



Article Effects of Salinity, pH, and Cu(II) on the Adsorption Behaviors of Tetracycline onto Polyvinyl Chloride Microplastics: A Site Energy Distribution Analysis

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Abstract: Microplastics (MPs), as vectors for various pollutants in the environment, have been arousing public concern in recent years. The extensive use of antibiotics has led to their frequent detection in water environments, where they inevitably coexist with MPs and are actively adsorbed onto MPs' surfaces. However, the information on the influence of the main environmental factors on the sorption behavior of MPs is not fully understood, and especially, information about the effect mechanism is limited. This study aims to comprehensively assess the main factors and mechanisms that affect antibiotic sorption onto microplastics. The results indicated that the adsorption of tetracycline (TC) onto PVC MPs fits the pseudo-second-order model well. The adsorption of TC onto PVC MPs decreased with increasing salinity and pH. With the help of SED analysis, the decrease at high salinity was attributed to the decreased quantities of the most distributed energy sites in high-salinity systems compared to freshwater. Additionally, the decreased adsorption capacity of TC onto MPs at high pH mainly resulted from the electrostatic repulsion between MPs and TC^{2-} . The coexisting Cu²⁺ and TC could improve the affinity between PVC MPs and TC via "MPs-TC-Cu²⁺" and "MPs-Cu²⁺-TC" bridges, boosting the capacity of PVC MPs to adsorb TC. This study provides comprehensive insights into the influence and mechanism of the main factors on the environmental behaviors of the coexistence of MPs with antibiotics, which is of great importance for evaluating and controlling their risks.

Keywords: microplastics; adsorption; antibiotics; salinity; pH; site energy distribution analysis

1. Introduction

Microplastics (MPs, \leq 5 mm) have been widely detected in aquatic environments, such as oceans, rivers, and lakes [1,2]. Every year, over 8 million tons of MPs are released into the oceans from terrestrial environments around the world. However, this statistic about the amount of MPs in soil and water may be incomplete, posing a potential risk to human health and environmental security. MPs can be easily ingested by organisms due to their small size, negatively impacting organisms and human health [3,4]. Additionally, one of the biggest concerns about MPs is their potential to become carriers of coexisting pollutants in water environments [5]. Given their relatively high specific surface area and hydrophobicity, MPs inevitably interact with other trace pollutants [6]. The presence of MPs in air, soil, water, sediment, salt, and food provides exposure pathways for plants, animals, and humans to a variety of harmful substances, pollutants, and pests [7]. Moreover, MPs can transport or exchange pollutants from different environmental compartments, even over long distances [8]. With MP pollution exacerbating and MP surfaces accumulating trace contaminants at higher concentrations than in the water, their environmental risk is further increasing via bioaccumulation [9,10]. Therefore, an improved understanding of



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Copyright: © 2023 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/). the interaction mechanisms between microplastics and trace pollutants is of significant importance for assessing their risk to water ecosystems.

Adsorption of trace pollutants onto MPs has been previously studied. Various types of pollutants in the water cycle, such as antibiotics, polycyclic aromatic hydrocarbons, heavy metals, and organic compounds, are absorbed by microplastics in water according to their distribution coefficients [11], revealing the importance of van der Waals forces, hydrophobic interactions, and electrostatic interactions [12,13]. Van der Waals forces are noncovalent interactions that are prone to occur in aliphatic polymers (e.g., polyvinyl chloride (PVC) and polyethylene (PE)) and aromatic polymers [14]. Hydrophobic interactions, also as a form of noncovalent bonds, are prone to take place in a polar medium [15]. Guo and Wang previously reported that the adsorption of sulfamethoxazole and cephalosporin C onto PE was affected by their hydrophobicity differences [16]. Regarding electrostatic interaction, this force arises when positively charged molecules are close to negatively charged molecules [17]. Notably, these interaction forces are inevitably affected by environmental factors (e.g., salinity, pH, metal ions, etc.), further altering the sorption capacity. For instance, electrostatic interactions are susceptible to solution pH and the charge of coexisting pollutants. Wang et al. reported that activated carbon fiber (ACF) positive surfaces exhibited higher adsorption capacity at low pH for anionic perfluorooctane sulfonates (PFOSs) than nonionic perfluorooctane sulfonates (FOSAs), which means that the adsorption of antibiotics with different ionic, and ionic and amphoteric chemical forms on MPs may exert differences at different pH values [18]. It has been confirmed that negatively charged MPs favor the adsorption of positively charged pollutants and exhibit higher adsorption efficiency than negatively charged pollutants [19]. However, the influence of the main factors on the sorption behavior of MPs has not yet been fully understood; especially, the information about the effect mechanism is limited.

Antibiotics, ubiquitously detected in global environments, have been arousing great concern due to the development of microbial antibiotic resistance [20]. Large quantities of antibiotics are discharged into water environments every year. In China alone, over 60,000 tons of antibiotics were released into various environments in 2018 [21]. MPs and antibiotics are two emerging kinds of contaminants, bringing great potential threats to water ecosystems and human health. According to Quan et al., the adsorption of various antibiotics by MPs may result in their long-range migration and lead to complex influences [22], and the interactions between antibiotics and MPs may aggravate the potential threat to human health. The concentrations of antibiotics in aquatic environments can even reach concentrations of $\mu g/L$ -mg/L. Tetracycline (TC) is a broad-spectrum antibiotic commonly used in human medical treatment and animal husbandry [15]. Approximately 70 to 90% of administered TC is not biologically degraded and is discharged into the environment through urine and feces [23]. Consequently, TC is frequently detected in the environment at concentrations reaching the $\mu g/L$ -mg/L range [24], attracting extensive attention as an emerging trace pollutant in recent years. When TC combines with MPs and is ingested by organisms, the toxicity may be increased. Therefore, it is of great importance to systematically evaluate the interactions between TC and MPs and their potential environmental risk, especially the influence of environmental factors (e.g., salinity, pH, metal ion) on their interaction in seawater.

To the best of our knowledge, some studies investigated the effects of pH, salinity, and metal ions on the adsorption of antibiotics onto microplastics, but there are still limitations regarding the underlying mechanism. More importantly, the variety of antibiotics and MPs used in these studies is extensive, and the adsorption of different antibiotics onto different types of MPs varies, resulting in changes in the influence of environmental factors (e.g., pH, salinity, and metal ions) accordingly. Puckowski et al. studied the adsorption of norfloxacin on low density polyethylene (LDPE), high density polyethylene (HDPE), polypropylene (PP), and PVC, and the results showed that LDPE and HDPE had peak adsorption on norfloxacin at pH 4 and pH 2, respectively, and the peaks of PP and PVC were adsorbed at pH 12 [25]. Guo et al. showed that the adsorption of sulfamethoxazole

and sulfamethazine onto PE, polystyrene (PS), polyamide (PA), PVC, PP, and polyethylene glycol terephthalate (PET) showed a decreasing trend with increasing NaCl concentration (10%, 20%, and 35%) [26]. Fei et al. discovered that the presence of Cu^{2+} , Zn^{2+} , and Cr^{3+} improved the adsorption performance of levofloxacin (OFL) onto polyvinyl chloride (PVC) in aqueous solution, but the presence of Cd^{2+} and Pb^{2+} ions inhibited the adsorption, and this was related to the type and concentration of heavy metals [27]. However, further research is required to clarify the influence of these factors on the adsorption properties of antibiotics onto MPs.

In the present study, we aim to investigate and reveal the effects and mechanisms of salinity, pH, and main metal ions on the adsorption behaviors of antibiotics onto MPs. To this end, PVC, the common MP in aquatic environments, was selected to examine the adsorption behavior of TC onto MPs. Notably, the influence of the main environmental factors (i.e., salinity, pH, and Cu²⁺) on the adsorption behavior of TC onto MPs was further explored. Furthermore, site energy diffusion theory (SED) was employed to reveal the influence mechanism of these factors, given that SED can provide the energy magnitude and corresponding distribution function of adsorbent surface sites. This study reveals the underlying influence and mechanisms of salinity, pH, and Cu²⁺ on the environmental behaviors of PVC MPs adsorbing TC to evaluate and control their coexistence risk.

2. Materials and Methods

2.1. Materials

Tetracycline (TC, purity 99%) was acquired from J&K Scientific Chemical Co., Ltd. (Shanghai, China), and the main physicochemical properties of TC were: MW: 444.43; aqueous solubility of 0.52–117 mmol/L; $\log K_{ow}$ of 20,131.97 to -0.47; and pK_a , values of 3.3, 7.7 and 9.7. Molecular structure of tetracycline and its speciation as a function of pH are presented in Figure S1 [28]. Analytical grade reagents of sodium chloride (NaCl), sodium hydroxide (NaOH), potassium chloride (KCl), calcium chloride (CaCl₂), magnesium chloride (MgCl₂), magnesium sulfate (MgSO₄), and copper sulfate (CuSO₄) were also obtained from J&K Scientific Chemical Co., Ltd. Co., Ltd. (Shanghai, China). Here, NaCl, NaOH, KCl, CaCl₂, MgCl₂, and MgSO₄ were used for preparation of simulated seawater; the detailed preparation method is referred to in previous reports [29]. PVC MPs (100–200 µm) were obtained from Seedior Co., Ltd. (Guangzhou, China). Water for environments (18.25 MΩ·cm) was prepared via Milli-Q purification equipment.

2.2. Characterization

The characterization of MPs references methods in previous literature [30–32]. Scanning electron microscopy (Sigma 300, Zeiss AG, Oberkochen, Germany) was used to study the surface morphology of the PVC MPs. The element composition and association of MPs were analyzed using X-ray photoelectron spectroscopy (XPS, K-alpha, Thermo Co., Waltham, MA, USA). The crystal structure of MPs was determined using X-ray diffraction (XRD, Ultima VI, Rigaku Co., Tokyo, Japan). A specific surface area and pore size analyzer (ASAP2460, Micromeritics Co., Norcross, GA, USA) was used to analyzed MPs' specific surface properties under N_2 adsorption (77.35 K).

2.3. Sorption Experiments

The MPs (100 mg) and TC (10 mg/L initially) were mixed in a conical flask (60 mL, cover with tinfoil paper) and placed in thermostatic oscillators at different temperatures (i.e., 288 K, 298 K, and 308 K) for kinetic tests at 180 RPM. The pretest results show that the adsorption can reach equilibrium within 24 h. Then, 0.5 mL sample was taken at specific time interval and filtered via 0.45 μ m glass fiber membrane for analysis. All adsorption experiments were carried out three times, and the mean values were determined.

Regarding adsorption isothermal experiment, concentrations of TC (1-40 mg/L) were prepared in a conical flask reactor with 100 mg MPs and placed in the oscillator at 288 K,

298 K, 308 K, and 180 rpm for 24 h. A 0.45 μm glass fiber membrane was used for solid–liquid separation.

In order to verify the influence of salinity, pH, and Cu on TC concentration in the absence of MPs, TC concentration was measured under different salinity (seawater, half seawater, and freshwater), different pH (pH = 5, 8.1, and 11), and different Cu ion concentrations (Cu: TC = 0, 0.5, and 1). The changes in C/C_0 over time are shown in Figure S2. As shown in Figure S2, C/C_0 decreased slightly (<3%) over time, and the blank experiment without MPs shows that the change in TC concentration can be ignored.

2.4. Adsorption Kinetics of TC onto MPs

 Q_t (i.e., adsorption amount of TC onto MPs (mg/g)) was obtained via Equation (1) as follows:

$$Q_t = V(C_0 - C_t)/m \tag{1}$$

Here, subscript *t* represents the adsorption time (h); *V* represents the adsorption solution volume (L); C_0 and C_t represent the TC concentrations at initial time and adsorption time *t* (mg/L); *m* represents the MPs used in adsorption environment mass (g); and Q_t represents the solute adsorption amount of TC onto the per unit mass of MPs at adsorption time *t* (mg/g). Upon adsorption achieving equilibrium, TC concentration is expressed as C_e ; meanwhile, the solute adsorption amount of TC onto PVC MPs is expressed as Q_e . The adsorption kinetics of TC onto MPs were fitted using pseudo-first-order and pseudo-second-order models, respectively [33,34]. The diffusion process was fitted by intraparticle diffusion models [35].

2.5. The Site Energy Distribution (SED) Analysis

The site energy distribution (SED) analysis method was determined based on previous studies [36]. In addition, the calculation of standard deviation refers to the research of Shen et al. [37]. In detail, SED, on basis of heterogeneous surface adsorption theory, was calculated via an equation as follows:

$$Q_e(C_e) = \int_0^{+\infty} q_h(E, C_e) F(E) dE$$
⁽²⁾

Here, $q_h(E, Ce)$ represents the adsorption isotherm of local adsorption site. F(E) presents the frequency distribution function of local adsorption site energy. An approximate method based on the heterogeneous surface adsorption theory proposed by Cerofolini [38,39] was also used, in which, the relationship between E^* and C_e (Equation (3)) can be obtained via approximate condensation method proposed by Cerofolini:

$$C_e = C_s \exp[-(E - E_s)/RT] = C_s \exp(-E^*/RT)$$
 (3)

Here, C_s represents the maximum solubility of adsorbate (i.e., antibiotic in this study), C_e represents the antibiotic concentration in solution when adsorption equilibrium is achieved, and E represents the adsorption energy of C_e . E_s represents adsorption energy of C_s . E^* represents the difference in adsorption energy between adsorbate and solvent on the surface of MPs based on E_s . In the present study, the greater E^* indicates that desorption of antibiotics from MPs required more energy, and thus the adsorption is considered to be more persistent. Upon $C_e = C_s$ and $E^* = 0$, the capacity of the MPs to adsorb antibiotics on their surface is lowest. On basis of the calculated C_e and E^* and their relationship, the adsorption isotherm model was obtained and expressed as the equation of $Q_e(E^*) - E^*$. As a consequence, the SED equation $F(E^*)$ could be defined via $Q_e(E^*)$ as follows:

$$F(E^*) = -dQ_e(E^*)/dE^*$$
 (4)

The SED curve could illustrate the change in adsorption site energy related to the accessible adsorption site frequency. Additionally, the standard deviation () was used to

denote heterogeneity of their energy. The values of E^* and E^{*2} are determined via $\mu(E^{*2})$ and $\mu(E^*)^2$, and the equation is as follows:

$$\sigma_e^* = \sqrt{\mu(E^{*2}) - \mu(E^*)^2} \tag{5}$$

$$\mu(E^*) = \frac{\int_{E_1^*}^{E_2^*} E^* \cdot F(E^*) d(E^*)}{\int_{E_1^*}^{E_2^*} F(E^*) d(E^*)}$$
(6)

$$\mu(E^{*2}) = \frac{\int_{E_1^*}^{E_2^*} E^{*2} \cdot F(E^*) d(E^*)}{\int_{E_1^*}^{E_2^*} F(E^*) d(E^*)}$$
(7)

Theoretically, E_1^* and E_2^* are equivalent to the E^* at low-energy and high-energy sites when $F(E^*) = 0$. In the present study, E_1^* and E_2^* represent the minimum and maximum expectation values, respectively.

Notably, the sorption isotherms (i.e., Langmuir, Freundlich, and Langmuir–Freundlich) were used in our study (Figure S3 and Table S2); the Langmuir–Freundlich model was the most suitable for the three temperatures (adjusted- $R^2 > 0.987$), suggesting that the process is monolayer sorption in heterogeneous systems. Based on the Langmuir–Freundlich model and Equations (2) and (3), the SED frequency function *F*(*E**) was acquired via Equation (S1).

2.6. The Analysis Method of Antibiotics

In the present study, tetracycline (TC) as a spectral antibiotic was selected to investigate its adsorption behavior on PVC MPs due to its frequent detection in water environments. High-performance liquid chromatography was applied to detect the residue of tetracycline in the solution. The mobile phase of analyzing TC was as follows: acetonitrile (30%) and 0.01 mol/L oxalic acid (70%), and flow rate was 0.7 mL/min. The detection wavelength was set at 365 nm.

3. Results and Discussion

3.1. The Adsorption Kinetics of TC by MPs

Characterization of PVC MPs. The SEM images, XPS, and XRD spectra of PVC MPs are shown in Figure 1. The size of MPs used in this study is about 100–200 μ m (Figure 1a), and the appearance of PVC MPs involves some obvious cracks, exhibiting obvious characteristics of roughness and irregularity (Figure 1b). This result is consistent with previous reports [12,13]. The PVC MPs' high surface roughness results in a big specific surface area, as shown in Table S1. The surface area was detected to be 1941 m²/g, the single point pore volume was 0.003113 cm³/g, and the average pore size was 6.415 nm. The higher specific surface area makes them more susceptible to the adsorption of coexisting trace contaminants.

The crystallinity of the MPs was also analyzed via XRD. As shown in Figure 1c, the MPs are amorphous, with a crystallinity of 24.14% based on Text S2. The surface element of the MPs was observed via XPS, as shown in Figure 1d. The full spectrum indicates that elements of the MPs mainly consist of C and Cl, with the presence of O in the composition of PVC MPs. The presence of oxygen may be attributed to the generation of oxygen-containing function groups during the preparation of microplastics. The generated oxygen-containing groups on the surface of MPs can increase their hydrophilicity, favoring the adsorption of polar trace pollutants via hydrogen bonds [40].

The adsorption kinetics of TC by MPs. The kinetic models fitted to the PVC MPs adsorbing TC are exhibited in Figure 2a,b and Table S3. It was shown that the pseudo-second-order model fitted the process of PVC MPs adsorbing TC well (adjusted- $R^2 = 0.824$ at 288 K, adjusted- $R^2 = 0.892$ at 298 K, and adjusted- $R^2 = 0.860$ at 308 K). The maximum adsorption capacities at 288 K, 298 K, and 308 K were found to be 0.538, 0.637, and 0.688 mg/g, respectively. Here, the adsorption processes were influenced by several factors, including

external diffusion of the liquid film, surface adsorption, and internal diffusion of particles. In the initial stage of adsorption, the observed rapid adsorption of TC was probably attributed to the abundant amounts of adsorption sites on the MPs. With the adsorption sites on the surface of MPs occupied, the adsorption rate slowed gradually, and finally, the adsorption achieved equilibrium after 24 h. The results from the intraparticle diffusion model obtained via Q_t - $t^{0.5}$ are shown in Figure 2b. The adsorption process was completed in three stages. First, TC was rapidly attached to the PVC MP external surfaces; in this stage, the slope reached a maximum. Second, TC molecules were transported to the internal pores of the PVC MPs. Finally, the adsorption process gradually reached a pseudo-equilibrium state [41].



Figure 1. The XPS patterns of PVC MPs and characterization of PVC MPs: (**a**) SEM images (200×); (**b**) SEM images (20,000×); (**c**) XRD analysis; (**d**) XPS analysis.



Figure 2. Adsorption kinetics of TC onto PVC MPs at three temperatures (**a**) and intraparticle diffusion model for sorption of TC onto PVC MPs (**b**). Experimental conditions: initial concentration 10 mg/L in freshwater with pH 6.5 ± 0.2 .

3.2. Effects of Salinity on Adsorption Kinetics of TC onto PVC MPs

The influence of salinity on the adsorption capacity of MPs was investigated (Figure 3). With the increase in salinity, the adsorption capacity of PVC MPs for TC exhibited an obvious decrease. When the initial TC concentrations were 4, 8, 12, and 16 mg/L, the theoretical maximum adsorption capacity Q_g of seawater decreased by 16.60%, 10.71%, 12.24%, and 7.91%, respectively, compared with in freshwater. This is consistent with previous reports; when the NaCl concentration was increased from 8.8% to 35%, the adsorption capacity of PVC MPs for ciprofloxacin decreased gradually [42]. The increase in salinity enhances the ionic strength. In this case, cations are adsorbed onto negatively charged MPs through electrostatic interaction and ion exchange competing with TC for adsorption sites [43]. In addition, Na⁺ may inhibit the formation of hydrogen bonds by substituting H⁺ to reduce the adsorption of TC on MPs [44]. Therefore, the adsorption of TC on PVC MPs would be inhibited in high salinity systems.



Figure 3. The effects of salinity on adsorption of TC onto PVC MPs. Experimental conditions: pH 6.8 \pm 0.2.

The site energy distribution of PVC MPs in three salinity systems was further explored; the $F(E^*)$ – E^* curves are displayed in Figure 4, and the key SED parameters are shown in Table S4. The $\sigma(*)$ of PVC MPs ranged from 2.702 to 2.729 in three salinity systems. The values of $F(E^*)$ for PVC MPs decreased from 174.532 to 142.153 with increasing salinity (decreasing 22.78%), indicating that the quantities of the most distributed energy sites were decreased significantly in high-salinity systems compared to freshwater, which further boosted the adsorption capacity. Therefore, in low salinity conditions, the promotion may be attributed to TC molecules preferentially occupying high-energy adsorption sites, with the adsorption site energy changing from low energy to high energy.



Figure 4. SED analysis of adsorption at different salinity (freshwater, half seawater, and seawater environments).

3.3. Effects of pH on Adsorption of TC onto PVC MPs

The pH of natural water is typically between 5 and 9, but the pH can alter erratically due to various coexisting contamination. We investigated the adsorption capacity of MPs for TC at different pH levels to evaluate the effects of pH on the process of MPs adsorbing TC, and the results are shown in Figure 5. When the initial TC concentrations were 4, 8, 12, and 16 mg/L, the theoretical maximum adsorption capacity Q_g at pH 11 decreased 31.61%, 30.64%, 12.18%, and 16.07%, respectively, compared with that at pH 5. Similar adsorption behavior of sulfamethoxazole and tylosin onto PVC and PP has been confirmed [43,45]. This result is attributed to the species of TC present as a function of pH. In detail, at pH 5, TC existed as neutral molecules, and when the pH is at 11, TC existed in the form of ionizable compounds (i.e., TC^{2-}), which is related to its dissociation constant [46]. As MPs are negatively charged, and the PZC is in an acidic condition, and with the increase in pH, the charge of MPs will change from a positive charge to zero (pH = PZC) and then to a negative charge. When antibiotics exist in the form of ionizable compounds, electrostatic repulsion occurs between MPs and antibiotics [47].

Based on SED theory, the site energy distribution of PVC MPs at different pH was further explored; the $F(E^*)$ – E^* curves are shown in Figure 6. At pH 5, more adsorption sites were available, and the pattern exhibited the tendency to move toward high-energy sites, leading to more adsorption sites being activated in this condition, and TC always occupied the high-energy sites. The average site energy $\mu(E^*)$ also reached the maximum value at pH 5 (i.e., 21.023) and the minimum value at pH 11 (i.e., 20.927), resulting in the highest affinity at pH 5 and the lowest at pH 11 [48]. At pH 11, PVC MPs were negatively charged, producing electrostatic repulsion with TC^{2–}, but at pH 5, TC molecules were uncharged, and hydrophobic interactions played a dominant role in the adsorption process [49]. Additionally, the value of $F(E^*)$ for PVC MPs decreased from 171.291 at pH 5 to 126.299 at pH 11 (decreasing by 26.27%). This result demonstrated that the decreased adsorption capacity of TC onto MPs mainly resulted from electrostatic repulsion between MPs and TC^{2–}.



Figure 5. Effects of pH on adsorption of TC onto PVC MPs. Experimental conditions: the experiments were conducted in freshwater for 24 h.



Figure 6. SED of TC adsorption onto PVC MPs at pH 5, pH 8.1, and pH 5. Experimental conditions: the experiments were conducted in freshwater.

3.4. The Effects of Cu^{2+} on Adsorption of TC onto PVC MPs

Different trace metal ions also affect each other. At present, many studies have reported the presence of a variety of heavy metals on the surface of MPs, including Cu, Zn, Cd, Cr, Pb, Co, Ni, Al, Mn, Fe, Ca, Ag, and Hg. Cu is a common metal element in water environments and has been widely studied. In addition, TC contains electron donor groups that can bind to metal ions, such as Cu, thereby affecting the behavior of TC and heavy metals in the environment. Studies have shown that the combination of antibiotics and heavy metals promotes their adsorption under certain conditions [50]. The complex and competitive behavior of Cu²⁺ and TC plays an important role in the adsorption process [48].

Cu²⁺ was selected to investigate the influence of metal ions in half seawater at 298 K. The adsorption capacity of MPs for TC in the presence of Cu²⁺ is shown in Figure S4, and the results showed that the adsorption capacity of MPs to TC increased with the increase in copper ion concentration. The SED patterns are shown in Figure 7. According to the area under the SED curve, it is clear that the adsorption capacity of PVC MPs for TC increased significantly in the presence of Cu²⁺. Additionally, the SED curve of PVC MPs became "short and fat" in the presence of Cu²⁺, indicating the most distributed energy sites $F(E_0^*)$ transformed to sites with other energy and caused an increase in the unevenness degree. This increase may be attributed to the complexation of Cu²⁺ with TC. It was previously reported that [TC-Cu]⁰ is the main complexation form when pH > 5 [51]. The coexistence of Cu²⁺ and TC could realize the synergistic adsorption between each other through the bridging form of "MPs-TC-Cu²⁺" and "MPs-Cu²⁺-TC". The affinity between the PVC MPs and TC was increased via complexation. Therefore, the adsorption capacity of PVC MPs in the presence of Cu²⁺ was relatively improved [50].



Figure 7. SED of TC adsorption onto PVC MPs in the presence of Cu²⁺. Experimental conditions: the concentration of Cu to TC was in mg/L, the experiments were conducted in freshwater at pH 6.8 \pm 0.2.

4. Conclusions

In the present study, batch adsorption experiments were conducted under various conditions to explore the influence of salinity and pH on the adsorption of TC onto MPs. A pseudo-second-order model was found to accurately describe the adsorption of TC onto PVC MPs, and the adsorption capacity increased with temperature (288K, 0.538 mg/g; 298K, 0.637 mg/g; 308K, 0.688 mg/g). According to SED analysis, with the increase in salinity, the number of active sites on MPs will decrease, thus reducing the capacity of MPs to adsorb TC. As for the effect of pH on the adsorption capacity of MPs, SED analysis

indicated that the increase in pH enhanced the electrostatic repulsion between MPs and TC, leading to a decrease in adsorption capacity. In addition, Cu^{2+} can realize the synergistic adsorption between TC and MPs-TC- Cu^{2+} through the form of "MPs- Cu^{2+} " and "MPs- Cu^{2+} -TC" bridges and through complexation, improve the affinity of PVC MPs for TC. This study explored the adsorption properties of MPS on TC under different environmental conditions, which is helpful to further understand the interaction between MPs and TC in different real environments.

Supplementary Materials: The following supporting information can be downloaded at: https:// www.mdpi.com/article/10.3390/w15101925/s1, Text S1: SED frequency function F(E*); Text S2: The calculation of relative crystallinity; Figure S1: Molecular structure of TC; Figure S2: The control experiments for all explored conditions; Figure S3: The sorption isotherm of virgin and aged PVC MPs at three temperatures; Figure S4: The adsorption of TC onto PVC MPs in the presence of Cu²⁺; Table S1: The results of BET test; Table S2: Parameters for three sorption isotherms of virgin and aged PVC MPs and TC at three temperatures; Table S3: The parameters of sorption kinetics for PVC MPs adsorbing TC; Table S4: The SED parameters of PVC MPs adsorbing TC in three salinity systems.

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References

- Law, K.L.; Morét-Ferguson, S.E.; Goodwin, D.S.; Zettler, E.R.; DeForce, E.; Kukulka, T.; Proskurowski, G. Distribution of surface plastic debris in the eastern Pacific Ocean from an 11-year data set. *Environ. Sci. Technol.* 2014, 48, 4732–4738. [CrossRef] [PubMed]
- Zhang, K.; Xiong, X.; Hu, H.; Wu, C.; Bi, Y.; Wu, Y.; Liu, J. Occurrence and characteristics of microplastic pollution in Xiangxi Bay of Three Gorges Reservoir, China. *Environ. Sci. Technol.* 2017, *51*, 3794–3801. [CrossRef] [PubMed]
- Cox, K.; Covernton, G.; Davies, H.; Dower, J.; Juanes, F.; Dudas, S. Human consumption of microplastics. *Environ. Sci. Technol.* 2019, 53, 7068–7074. [CrossRef] [PubMed]
- 4. Cris, B.; Gomez, C.; Gomez, B.C.; Adzel, A.G.; Escalante, O. The occurrence of microplastics in the gastrointestinal tract of demersal fish species. *Int. J. Biosci.* **2020**, *16*, 152–162.
- Yuan, J.; Ma, J.; Sun, Y.; Zhou, T.; Zhao, Y.; Yu, F. Microbial degradation and other environmental aspects of microplastics/plastics. *Sci. Total Environ.* 2020, 715, 136968. [CrossRef] [PubMed]
- 6. Torres, F.G.; Dioses-Salinas, D.C.; Pizarro-Ortega, C.I.; De-la-Torre, G.E. Sorption of chemical contaminants on degradable and non-degradable microplastics: Recent progress and research trends. *Sci. Total Environ.* **2021**, *757*, 143875. [CrossRef] [PubMed]
- Prata, J.C.; da Costa, J.P.; Lopes, I.; Duarte, A.C.; Rocha-Santos, T. Environmental exposure to microplastics: An overview on possible human health effects. *Sci. Total Environ.* 2020, 702, 134455. [CrossRef]
- Schwarz, A.E.; Ligthart, T.N.; Boukris, E.; van Harmelen, T. Sources, transport, and accumulation of different types of plastic litter in aquatic environments: A review study. *Mar. Pollut. Bull.* 2019, 143, 92–100. [CrossRef]
- 9. Ding, J.; Zhang, S.; Razanajatovo, R.M.; Zou, H.; Zhu, W. Accumulation, tissue distribution, and biochemical effects of polystyrene microplastics in the freshwater fish red tilapia (Oreochromis niloticus). *Environ. Pollut.* **2018**, 238, 1–9. [CrossRef]
- Green, D.S.; Boots, B.; O'Connor, N.E.; Thompson, R. Microplastics affect the ecological functioning of an important biogenic habitat. *Environ. Sci. Technol.* 2017, 51, 68–77. [CrossRef]
- 11. Tang, Y.Q.; Liu, Y.G.; Chen, Y.; Zhang, W.; Zhao, J.M.; He, S.Y.; Yang, C.P.; Zhang, T.; Tang, C.F.; Zhang, C. A review: Research progress on microplastic pollutants in aquatic environments. *Sci. Total Environ.* **2021**, *766*, 142572. [CrossRef] [PubMed]
- 12. Lin, L.; Tang, S.; Wang, X.S.; Sun, X.; Han, Z.; Chen, Y. Accumulation mechanism of tetracycline hydrochloride from aqueous solutions by nylon microplastics. *Environ. Technol. Innov.* **2020**, *18*, 100750. [CrossRef]
- 13. Wang, Y.; Wang, X.; Li, Y.; Li, J.; Wang, F.; Xia, S.; Zhao, J. Biofilm alters tetracycline and copper adsorption behaviors onto polyethylene microplastics. *Chem. Eng. J.* **2020**, *392*, 123808. [CrossRef]

- 14. Li, J.; Zhang, K.; Zhang, H. Adsorption of antibiotics on microplastics. Environ. Pollut. 2018, 237, 460–467. [CrossRef] [PubMed]
- 15. Xiang, Y.; Xu, Z.; Wei, Y.; Zhou, Y.; Yang, X.; Yang, Y.; Yang, J.; Zhang, J.; Luo, L.; Zhou, Z. Carbon-based materials as adsorbent for antibiotics removal: Mechanisms and influencing factors. *J. Environ. Manag.* **2019**, *237*, 128–138. [CrossRef]
- 16. Guo, X.; Wang, J. Sorption of antibiotics onto aged microplastics in freshwater and seawater. *Mar. Pollut. Bull.* **2019**, *149*, 110511. [CrossRef]
- 17. Razanajatovo, R.M.; Ding, J.; Zhang, S.; Jiang, H.; Zou, H. Sorption and desorption of selected pharmaceuticals by polyethylene microplastics. *Mar. Pollut. Bull.* **2018**, *136*, 516–523. [CrossRef]
- 18. Wang, Y.J.; Niu, J.F.; Li, Y.; Zheng, T.J.; Xu, Y.; Liu, Y. Performance and mechanisms for removal of perfluorooctanoate (PFOA) from aqueous solution by activated carbon fiber. *RSC Adv.* **2015**, *5*, 86927–86933. [CrossRef]
- Zhang, R.; Pei, J.; Zhang, R.; Wang, S.; Zeng, W.; Huang, D.; Wang, Y.; Zhang, Y.; Wang, Y.; Yu, K. Occurrence and distribution of antibiotics in mariculturefarms, estuaries and the coast of the Beibu Gulf, China: Bioconcentration and diet safety of seafood. Ecotoxicol. *Environ. Saf.* 2018, 154, 27–35. [CrossRef]
- 20. Tolls, J. Sorption of veterinary pharmaceuticals in soils: A review. Environ. Sci. Technol. 2001, 35, 3397–3406. [CrossRef]
- 21. Ying, G. Chinese Antibiotic Use and Watershed Pollution. Chin. Chem. Soc. 2016, 144, 26-I-005. (In Chinese)
- Quan, B.; Li, X.; Zhang, H.; Zhang, C.; Ming, Y.; Huang, Y.; Tang, Y. Technology and principle of removing triclosan from aqueous media: A review. *Chem. Eng. J.* 2019, 378, 122185. [CrossRef]
- Pulicharla, R.; Brar, S.K.; Rouissi, T.; Auger, S.; Drogui, P.; Verma, M.; Surampalli, R.Y. Degradation of chlortetracycline in wastewater sludge by ultrasonication, Fenton oxidation, and ferro-sonication. *Ultrason. Sonochem.* 2017, 34, 332–342. [CrossRef] [PubMed]
- 24. Zhou, M.; Zhu, T.; Fei, X. Enhanced adsorption performance of oxytetracycline by desugared reed residues. *Int. J. Environ. Res. Public Health* **2018**, *15*, 2229. [CrossRef]
- Puckowski, A.; Cwiek, W.; Mioduszewska, K.; Stepnowski, P.; Bialk-Bielinska, A. Sorption of pharmaceuticals on the surface of microplastics. *Chemosphere* 2021, 263, 127976. [CrossRef]
- Guo, X.; Chen, C.; Wang, J. Sorption of sulfamethoxazole onto six types of microplastics. *Chemosphere* 2019, 228, 300–308. [CrossRef]
- Yu, F.; Li, Y.; Huang, G.Q.; Yang, C.F.; Chen, C.; Zhou, T.; Zhao, Y.C.; Ma, J. Adsorption behavior of the antibiotic levofloxacin on microplastics in the presence of different heavy metals in an aqueous solution. *Chemosphere* 2020, 260, 127650. [CrossRef]
- 28. Liu, H.; Yang, Y.; Kang, J.; Fan, M.; Qu, J. Removal of tetracycline from water by Fe-Mn binary oxide. J. Environ. Sci. 2012, 24, 242–247. [CrossRef]
- Kuniki, H.; Tomonori, S.; Takafumi, M.; Fumiyoshi, U.; Satoshi, H.; Shigeki, K.; Takashi, T. Simulation for radiolytic products of seawater: Effects of seawater constituents, dilution rate, and dose rate. J. Nucl. Sci. Technol. 2016, 8, 1183–1191.
- Wu, X.; Liu, P.; Shi, H.; Wang, H.; Huang, H.; Shi, Y.; Gao, S. Photo aging and fragmentation of polypropylene food packaging materials in artificial seawater. *Water Res.* 2021, 188, 116456. [CrossRef]
- 31. Shi, Y.; Liu, P.; Wu, X.; Shi, H.; Huang, H.; Wang, H.; Gao, S. Insight into chain scission and release profiles from photodegradation of polycarbonate microplastics. *Water Res.* **2021**, *195*, 116980. [CrossRef] [PubMed]
- 32. Wu, J.; Xu, P.; Chen, Q.; Ma, D.; Ge, W.; Jiang, T.; Chai, C. Effects of polymer aging on sorption of 2, 2', 4, 4'-tetrabromodiphenyl ether by polystyrene microplastics. *Chemosphere* **2020**, 253, 126706. [CrossRef] [PubMed]
- 33. Lagergren, S. Zur theorie der sogenannten adsorption geloster stoffe. Kungliga svenska vetenskapsakademiens. Handlingar 1898, 24, 1–39.
- 34. Ho, Y.S.; McKay, G. Pseudo-second order model for sorption processes. Process Biochem. 1999, 34, 451–465. [CrossRef]
- 35. Weber, W.J., Jr.; Morris, J.C. Kinetics of adsorption on carbon from solution. J. Sanit. Eng. Div. 1963, 89, 31–59. [CrossRef]
- Carter, M.C.; Kilduff, J.E.; Weber, W.J. Site energy distribution analysis of preloaded adsorbents. *Environ. Sci. Technol.* 1995, 29, 1773–1780. [CrossRef]
- 37. Cerofolini, G.F. Localized adsorption on heterogeneous surfaces. Thin Solid Film. 1974, 23, 129–152. [CrossRef]
- 38. Shen, X.; Guo, X.; Zhang, M.; Tao, S.; Wang, X. Sorption mechanisms of organic compounds by carbonaceous materials: Site energy distribution consideration. *Environ. Sci. Technol.* **2015**, *49*, 4894–4902. [CrossRef]
- He, J.; Guo, J.; Zhou, Q.; Yang, J.; Fang, F.; Yang, H. Analysis of 17a-ethinylestradiol and bisphenol A adsorption on anthracite surfaces by site energy distribution. *Chemosphere* 2019, 216, 59–68. [CrossRef]
- 40. Liu, G.; Zhu, Z.; Yang, Y.; Sun, Y.; Yu, F.; Ma, J. Sorption behavior and mechanism of hydrophilic organic chemicals to virgin and aged microplastics in freshwater and seawater. *Environ. Pollut.* **2019**, *246*, 26–33. [CrossRef]
- 41. Ma, J.; Zhao, J.; Zhu, Z.; Li, L.; Yu, F. Effect of microplastic size on the adsorption behavior and mechanism of triclosan on polyvinyl chloride. *Environ. Pollut.* **2019**, 254, 113104. [CrossRef] [PubMed]
- Liu, J.; Zhang, T.; Tian, L.; Liu, X.; Qi, Z.; Ma, Y.; Chen, W. Aging significantly affects mobility and contaminant-mobilizing ability of nanoplastics in saturated loamy sand. *Environ. Sci. Technol.* 2019, 53, 5805–5815. [CrossRef] [PubMed]
- 43. Guo, X.; Liu, Y.; Wang, J. Sorption of sulfamethazine onto different types of microplastics: A combined experimental and molecular dynamics simulation study. *Mar. Pollut. Bull.* **2019**, *145*, 547–554. [CrossRef]
- 44. Aristilde, L.; Marichal, C.; Miéhé-Brendlé, J.; Lanson, B.; Charlet, L. Interactions of oxytetracycline with a smectite clay: A spectroscopic study with molecular simulations. *Environ. Sci. Technol.* **2010**, *44*, 7839–7845. [CrossRef]
- Guo, X.; Pang, J.; Chen, S.; Jia, H. Sorption properties of tylosin on four different microplastics. *Chemosphere* 2018, 209, 240–245. [CrossRef] [PubMed]

- 46. Pulicharla, R.; Hegde, K.; Brar, S.K.; Surampalli, R.Y. Tetracyclines metal complexation: Significance and fate of mutual existence in the environment. *Environ. Pollut.* **2017**, 221, 1–14. [CrossRef]
- 47. Wang, Y.; Yang, Y.; Liu, X.; Zhao, J.; Liu, R.; Xing, B. Interaction of microplastics with antibiotics in aquatic environment: Distribution, adsorption, and toxicity. *Environ. Sci. Technol.* **2021**, *55*, 15579–15595. [CrossRef]
- Yan, B.; Niu, C.H.; Wang, J. Analyses of levofloxacin adsorption on pretreated barley straw with respect to temperature: Kinetics, π–π electron-donor–acceptor interaction and site energy distribution. *Environ. Sci. Technol.* 2017, *51*, 8048–8056. [CrossRef]
- 49. Zhang, H.; Wang, J.; Zhou, B.; Zhou, Y.; Dai, Z.; Zhou, Q.; Luo, Y. Enhanced adsorption of oxytetracycline to weathered microplastic polystyrene: Kinetics, isotherms and influencing factors. *Environ. Pollut.* **2018**, 243, 1550–1557. [CrossRef]
- 50. Ma, X.; Yang, C.; Jiang, Y.; Zhang, X.; Wang, Q.; Dang, Z. Desorption of heavy metals and tetracycline from goethite-coated sands: The role of complexation. *Colloids Surf. A Physicochem. Eng. Asp.* **2019**, *573*, 88–94. [CrossRef]
- Wang, Y.; Wang, X.; Li, J.; Li, Y.; Xia, S.Q.; Zhao, J.F.; Minale, T.M.; Gu, Z.L. Coadsorption of tetracycline and copper (II) onto struvite loaded zeolite–An environmentally friendly product recovered from swine biogas slurry. *Chem. Eng. J.* 2019, 371, 366–377. [CrossRef]

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