h. The initial sorption rate of PP is not as fast as that of PVC, and it takes longer to reach sorption equilibrium. After 4 h, the sorption of MTL by PP reached more than 70% of the equilibrium sorption capacities. The equilibrium sorption capacities of MTL on the PVC and PP were also varied, and the order of sorption capacity was PVC > PP. The difference in sorption capacity between PVC and PP was evaluated by



$t$ -test and  $p < 0.001$  was obtained, indicating that there was significant difference in sorption capacity between PVC and PP (Figure S4a).



**Figure 7.** Sorption kinetics of MTL on MPs.

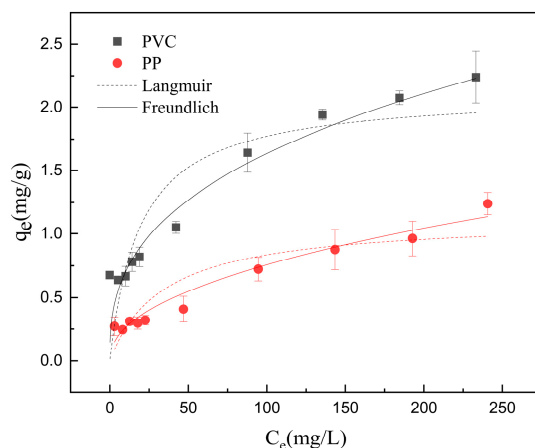
The parameters of the dynamic fitting curve are shown in Table 1. The results showed that the sorption process was fitted by the pseudo-second-order kinetic model with  $R^2 > 0.99$ , better than the pseudo-first-order model. This indicated that chemical sorption existed in the sorption of MTL on the MPs [38]. The results are in line with previous research that confirmed the sorption of pharmaceuticals including  $\beta$ -blockers onto MPs, fitting the pseudo-second-order model [2,34].

**Table 1.** Parameters obtained by different kinetic models for MTL adsorbed onto MPs.

MTL	MPs	Pseudo-First-Order Kinetics			Pseudo-Second-Order Kinetics		
		$K_1/(L/min)$	$q_e/(mg/g)$	$R^2$	$K_2/(g/(g \cdot min))$	$q_e/(mg/g)$	$R^2$
	PVC	0.0773	0.7307	0.9234	0.0879	0.7669	0.9976
	PP	0.0035	0.3252	0.9897	0.0089	0.3882	0.9924

### 3.4. Sorption Isotherms

Figure 8 depicts the sorption isotherm of MTL on the MPs, which were fitted with the Langmuir and Freundlich models to evaluate the sorption capacity of the MPs for MTL. As shown in Figure 8, the sorption capacity for MTL increased with increasing equilibrium concentration, while the rate of increase showed a tendency to become slower with increasing equilibrium concentration, suggesting that the sorption of the MPs gradually became saturated with the increase in equilibrium concentration [1]. The sorption capacity of PVC for MTL was greater than that of PP, which was consistent with the kinetics result. The difference in sorption capacity between PVC and PP was evaluated through  $t$ -test and  $p < 0.05$  was obtained (Figure S4b). The equilibrium sorption isotherms of MTL were generally better represented by the Freundlich isotherm, suggesting that the sorption of MTL on the MPs presents a multilayer sorption process [38]. The fitting parameters of two isotherm models are listed in Table 2. In contrast with the determination coefficient of the MPs adsorb MTL, the Langmuir  $R^2$  values were  $< 0.9$ , while that of the Freundlich equation ranged from 0.94 to 0.98. This also explained that the Freundlich model was more appropriate to simulate the sorption of MTL and the sorption was heterogeneous on the surface of PVC and PP [38]. In this study, the  $n$  values were all greater than 1 for MTL, which indicated that the chemical sorption process was not the only element between MTL and the MPs [39].



**Figure 8.** Sorption isotherms of the MTL by MPs.

**Table 2.** Parameters obtained by different isotherms models for the MTL adsorbed onto MPs.

MTL	MPs	Langmuir			Freundlich		
		$K_l$ ( $L \cdot mg^{-1}$ )	$Q_e$ ( $mg \cdot g^{-1}$ )	$R^2$	$n$	$K_f$ ( $mg \cdot g^{-1}$ )	$R^2$
	PVC	0.0502	2.1258	0.8469	2.7252	0.3018	0.9720
	PP	0.0356	1.4024	0.7534	2.5848	0.1190	0.9406

#### 4. Conclusions

This research investigated the sorption properties of the typical  $\beta$ -blocker MTL by two different MPs (PVC and PP). The results showed that elevated pH and low salinity favored the sorption of MTL on the MPs to some extent. When pH = 10, the sorption of MTL by the two MPs has reached the maximum. In the concentration range of 5–250 mg/L, the presence of  $Na^+$  and  $Ca^{2+}$  inhibited the sorption of the MPs for MTL. HAs also play a vital role in the sorption affinity of  $\beta$ -blockers and MPs. Low concentrations of HAs promoted the sorption of MTL by the MPs, while high concentrations of HAs (> 100 mg/L) inhibited its sorption. In the kinetic analysis, the sorption of MTL on the MPs followed the pseudo-second-order kinetic model, and the sorption amount of MTL was PVC > PP. *t*-test was used to evaluate the difference in sorption capacity between PVC and PP, and  $p < 0.001$  was calculated, indicating that the sorption capacity of MTL on PVC was significantly greater than that of PP. In the isotherm analysis, the sorption of MTL on the MPs fitted the Freundlich isotherm model, manifesting that the sorption process is a multilayered heterogeneous sorption. The statistical analysis also showed that the sorption capacity of PVC was significantly greater than that of PP (*t*-test,  $p < 0.05$ ), which may be ascribed to the specific surface area, crystallinity and surface functional group of the different MPs. The main sorption mechanisms of the MPs on MTL may be electrostatic interactions, cation exchange, hydrophobic interaction and halogen bonding. These findings elucidated the interaction behaviors and mechanisms between PVC or PP and MTL in natural water, which could be meaningful for further research into the environmental behavior of MPs and  $\beta$ -blockers in natural water. It is remarkable that our study focused on the sorption of pristine MPs for MTL. However, MPs are susceptible to natural aging under real environmental conditions, their properties change significantly after aging, and the sorption behavior of pollutants onto MPs was also affected. Therefore, in the future, attention should be paid to the sorption behavior of MPs after natural aging in order to further accurately evaluate the fate of MPs in the real environment.

**Supplementary Materials:** The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/w16223278/s1>, Figure S1: The significant differences analysis of the sorption capacity between PVC and PP under different experimental conditions (pH (a),  $Na^+$  (b),

Ca<sup>2+</sup> (c) and HAs (d)); Figure S2: The significant correlation indexes between the sorption of MPs and the environmental factors (pH and HAs); Figure S3: The significant differences analysis in the increase/decrease of MPs sorption capacity caused by environmental changes compared to control conditions; Figure S4: The significant differences analysis of the sorption capacity between PVC and PP in the sorption kinetics (a) and the sorption isotherms (b); Table S1: The significant correlation indexes between the sorption of MPs and salinity (Na<sup>+</sup> and Ca<sup>2+</sup>).

**Author Contributions:** T.P.: conceptualization, resources, funding acquisition, writing review and editing; Z.Y.: investigation, formal analysis, visualization, writing—original draft; D.C.: investigation, visualization, writing—original draft; H.C.: investigation, visualization, formal analysis, writing original; Y.D.: conceptualization, resources, methodology, writing review and editing; W.Z.: conceptualization, resources, writing review and editing. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research received no external funding.

**Data Availability Statement:** Data is contained within the article.

**Conflicts of Interest:** The authors declare no conflicts of interest.

## References

1. Xue, X.; Hong, S.; Cheng, R. Adsorption characteristics of antibiotics on microplastics: The effect of surface contamination with an anionic surfactant. *Chemosphere* **2022**, *307*, 136195. [[CrossRef](#)] [[PubMed](#)]
2. Yu, F.; Li, Y.; Huang, G. Adsorption behavior of the antibiotic levofloxacin on microplastics in the presence of different heavy metals in an aqueous solution. *Chemosphere* **2020**, *260*, 127650. [[CrossRef](#)] [[PubMed](#)]
3. Kinigopoulou, V.; Pashalidis, I.; Kalderis, D. Microplastics as carriers of inorganic and organic contaminants in the environment: A review of recent progress. *J. Mol. Liq.* **2022**, *350*, 118580. [[CrossRef](#)]
4. Mao, R.; Lang, M.; Yu, X. Aging mechanism of microplastics with UV irradiation and its effects on the adsorption of heavy metals. *J. Hazard. Mater.* **2020**, *393*, 122515. [[CrossRef](#)] [[PubMed](#)]
5. Guo, X.; Chen, C.; Wang, J. Sorption of sulfamethoxazole onto six types of microplastics. *Chemosphere* **2019**, *228*, 300–308. [[CrossRef](#)]
6. Ma, J.; Zhao, J.; Zhu, Z. Effect of microplastic size on the adsorption behavior and mechanism of triclosan on polyvinyl chloride. *Environ. Pollut.* **2019**, *254*, 113104. [[CrossRef](#)]
7. Wang, T.; Yu, C.; Chu, Q. Adsorption behavior and mechanism of five pesticides on microplastics from agricultural polyethylene films. *Chemosphere* **2020**, *244*, 125491. [[CrossRef](#)]
8. Rubin, A.E.; Zucker, I. Interactions of microplastics and organic compounds in aquatic environments: A case study of augmented joint toxicity. *Chemosphere* **2022**, *289*, 133212. [[CrossRef](#)]
9. Wang, T.; Wang, L.; Chen, Q. Interactions between microplastics and organic pollutants: Effects on toxicity, bioaccumulation, degradation, and transport. *Sci. Total Environ.* **2020**, *748*, 142427. [[CrossRef](#)]
10. Tourinho, P.S.; Kočí, V.; Loureiro, S. Partitioning of chemical contaminants to microplastics: Sorption mechanisms, environmental distribution and effects on toxicity and bioaccumulation. *Environ. Pollut.* **2019**, *252*, 1246–1256. [[CrossRef](#)]
11. Fred-Ahmadu, O.H.; Bhagwat, G.; Oluyoye, I. Interaction of chemical contaminants with microplastics: Principles and perspectives. *Sci. Total Environ.* **2020**, *706*, 135978. [[CrossRef](#)] [[PubMed](#)]
12. Wang, Z.; Ding, J.; Razanajatovo, R.M. Sorption of selected pharmaceutical compounds on polyethylene microplastics: Roles of pH, aging, and competitive sorption. *Chemosphere* **2022**, *307*, 135561. [[CrossRef](#)] [[PubMed](#)]
13. Guo, X.; Liu, Y.; Wang, J. Equilibrium, kinetics and molecular dynamic modeling of Sr<sup>2+</sup> sorption onto microplastics. *J. Hazard. Mater.* **2020**, *400*, 123324. [[CrossRef](#)] [[PubMed](#)]
14. Guo, X.; Hu, G.; Fan, X. Sorption properties of cadmium on microplastics: The common practice experiment and a two-dimensional correlation spectroscopic study. *Ecotoxicol. Environ. Saf.* **2020**, *190*, 110118. [[CrossRef](#)]
15. Elizalde-Velázquez, A.; Subbiah, S.; Anderson, T.A. Sorption of three common nonsteroidal anti-inflammatory drugs (NSAIDs) to microplastics. *Sci. Total Environ.* **2020**, *715*, 136974. [[CrossRef](#)]
16. Chen, Y.; Tang, H.; Cheng, Y. Interaction between microplastics and humic acid and its effect on their properties as revealed by molecular dynamics simulations. *J. Hazard. Mater.* **2023**, *455*, 131636. [[CrossRef](#)]
17. Du, H.L.; Zhang, Y.S.; Wang, H. Adsorption behavior of methylene blue on diverse microplastics. *Environ. Chem.* **2022**, *41*, 2803–2812.
18. Sun, M.; Yang, Y.; Huang, M.; Fu, S.; Hao, Y. Adsorption behaviors and mechanisms of antibiotic norfloxacin on degradable and nondegradable microplastics. *Sci. Total Environ.* **2022**, *807*, 151042. [[CrossRef](#)]
19. Guo, X.; Pang, J.; Chen, S. Sorption properties of tylosin on four different microplastics. *Chemosphere* **2018**, *209*, 240–245. [[CrossRef](#)]
20. Fu, L.; Li, J.; Wang, G. Adsorption behavior of organic pollutants on microplastics. *Ecotoxicol. Environ. Saf.* **2021**, *217*, 112207. [[CrossRef](#)]

21. Barbieri, M.; Licha, T.; Nödler, K. Fate of  $\beta$ -blockers in aquifer material under nitrate reducing conditions: Batch experiments. *Chemosphere* **2012**, *89*, 1272–1277. [[CrossRef](#)] [[PubMed](#)]
22. Yi, M.; Sheng, Q.; Sui, Q.  $\beta$ -blockers in the environment: Distribution, transformation, and ecotoxicity. *Environ. Pollut.* **2020**, *266*, 115269. [[CrossRef](#)] [[PubMed](#)]
23. Puckowski, A.; Cwiąg, W.; Mioduszevska, K.; Stepnowski, P. Sorption of pharmaceuticals on the surface of microplastics. *Chemosphere* **2021**, *263*, 127976. [[CrossRef](#)] [[PubMed](#)]
24. McDougall, L.; Thomson, L.; Brand, S. Adsorption of a diverse range of pharmaceuticals to polyethylene microplastics in wastewater and their desorption in environmental matrices. *Sci. Total Environ.* **2022**, *808*, 152071. [[CrossRef](#)] [[PubMed](#)]
25. Luo, H.; Liu, C.; He, D.; Sun, J.; Zhang, A.; Li, J. Interactions between polypropylene microplastics (PP-MPs) and humic acid influenced by aging of MPs. *Water Res.* **2022**, *222*, 118921. [[CrossRef](#)]
26. Titov, I.; Semerád, J.; Boháčková, J. Microplastics meet micropollutants in a central european river stream: Adsorption of pollutants to microplastics under environmentally relevant conditions. *Environ. Pollut.* **2024**, *360*, 124616. [[CrossRef](#)]
27. Wang, L.; Yang, H.; Guo, M.H. Adsorption of antibiotics on different microplastics (MPs): Behavior and mechanism. *Sci. Total Environ.* **2023**, *863*, 161022. [[CrossRef](#)]
28. He, S.; Sun, S.; Xue, H.; Kang, C. Polypropylene microplastics aging under natural conditions in winter and summer and its effects on the sorption and desorption of nonylphenol. *Environ. Res.* **2023**, *225*, 115615. [[CrossRef](#)]
29. Ding, L.; Yu, X.; Guo, X.; Zhang, Y.; Ouyang, Z.; Liu, P. The photodegradation processes and mechanisms of polyvinyl chloride and polyethylene terephthalate microplastic in aquatic environments: Important role of clay minerals. *Water Res.* **2022**, *208*, 117879. [[CrossRef](#)]
30. Yza, B.; Yyac, D.; Glac, D. Adsorption mechanism of cadmium on microplastics and their desorption behavior in sediment and gut environments: The roles of water pH, lead ions, natural organic matter and phenanthrene. *Water Res.* **2020**, *184*, 116209.
31. Huang, D.; Xu, Y.; Yu, X. Effect of cadmium on the sorption of tylosin by polystyrene microplastics. *Ecotoxicol. Environ. Saf.* **2020**, *207*, 111255. [[CrossRef](#)] [[PubMed](#)]
32. Mei, W.; Chen, G.; Bao, J.; Song, M.; Li, Y.; Luo, C. Interactions between microplastics and organic compounds in aquatic environments: A mini review. *Sci. Total Environ.* **2020**, *736*, 139472. [[CrossRef](#)] [[PubMed](#)]
33. Deng, Y.; Li, Y. Surface-bound humic acid increased propranolol sorption on Fe<sub>3</sub>O<sub>4</sub>/attapulgit magnetic nanoparticles. *Nanomaterials* **2020**, *10*, 205. [[CrossRef](#)]
34. Zhang, H.; Wang, J.; Zhou, B. Enhanced adsorption of oxytetracycline to weathered microplastic polystyrene: Kinetics, isotherms and influencing factors. *Environ. Pollut.* **2018**, *243*, 1550–1557. [[CrossRef](#)] [[PubMed](#)]
35. Wu, J.; Xu, P.; Chen, Q. Effects of polymer aging on sorption of 2, 2', 4, 4'-tetrabromodiphenyl ether by polystyrene microplastics. *Chemosphere* **2020**, *253*, 126706. [[CrossRef](#)] [[PubMed](#)]
36. Wagstaff, A.; Lawton, L.A.; Petrie, B. Polyamide microplastics in wastewater as vectors of cationic pharmaceutical drugs. *Chemosphere* **2021**, *288*, 132578. [[CrossRef](#)] [[PubMed](#)]
37. Wang, X.; Diao, Y.; Dan, Y. Effects of solution chemistry and humic acid on transport and deposition of aged microplastics in unsaturated porous media. *Chemosphere* **2022**, *309*, 136658. [[CrossRef](#)]
38. Zhang, J.; Zhan, S.; Zhong, L.B. Adsorption of typical natural organic matter on microplastics in aqueous solution: Kinetics, isotherm, influence factors and mechanism. *J. Hazard. Mater.* **2023**, *443*, 130130. [[CrossRef](#)]
39. Li, L.; Zhao, X.L.; Liu, D. Occurrence and ecological risk assessment of PPCPs in typical inflow rivers of Taihu lake, China. *J. Environ. Manag.* **2021**, *285*, 112176. [[CrossRef](#)]

**Disclaimer/Publisher's Note:** The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.