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Study on the Adsorption Characteristics of Heavy Metal Cadmium Cd (II) by Microplastics

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Abstract: *Microplastics and heavy metal cadmium Cd (II) are common pollutants in the environment, and their presence poses a potential threat to ecosystems and human health. In this experiment, different types of microplastics were subjected to ultraviolet aging, and the original and ultraviolet aging PVC (polyvinyl chloride), PS (polystyrene), ABS (acrylonitrile-butadiene-styrene copolymer), PMMA (polymethyl methacrylate), PBAT (polybutylene-terephthalic acid-polybutylene-butanediol ester) and PBS (polybutylene-styrene-polystyrene) were used to adsorb Cd (II) in aqueous solution. The physical and chemical properties of microplastics before and after UV aging were observed by SEM, XRD and FT-IR. The results showed that the surface roughness, pore volume and oxygen-containing functional groups of microplastics after UV aging increased to varying degrees, and the degree of crystallization decreased. The results of adsorption kinetics and isotherms indicated that UV aging changed the physical and chemical properties of the surface of microplastics, and the covalent bond force and heterogeneity were enhanced. The effect of changing the pH of the water on Cd (II) on the six microplastics was basically the same. With the increase of pH, the adsorption capacity of microplastics to Cd (II) increased.*

Keywords: *microplastics; heavy metal Cd; adsorption; UV aging effect*

1. Introduction

Microplastics are small plastic particles that are widely distributed in the environment. They are usually less than 5 mm in diameter, including some nano-sized particles. These tiny plastic particles are mainly derived from the decomposition of large plastic products, microfibers released during washing, and microbeads in some personal care products and cosmetics. Most of the plastic products are difficult to be recycled[1]. Over time, microplastics have gradually accumulated in water, soil and atmosphere, becoming a global environmental problem. Microplastics enter ecosystems, food chains and drinking water through water bodies[2], and may eventually be ingested by humans through consumption[3], causing potential health risks; at the same time, the surface of microplastics may adsorb harmful chemicals, which may be released and have additional effects on the environment and ecosystems. Heavy metal cadmium is a toxic metal that usually enters the environment due to industrial emissions, waste treatment and agricultural activities. Heavy metal cadmium accumulates in the human body for a long time, which has toxic effects on the kidney and skeletal system, causing chronic kidney disease and osteoporosis. In addition, the reproductive system and respiratory system will also be seriously affected[4].

In order to deal with the problems caused by microplastics and study the interaction between microplastics and heavy metals[5], all walks of life are strengthening their understanding of plastic pollution. The purpose of this study is to explore the effect of microplastics with different aging degrees on the adsorption and desorption of heavy metal Cd (II). By understanding the interaction between microplastics and heavy metals, we are expected to have a more comprehensive understanding of the behavior of microplastics in the environment and provide a scientific basis for mitigating their potential hazards to ecosystems.

2. Method and experimental design

2.1. Experimental materials and reagents

PVC, PS, ABS, PMMA, PBAT, and PBS microplastics were all purchased from Huachuang Plastics Co., Ltd. Nitric acid was purchased from Merck (Germany), and cadmium nitrate tetrahydrate was

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purchased from Shanghai Aladdin Biochemical Technology Co., Ltd.

2.2. Methods of experiment

2.2.1. Cleaning and pickling of microplastics

The microplastics were first washed three times with water to remove impurities, then soaked in 5% nitric acid for 24 h, rinsed with pure water three times, dried, and stored in a sealed condition.

2.2.2. Ultraviolet lamp radiation aging of microplastics[6]

The dried microplastics were spread into a layer (thickness < 2 mm), irradiated with a 175 W UV lamp at a distance of 50 cm for 96 h, collected, and stored in a sealed dry environment.

2.2.3. Experiments on adsorption kinetics of Cd (II) by original and UV-aged microplastics

Accurately weigh 20 mg of microplastics, place them into a metal mesh bag, seal it, and transfer it into a 100-mL conical flask containing 50 mL of 10 mg/L Cd(II) solution. Incubate in a thermostatic shaking incubator at 25 °C and 150 r/min with water-bath shaking. At time points of 2, 5, 10, 15, 20, 25, 30, 60, 120, 240, 480, and 760 min, collect three replicate samples each. Filter the samples through a 0.45 μm membrane filter, dilute 20-fold according to the upper detection limit of the flame atomic absorption spectrometer, store the diluted solutions in centrifuge tubes, and determine the Cd(II) concentration as soon as possible.

2.2.4. Adsorption isotherm experiments of Cd (II) onto pristine and UV-Aged Microplastics

The Cd(II) stock solution was diluted to a series of concentrations of 1, 2, 5, 8, 10, 15, 20, and 30 mg/L. For each concentration, 20 mg of microplastics were placed into a metal mesh bag and immersed in 50 mL of the solution. The system was incubated in a thermostatic shaking incubator at 25 °C and 150 r/min with water-bath shaking for 24 h. Three replicates were set for each group, and the sampling and subsequent procedures were the same as those in the kinetic experiment. Additionally, a blank control group without microplastics was set up to determine the initial Cd(II) concentration.

2.2.5. Effect of pH on the adsorption of Cd (II) by pristine and UV-aged microplastics

Using 0.01 mol/L NaOH and HNO_3 to adjust the pH value of the pure water used in the experiment, the pH value was adjusted to the range of 3-7.5, and a gradient of 1.5 was set to prepare a series of ionic water with different pH values.

2.2.6. Data fitting and analysis

Origin7.5 software is used for fitting and analyzing the experimental data. All experimental processes are conducted with three parallel samples, and their average values are taken as the final results. The adsorption data analysis models and parameters are shown in Table 1.

Table 1: Adsorption data analysis models and parameters.

Type of calculation	*Mathematical expression*	*Meaning of parameters*
Calculation of adsorption quantity	$Qe=\frac{(C\text{-}Ce)}{m}V$ $Qt=\frac{(C\text{-}Ct)}{m}V$	*Q_e is equilibrium adsorption capacity (mg· g^{-1}); Q_t is adsorption capacity at time t (mg· g^{-1}); V is volume of the Cd (II) solution (mL); m is dosage of the microplastics t (mg).*
Pseudo-first-order *adsorption kinetics*	$ln(Qe-Qt)=lnQe-k_1t$	*k_1 is adsorption rate constant (min^{-1}).*
Pseudo-second-order adsorption kinetics	$\frac{t}{Qt}=\frac{1}{Qe^2k_2}+\frac{t}{Qe}$	*k_2 is adsorption rate constant (g·mg^{-1}· min^{-1})*
Langmuir model	$\frac{Ce}{Qe}=\frac{1}{QmK_L}+\frac{Ce}{Qm}$	*C_e is concentration of the adsorbate in the liquid phase at equilibrium (mg·L^{-1}). q_m is maximum adsorption capacity for monolayer coverage (mg·mg^{-1}); KL is adsorption equilibrium constant related to adsorption heat (L·mg^{-1})*
Freundlich model	$ln(Qe)=lnK_F+\frac{1}{n}lnCe$	*K_F is Freundlich constant related to adsorption capacity [(mg/g)(L/mg)^n]. n is constant related to the intensity of adsorption.*

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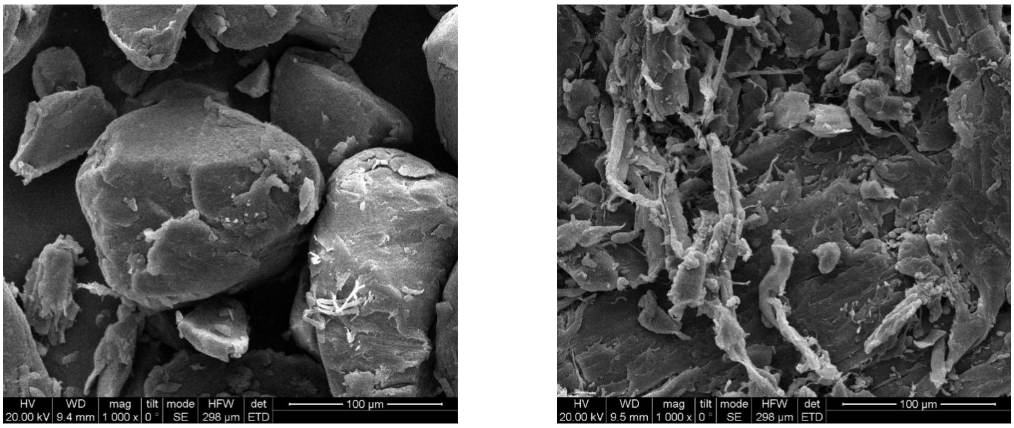
3. Results and discussion

3.1 Comparative analysis of the properties of original and aged microplastics



(a) original microplastics *(b) aging microplastics*

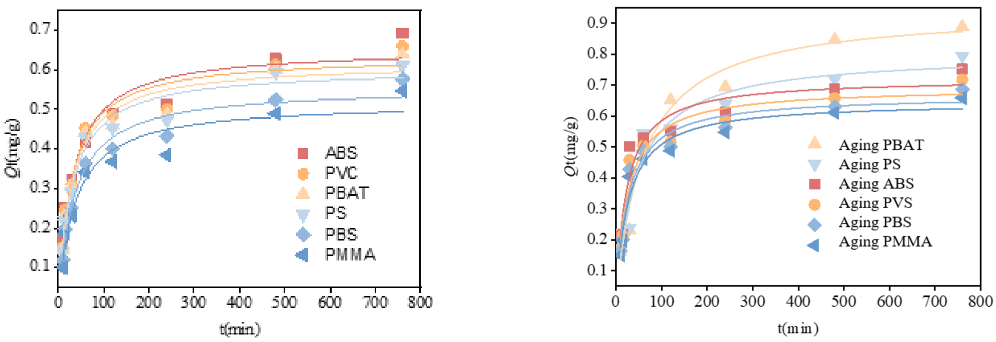
Fig.1 Microplastic scanning electron microscope

According to the observation results in Fig.1, it can be seen that the microplastics in the initial state have a smooth overall surface, a compact structure, and no obvious pore structure. However, through the ultraviolet aging process, it has undergone a process of accelerated decomposition, resulting in significant changes in its surface morphology. After aging, microplastics mostly show cracks, debris, uneven surface, and some holes[7].

3.2. Experiments on the adsorption of Cd (II) by original and aged microplastics

The sampling time points in this study were set at 2, 5, 10, 15, 30, 60, 120, 240, 480, and 760 minutes. In the first 200 minutes, the adsorption of Cd(II) by microplastics was rapid, while the adsorption between 200 and 760 minutes tended to stabilize. This trend was mainly because there were a large number of adsorption sites on the surface of the microplastics initially, along with a high specific surface area, which enabled Cd(II) in the solution to quickly reach the surface and occupy the adsorption sites. However, over time, the number of available adsorption sites gradually decreased. As the Cd(II) concentration in the solution decreased, the adsorption rate gradually slowed down, and finally reached adsorption equilibrium. These results are consistent with the findings of Zhang et al[8] [9].

In order to further understand the adsorption kinetics of heavy metals on the surface of microplastics, the quasi-first-order and quasi-second-order kinetic models were used to fit the data. The relevant fitting parameters are shown in Figs. 2 and 3, and are listed in Table 2.



(a) Primitive microplastics adsorb Cd (II) *(b) Aging microplastics adsorb Cd (II)*

Fig. 2 Quasi-first-order kinetic fitting of Cd (II) adsorption by MPs

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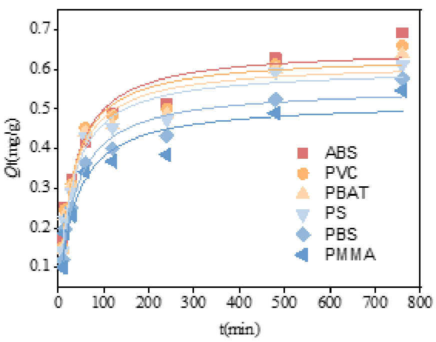
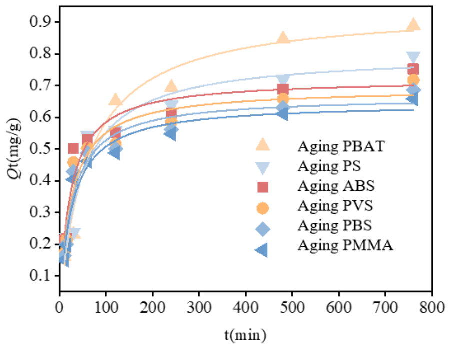


(a) Primitive microplastics adsorb Cd (II)



(b) Aging microplastics adsorb Cd (II)

Fig. 3 Quasi-second-order kinetic fitting of Cd (II) adsorption by microplastics

According to the fitting data, the pseudo-second-order kinetic model is more consistent with the adsorption process than the pseudo-first-order model. Pseudo-first-order is usually suitable for physical adsorption, and pseudo-second-order is more suitable for chemical adsorption. Due to the change of specific surface area, porosity and polarity, the physical adsorption of ultraviolet aging microplastics was enhanced, which slightly improved the fitting of pseudo-first-order, but still more in line with the pseudo-second-order model. Therefore, the pseudo-second-order model is more suitable to describe the adsorption of heavy metals on the surface of microplastics. This process is dominated by chemical adsorption, accompanied by partial physical adsorption, showing a heterogeneous adsorption mechanism of physical-chemical mixing.

Table 2 Fitting parameters of Cd (II) adsorption kinetic model

MPs types	Quasi-first-order model			Quasi-second-order model		
	Qe(mg/g)	K1	R2	Qe(mg/g)	K2	R2
ABS	0.6388	0.0332	0.8944	0.6413	0.0313	0.9993
aging ABS	0.7216	0.0201	0.8934	0.7419	0.0044	0.9966
PVC	0.6033	0.0393	0.9153	0.6022	0.0417	0.9974
aging PVC	0.6563	0.0172	0.9153	0.6933	0.0027	0.9913
PBAT	0.5589	0.0317	0.8872	0.5603	0.0536	0.9748
aging PBAT	0.8338	0.0183	0.9197	0.8102	0.0032	0.9732
PS	0.5129	0.0329	0.9037	0.5313	0.0318	0.9891
aging PS	0.7544	0.0297	0.9101	0.7877	0.0121	0.9766
PBS	0.4313	0.0342	0.8798	0.4722	0.0472	0.9883
aging PBS	0.6449	0.0277	0.8993	0.6516	0.0017	0.9308
PMMA	0.4127	0.0331	0.8525	0.4344	0.0552	0.9772
aging PMMA	0.6177	0.0176	0.8885	0.6117	0.0029	0.9451

Table 3 Microplastic adsorption of Cd (II) isotherm fitting parameters

MPs types	Langmuir Model			Freundlich Model		
	Qm (mg/g)	K_L	R^2	K_F(mg/g)	n	R^2
PVC	0.0574	0.0724	0.9774	0.0587	1.4317	0.9948
aging PVC	0.0644	0.0892	0.9872	0.0604	1.1292	0.9943
PBAT	0.0511	0.0589	0.9934	0.0531	1.4812	0.9956
aging PBAT	0.0778	0.0664	0.9586	0.0784	1.1282	0.9913
PBS	0.0461	0.0562	0.9847	0.0421	2.7873	0.9895
aging PBS	0.0413	0.0662	0.9683	0.0483	1.4882	0.9923
PS	0.0485	0.0392	0.9893	0.0512	1.6716	0.9923
aging PS	0.0663	0.0871	0.9688	0.0723	1.1891	0.9932
ABS	0.0585	0.0201	0.9683	0.0621	1.9933	0.9942
aging ABS	0.0654	0.0811	0.9688	0.0643	1.4738	0.9904
PMMA	0.0324	0.0112	0.9904	0.0333	1.3782	0.9976
aging PMMA	0.0283	0.0242	0.9898	0.0371	1.3281	0.9932

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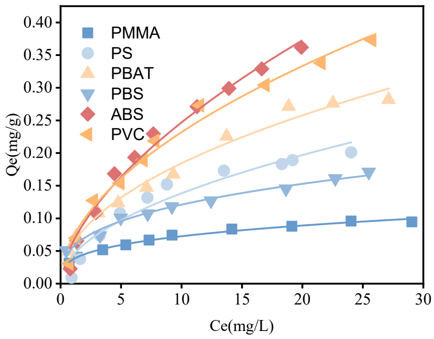
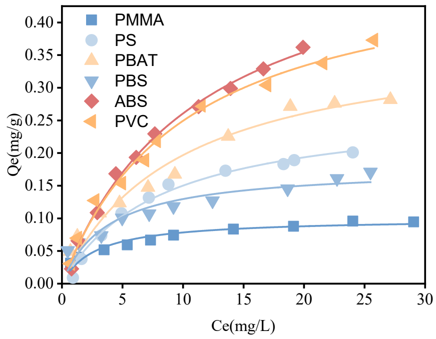
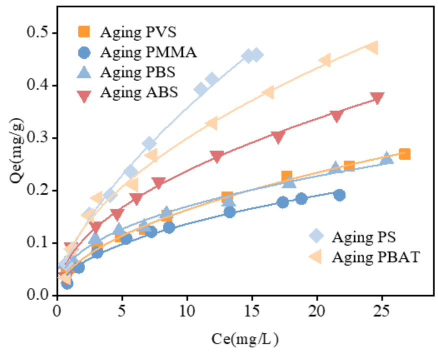


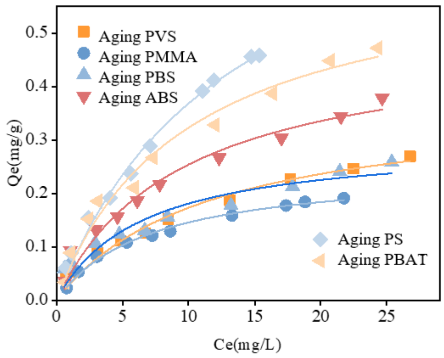
(a) The Langmuir model of Cd (II) adsorption on original microplastics



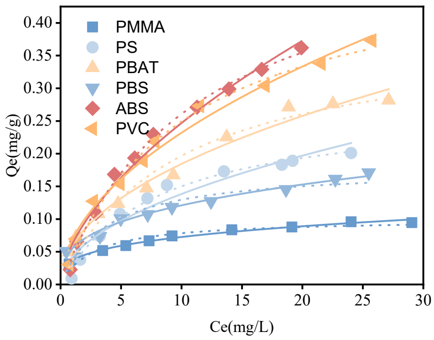
(b) The Freundlich model of Cd (II) adsorption on original microplastics



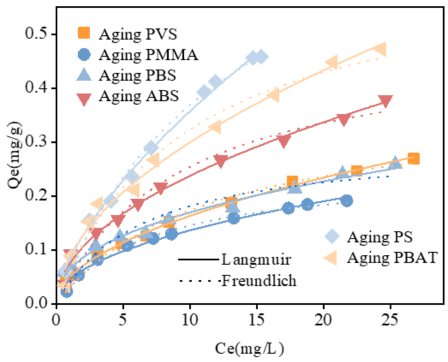
(c) Langmuir model of Cd (II) adsorption on aged microplastics



(d) Freundlich model of Cd (II) adsorption on aged microplastics



(e) Adsorption isotherm model of Cd (II) on original microplastics



(f) Cd (II) adsorption isotherm model of aged microplastics

Fig.4 Isothermal fitting of Cd (II) by microplastics

As shown in Fig.4 and Table 3, the adsorption capacity of microplastics for Cd(II) before aging, in descending order, was: PMMA, PBS, PS, PBAT, PVC, ABS. The adsorption capacity of aged microplastics for Cd(II) in descending order was: PMMA, PBS, PVC, ABS, PS, PBAT. This indicates that UV aging enhances the Cd(II) adsorption capacity of microplastics. UV aging alters the surface physicochemical properties of microplastics, increasing the specific surface area and porosity, creating more adsorption sites, and enhancing hydrophobic interactions[10]. Moreover, UV aging increases the hydrophilicity of microplastics, thereby enhancing their adsorption capacity for hydrophilic cations in the environment[11]. After aging, the oxygen-containing functional groups on the microplastic surface increase, which enhances the complexation between microplastics and heavy metal ions[12].

Fig. 5 shows the adsorption properties of six microplastics for Cd(II) under different pH conditions. The results show that the adsorption capacity increased with increasing pH. Under different pH conditions, the six microplastics exhibited similar trends in heavy metal adsorption. At low pH, a large number of H^+ ions in the solution compete with Cd(II) for adsorption sites, resulting in relatively low adsorption capacity. As the pH increases, the surface functional groups of the microplastics become deprotonated, increasing their negative charge, which further strengthens the electrostatic interaction

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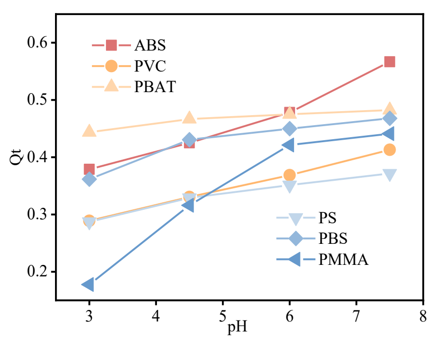
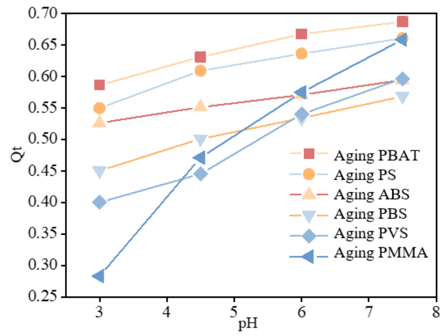
between the microplastics and Cd(II), thereby enhancing adsorption capacity[13]. Notably, the adsorption capacity of PMMA for Cd(II) increased significantly with pH, which is consistent with previous findings[14] [15]. Considering that the pH of natural waters typically ranges from 6.5 to 8.5, these results indicate that the six microplastics exhibit significant Cd(II) adsorption capacity within this pH range.



(a) The effect of pH on the adsorption of Cd (II) on microplastics



(b) Effect of pH on the adsorption of Cd (II) on aged microplastics

Fig.5 Effect of pH on the adsorption of heavy metals on microplastics

4. Conclusion and Prospect

This study investigated the adsorption behavior and related mechanisms of six types of microplastics for Cd(II) under different conditions. The microplastics were subjected to UV aging in the laboratory, and kinetic and isotherm models were fitted and analyzed. The effects of aging were characterized using relevant analytical methods. The experimental results show that UV-aged microplastics have a rougher surface, which increases their specific surface area and porosity, and they possess more oxygen-containing functional groups than pristine microplastics. In adsorption experiments, the adsorption capacity of aged microplastics for Cd(II) was greater than that of pristine microplastics. The adsorption capacity of the six pristine microplastics followed the order: PMMA > PBS > PS > PBAT > PVC > ABS. For aged microplastics, the order was: PMMA > PBS > PVC > ABS > PS > PBAT. Model fitting revealed that the adsorption of Cd(II) onto microplastics is primarily a heterogeneous process involving both physical and chemical interactions. The effect of solution pH on Cd(II) adsorption was similar across all microplastic types, with adsorption capacity increasing as pH increased.

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