

Adsorption and Desorption Behavior of Microplastics on Copper Ions in Aqueous Solution

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Abstract: The environmental pollution caused by microplastics has received extensive attention around the world, and it is of great significance to study the adsorption and desorption of heavy metals by microplastics to clarify the environmental behaviour and toxic effects of heavy metals. In this paper, the adsorption and desorption process and mechanism of microplastics (species, oxygen-containing functional groups, crystallinity, aging state) on copper ions in aqueous solution were studied, and six microplastics were selected, namely refractory microplastics, polyvinyl chloride (PVC), polymethyl methacrylate (PMMA), polystyrene (PS), acrylonitrile-butadiene-styrene copolymer (ABS), polypropylene (PP) and degradable microplastics polybutylene succinate (PBS) and polybutylene terephthalate-butylene adipate (PBAT). The adsorption results showed that the adsorption capacity of copper ions by six microplastics was arranged as PVC>PBAT> PBS> PS>ABS>PMMA, and the adsorption capacity of copper ions by each microplastic (MPs) after aging was higher than that of its fresh state. The desorption results showed that the larger the adsorption capacity, the greater the desorption amount. The desorption rate of copper ions by PVC, PBS and PBAT was lower than that of PS, ABS and PMMA. The desorption amount and desorption rate of degradable MPs to copper ions were higher than those of refractory MPs. The desorption rate of copper ions by each microplastic after aging is lower than that of fresh state. It shows that refractory microplastics, aging MPs have a stronger carrier effect on copper ions. In addition, the adsorption kinetics of copper ions by microplastics mostly conform to the quasi-secondary model, some conform to the quasi-primary model, and the adsorption and desorption isotherms basically conform to the Langmuir and Freundlich models.

Keywords: Microplastics; Copper ions; UV aging; Adsorption; Desorption

1. Introduction

Plastic products are discarded in the natural environment at will, and gradually become microplastics after wind action, water erosion, crushing and grinding^[1,2]. Due to the special physical properties, after enter the water environment, they significantly affect the environmental behavior of heavy metals through electrostatic interaction^[6]. Microplastics are difficult to exist alone, become the carrier of heavy metals, so it is also known as "PM2.5 in water"^[3,4], microplastics are becoming a global long-term pollution problem^[5]. Distribution of pollution status of microplastics in aquatic environment^[2]; Study on adsorption behavior of microplastics on heavy metal/organic pollutants^[6,7]; Biototoxicity studies of microplastics^[8]. However, there is a lack of intuitive comparison of the adsorption performance of different types of microplastics on heavy metals. The mechanism of adsorption and desorption performance of degradable microplastics is relatively lacking. In summary, the six microplastics were aged by ultraviolet lamp, characterize, and the linear relationship between the carbonyl index and the maximum adsorption capacity was established. This paper provides a reference for the study of the adsorption and desorption behavior of copper ions by microplastics.

2. Materials and Methods

2.1. Material Preparation and Pretreatment

The six microplastics were all purchased from HuaChuang Plasticization Co., Ltd. The laboratory uses ultraviolet light to irradiate MPs for aging, the time is controlled at about 96h.

2.2. Determination of Physical and Chemical Properties of Microplastics

Instruments used include: scanning electron microscope (SEM, Hitachi S-4800, 5kV); Fourier transform infrared spectrometer DTGS KBr; Atomic absorption spectrometer.

2.3. Adsorption Experiment of Microplastics on Cu²⁺

2.3.1. Adsorption kinetic experiment

Add the mesh bag to a 50mL 10mg/L copper ion conical flask, mix evenly in a 100mL conical flask, place the conical flask on a constant temperature shaker, and rotate at 150r/min at a temperature of 25°C. Samples were taken within the time period (1~1440min), filtered with a needle filter of 0.45µm, diluted in different gradients according to the detection limit of the instrument, and stored in centrifuge tubes for testing.

2.3.2. Adsorption isotherm experiment

Prepare 1g/L copper ion mother solution, dilute copper ion solutions with different concentration gradients (1~30mg/L), add 20mg MPs samples and 50mL copper ion solutions with different concentrations (1~30mg/L) into a 100mL Erlenmeyer flask, and mix evenly, place the Erlenmeyer flask on a constant temperature shaker with a rotation speed of 150r/min and a temperature of 25°C for oscillation.

2.3.3 Desorption Experiment of Microplastics After Adsorption in Pure Water

Conduct the desorption experiment on the saturated microplastics. After the adsorption experiment is completed, add MPs to 50mL of ultrapure water. Place it on a constant temperature shaker, with a rotation speed of 150r/min and a temperature of 25°C, 24 hours, the first desorption is completed; the net bag is also rinsed clean, and continues to be added to 50mL of ultrapure water, and the conical flask is placed in the A constant temperature shaker with a rotation speed of 150r/min and a temperature of 25°C. The desorption time is 24 hours, the second desorption is completed; then the third desorption is completed in the same way, and so on, until the concentration of copper ions in the desorption liquid is close to 0. Both the adsorption experiment and the desorption experiment need to set up two parallels to eliminate experimental errors.

2.4. Adsorption Model

In order to study the adsorption behavior and mechanism of different microplastics on the same ions, the pseudo-first-order kinetic model, pseudo-second-order kinetic model, and intra-particle diffusion model were used to perform fitting analysis on the experimental data to study the second adsorption behavior of Microplastics. The corresponding equations are shown in (1), (2), and (3).

$$\ln(Q_e - Qt) = \ln Q_e - k_1 t \quad (1)$$

$$\frac{t}{Qt} = \frac{1}{Q_e k_2} + \frac{t}{Q_e} \quad (2)$$

$$Qt = k_i + C \quad (3)$$

In the formula: Q_e is the equilibrium adsorption capacity (mg/g); Q_t is the adsorption capacity of heavy metals at time (mg/g); k_1 (min^{-1}) and K_2 ($\text{g}/(\text{mg} \cdot \text{min})$) are quasi-first-order models and rate constants for the pseudo-second-order model. k_i is the intra-particle diffusion constant ($\text{g}/(\text{g} \cdot \text{min}^{0.5})$); the intercept C is a constant related to the thickness of the particle boundary layer.

The model analysis adopts Langmuir (4) and Freundlich (5) [17].

$$\text{Langmuir: } \frac{C_e}{Q_e} = \frac{1}{Q_m K_L} + \frac{C_e}{Q_m} \quad (4)$$

In the formula: Q_e (mg/g) and C_e (mg/L) represent the equilibrium concentrations of the adsorbent and adsorbate, respectively; Q_{max} (mg/g) represents the theoretical maximum adsorption capacity; K_L (L/mg) is the index reflecting the adsorption capacity Equilibrium constant.

$$\text{Freundlich: } \ln Q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (5)$$

3. Results and Discussion

3.1. Crystallinity Analysis

The XRD patterns of six microplastics are shown in Figure 1. There are fine and sharp crystalline phase diffraction peaks in the PBS patterns before and after aging; there are amorphous phase diffraction peaks in the XRD patterns of PMMA, ABS, PS, and PVC before and after aging. Because they are all amorphous polymers, there are polar groups in the molecular chains of each microplastic, and the crystallinity is low [8], the XRD spectra of PBAT before and after aging not only have the diffraction peaks of the dispersed amorphous phase but also have fine particles. Comparing the XRD patterns of microplastics, it is found that the characteristic peaks of all microplastics become smaller after aging [9]. In addition, research by Velzebor [10] found that UV reduce the crystallinity of microplastics.

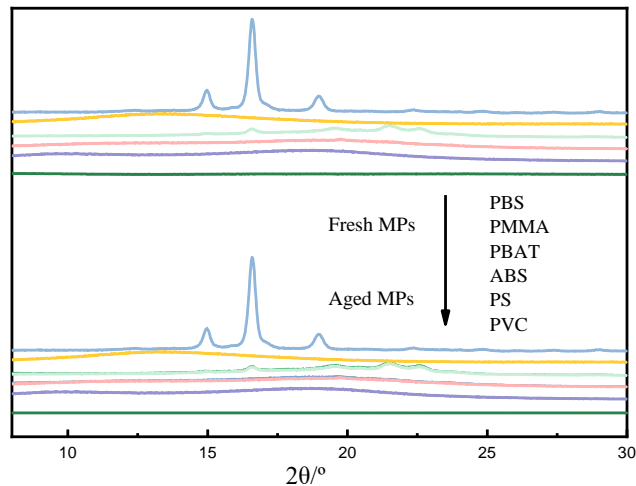
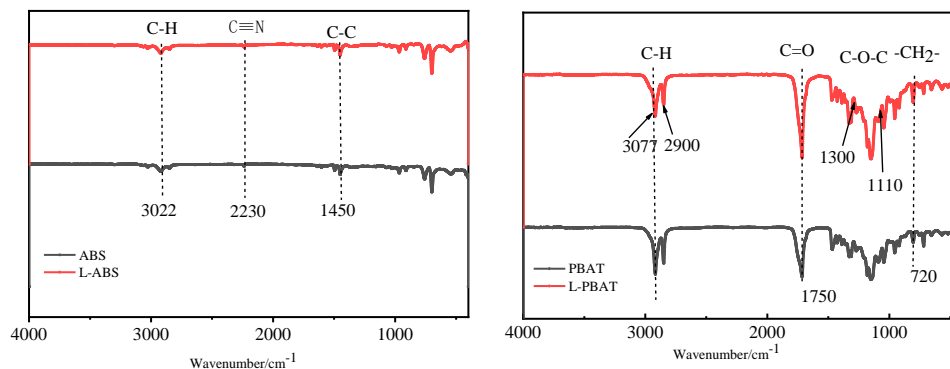


Figure 1: XRD patterns of microplastics before and after aging.

3.2. Surface Functional Group

Infrared spectroscopy was used to analyze the functional group changes of various microplastics before and after aging by ultraviolet irradiation, and the results were shown in Figure 2 below. The infrared spectrum of six microplastics had C-H telescopic vibration of methyl or methylene in the range of 3044-2848 cm^{-1} , the characteristic peak of infrared spectrum at 3500-3000 cm^{-1} was mainly caused by hydroxyl tensile vibration, and the absorption peak at 1700-1800 cm^{-1} was C=O stretching vibration [11]. The results of infrared spectroscopy showed that aging increased the number of carbonyl functional groups on the surface of microplastics, which was consistent with the results of Weniger [12] et al.



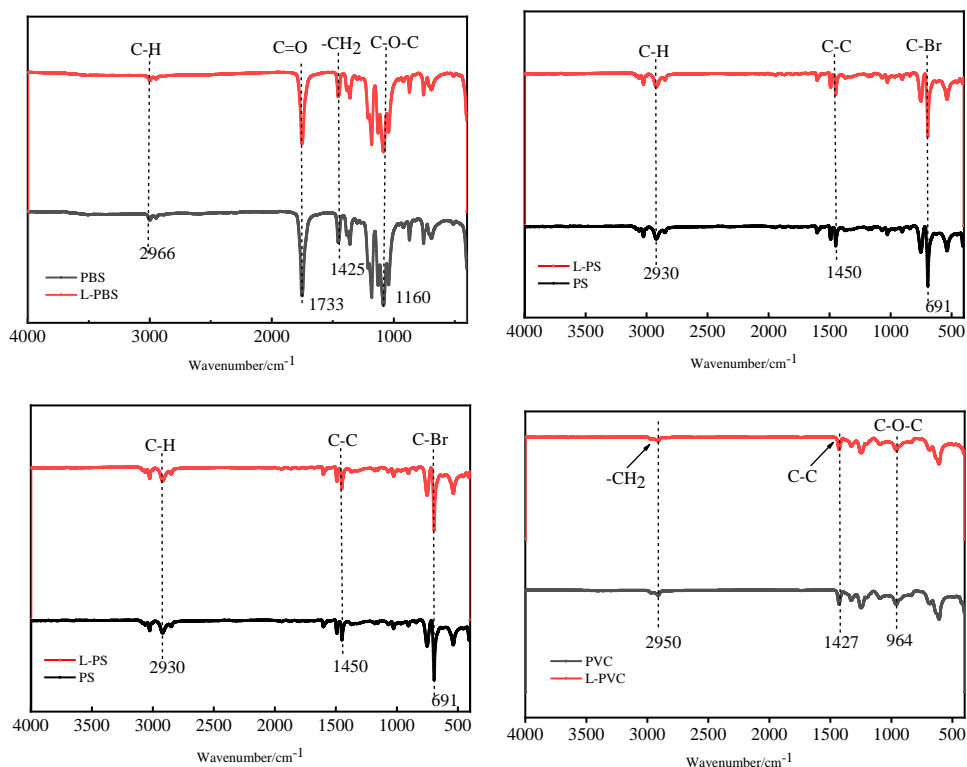


Figure 2: Infrared spectroscopy of microplastics before and after aging.

In order to more accurately quantify the aging degree of the six microplastics, the carbonyl index (CI) was used to measure. As one of the methods to quantitatively express the degree of material aging, CI is widely used in the study of material aging [13,14]. The calculation method is as follows:

$$CI = \frac{\text{carbonyl peak area(centred on 1700)}}{\text{peak area between } \Sigma 600 \sim 2000} \quad (6)$$

The experiments involved the carbonyl indices of six microplastics as shown in Table 1. The CI indices of the six MPs after aging were higher than those of the original state. The CI index order of MPs before and after aging is PVC>PBAT>ABS>PS>PBS>PMMA, and the aging effect makes the order of CI increase as follows: PBS>PS>PMMA>ABS>PVC>PBAT.

Table 1: Carbonyl index of microplastics before and after aging.

Types of Microplastics	CI
PBS	0.1185
L-PBS	0.1387
PMMA	0.1086
L-PMMA	0.1141
PBAT	0.1849
L-PBAT	0.1868
ABS	0.1175
L-ABS	0.1610
PS	0.1483
L-PS	0.1548
PVC	0.1942
L-PVC	0.1963

3.3. Adsorption Kinetics

Adsorption kinetics are often used to describe the equilibrium time, adsorption rate and adsorption mechanism of microplastics adsorbing heavy metals. In this paper, the adsorption kinetics of copper ions on microplastics within 760min were studied, and the experimental data were fitted using quasi-primary and quasi-secondary models as shown in Figure 3(a)(b)(c)(d) and Table 2, and the results were shown in Figure 3, and the kinetic fitting parameters were shown in Table 2. The drawing of the fitting results shows that the quasi-secondary kinetics is more suitable for describing the adsorption process of copper

ions on different microplastics, indicating that the chemical adsorption of copper ions by microplastics is mainly carried out, and the two are combined by electron sharing or transfer. The adsorption performance order of several microplastics in the fresh and aged state on copper ions is as follows: PMMA>ABS> PVC>PBS> PS>PBAT, and the changes in physical and chemical properties caused by ultraviolet aging make the adsorption capacity of microplastics on copper ions significantly enhanced. The internal diffusion model of particles was used for fitting. The results are shown in Figure 3(e)(f) and Table 3, which can divide the adsorption process into three stages: surface adsorption, intraparticle diffusion and adsorption equilibrium. Fit the diffusion rate constants $Kp1>Kp2>Kp3$. The diffusion fitting parameter C was greater than 0, and the fitting results showed that the adsorption of copper ions by microplastics was affected by internal diffusion and external diffusion, and adsorption was a multi-stage process [15]

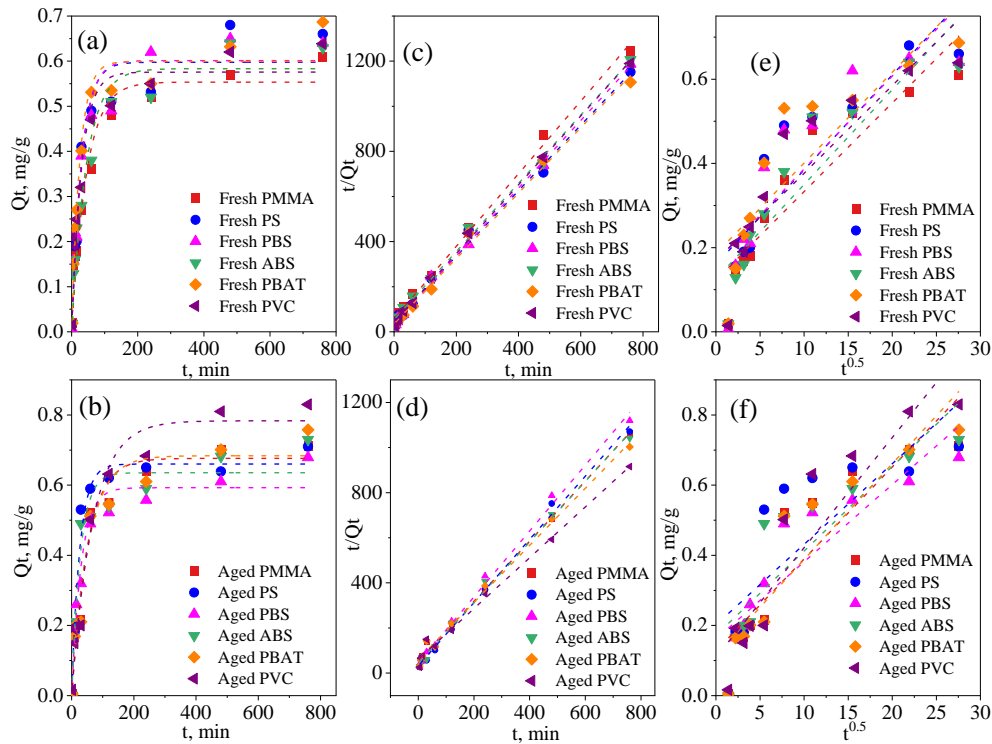


Figure 3: Kinetics of copper ion adsorption on microplastics and fitting curve of internal diffusion model.

Ultraviolet aging significantly increases the adsorption capacity of copper ions by microplastics, mainly due to: a) the physical and chemical properties have changed [16], and the hydrophobic partitioning effect has increased. b) Increased hydrophilicity, increased adsorption capacity of hydrophilic cations [17,18]. c) Surface oxygen-containing functional groups increase [16], covalent bond force increases, electronegativity increases, and adsorption capacity increases.

Table 2: Kinetic Model Parameters of Copper Ion Adsorption by Microplastics.

MPs	Pseudo-First Order Kinetic Model			Pseudo-second-order kinetic model		
	Q_e	K_1	R^2	Q_e	K_2	R^2
PBAT	0.5992	0.0401	0.9583	0.5902	0.0266	0.9956
L-PBAT	0.7838	0.0184	0.9687	0.7593	0.0026	0.9985
PVC	0.6012	0.0328	0.9472	0.6298	0.0594	0.9997
L-PVC	0.7834	0.0148	0.9519	0.7633	0.0013	0.9951
PBS	0.5898	0.0335	0.9391	0.5662	0.0622	0.9943
L-PBS	0.6764	0.0196	0.9453	0.7504	0.0341	0.9925
PS	0.5834	0.0226	0.9464	0.5614	0.0424	0.9964
L-PS	0.6621	0.0381	0.9581	0.6444	0.0143	0.9963
ABS	0.5756	0.0335	0.9243	0.5556	0.0559	0.9987
L-ABS	0.6357	0.0358	0.9327	0.6133	0.0613	0.9997
PMMA	0.5012	0.0328	0.9472	0.5098	0.0594	0.9997
L-PMMA	0.5834	0.0148	0.9519	0.5833	0.0013	0.9951

Table 3: Internal diffusion model parameters of copper ions adsorbed by microplastics.

MPs	Diffusion			Inner Diffusion			Membrane Adsorption		
	C ₁	K _{p1}	R ₁ ²	C ₂	K _{p2}	R ₂ ²	C ₃	K _{p3}	R ₃ ²
PBAT	4.238	0.018	0.961	3.583	0.006	0.968	3.583	0.0014	0.913
L-PBAT	3.232	0.014	0.956	2.929	0.003	0.958	1.489	0.0012	0.958
PVC	1.392	0.018	0.999	3.492	0.0054	0.968	2.595	0.0042	0.968
L-PVC	3.481	0.016	0.931	2.485	0.0043	0.958	3.492	0.0031	0.959
PBS	4.382	0.017	0.901	5.392	0.0086	0.957	4.538	0.0063	0.989
L-PBS	2.490	0.0121	0.922	3.578	0.0044	0.947	3.589	0.0042	0.958
PS	4.839	0.0164	0.991	3.589	0.0081	0.944	2.592	0.0052	0.958
L-PS	1.492	0.0130	0.948	1.492	0.0037	0.948	4.598	0.0012	0.990
ABS	7.839	0.0168	0.931	9.323	0.0094	0.944	8.857	0.0042	0.990
L-ABS	7.320	0.0148	0.973	6.573	0.0052	0.938	9.092	0.0021	0.975
PMMA	3.493	0.0172	0.918	3.857	0.0064	0.991	2.457	0.0033	0.928
L-PMMA	2.442	0.0147	0.992	2.574	0.0023	0.998	0.426	0.0011	0.958

3.4. Adsorption Isotherm

The isotherm data fitting adopts the Langmuir and Freundlich model [19]. The adsorption isotherm is shown in Figure 4, and the fitting data results are shown in Table 4. It can be seen that the Langmuir model is effective for the adsorption of copper ions on microplastics. The higher fitting degree shows that the adsorption capacity of microplastics to copper ions before and after aging is limited, and the adsorption mainly occurs on the adsorption sites on the surface of microplastics, and the adsorption sites are evenly distributed, which belongs to single-layer adsorption.

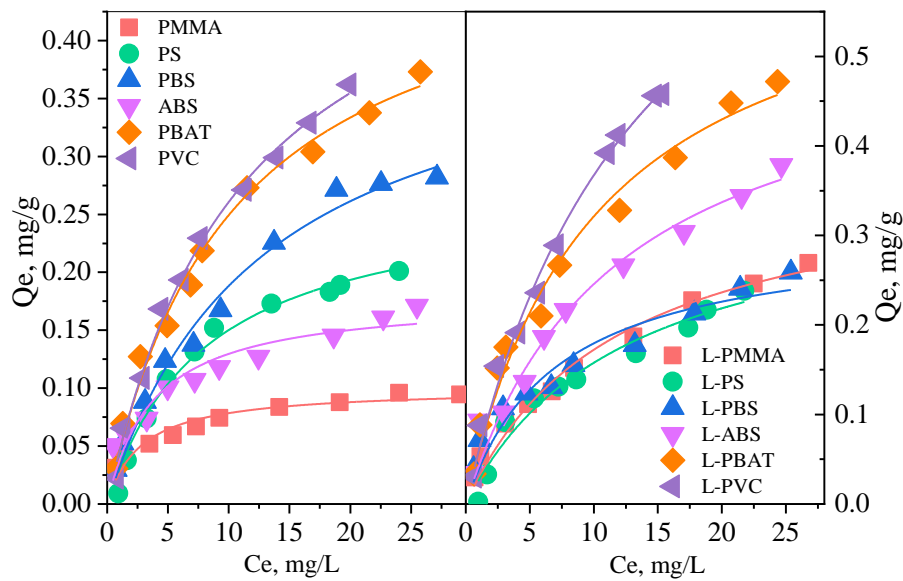


Figure 4: Adsorption isotherms of microplastics on copper ions before and after aging.

Table 4: Fitting model parameters of copper ion adsorption isotherm on microplastics.

MPs	Langmuir			Freundlich		
	Q _m	K _L	R ²	K _f	n	R ²
PVC	0.0627	0.0788	0.9863	0.0690	1.9128	0.9839
L-PVC	0.0722	0.0927	0.9912	0.0860	1.8538	0.9893
PBAT	0.0694	0.0591	0.9971	0.0672	1.6803	0.9826
L-PBAT	0.0758	0.0640	0.9939	0.0770	1.5055	0.9909
PBS	0.0578	0.0573	0.9848	0.0556	2.9635	0.9853
L-PBS	0.0683	0.0638	0.9208	0.0660	1.8402	0.9874
PS	0.0471	0.0123	0.9849	0.0499	1.8236	0.9708
L-PS	0.0576	0.0271	0.9846	0.0559	1.2434	0.9874
ABS	0.0493	0.0247	0.9253	0.0428	1.9611	0.9362
L-ABS	0.0428	0.0931	0.9671	0.0475	1.8790	0.9959
PMMA	0.0300	0.0363	0.9904	0.0365	1.9677	0.9879
L-PMMA	0.0318	0.0383	0.9873	0.0369	1.6487	0.9559

The maximum adsorption capacity of the aging PBAT is close to 3 times that of the fresh state, mainly due to changes caused by the increase of surface characteristics and oxygen-containing functional groups. MPs in fresh and aging states are more suitable for the Freundlich model to fit the adsorption process, indicating that the surface adsorption sites and functional groups of microplastics in these three states are unevenly distributed, and K_f increases after the aging of these three microplastics, The n value of all aging microplastics is less than that of the fresh state, because ultraviolet increased heterogeneity.

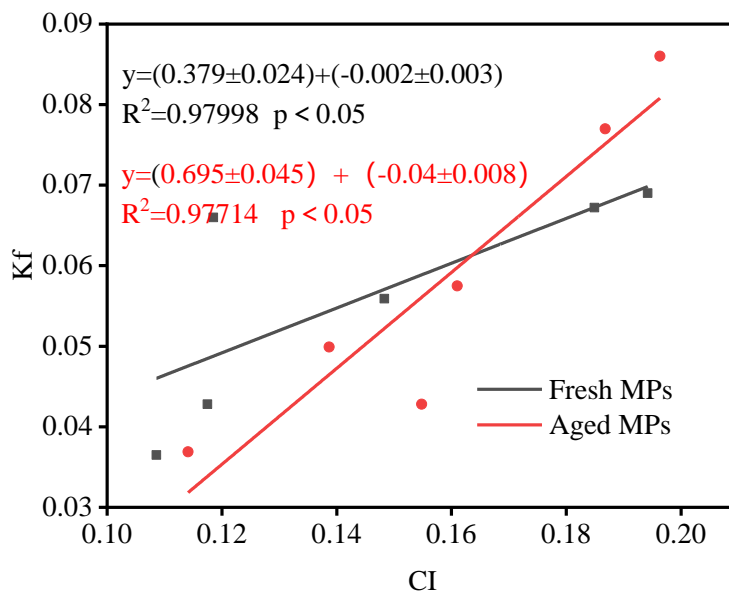


Figure 5: Linear fitting curve between carbonyl index and K_f .

The linear relationship between the carbonyl index of fresh and aged microplastics and the maximum adsorption capacity of copper ions was established isotherm is shown in Figure 5. The two are positively correlated and have a good linear relationship. It was indicated that the increase in the number of hydroxyl functional groups on the surface of microplastics would increase the adsorption capacity of microplastics.

The maximum adsorption capacity of PVC to copper ions was 0.00764mg/g [20], and the maximum adsorption capacity of PE to copper ions was 1.0432mg/g [21]. The microplastics selected in this experiment have a higher adsorption capacity for copper ions, and have greater research value and research significance for the removal of heavy metals in water.

3.5. Study on Desorption Behavior of Microplastics in Pure Water after Adsorption.

Heavy metal ions can be adsorbed on the surface of microplastics, and can also be desorbed from the surface of microplastics. The three desorption isotherm fitting curves are shown in Figures 6 and 7, and the three desorption fitting data parameters are shown in Tables 5, Tables 6, and Tables 7. The desorption order of microplastics to copper ions is arranged from large to small: PVC>PBAT>PBS>PS>ABS>PMMA. The larger the adsorption amount, the larger the desorption amount, and the desorption amount of degradable microplastics to copper ions is significantly higher than that of refractory microplastics. The desorption amount of the aged microplastics is higher than that of the fresh state. Aging will promote the desorption of copper ions by microplastics and release more copper ions, which will cause greater environmental harm. The third desorption generally decreased, which was related to the decrease in the amount of adsorbed copper ions and the weakening of the intermolecular van der Waals force.

The original has a similar desorption trend to PMMA and PS. The reason for the analysis is that the two MPs have fewer oxygen-containing functional groups and weaker adsorption capacity, which makes a large amount of Cu^{2+} desorbed and released. This is mutually confirmed by the FTIR results. The desorption trends of ABS, PVC, PBS, and PBAT are the same, mainly because the four kinds of MPs have more oxygen-containing functional groups, and the stronger adsorption capacity makes the desorption and release of Cu^{2+} difficult. The desorption trend of PVC after aging is obviously different, because the aging effect significantly increases the number of its active sites, and the excess adsorption sites make it difficult for Cu^{2+} to desorb from PVC, and it also interacts with the oxygen-containing functional groups and polar groups after aging. This is consistent with the FTIR.

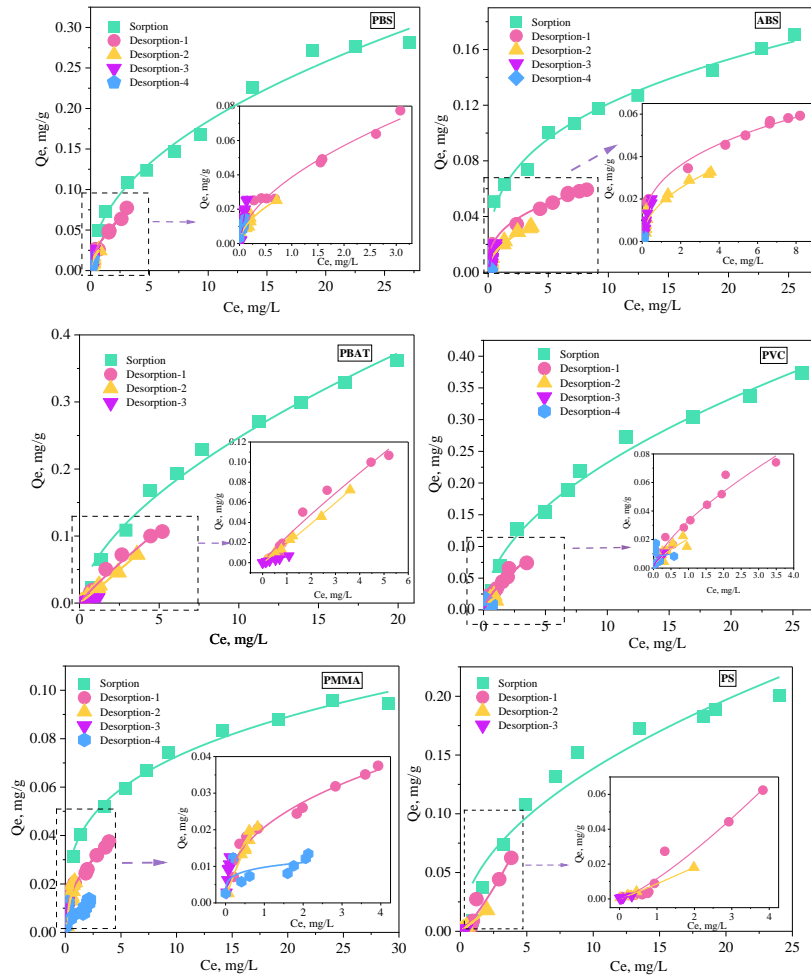
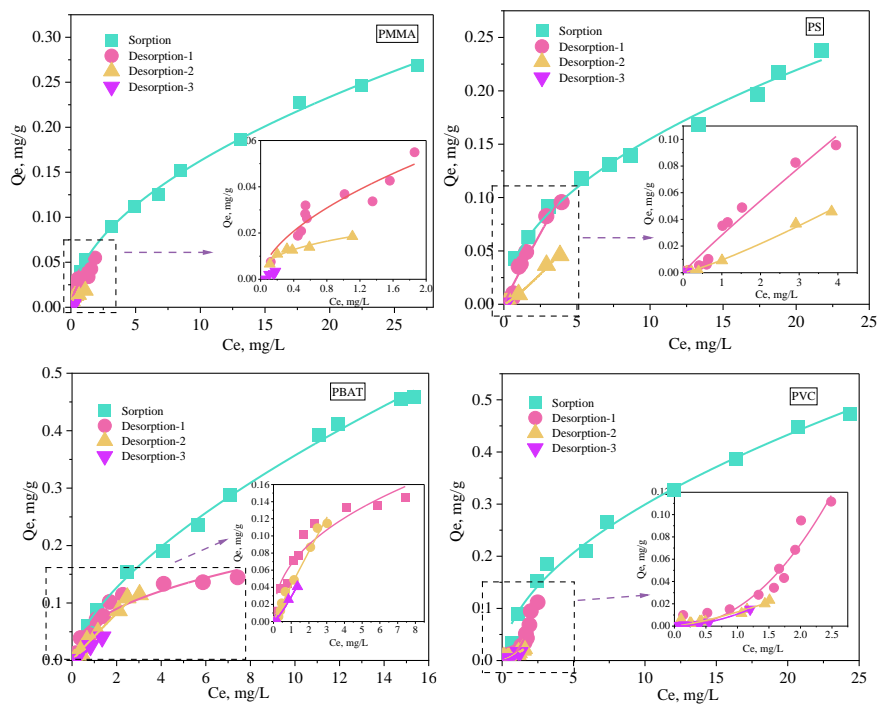


Figure 6: Desorption curve of microplastics to copper ions before aging.



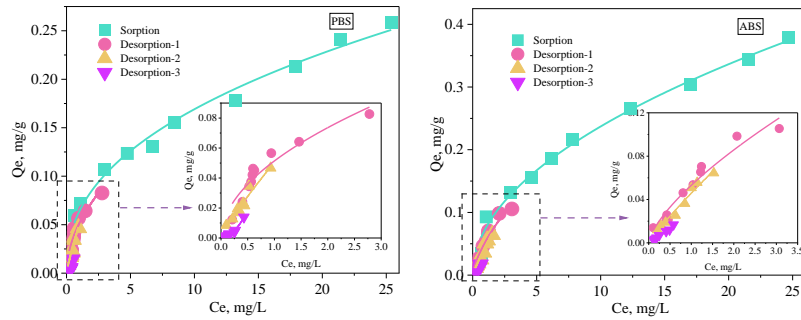


Figure 7: Desorption curve of microplastics to copper ions after aging.

It is the same as the ranking of the maximum adsorption amount of Cu^{2+} by MPs, and it can be obtained that the larger the adsorption amount, the greater the desorption amount. This conclusion is consistent with the desorption results of PA for typical heavy metals studied by Zhang Jinghan [23].

Table 5: Fitting model parameters of microplastics to copper ion primary desorption isotherm.

MPs	Langmuir			Freundlich		
	Q_m	K_L	R^2	Kf	n	R^2
PVC	0.0386	0.2864	0.9493	0.0352	1.4472	0.9017
L-PVC	0.0668	0.8726	0.9608	0.0699	0.4683	0.9133
PBAT	0.0331	0.7216	0.9762	0.0367	1.1185	0.9011
L-PBAT	0.0531	0.5996	0.9301	0.0581	1.0325	0.9019
PBS	0.0282	0.5985	0.9152	0.0307	1.7836	0.8912
L-PBS	0.0514	0.8575	0.9375	0.0519	1.7296	0.9075
PS	0.0281	0.0007	0.9240	0.0261	0.7937	0.8893
L-PS	0.0467	0.0060	0.9618	0.0451	0.0675	0.9076
ABS	0.0259	0.3217	0.9029	0.0396	2.8401	0.8313
L-ABS	0.0352	0.3312	0.9707	0.0321	1.4468	0.9012
PMMA	0.0207	1.3189	0.9747	0.0202	2.4297	0.8890
L-PMMA	0.0282	0.9138	0.9611	0.0262	1.7593	0.9162

Table 6: Parameters of fitting model for secondary desorption isotherm of microplastics on copper ions.

MPs	Langmuir			Freundlich		
	Q_m	K_L	R^2	Kf	n	R^2
PVC	0.0374	0.0228	0.9935	0.0302	1.5374	0.8833
L-PVC	0.0574	0.0251	0.9201	0.0527	0.7724	0.8893
PBAT	0.0291	0.0315	0.9704	0.0287	0.9509	0.9109
L-PBAT	0.0421	0.0523	0.9141	0.0488	0.8394	0.9869
PBS	0.0249	0.2841	0.8457	0.0263	1.9396	0.8095
L-PBS	0.0383	0.1410	0.9203	0.0404	1.1582	0.9708
PS	0.0193	0.0042	0.9938	0.0187	0.933	0.9919
L-PS	0.0253	0.0022	0.9938	0.0195	0.0837	0.9873
ABS	0.0162	0.1128	0.9312	0.0182	1.1102	0.9159
L-ABS	0.0221	0.0140	0.9710	0.0258	1.0213	0.9708
PMMA	0.0115	0.6839	0.9616	0.0153	1.2989	0.9121
L-PMMA	0.0147	0.4242	0.9304	0.0179	1.2691	0.9352

Table 7: Isotherm fitting model parameters of tertiary desorption of copper ions by microplastics.

MPs	Langmuir			Freundlich		
	Q_m	K_L	R^2	Kf	n	R^2
PVC	0.0149	0.0239	0.7523	0.0199	1.6744	0.9891
L-PVC	0.0214	0.0008	0.8785	0.0228	0.5512	0.9943
PBAT	0.0053	0.0014	0.7466	0.0069	0.9855	0.9799
MPs	Langmuir			Freundlich		
	Q_m	K_L	R^2	Kf	n	R^2
L-PBAT	0.0118	0.0037	0.9723	0.0108	0.7950	0.9888
PBS	0.0058	0.0045	0.8921	0.0067	0.8901	0.8942
L-PBS	0.0098	0.0024	0.7919	0.0097	0.0524	0.9805
PS	0.0024	0.0053	0.8786	0.0021	1.8635	0.9267
L-PS	0.0067	0.0004	0.8840	0.0074	0.8755	0.9303
ABS	0.0051	0.0544	0.939	0.0039	1.1271	0.9402
L-ABS	0.0088	0.0011	0.9724	0.0049	0.8770	0.9824
PMMA	0.0036	0.0037	0.8819	0.0029	1.2939	0.8829
L-PMMA	0.0049	0.0079	0.9215	0.0039	0.8550	0.9288

In the third cycle, the desorption amount of Cu^{2+} by original MPs was between 0.0036-0.0149mg/g, and the desorption amount of Cu^{2+} by aged MPs was between 0.0039-0.0228mg/g. The maximum desorption amount of the three cycles of desorption gradually decreased, and Green found that this was related to the reduction of intermolecular van der Waals force [24].

3.6. Desorption Hysteresis Coefficient.

The adsorption and retention characteristics of copper ions by each microplastic were measured by calculating the hysteresis coefficient [25]. The hysteresis coefficient (HI) to describe its calculation formula is:

$$\text{HI} = \frac{q_e^d - q_e^s}{q_e^s} T, \text{Ce} \quad (7)$$

Where: T represents temperature, Ce equilibrium concentration, and superscripts d and s represent solid phase concentrations during desorption and adsorption. The HI value of three desorption is calculated, the data are shown in Table 8.

Table 8: Desorption hysteresis coefficients of different microplastics.

MPS Form	PVC		PS		PBAT		ABS		PMMA		PBS	
	Fresh	Aged	Fresh	Aged	Fresh	Aged	Fresh	Aged	Fresh	Aged	Fresh	Aged
1	-0.41	-0.51	-0.37	-0.42	-0.35	-0.44	-0.44	-0.57	-0.37	-0.45	-0.47	-0.52
2	-0.23	-0.26	-0.31	-0.25	-0.26	-0.29	-0.32	-0.25	-0.24	-0.29	-0.31	-0.36
3	-0.22	-0.24	-0.34	-0.27	-0.31	-0.22	-0.30	-0.23	-0.22	-0.26	-0.33	-0.38

HI was less than 0, indicating that the desorption hysteresis phenomenon was not significant, and HI (first cycle), < HI (second cycle) < HI (third cycle) were mainly related to the small q_e^s value in the first cycle. Comprehensive comparison shows that HI (degradable MPs), < HI (refractory MPs), HI (aging MPs) < HI (original MPs) further illustrate the aging state MPs, the irreversible desorption of degradable MPs is more, the desorption effect is more obvious, and the results of the three-cycle desorption isotherm of the MPs carrier tape Cu (II) have been mutually confirmed.

4. Conclusions

In this study, six microplastics were selected as the research objects to characterize the crystallinity of microplastics and the number of hydroxyl functional groups on the surface of microplastics. Through the adsorption experiment to explore the characteristics and maximum adsorption capacity of adsorption, investigate the desorption behavior in pure water, and study the adsorption-desorption mechanism, the main conclusions are: aging has caused the physical and chemical properties of the six microplastics to change to varying degrees, and the crystallinity has been reduced to a certain extent, which is calculated by the carbonyl index: degradable microplastics are more prone to aging and decomposition, the original physical and chemical properties are more likely to change, and there is also a linear relationship between the carbonyl index and the maximum adsorption capacity. The quasi-secondary kinetic model can better describe the adsorption process of copper ions by six microplastics, and the isotherm model is better fitted with the Freundlich model, indicating that it is a multilayer adsorption process. The aging effect significantly improves the adsorption capacity of microplastics to copper ions. The adsorption mechanism of aging microplastics is mainly electrostatic and complexation, and the desorption mechanism is mainly electrostatic repulsion and decomplexation. And the larger the adsorption capacity, the greater the resolution, degradable microplastics compared to refractory microplastics, aging microplastics compared to fresh microplastics irreversibly desorption, will cause more serious water environmental risks.

References

- [1] Rilling M C. Microplastic inter retrieval ecosystems and the soil?[J]. *Environmental Science & Technology*, 2012, 46(12): 6453-6454.
- [2] Andrady A L. The Plastics Microplastics: are view[J]. *Marine Pollution Bulletin*, 2017(1):119.
- [3] Chio J S, Hong S H, Park J W. Evaluation of Microplastic to xi city in accordance with different sizes and exposure times in the marine copepod *Tigriopus japonicus*[J]. *Marine Environmental Research*, 2020, 153: 104838.
- [4] Li U G, Jian G R, You J, et al. Microplastic impacts on microalgae growth: effects of size and humic acid [J]. *Environmental Science & Technology*, 2020, 54(3): 1782-1785.
- [5] Auta H S, Emenike C U, Fauzian S H. Distribution and importance of microplastics in the marine

- environment: a review of the Sources, Fate, Effects, and potential solutions[J]. *Environment International*, 2017, 12(102): 175-176.
- [6] Ma S R, Li S X, Guo X T, et al. A review on aging characteristics, mechanism of microplastics and their effects on the adsorption behaviors of pollutants[J]. *China Environmental Science*, 2020, 40(9): 3992-4003.
- [7] Mato Y, Isobe T, Takada H, et al. Plastic resin pellets as a transport medium for toxic chemicals in the marine environment [J]. *Environmental Science & Technology*, 2001, 35(2): 318-324.
- [8] Andrady A L. The plastic in microplastics: A review [J]. *Marine Pollution Bulletin*, 2017(119): 12-22.
- [9] Rouillon C, Bussiere P O, Desnoux E, et al. Is carbonyl index a quantitative probe to monitor polypropylene photodegradation?[J]. *Polymer Degradation and Stability*, 2016(128):200-208.
- [10] Chen S Y. The aging process of microplastics and its influence on the sorption of pollutants[D]. Huainan: An Hui University of Science and Technology, 2019.
- [11] Velzeboer I, Kwadijk C, Koelmans A, et al. Strong Sorption of PCBs to plastics, microplastics, carbon nanotubes, and fullerenes[J]. *Environmental Science and Technology*, 2014, 48(9): 4869-4876.
- [12] Liu G, Zhu Z, Yang Y, et al. Sorption behavior and mechanism of hydrophilic organic chemicals to virgin and aged microplastics in freshwater and seawater[J]. *Environmental Pollution*, 2019(246)26- 33.
- [13] Hueffer, Thorsten, Weniger, et al. Sorption of organic compounds by aged polystyrene microplastic particles [J]. *Environmental Pollution*, 2018, 236: 218-225.
- [14] Subowo W S, Barmawi M, Liang O B, et al. Growth of carbonyl index in the degradation of polypropylene by UV irradiation[J]. *Journal of Polymer Science Part A Polymer Chemistry*, 1986, 24(6): 1351-1362.
- [15] Wieslander A, Linden T, Musi B, et al. Exogenous uptake of carbonyl stress compounds promoting AGE formation from peritoneal dialysis fluids[J]. *Contributions to Nephrology*, 2001(131):82-89.
- [16] Rainieris, Conlledon, Larsenbk, et al. Combine defects of microplastics and chemical contaminants on the organ toxicity of zebra fish (*Daniorerio*)[J]. *Environmental Research*, 2018(162): 135-143.
- [17] Liu G, Jiang R, You J, et al. Microplastic impacts on microalgae growth: effects of size and humic acid [J]. *Environmental Science & Technology*, 2020, 54(3):1782-1789.
- [18] Zhu J. Current status of microplastics pollution in Tianjin coastal waters[J]. *IOP Conference Series: Earth and Environmental Science*, 2020, 546(3): 032033.
- [19] Liu Bian, He Wang. Effects of carbon nanotubes on phosphorus adsorption behaviors on aquatic sediments [J]. *Ecotoxicology & Environmental Safety*, 2017(142):230-236.
- [20] Ahmad S, Wan N, Ismail A F, et al. Adsorptive removal of heavy metal ions using graphene-based nanomaterials: Toxicity, roles of functional groups and mechanisms [J]. *Chemosphere*, 2020(248): 126008
- [21] Wang J, Peng J, Tan Z, et al. Microplastics in the surface sediments from the Beijiang River littoral zone: Composition, abundance, surface textures and interaction with heavy metals [J]. *Chemosphere*, 2017(171):248-258.
- [22] Lin Y Q, Ma Q, Yuan C X, et al. Study on copper ion adsorption in waters by micro plastics [J]. *Chemical Engineer*, 2019(10):76-79.
- [23] Du J. Study on the adsorption effect of PE microplastics on heavy metal ions in water [J]. *Plastics Science and Technology*, 2020(7):56- 59.
- [24] Green D S, Colgan T J, Thompson R C, et al. Exposure to microplastics reduces attachment strength and alters the haemolymph proteome of blue mussels(*Mytilus edulis*)[J]. *Environmental Pollution*, 2019(246):423-434.
- [25] Weber W J, Jr Huang, Wu H, et al. Hysteresis in the sorption and desorption of hydrophobic organic contaminants by soils and sediments. Effects of soil organic matter heterogeneity[J]. *Journal of Contaminants Hydrology*, 1998(31):149—16.