Study on Adsorption of Heavy Metals Cu and Zn by Microplastics Under Different Aged Factors

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Abstract. Microplastics are widely distributed in a variety of environments, absorbing heavy metals in the environment while aging due to various environmental factors. In this paper, the effects of different aging factors (pH, DOM, and H_2O_2) on the adsorption capacity of heavy metals Cu and Zn on polyethylene microplastics (PE-MPs) were investigated, and the changes in physical and chemical properties of PE microplastics were analyzed. The results demonstrate that H_2O_2 aging bears the greatest effect on the adsorption effect of PE microplastics, dissolved organic matter (DOM) aging has the least effect on the adsorption effect of PE microplastics, and the adsorption effect of microplastics aged with pH=9 is stronger than that aged with pH=4; the adsorption kinetics model of microplastics fitted to the pseudo-second-order kinetic model, and the thermodynamic model fitted to Langmuir model; aging mainly changed the surface structure of microplastics, increased the Zeta potential of microplastics, introduced more oxygen-containing functional groups, and finally affected the ability of microplastics to adsorb heavy metals. The research provides data reference for understanding the influence of different aging on the adsorption capacity of heavy metals in microplastics.

1. Introduction

Plastic products are important basic materials, and with the development and increasing demand, plastic waste is inevitably produced. Plastic waste is broken into plastic particles with smaller particle sizes under the influence of environmental factors, and those with particle sizes of less than 5 mm are called microplastics (MPs) [1]. MPs witnessed widespread distribution in various environments and are competent to adsorb heavy metals from the environment on account of their small particle size, a large number of pores, and large specific surface areas [2]. Ashton et al. [3] set up suspended original PE in port for 8 weeks, and they found that it can adsorb heavy metals in seawater; Guo also found that polystyrene (PS) and polyvinyl chloride (PVC) could adsorb many heavy metals in the environment after they were set up for three months [4]. There are more concentrations of microplastics in landfills and other environments, which can continuously saturate and adsorb high concentrations of heavy metal ions in the environment [5,6]. Microplastics adsorbed with heavy metals may be eaten by other organisms in the environment, causing greater harm [7,8]. Charging characteristics, polarity, and hydrophobicity of MPs may affect the interaction between MPs and heavy metals [9].

While microplastics adsorb other pollutants in the environment, they are also subjected to aging in response to environmental influences, and aging microplastics usually exhibit a stronger adsorption capacity [10,11]. Mao et al. [12] discussed the influence of ultraviolet on the adsorption of heavy metals by plastics in different background environments, mainly affecting the surface roughness of MPs and the formation of oxygen-containing functional groups. Other types of advanced oxidation (such as hydrogen peroxide and Fenton) are similar to ultraviolet effects, introducing carbonyl and carboxyl groups on MPs surface [13]. In addition, pH, salinity, and DOM in background conditions may also change the surface roughness and electronegativity of MPs, and then affect the adsorption effect of MPs and heavy metals [14]. At present, the research mainly simulates the aging of MPs in the background environment such as river water and seawater [15,16], but there is a lack of research on aging in landfills, soils and groundwater, which are susceptible to the influence of multiple factors.

Different kinds of factors have varying effects on the aging of microplastics. In order to evaluate the continuous aging effect of common environmental factors on microplastics, PE-MPs were selected as the research object in this paper, and four factors were used to age MPs for a long time. The adsorption capacity of Cu (II) and Zn (II) ions and the changes in physicochemical properties of

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MPs after aging were analyzed, which provided a reference for investigating the contamination of aging MPs.

2 Materials and Methods

2.1 Experimental materials

In the aging and adsorption experiments, PE-MPs with a particle size of 13 μm were used as the research object to explore the ability of MPs to adsorb heavy metals after long-term aging. pH, humic acid, and oxidation were selected as aging factors of MPs. All experiments were conducted in a dust-free environment, and the glassware used was washed with ultrapure water at least three times before use and dried in an oven.

2.2 MPs aging

0.1 M HCl and NaOH solution with pH=4 and pH=9 were used to simulate acid-base aging, fulvic acid with 1000 mg/L DOC was used to simulate humic acid aging, and 30% hydrogen peroxide solution was used to simulate oxidative aging. The aging time was set to 50 days. 500 mL background solution and 0.5 g MPs were mixed in a beaker and stirred continuously by a magnetic stirrer to enhance the dispersion effect of MPs. The mixed solution was aged at room temperature (25 ℃), and the rotating speed of the magnetic stirrer was 250 r/min.

After 50 days of aging, the MPs mixture was filtered several times by vacuum suction filter on a filter membrane of 0.22 μm. After filtration, MPs were washed repeatedly with ultrapure water to remove residual liquid. After washing, MPs were transferred to a 60 ℃ oven for drying, and then sealed and stored for subsequent use.

2.3 MPs adsorption experiment

Before the adsorption experiment, 0.1 M HCl and 0.1 M NaOH were used to adjust the pH of the background solution to 6 to avoid metal ion precipitation. In the experiment of adsorption kinetics, the original and different aged MPs were 10 mg, and the adsorbates were 10 mg/L Cu (II) and 100 mL Zn (II) solution. Adsorption was carried out in a 200 r/min magnetic stirrer at room temperature. Samples were taken at different time intervals (0, 1, 2, 4, 8, 12, 24, 36, and 48 h). After sampling, the samples were filtered by a 0.22 μm filter membrane and stored in a refrigerator at 5 ℃. All experiments were set in triplicate as controls.

In the experimental adsorbent isokinetic experiments of adsorption isotherms, adsorbents of Cu (II) with different concentration gradients (1, 5, 10, 20, 30 mg/L) and 100 mL Zn (II) solution were adsorbed in a 200 r/min magnetic stirrer for 48 h at a room temperature. After reaching the time, samples were taken and filtered by 0.22 μm filter membrane and stored in a refrigerator at a low temperature of 5 ℃. All experiments were set in triplicate as controls.

Cu (II) and Zn (II) in all samples were determined by inductively coupled plasma mass spectrometer (ICP-MS), and the concentration of heavy metals adsorbed on MPs was calculated by the difference method. The results of adsorption kinetics were fitted by pseudo-first-order kinetics and pseudo-second-order kinetics. The pseudo-first-order kinetics usually represents a higher initial adsorption concentration and fewer adsorption sites, while pseudo-second-order kinetics generally stands for a lower initial adsorption concentration and more adsorption sites. The adsorption isotherms were fitted by the Langmuir model and Frendichi model.

Pseudo-first-order kinetics and pseudo-second-order kinetics are often used to analyze the adsorption kinetics between adsorbate and adsorbent, and the specific calculation formula is as follows [17]:

Pseudo-first-order dynamic model

$$\ln\left(Q_e - Q_t\right) = \ln Q_e - k_1 t \quad (1)$$

$$t / Q_t = 1 / \left(k_2 Q_e^2\right) + t / Q_e \quad (2)$$

Where:

Q_e- The maximum adsorption capacity of MPs for heavy metals (μg/g);

Q_t- The capacity of adsorption for t hours (μg/g);

T- Time (h);

k_1- The pseudo-first-order kinetic adsorption rate (h^{-1});

k_2- The pseudo-second-order kinetic adsorption rate ($g\cdot(mg\cdot h)^{-1}$).

Langmuir model and Frendichi model are commonly deployed to analyze the relationship between the maximum adsorption capacity and adsorption equilibrium between adsorbate and adsorbent, and the calculation formula is as follows [18]:

Langmuir model

$$Q_e = Q_m C_e K_l / \left(1 + C_e K_l\right) \quad (3)$$

Frendichi model

$$Q_e = K_f C_e^{1/n} \quad (4)$$

Where:

Q_e- Adsorption capacity of MPs (μ g/g);

Q_m- Saturated adsorption capacity of MPs surface monolayer (μ g/g);

K_l- Adsorption equilibrium constant of MPs;

K_f- Equilibrium constant;

n- The degree of nonlinearity of fitting isotherms.

2.4 MPs characterization

Samples of four types of aged MPs and an original MP were characterized. The surface structure of MPs was characterized by scanning electron microscope (SEM), functional groups were determined by Fourier transform infrared spectroscopy (FTIR), the surface potential was measured by Zeta-plus analyzer, and surface elements were determined by X-ray photoelectron spectroscopy (XPS).

3 Results and Discussion

In this study, pH=4, pH=9, 1000 mg/L DOC, and 30% H_2O_2 were selected as aging factors for 50 days of the original PE-MPs. The adsorption effects of original and

aged MPs on Cu (II) and Zn (II) were analyzed. Pseudo-first-order and pseudo-second-order adsorption kinetic models and isotherm models of Langmuir and Freundlich adsorption were established.

3.1 Adsorption kinetics of aging MPs

The adsorption kinetics fitting of metal ions adsorbed by different aged MPs is depicted in Fig 1, and the kinetic fitting parameters are described in Table 1. From the adsorption process, the adsorption capacity of MPs increased rapidly from 0 to 8 h, the adsorption rate decreased gradually from 8 to 12 h, the adsorption capacity of MPs tended to be equilibrium from 12 to 24 h, and MPs remained stable after 24 h. Therefore, it was considered that the adsorption time of Cu (II) by different types of MPs reached equilibrium at 24 h. From the comparison of adsorption equilibrium, the results of the two kinetic fitting effects are similar. From the adsorption model, the pseudo-second-order kinetic model R^2 is higher than the pseudo-first-order kinetic model R^2, so, suffice it to say that the pseudo-second-order model is more in line with the adsorption process of Cu (II) by aging MPs, which is similar to other studies [19,20]. The pseudo-first-order kinetic model explains the rate relationship between adsorbate and adsorbent, which is used to analyze the rate change in MPs adsorption process; the pseudo-second-order kinetic model shows that the adsorption process of heavy metals by MPs is mainly affected by chemical adsorption process [21].

According to the pseudo-second-order kinetics, the adsorption of Cu (II) by five types of MPs can be divided into three types with different adsorption effects according to the maximum adsorption capacity of MPs. Aging with H_2O_2 increased the maximum adsorption capacity of PE-MPs by about 118.51%, aging with pH=9 increased the maximum adsorption capacity by about 97.46%, aging with pH = 4 increased the maximum adsorption capacity by about 81.01%, and aging with DOM increased the maximum adsorption capacity by about 8.64%. To put it in a nutshell, aging with H_2O_2 significantly changed the overall adsorption effect of MPs Cu (II), and the adsorption effect at different pH was relatively close but the aging effect was more obvious at pH=9. DOM has no obvious effect on the adsorption effect.

The adsorption process of Zn (II) on MPs was similar to that of Cu (II), both of which approached equilibrium at 24 h. The enhancement effect of different analogous aging on adsorption is similar to that of Cu (II), indicating that H_2O_2 displayed the most obvious enhancement effect, and the fitting effect of the pseudo-second-order dynamics is better. On the whole, the adsorption kinetics of Cu (II) and Zn (II) by MPs is roughly the same. In terms of data, aging with H_2O_2 increased the maximum adsorption capacity of PE-MPs by about 125.07%, aging with pH=9 increased the maximum adsorption capacity by about 61.11%, aging with pH=4 increased the maximum adsorption capacity by about 54.089%, and aging with DOM increased the maximum adsorption capacity by about 6.49%. Generally speaking, the adsorption properties of Cu (II) and Zn (II) by MPs are similar, but the adsorption capacity of Cu (II) by different types of MPs is higher than that of Zn (II).

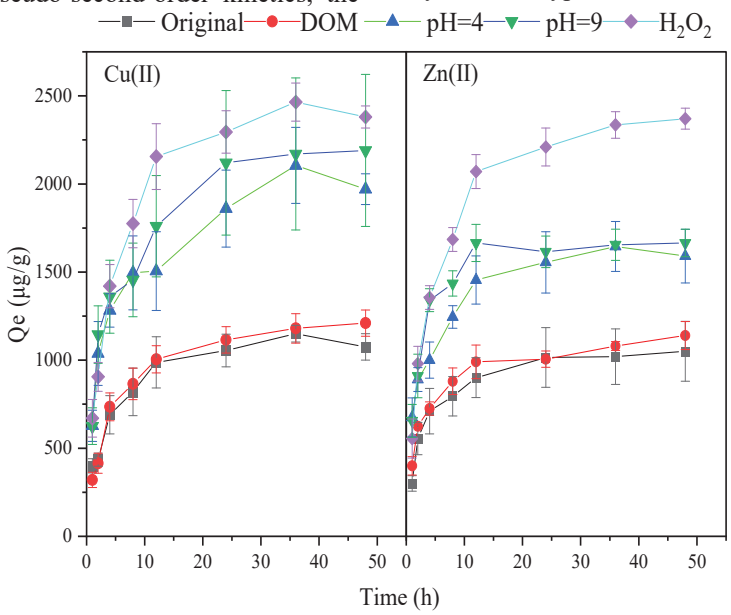

Fig 1. Adsorption curves of different types of MPs

Table 1. Dynamic fitting parameters of MPs

Metal ion	MPs type	Pseudo-first-order dynamic model			Pseudo-second-order dynamic model		
		Q_e (μg/g)	k_1 (h^{-1})	R^2	Q_e (μg/g)	k_2 (g(mg h)$^{-1}$)	R^2
Cu (II)	Original MPs	981.728	0.334	0.934	1080.98	0.171	0.981
	Aging MPs with DOM	1030.348	0.385	0.902	1168.16	0.508	0.971
	Aging MPs with pH=4	1517.791	0.366	0.845	1956.76	1.707	0.974
	Aging MPs with pH=9	1622.563	0.433	0.968	2134.567	1.329	0.979

	Aging MPs with H_2O_2	2268.135	0.223	0.969	2362.100	1.045	0.977
Zn (II)	Original MPs	981.728	0.334	0.934	1023.031	0.318	0.988
	Aging MPs with DOM	1030.348	0.385	0.902	1089.454	0.356	0.987
	Aging MPs with pH=4	1517.791	0.366	0.845	1584.6151	1.235	0.991
	Aging MPs with pH=9	1622.563	0.433	0.968	1648.233	1.596	0.995
	Aging MPs with H_2O_2	2268.135	0.223	0.969	2302.574	2.614	0.977

3.2 Adsorption isotherm of aged MPs

The adsorption isotherm models of MPs under five Cu (II) concentration gradients of 1, 5, 10, 20, and 30 mg/L were established. The adsorption isotherm fitting of different kinds of MPs and metal ions is shown in Fig 2, and the isotherm fitting parameters are shown in Table 2. According to the results of different concentration gradients of Cu (II) adsorption on MPs, the adsorption capacity of aging MPs with DOM increased from 190 to 2435 μg/g, and the fitted maximum adsorption capacity was 4914 μg/g; the adsorption capacity of aging MPs with pH = 4 increased from 316 to 3250 μg/g, and the fitting maximum adsorption capacity was 5119 μg/g; the adsorption capacity of aging MPs with pH=9 increased from 335 to 3575 μg/g, and the fitting maximum adsorption capacity was 5553 μg/g; the adsorption capacity of aging MPs with H_2O_2 increased from 500 to 4065 μg/g, and the fitting maximum adsorption capacity was 5732 μg/g. By and large, the aging effect enhanced the adsorption capacity and the maximum saturated adsorption capacity of MPs at different adsorbate concentrations, and the effects of different aging were consistent with adsorption kinetics. Adsorption isotherm is a model based on the maximum adsorption of adsorbents under different concentrations of adsorbate, which analyzes the influence of MPs concentration on the adsorption effect and discusses the interaction characteristics between MPs and heavy metals. From the fitting results, Langmuir isotherm model R^2 is generally higher under various influencing factors, and the fitting effect is better, which indicates that the adsorption of Cu (II) by MPs is single-layer adsorption, and there is no other interaction between adsorbate molecules [22]. Nonlinear fitting shows that the surface adsorption of MPs is the dominant factor, and the hydrogen bond, electrostatic interaction, and π-π bond binding on the surface may be the reasons for promoting adsorption [23].

According to the results of different concentration gradients of Zn (II) adsorbed by MPs, the adsorption capacity of aging MPs with DOM increased from 175 to 2218 μg/g, and the fitting maximum adsorption capacity was 3733 μg/g; the adsorption capacity of aging MPs with pH = 4 increased from 305 to 2930 μg/g, and the fitting maximum adsorption capacity was 4751 μg/g; the adsorption capacity of aging MPs with pH=9 increased from 308 to 3180 μg/g, and the fitting maximum adsorption capacity was 5293 μg/g; the adsorption capacity of aging MPs with H_2O_2 increased from 465 to 3930 μg/g, and the fitting maximum adsorption capacity was 5528 μg/g. Generally speaking, the adsorption isotherm fitting results of Zn (II) are similar to those of Cu (II), the Langmuir model fits well as a whole, and the adsorption performance is similar. At the same time, the maximum adsorption capacity of Cu (II) is higher than that of Zn (II) in the whole data of the isotherm model.

Combined with the above results, it is found that the adsorption effect of Cu (II) by different types of MPs is better than that of Zn (II). At present, some studies have reported the difference in the adsorption capacity of different metals with the same valence [19]. The hydration ion radii of Cu (II) and Zn (II) are 0.419 nm and 0.430 nm, respectively. Considering that MPs aged in the same batch and stirred by a magnetic stirrer every time, the difference in materials can be ignored. At this time, the surface potential of MPs is essentially identical, so the adsorption affinity is affected by different hydration radii, showing an inverse relationship [24]. The electronegativity of Cu and Zn is 1.9 and 1.65, respectively, so the electrostatic attraction is different [25]. Comprehensive analysis shows that electrostatic attraction may be the key factor for MPs to adsorb heavy metals, and aging will also change the distribution of surface charge of MPs to a certain extent, which will affect its electrostatic force.

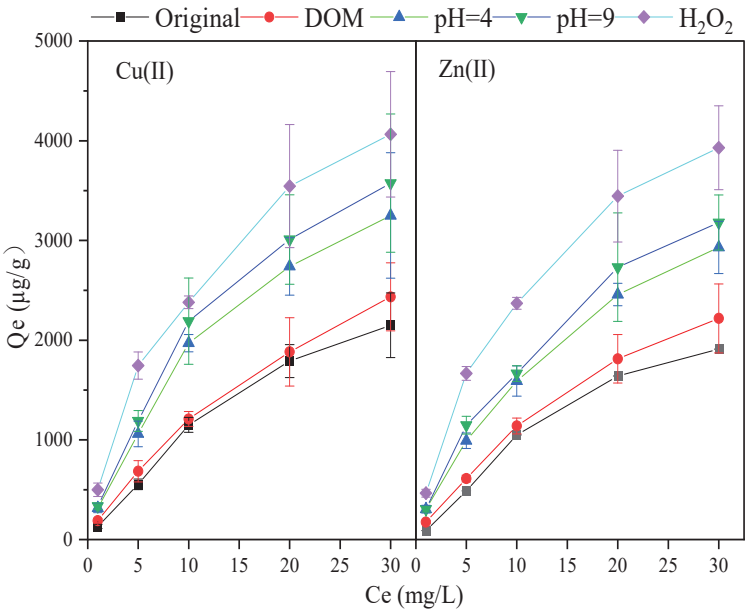

Fig 2. Adsorption isotherms of different types of MPs

Table 2. Fitting parameters of MPs isotherm

Metal ion	MPs type	Langmuir model			Freundlich model		
		Q_e (μg/g)	K_l (L/mg)	R^2	K_f (mg/g)	1/*n*	R^2
Cu (II)	Original MPs	4242.451	0.0352	0.994	0.217	0.684	0.979
	Aging MPs with DOM	4913.811	0.0321	0.998	0.238	0.686	0.997
	Aging MPs with pH=4	5119.871	0.0582	0.993	0.461	0.583	0.977
	Aging MPs with pH=9	5553.503	0.0603	0.996	0.516	0.578	0.976
	Aging MPs with H_2O_2	5713.929	0.0796	0.992	0.713	0.520	0.988
Zn (II)	Original MPs	3733.764	0.0367	0.989	0.196	0.683	0.967
	Aging MPs with DOM	4357.923	0.0349	0.998	0.228	0.676	0.990
	Aging MPs with pH=4	4868.511	0.0504	0.997	0.387	0.603	0.992
	Aging MPs with pH=9	5293.233	0.0508	0.995	0.424	0.602	0.987
	Aging MPs with H_2O_2	5528.972	0.0811	0.996	0.659	0.519	0.982

3.3 Aging MPs characterization

It can be seen from the adsorption results that the adsorption capacity of MPs changes with aging, and the enhancement effect varies. At present, it has been reported that the surface properties of MPs will change after aging, which will affect the interaction between MPs pollutants. Therefore, SEM, Zeta potential analysis, XPS analysis, and FTIR analysis were used to study the mechanism of different aging on MPs.

A scanning electron microscope is used to analyze the surface structure changes of MPs, and the results are shown in Fig 3. Compared with the original MPs, aging mainly affects the wrinkle degree and surface integrity of MPs [12]. Since MPs are derived from broken larger plastic pellets, the surface of the original MPs already has a certain degree of the wrinkling phenomenon and there are certain tear marks, but the overall is relatively intact with fewer holes. After the aging of DOM, the wrinkling phenomenon on the surface of MPs intensified, and a certain degree of chapping occurred, with bulbous projection phenomenon and a gradual increase of fine porosity. For the aging with pH=4, the surface of MPs showed more detailed and dense wrinkles, enhanced spherical projections, more obvious erosion of the surface, enlargement of fine pores, and more wrinkles inside the pores. Under the aging with pH=9, chapping gradually increased, the surface shape became more irregular, the holes increased substantially, the wrinkles in the holes became denser and more detailed, and the internal structure turned over. Under the aging with H_2O_2, chapping traces were the most obvious and gradually diffused, the roughness was extremely high, the holes appeared the most, and the overall structure of MPs surface was incomplete, with traces of breakage and a large number of spherical projections, enhancing the rollover phenomenon.

As a general rule, the surface roughness of MPs under different aging conditions is different, and the roughness is matched with the aging-enhanced MPs adsorption. The change of MPs' surface affects the number of adsorption sites of MPs. When MPs remain flat and smooth, only the single layer of the surface can contact heavy metals. However, with the gradual corrosion of the MPs surface

layer, the internal skeleton is exposed, and the internal pore size begins to adsorb heavy metals, which enhances the adsorption effect [2]. When aging seriously affects the integrity of MPs skeleton, the specific surface area rapidly enlarges and the adsorption sites rapidly increase, so the overall adsorption enhancement effect of H_2O_2 is the best.

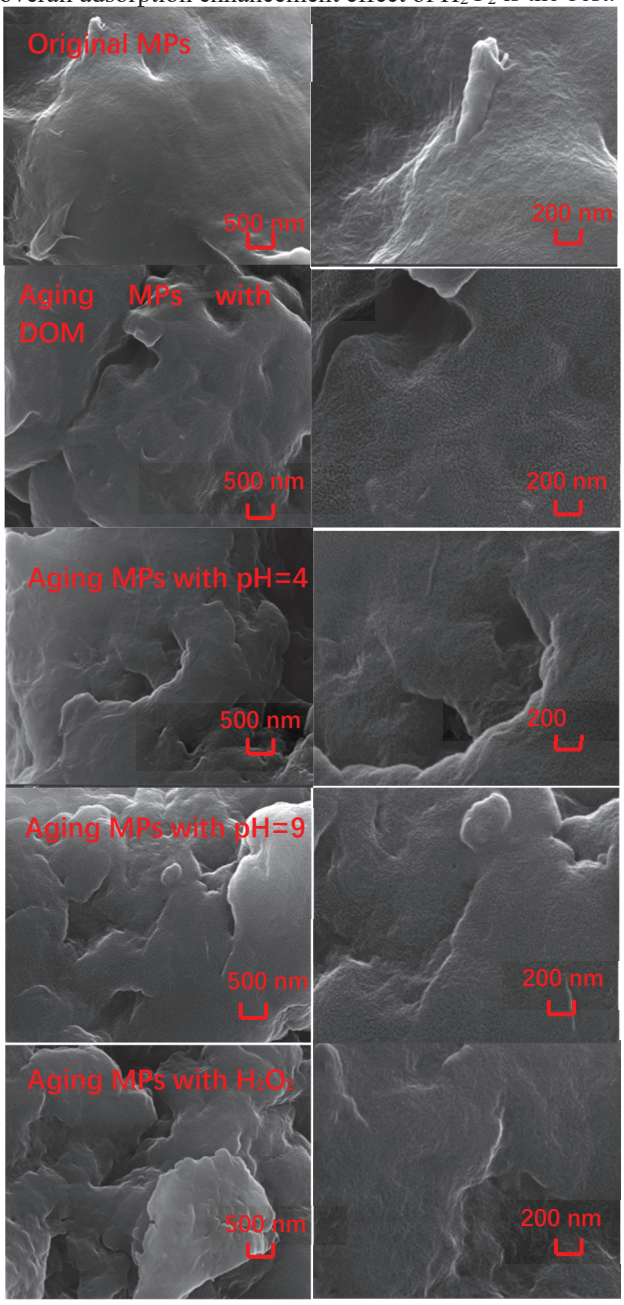

Fig 3. Scanning electron microscope graph of different types of MPs

Because the electrostatic repulsion may affect the adsorption characteristics of heavy metals by MPs, the Zeta potential values of MPs under different aging conditions were measured [25]. As shown in Table 3, the Zeta potential of different aging degrees is different, and the comparison of Zeta potential values matches the comparison of adsorption capacity. Aging strengthens the electronegativity of MPs surface, enhances the electrostatic mutual attraction between MPs and metal cations, and changes the adsorption effect of MPs.

Table 3. Zeta potentials of different types of MPs

MPs type	Zeta potential (mV)
Original MPs	-1.17 ± 0.53
Aging MPs with DOM	-1.22 ± 0.58
Aging MPs with pH=4	-3.63 ± 0.62
Aging MPs with pH=9	-4.17 ± 0.47
Aging MPs with H_2O_2	-4.66 ± 0.12

XPS is used to analyze the elemental composition and carbon bond morphology ratio of MPs under different aging degrees, with the results shown in Table 4 and Fig 4. The characteristic peaks of several aging MPs were found at 284.8, 286.07, 288.34, and 289.30 eV, which belonged to C-C, C-O, C=O, and C-OOH bonds respectively. The signal intensity of different types of MPs was different [26]. The results show that the aging of MPs will significantly reduce the C/O ratio on the surface of MPs, and other factors except DOM show a trend of matching with the adsorption results, indicating that the increase of oxygen content is an important factor to enhance the adsorption of heavy metals by MPs [27]. Compared with the original MPs, the proportion of oxygen-containing functional groups increased significantly, and the C-O functional groups had the biggest change trend, while C=O and C-OOH had a lower change range.

DOM has a special influence mechanism, and the oxygen content of the oxygen element increases the most. However, the proportion of oxygen-containing functional groups changes relatively insignificantly, and the surface COOH functional groups are increased mainly. At the same time, the adsorption capacity of MPs for heavy metals is the weakest among aging MPs. This may be due to the fact that DOM competes with heavy metals for adsorption sites on the surface of MPs, which affects the effect of the adsorption of heavy metals by MPs. Meanwhile, it can be found that DOM has the least influence on the surface structure of MPs, and the increased adsorption sites occupy fewer adsorption sites than DOM, thus causing the difference between the adsorption effect and oxygen content [14].

Table 4. Element composition and proportion of various forms of carbon bonds (%)

MPs type	O/C	C-C	C-O	C = O	C-OOH
Original MPs	5.72	98.71	0.64	0.51	0.14
Aging MPs with DOM	11.23	95.69	2.30	0.86	1.14
Aging MPs with pH=4	9.19	96.11	2.74	0.67	0.48
Aging MPs with pH=9	9.82	95.33	3.19	0.89	0.59
Aging MPs with H_2O_2	10.97	92.91	5.05	0.82	1.22

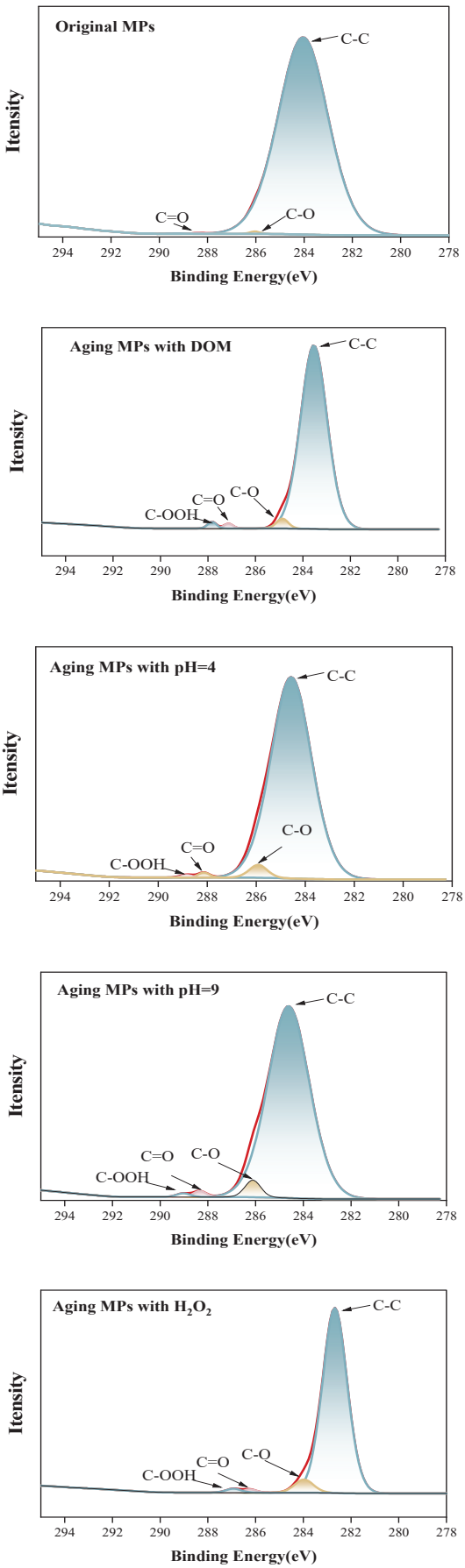

Fig 4. XPS spectra of different types of MPs

FTIR is oriented to analyze the changes of functional groups of MPs under different aging conditions, and also to verify the analysis results in XPS. The infrared analysis results are shown in Fig 5. The characteristic peaks of PE-MPs were observed at 721, 1468, 2849, and 2919 cm-1 by FTIR analysis, and the characteristic peaks of C-O, C = O, and C-OOH were observed at 1373, 1635, and 2648 cm^{-1}, which matched the carbon bond morphology observed in XPS [28]. The results of FTIR and XPS are similar, except for the DOM, where the intensity of the signal is matched with the adsorption performance. The infrared signal of DOM is much higher than that of other aging MPs. It is speculated that this phenomenon is also related to DOM adsorption at MPs.

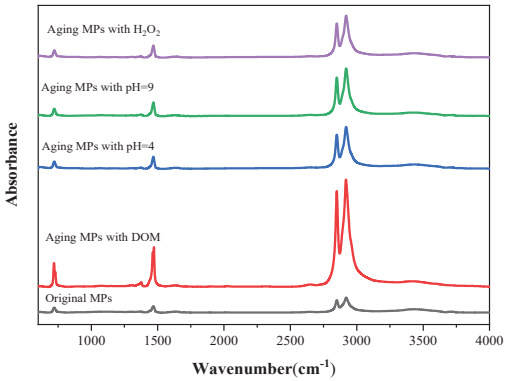

Fig. 5 FTIR spectra of different types of MPs

According to the above analysis, the effect of aging on the adsorption properties of MPs mainly changes the surface structure and oxygen-containing functional groups of MPs. The change of surface structure will affect the adsorption point of heavy metal ions on MPs and the charge distribution on MPs surface, and then the adsorption relationship between MPs and metal cations will change; the increase of oxygen-containing functional groups on the surface can provide coordination groups for the complexation of metal ions and enhance the hydrophilicity of MPs [29,30].

4 Conclusion

In this chapter, the adsorption properties of PE-MPs were studied under the influence of different aging factors (pH=4, 9, DOM, H_2O_2) for a long time, and the mechanism of adsorption changes of MPs was analyzed by characterization. The main conclusions are drawn as follows:

(1) The adsorption capacity of Cu (II) and Zn (II) on MPs was enhanced by four aging factors. The adsorption kinetics model accorded with the pseudo-second-order kinetics model, the adsorption isotherm model accorded with the Langmuir isotherm model, and the adsorption effect was enhanced most by H_2O2. The adsorption capacity of MPs for Cu (II) was stronger than that of Zn (II).

(2) Four kinds of aging factors changed the surface characteristics of MPs, made the surface of MPs rougher, produced more pore size, and destroyed the integrity of MPs' surface. The changes of surface structure and Zeta potential are similar to the adsorption properties of MPs.

(3) Aging increased the proportion of oxygen elements, affected the oxygen-containing functional groups on the surface of MPs, and finally enhanced the adsorption effect. DOM has the greatest influence on the changes of elements on MPs surface, but at the same time, it occupies adsorption sites on MPs surface, which inhibits the adsorption effect of heavy metals.

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