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Adsorption properties and mechanism of Cu(Ⅱ) on virgin and aged microplastics in the aquatic environment

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Abstract

Microplastics (MPs) bind to heavy metals in the aquatic environment and move into groups as carriers. They are prone to aging due to UV irradiation, which affects their adsorbability and mechanisms. The physicochemical properties Polyamide (PA) and polylactic acid (PLA) MPs were characterized. The impact and mechanism of UV aging on the adsorption of typical Cu(II) contaminants by MPs were investigated. The findings demonstrated that UV aging increased the specific surface area (S_{BET}) and amount of oxygen-functional groups, decreased crystallinity, and generated pits on superficies of the MPs. Before and after aging, the adsorption behavior of the MPs on Cu(II) complied with the pseudo-second-order and Langmuir isotherm models. The primary adsorption processes, which were predominantly single-layer chemical reactions, were liquid-film and intra-particle diffusion. Compared to virgin MPs, the aged MPs had a higher adsorbability, which was primarily explained by the electrostatic attraction and complexation of the oxygen-functional groups with Cu(II). Cu( ) adsorption by MPs was significantly affected by pH and salinity. At pH 5, the maximum adsorbability was noted, and increasing salinity reduced the MPs' ability to bind Cu(II). The equilibrium Cu( ) adsorbability and MPs dosage were negatively correlated. These findings provide a scientific foundation for ecological environment risk assessment when MPs coexist with heavy metals.

1. Introduction

Plastic is an important basic material developed by humans. Owing to its high-quality characteristics, such as its portability, affordability, great plasticity, and endurance, it is extensively employed in daily life, agriculture, industry, and the military (Tan et al. 2020), bringing great convenience to production and people's lives. According to statistics, global plastic manufacturing will reach 367 million tons in 2020 (Chen et al. 2023), and by 2050, global plastic output is anticipate to total 34 billion tons (Petersen & Hubbart 2021). Despite the huge output, only 6–14% of plastics are recycled (Alimi et al. 2018). Most plastics enter the environment without proper treatment and gradually break and disintegrate into plastic fragments with smaller particles under environmental stress, such as weathering, mechanical crushing, UV irradiation, chemical reactions, and microbial degradation (De Gisi et al. 2022, Lionetto et al. 2023). When plastic fragments or particles are smaller than 5 mm in diameter, they are generlly called MPs (Thompson et al. 2004). When the plastic debris or particle size is less than 5 mm, it is called MPs.

MPs are a new global environmental pollutant, widely distributed in oceans, rivers, lakes, sediments, soils, and other environmental media (Fiore et al. 2022, Hu et al. 2021, Li et al. 2018, Li et al. 2021, Shen et al. 2018), and are even found in polar areas (Bergmann et al. 2019, Ding et al. 2023). MPs have also entered the food chain (Wang et al. 2021a). Humans ingest MPs through their diet, respiration, or skin contact, and they could harm human health (Carbery et al. 2018, Rubio et al. 2020), which also presents an immense risk to ecological environmental security and biodiversity (Rahman et al. 2021). Compared with large plastics, MPs have a small particle size, high S_{BET}, high hydrophobicity, and are difficult to degrade (Leng et al. 2023, Liu et al. 2018), and they readily serve as carriers to adsorb and enrich various organic compounds, heavy metals, and microorganisms from external phases (Ahechti et al. 2022, Loncarski et al. 2021, Torres et al. 2021, Upadhyay et al. 2022). These pollutants also enter the food chain with MPs, and are transmitted and enriched between food chains, posing a serious risk to human wellness (Luo et al. 2023, Zhuang & Wang 2023). MPs help pollutants migrate into the environment through water transport or atmospheric flow, and can also interact with pollutants to produce combined effects, causing joint toxicity to organisms and ecosystems (Lv et al. 2022, Mejias et al. 2023). Consequently, the high concentrations of MPs in the environment and their environmental risks have attracted worldwide attention in recent years. MPs inevitably experience UV irradiation, thermal radiation, physical wear, chemical oxidation, and biological action in nature (Lang et al. 2020, Liu et al. 2020, Wang et al. 2021c), leading to different degrees of aging and resulting in changes in the surface morphology, functional group composition, crystallinity, and hydrophobicity of MPs (Liu et al. 2021b, Wright et

al. 2013). The adsorbability and mechanism of MPs will also change, and their toxicity to organisms may also change accordingly. Cracks and gullies appear on MPs after aging (Liu et al. 2019), increasing both the pore structure and S_{BET} (Fan et al. 2021b), and oxygen-functional groups (Brennecke et al. 2016, Kalcikova et al. 2020). Thus, there are more oxidation-binding sites on MPs and their adsorbability is improved (Wang et al. 2023), both of which indirectly raise ecological and environmental concerns. The aging of MPs affects their ability to absorb contaminants (Lin et al. 2021), which, in turn, affects the mechanism by which MPs adsorb pollutants.

Due to the rapid socioeconomic development and ongoing growth of metal electroplating, fertilizer manufacturing, mining, papermaking, and other industries, heavy metal ion-containing wastewater is being released into the environment in increasing amounts. (Dong et al. 2019, Wu et al. 2020, Xie et al. 2022), and heavy metal pollution in water frequently occurs; Cu(II) is a common heavy metal pollutant in water (Cherono et al. 2021, Wang et al. 2021b). Heavy metals are persistent contaminants that can bioaccumulate, persist in the environment, and are toxic (Sheng et al. 2022, Velusamy et al. 2021). At lower concentrations, heavy metals as Cu, Cd, Cr, As, and Pb can also have harmful consequences. Heavy metals are extremely difficult to biodegrade; thus, they can be enriched in the human body after diffusion, transfer, and dispersion under the amplification of organisms in the food chain, resulting in significant toxic effects (O 'Connor et al. 2020). Among the toxic pollutants adsorbed on MPs, heavy metals are representative of toxic inorganic pollutants (Foshtomi et al. 2019, Marsic-Lucic et al. 2018), and their physical and chemical characteristics, such as their structure, S_{BET}, and age, affect their adsorption ability (Luo et al. 2022). Recently, the reciprocity between heavy metals and MPs has attracted extensive attention from the academic community. The potential hazards to the aquatic environment could be worsened by heavy metal ion adsorption on MPs (Khalid et al. 2021) and produce a compound toxic effect on organisms. The foundation for disclosing the environmental behavior and dangers of MPs and coexisting heavy metal ions in a combined contaminated aquatic environment is delineating the interaction strength and mechanism between MPs and coexisting heavy metal ions.

Owing to its good mechanical properties, heat resistance, and chemical stability, polyamide (PA) is widely used in the fields of automobiles, electronics, machinery, rail transit, sports equipment, and so on (Crespo et al. 2019, Reinaldo et al. 2020). Polylactic acid (PLA) is a transparent and environmentally friendly biomaterial with high strength, high modulus, and good formability with great application value in various fields (Geng et al. 2020, Sun et al. 2022). PA and PLA MPs have been detected in many aquatic environments (Jang et al. 2020, Naji et al. 2021, Obbard et al. 2014, Yan et al. 2019). At present, investigation on MPs in the environment has mainly focused on original MPs, whereas the carrier effect of aged MPs remains to be studied. Therefore, two types of polymer particles with different functional groups, PA and PLA, were used as the target MPs in this study. Cu(II) was selected as the coexisting MPs pollutant with the highest detection rate in the aquatic environments. Scanning electron microscopy (SEM), Brunauer-EmmettTeller (BET), Fourier transform infrared spectroscopy (FT-IR), and X-ray diffraction (XRD) measurements were used to describe the structure of MPs both before and after simulated UV aging. The isotherms and kinetics of the adsorption characteristics of Cu(II) in an aquatic environment by the two types of MPs were compared. From the viewpoint of the physicochemical properties of MPs, the affecting factors of pH, salinity, and MPs dosage on Cu(II) adsorption were investigated and the relevant mechanisms were elucidated. To provide basic data with scientific value for a deeper understanding of the environmental performance of the interactions between MPs and traditional heavy metal contaminants in nature, it is helpful to expand our understanding of the ecological and environmental effects of MPs.

2. Materials and methods

2.1. Materials and reagents

PA and PLA MPs with grain diameter of approximately 50–100 μm were purchased from Guangdong Zhongcheng Plasticizing Co., Ltd. To remove metal ions and organic impurities from the MPs, the purchased MPs were first soaked in ultrapure water for 36 h, then soaked in 12% hydrochloric acid for 36 h, cleaned three times each with dehydrated ethanol and ultrapure water, and finally filtered MPs; after drying in a vacuum drying oven at 50°C for 36 h, the MPs stored in a sample bag for further testing. The Cu(II) solution required for the experiment was prepared from $CuSO_4 \cdot 5H_2O$ purchased from Shanghai Macklin Biochemical Technology Co., Ltd., with a purity of 99.99%. Sinopharm Chemical Reagents Co., Ltd. provided the NaOH and HCl. The test vessels were immersed in 10% nitric acid for over 24 h before being flushed with ultrapure water. The chemicals used in the experiment were all analytically pure, and ultrapure water was used to configure the solution.

2.2. Preparation of aged PA and PLA

To simulate the photoaging process of MPs in nature, the MPs were aged using UV irradiation. UV light with a wavelength of 340 nm was used to irradiate a certain number of PA and PLA MPs placed in a quartz tube, and the aging time was 240 h. To ensure uniformity of irradiation, the MPs were flipped every 12 h. After aging, the MPs were dried at 50°C after being rinsed with ultrapure water. Finally, the aged PA and aged PLA were obtained and sealed for storage.

2.3. Characterization of MPs

The S_{BET} and pore size of the MPs were determined using an automatic S_{BET} and porosity analyzer (BET; Micromeritics ASAP 2460, USA). High-resolution SEM (ZEISS Gemini 300, Germany) was used to examine the morphology and microscopic structure of the MPs. FT-IR (Nicolet 5700, USA) was used to examine the functional group composition of the MPs. The crystallinity of the MPs was examined using XRD (Rigaku Ultima IV, Japan).

2.4. Batch adsorption experiments

2.4.1. Adsorption kinetics experiments

In a 50-mL brown glass bottle, 0.20 g of virgin PA, aged PA, virgin PLA, and aged PLA MPs were placed, along with 50 mL of Cu(II) solution with a density of 5.0 mg/L. The MP solutions were then oscillated in a uniform-temperature reciprocating oscillator at a speed of 200 r/min at 25°C and collected at 0.25, 0.5, 1, 2, 4, 8, 12, 24, and 36 h; supernatant was taken out and 5 mL of it was passed through a 0.22-μm needle filter. The density of Cu(II) in the filtrate was determined by an atomic absorption spectrometer (AA320N, Shanghai Instrument Electroanalytical Instrument Co., Ltd.). Three replicates were set for each group, and a blank control without MPs was also used.

2.4.2. Adsorption isotherm experiments

The Cu(II) stock solution was diluted to 1, 2, 5, 10, and 20 mg/L. Adsorption equilibrium was reached at ambient temperature for 36 h in a thermostatic oscillator. After adsorption, the test samples were treated in the same manner as those used to determine the kinetics.

2.4.3. Influencing factors experiments

The solution was adjusted to pH 1, 2, 3, 4, 5, 6, and 7 using 0.1 mol/L HCl and NaOH to determine its impact on the adsorption by MPs. The effects of salinity were evaluated using NaCl solution diluted to a series of salinities (0.5, 1.0, 1.5, 2.0, 2.5, 3.0, and 3.5 wt.%). To investigate the effect of MPs dosage, the MPs were added at various densities (1.0, 2.0, 4.0, 6.0, and 8.0 g/L).

2.5. Adsorption model and statistical analysis

Data processing and statistical analyses, such as the t-test and Pearson correlation analysis of paired samples, were performed using SPSS 26.0. Origin software (version 22.0) was used for drawing graphs. The result of Eq. (1) was ascertained the amount of Cu(II) adsorbed on the MPs.

$$\mathrm{q_e} = \frac{(\mathrm{C_0} - \mathrm{C_e})}{\mathrm{m}}\mathrm{V}$$

1

where $\mathrm{C_0}$ (mg/L) and $\mathrm{C_0}$ (mg/L) are the initial and adsorption equilibrium concentrations of Cu(II), respectively; m (g) is the mass of the added MPs; V (L) is the volume of the Cu(II) solution; and $\mathrm{q_e}$ (mg/g) is the adsorbability of Cu(II) at equilibrium.

To match the kinetic data, Pseudo-first-order, pseudo-second-order, and intra-particle diffusion models models were used to look into the process by which MPs adsorb Cu(II) (Betianu et al. 2020, Zhang et al. 2023). The fitting formulas are Equations(2), (3), and (4).

$$\mathrm{q_t} = \mathrm{q_e}(1 - \mathrm{e}^{-\mathrm{K_1 t}})$$

2

$$\mathrm{q_t} = \frac{\mathrm{q_e^2 k_2 t}}{1 + \mathrm{q_e k_2 t}}$$

3

$$\mathrm{q_t} = \mathrm{k_p t}^{0.5} + \mathrm{C}$$

4

where $\mathrm{q_e}$ (mg/g) is the equilibrium adsorbability; $\mathrm{q_t}$ (mg/g) is the adsorbability at a certain time; $\mathrm{k_1}$ (h^{-1}) is the rate constant of the Lagrange pseudo-first-order adsorption reaction; $\mathrm{k_2}$ ($g/(mg \bullet h)$) is the Lagrange pseudo-second-order adsorption reaction rate constant; $\mathrm{k_p}$ ($\mathrm{mg/(g \bullet h^{0.5})}$) is the interparticle diffusion rate constant; and C is a constant associated with the boundary layer's thickness.

Linear, Freundlich, and Langmuir isotherm models were used to fit the isothermal data on adsorption (Sackey et al. 2021, Zhao et al. 2013), and the expressions are shown in Equations (5), (6), and (7), respectively.

$$\mathrm{q_e} = \mathrm{q_m}\frac{\mathrm{K_L C_e}}{1 + \mathrm{K_L C_e}}$$

5

$$\mathrm{q_e} = \mathrm{K_F C_e^{1/n}}$$

6

$$\mathrm{q_e} = \mathrm{K_d C_e}$$

7

where q_m (mg/g) is the maximum monolayer adsorbability of Cu(II) on the MPs calculated using the Langmuir model; K_L (L/mg) is the adsorption constant of the Langmuir model associated with the adsorption free energy; K_F (L/mg) is the adsorption constant of the Freundlich model connected to the adsorbability of the MPs; $1/n$ is the Freundlich model constant reflecting the adsorption intensity; and K_d (L/mg) is the distribution coefficient of the linear model.

3. Results and discussion

3.1. Characterization of MPs

The apparent color of the PA and PLA MPs after aging changed significantly from white to yellow, which may have been due to the oxidation of MPs in this process, resulting in the generation of chromogenic group substances (Li et al. 2023b, Liu et al. 2022b). The morphology of the MPs before and after aging was examined using SEM (Fig. 1). The surface of the virgin MPs was dense, smooth, and less wrinkled, whereas the surface of the MPs after UV aging was rough, accompanied by cracks, pits, and other phenomena. In addition to stacked folds and gullies, an abundance of MP structures was found on the surface of aged PA, which may have provided points to adsrob Cu (II) (Guo et al. 2023). The roughness of the aged MPs did not change significantly, but some cracks appeared on the particle surface, which increased the S_{BET}, thus improving the pollutant adsorption capacity of the MPs. PA-MPs are more susceptible to UV irradiation in natural environments. UV radiation can cause the C–C main chain in the polymer to break and degrade to form low-molecular-weight polymer fragments. Generally, similar to previous studies, the morphology of MPs was dramatically altered by UV aging (Gao et al. 2021).

Table 1 illustrates the differences in the S_{BET}, pore volume, and pore diameter of the MPs before and after aging. After UV aging, the S_{BET} of PA increased from 0.4482 to 0.6716 m^2/g, and the S_{BET} of PLA increased from 0.2789 to 0.3357 m^2/g. In contrast to virgin MPs, the S_{BET} of aged PA and PLA increased by 49.84% and 20.36%, respectively. These results show that UV irradiation led to cracks and pits on PA and PLA MPs, which decreased the particle size and increased the S_{BET}, consistent with the SEM analysis conclusions. Furthermore, in comparison with virgin MPs, the pore volume and diameter increased significantly after aging. The increase in pore volume indicates that the structure of the aged MPs was more developed and could provide more internal adsorption sites, which is consistent with previous research related to UV aging (Fan et al. 2021a). The above results show that, under the action of photooxidation, the S_{BET} and pore diameter of MPs increased, which was more beneficial for the ions of heavy metals sticking on MPs' surface, leading to adsorption (Wang et al. 2022a).

Table 1 Pore structure parameters of MPs

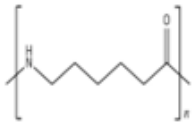
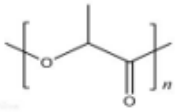
Samples	Structure	$S_{BET}(m^2/g)$	$V_p(cm^3/g)$	$d_p(nm)$
Virgin PA		0.4482	0.000965	5.5359
Aged PA		0.6716	0.001169	6.3410
Virgin PLA		0.2789	0.000468	5.4013
Aged PLA		0.3357	0.000629	5.9536

Figure 2 shows the the MPs FTIR spectra both prior to and upon aging. By analyzing and comparing the functional groups of PA MPs, it was found that the feature peaks at 3301 cm^{-1}, 2935 cm^{-1}, 1640 cm^{-1}, and 1541 cm^{-1} were the N–H stretching vibration absorption peak, the stretching vibration absorption peak of CH_2, the stretching vibration absorption peak of C = O, and the absorption peaks caused by the coupling of the amide group's C–N stretching vibration and N–H bending vibration, respectively. These are characteristic bands of PA (Du et al. 2022, Liu et al. 2023). The position of absorption peaks at these features after aging did not change significantly; however, the absorption peaks' strengths were noticeably higher, suggesting that the oxygen-containing functional groups on MPs' surfaces increased as a result of UV aging, and improved their adsorbability (Li et al. 2022). It is evident from the examination and comparison of the PLA functional groups after aging that the pinnacle of the O–H stretching vibration absorption was located at 3449 cm^{-1}, the stretching vibration absorption peak of $-CH_2$ is located at 3000 cm^{-1}, and the stretching vibration of C = O was responsible for the feature peak at 1755 cm^{-1} (Fan et al. 2023, Liang et al. 2023). The two absorption peaks of the aged PLA at 3449 and 1755 cm^{-1} exhibited noticeably increased intensities, indicating that PLA reacted with oxygen in air under UV irradiation and generated additional functional groupings containing oxygen. In general, the increases in the functional groups –OH and C = O and the decrease in the functional group CH_2 suggested that the affinity of aged MPs for contaminants increased.

Figure 3 is the XRD pattern of the crystal structure and crystallinity of MPs before and after aging. Both PA and PLA showed sharp diffraction peaks and diffraction peaks of the dispersed amorphous phase in the XRD spectra, indicating that they were partially crystalline polymers. The peak of the aged MPs did not shift significantly relative to that of the virgin MPs, implying that aging did not change the crystal size. However, the diffraction peaks of the MPs after aging were weaker than those of virgin MPs, indicating a decrease in crystallinity (Li et al. 2023a). The crystallinity analysis showed that the crystallinity of PA decreased from 69.47–61.02% and that of PLA decreased from 77.39–26.25% after aging. This indicates that UV aging promoted the expansion of the amorphous region in the MPs. This may be because the ordered structure in the crystal polymer chains of MPs is destroyed by UV light and some molecular chains can undergo oxidative damage during aging (Velzeboer et al. 2014). As evidenced by the lower crystallinity of the aged MPs, which is consistent with the experimental findings, the aged MPs had a higher adsorption capacity than virgin MPs.

3.2. Adsorption kinetics

The Cu(II) adsorption kinetic fitting curves before and after MP aging are presented in Fig. 4. The adsorption of Cu(II) on PA and PLA showed a similar trend, that is, rapid adsorption within the initial time of 1–4 h, after which the

adsorption slowly reached equilibrium. As MPs have many adsorption sites, the adsorption process proceeds rapidly in the first stage. Subsequently, the MPs' surface adsorption sites are progressively filled, the adsorption rate slows down (Leng et al. 2023), and the adsorption reaches equilibrium at 36 h. The order of equilibrium adsorption capacity for the MPs was as follows: aged PA > aged PLA > virgin PA > virgin PLA.

Pseudo-first- and -second-order models were used to fit the kinetic data. Table 2 lists the corresponding parameters for the fitting. The experiment date showed that the adsorption processes of by PA and PLA were more consistent with the pseudo-second-order model, having correlation values higher than 0.950. Cu(II) is mostly chemically adsorbed onto MPs via methods such as surface adsorption and external liquid film diffusion (Liu et al. 2022a). Based on the fitted rate constant and equilibrium adsorption capacity data, the UV aging treatment accelerated the process by which MPs adsorbed Cu(II) and enhanced the adsorbability. The adsorbability of aged PA and PLA to Cu(II) increased to 1.59 and 1.76 times those of virgin PA and virgin PLA, respectively. Moreover, the smaller the k_2 value, the slower the adsorption rate of MPs on heavy metal ions, and the quantity of available adsorption sites determines the adsorption rate (Han et al. 2021, Wang et al. 2020), which is similar to the SEM and S_{BET} analysis results for MPs. Aged MPs generally have a higher adsorption rate constant than virgin MPs, indicating that aging increases the adsorption rate. This indicates that the cracks and pits on the surface of MPs caused by the aging process increased their S_{BET}, thereby increasing the number of adsorption sites on their surfaces and improving their ability to adsorb contaminants (Fu et al. 2021).

Table 2
Kinetic model parameters of Cu(II) adsorption by virgin and aged PA and PLA

Samples	Pseudo-first-order model			Pseudo-second-order model		
	$k_1\left(h^{-1}\right)$	$q_e(mg/g)$	R^2	$k_2\left[\mathrm{g/\ mg \bullet h}\right]$	$q_e(mg/g)$	R^2
Virgin PA	1.968	0.360	0.884	4.642	0.382	0.958
Aged PA	3.110	0.574	0.972	11.945	0.606	0.997
Virgin PLA	3.336	0.315	0.953	7.724	0.326	0.983
Aged PLA	2.620	0.548	0.974	16.372	0.575	0.998

To advance further understand the adsorption progress of Cu(II) by MPs before and after aging, the adsorption kinetics were investigated using an intra-particle diffusion model. Table 3 and Fig. 5 present the fitting results. There are three stages of Cu(II) adsorption on both virgin and used PA and PLA (Ma et al. 2019, Sun et al. 2023). The fitting line did not cross the origin ($C \neq 0$) in the first stage, which was the rapid adsorption stage, suggesting that there are more steps to influence the adsorption process besides intra-particle diffusion. This stage was the result of the interaction between intra-particle diffusion and surface adsorption. Intra-particle diffusion was the second stage. Cu(II) gradually permeated the interior surface of the MPs from the outer liquid sheet. The gradient of the fitting line was lower than Stage I, which was mainly due to the decrease in the intra-particle diffusion rate of MPs caused by the decrease in the Cu(II) density of the solution. The third phase was the adsorption equilibrium stage. The velocity ratio of intra-particle diffusion continued to decline and the residual Cu(II) density in the aquatic environment was extremely low at this point. The diffusion rate constants of the three stages of adsorption of Cu(II) by the virgin and aged PA and PLA MPs were as follows: $\mathrm{K_{p1}} > \mathrm{K_{p2}} > \mathrm{K_{p3}}$, showing that the order of the three stages' adsorption rates was stage I > stage II > stage III. The intercept C values of the aged MPs in the three stages of adsorption were

greater than those of the virgin MPs, which was mostly caused by the MPs' surfaces exhibiting more adsorption sites as they aged, which increased the mass transfer driving force of Cu(II) in MPs intra-particle diffusion (Fan et al. 2022).

Table 3
Intra-particle diffusion model parameters of Cu(II) adsorption by virgin and aged MPs

Samples	Stage			Stage			Stage		
	C_1	k_{p1}	R_1^2	C_2	k_{p2}	R_2^2	C_3	k_{p3}	R_3^2
Virgin PA	0.211	0.066	0.812	0.245	0.042	0.979	0.343	0.013	0.930
Aged PA	0.152	0.275	0.938	0.478	0.032	0.980	0.557	0.007	0.994
Virgin PLA	0.205	0.061	0.950	0.251	0.026	0.985	0.338	0.002	0.987
Aged PLA	0.219	0.216	0.902	0.482	0.023	0.839	0.523	0.011	0.812

3.3. Adsorption isotherms

The adsorption datum were fitted by Langmuir, Freundlich, and linear isothermal models to comprehend the adsorption properties of MPs before and after aging. Figure 6 and Table 4 exhibit the fitting findings. Evidently, when the initial density of Cu(II) increased, the equilibrium adsorbability gradually increased. Comparing the three isothermal adsorption models, the R^2 values of the Langmuir and Freundlich models in the experimental analysis were higher, but the Langmuir isothermal adsorption model ($0.964 < R^2 < 0.996$) was better suited to explaining the isothermal adsorbent process of Cu(II) on PA and PLA than the Freundlich and Linear models. This indicated that the adsorption occurred on superficies of the MPs. The adsorption of Cu(II) by MPs before and after aging is mainly chemical, and the adsorption process is monolayer adsorption (Loncarski et al. 2021). In contrast to virgin and aged MPs had a higher maximum adsorbability (q_m) for Cu(II), and the q_m value of the aged PA increased from 0.964 to 1.415 mg/g. Similarly, the q_m value of the PLA increased from 0.951 to 1.398 mg/g after aging, which is consistent with the kinetic process. This suggests that increasing the number of adsorption sites on superficies of the MPs following aging can improve the adsorbability of PA and PLA for Cu(II).

Table 4
Adsorption isotherm parameters of Cu(II) adsorption by virgin and aged MPs

Samples	Langmuir model			Freundlich model			Linear model	
	$q_m(mg/g)$	$k_L(L/mg)$	R^2	n	$K_F(\mathrm{L/mg})$	R^2	$K_d(L/mg)$	R^2
Virgin PA	0.964	0.177	0.978	1.914	0.180	0.963	0.042	0.893
Aged PA	1.415	0.260	0.983	2.056	0.322	0.930	0.070	0.815
Virgin PLA	0.951	0.129	0.996	1.693	0.141	0.990	0.042	0.963
Aged PLA	1.398	0.194	0.964	1.821	0.267	0.904	0.073	0.805

Furthermore, PA had a higher adsorption intensity and adsorbability for Cu(II) than PLA, both before and after aging. This is primarily because the two types of MPs exhibited different physical and chemical characteristics. Compared with the PLA MPs, the surfaces of the PA MPs contained more oxygen-functional groups, which could produce more hydrogen bonds with the surrounding water, thus enhancing the intensity of Cu(II) adsorption in water. Meanwhile, the S_{BET} of the PA MPs was larger than PLA MPs, which caused superficies of the PA MPs to exhibit more adsorption sites, leading to increases in the adsorption rate and adsorbability. In general, UV aging treatment has the potential to enhance the danger of MPs in aquatic environments while drastically altering their physical and chemical features.

3.4. Influencing factors

3.4.1 Effect of pH

The pH has a significant impact on the surface charge state of MPs, the solution's concentration of heavy metal ions, and the MPs' ability to adsorb heavy metals. The adsorption of Cu(II) with various pH values was investigated. According to Fig. 7(a), the initial pH had a consistent impact on adsorption by the MPs, both before and after aging, which first increased and subsequently decreased as the pH value increased. At pH 5, the adsorbability achieved a maximum of 0.63 mg/g. This is because, when the pH of a solution is low, the zeta potential is positive, electrostatic repulsion is large, and the density of H^+ in the acidic environment is comparatively high. In solution, H^+ competes with Cu(II) for adsorption, and H^+ occupies the adsorption sites of MPs, resulting in a low Cu(II) adsorption effect (Allouss et al. 2020). When the pH value exceeds 5, the increase in OH^- in the solution causes the Cu(II) to react with the OH^- in water and precipitate, which affects the adsorption of Cu(II) by MPs. In addition, compared with virgin MPs, Cu(II) has a much larger potential to bind to aged PA and PLA because aged MPs have more oxygen-functional groups and their S_{BET} is higher.

3.4.2. Effects of salinity

The adsorption behavior of Cu(II) on MPs before and after aging was investigated by simulating the saline environments of rivers, estuaries, and seas using a gradient NaCl solution. According to Fig. 7 (b), the adsorbability of Cu(II) on MPs decreased gradually when the salinity increased from 0 to 3.5%, and the effect of salinity on MPs after aging was lower than that on virgin MPs. In addition, Na^+ near MPs may compete with free Cu(II) for adsorption sites on their surfaces, thereby inhibiting the adsorption of Cu(II) (Wang et al. 2022b). The above discussion shows that PA and PLA MPs are more likely to enrich heavy metal pollutants in freshwater environments than in seawater.

3.4.3. Effect of dosage

Figure 7 (c) illustrates how the MPs dosage affected Cu(II) adsorption. both before and after aging. The adsorbability of the MPs at equilibrium steadily enhanced as the MPs dosage increased from 1 to 8 g/L. Virgin PA's adsorption capacity descended from 0.68 to 0.23 mg/g, and that of virgin PLA decreased from 0.62 to 0.22 mg/g. This is because, when the original concentration and volume of the adsorbate were constant, as the dosage of the adsorbent increased, less Cu(II) was absorbed per unit mass of the adsorbent. However, Cu(II) adsorption by the MPs increased rapidly as the dosage increased. The adsorption percentages of virgin PA and PLA increased from 13.55–37.41% and 12.31–35.01%, respectively. This is mainly because, as the dosage of MPs enhanced, the adsorption sites increased, which was helpful for the adsorption of Cu(II). The adsorbability of MPs on Cu(II) tended to be steady at dosages greater than 4 g/L, and the adsorption rate increased slowly. This may be mainly due to the formation of large particle clusters due to the interaction between MP particles, hindering the normal diffusion of Cu(II) to the MPs' surfaces (He et al. 2020) and causing the adsorbent particles in the solution to be overcrowded, resulting in the overlapping of adsorption binding sites and the unsaturated utilization of active binding sites during the adsorbent process

(Chaturvedi et al. 2020), causing the adsorbability of the unit to gradually decline. In addition, the aged MPs had a larger Cu (II) adsorbability and adsorption rate than the virgin MPs, which agrees with what other research has found.

3.5. Adsorption mechanisms

In general, three different ways to describe the procedure of heavy metal adsorption on MPs: (1) heavy metal surface diffusion on films near MPs, (2) heavy metal diffusion via MPs' pores, and (3) heavy metal adsorption on MPs active sites (Guo & Wang 2019, Suzaki et al. 2017). The adsorption for heavy metals on MPs in the aquatic environment can be divided into physical mechanism and chemical mechanism. (Liu et al. 2021a). The physical mechanism involves MPs using their own pore structure and S_{BET} to adsorb heavy metal ions on the surface or in the pores through van der Waals forces, including electrostatic interactions, and internal and external diffusion (Holmes et al. 2014). The chemical mechanism refers to the direct adsorption and fixation of heavy metal ions by MPs using functional groups rich on their own surface, including ion exchange, functional group complexation, precipitation, and cation-π interactions (Huang et al. 2020, Zhou et al. 2020). Owing to the distinct physical and chemical properties, the adsorption of heavy metals by MPs could be either physical or chemical. The pH value in the aquatic environment has an impact on the negative charge of MPs. The adsorbability of Cu(II) by the MPs first increased and then decreased as the pH increased from 1 to 7 (Fig. 7). This demonstrates that the adsorption is affected by the shift in the negative charge on their surfaces, demonstrating the involvement of electrostatic attraction in this process. While the adsorption in this study exhibited more congruence with the Langmuir model, the R^2 value of the fitting parameters of the Freundlich model was also relatively high ($0.904 < R^2 < 0.990$). The n value in the model is greater than 1 (1.693–2.056, Table 4), indicating nonlinear adsorption; therefore, adsorption may be controlled by electrostatic attraction. In addition, this study showed that physical adsorption occurred when the n value in the Freundlich model was > 1. UV aging inevitably changed the ability of MPs to bind Cu(II) owing to changes in the microscopic morphology, S_{BET}, oxygen-functional groups, and other physicochemical properties of MPs.

Based on results of the experiments and related characterization of MPs after UV aging, this study shows that the aging action may promote the absorption of heavy metals on MPs, and its promotion effect is mainly reflected in the following aspects: (1) After aging, MPs develop large cracks and have a rough surface, increasing the S_{BET} and porosity of MPs (Ammala et al. 2011), providing more adsorption sites, and enhancing the physical adsorption of Cu(II) by MPs. (2) Compared with virgin MPs, aging increased the number of oxygen-functional groups on MPs. The increased oxygen-functional groups could combine with Cu(II) to form a complex, thereby enhancing the complexation between MPs and Cu(II) (Arp et al. 2021); the abundant oxygen-functional groups and negative charges had a strong electrostatic attraction to Cu(II), thereby enhancing the electrostatic adsorption of MPs on Cu(II) (Purwiyanto et al. 2020).

4. Conclusions

In the present research, batch test and experimental characterization were used to examine the Cu(II) adsorption behavior and mechanism of PA and PLA MPs before and after UV aging. After UV aging, the smooth outer surfaces of the PA and PLA became rough with cracks and gullies. The quantity of of oxygen-functional groups, as carbonyl and hydroxyl groups, enhanced and the surface charge of the aged MPs increased considerably. These factors promoted the Cu(II) enrichment ability of aged MPs in a water environment, and the main mechanisms of action were electrostatic attraction and oxygen-functional groups complexation with Cu(II). The adsorption by MPs before and after aging is a fast–slow process, which can be explained by the pseudo-second-order and Langmuir models, suggesting that it mainly involves monolayer chemical adsorption, and adsorption occurs through liquid-film diffusion and intra-particle diffusion. The adsorption was significantly affected by pH and salinity. The adsorption amount of

Cu(II) was the highest at pH 5, and it considerably decreased as salinity increased. The dosage of MPs showed a negative correlation with the equilibrium adsorption of Cu(II) and a positive correlation with the adsorption rate. The results of this study prove that aged MPs can be used as carriers to enrich Cu(II) in aquatic environments, affect their migration and transformation pathways, and increase biological toxicity and ecological risks.

Declarations

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Figures

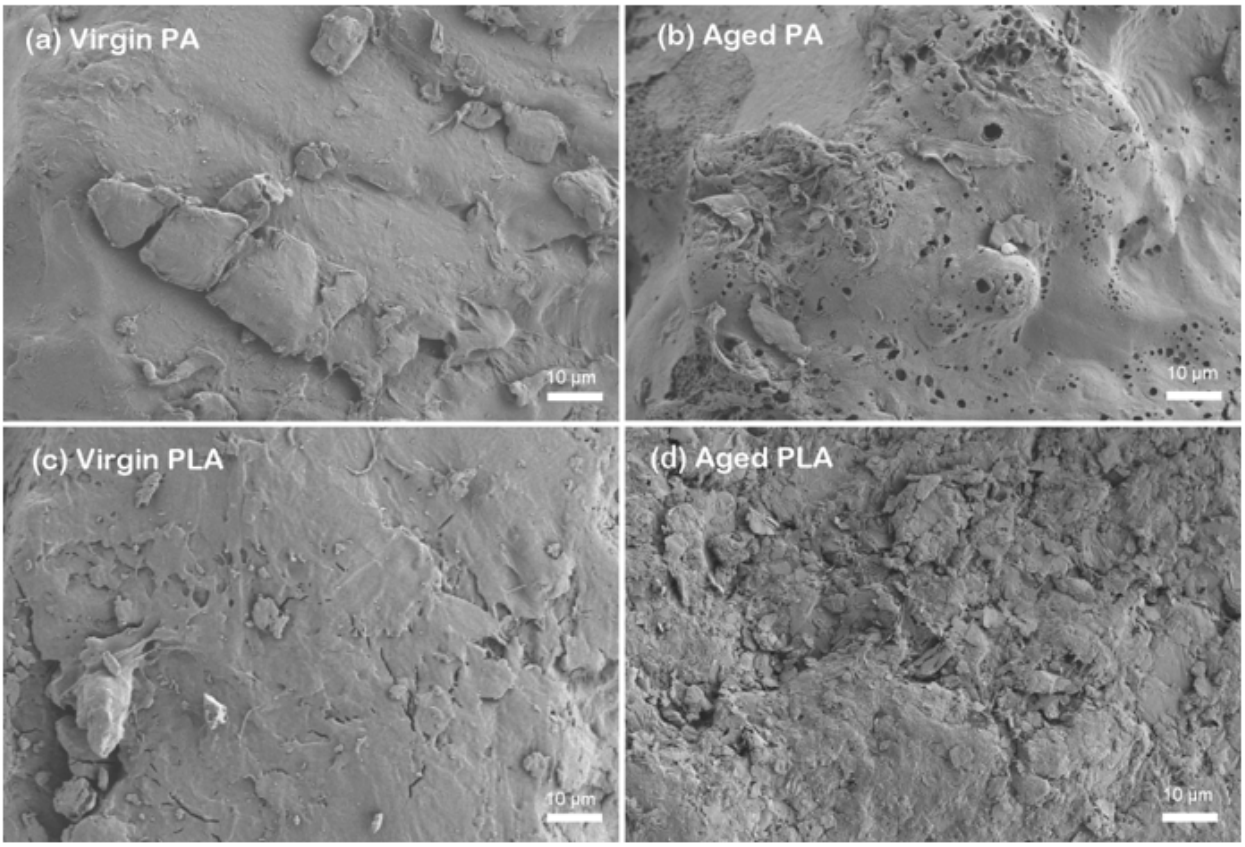


Figure 1

SEM photographs of virgin and aged MPs: (a) virin PA, (b) aged PA, (c) virgin PLA, and (d) aged PLA

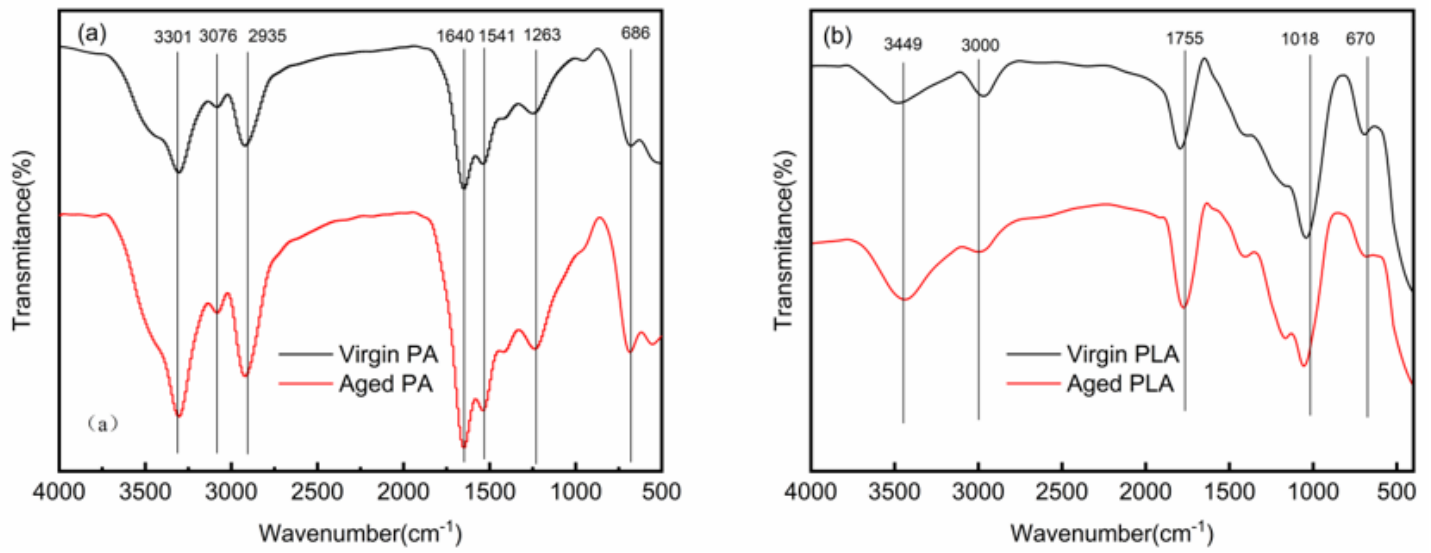


Figure 2

FTIR spectra of virgin and aged MPs: (a) PA MPs, and (b) PLA MPs

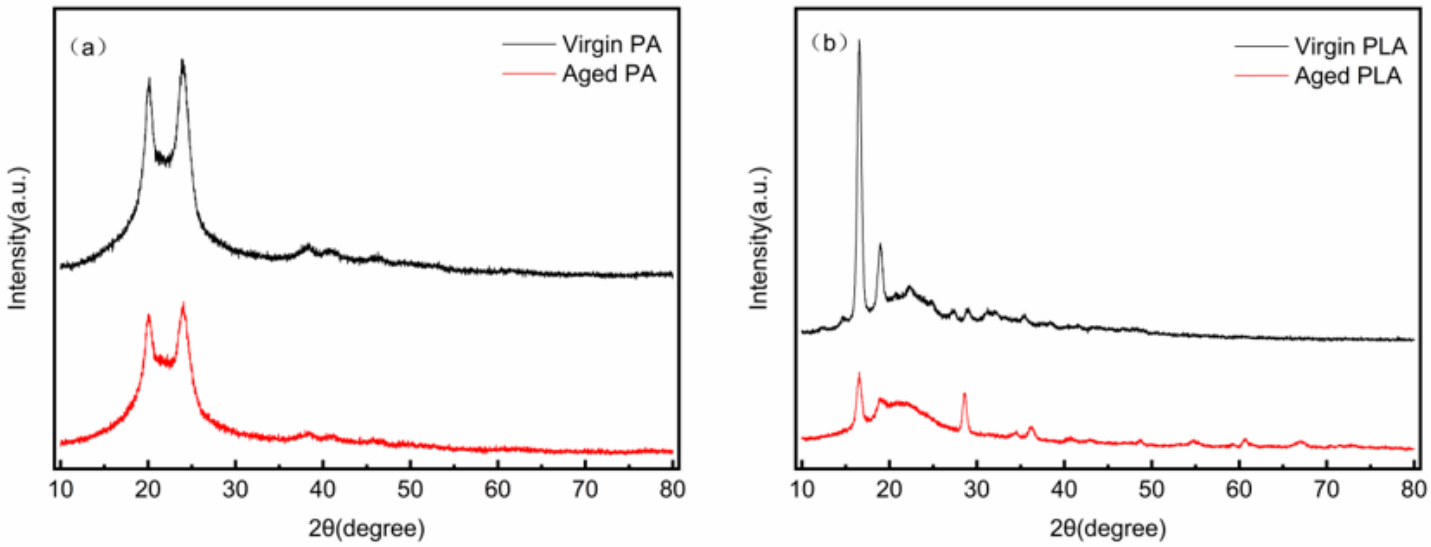


Figure 3

XRD patterns of virgin and aged MPs: (a) PA MPs, and (b) PLA MPs

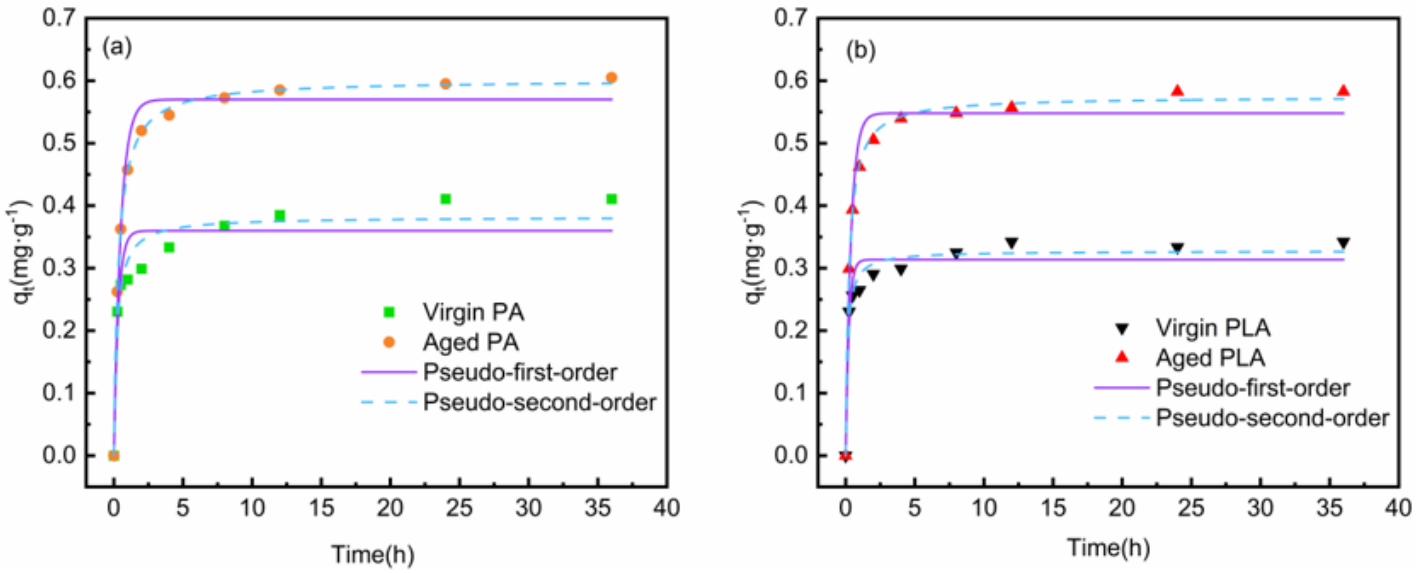


Figure 4

The adsorption kinetics of virgin and aged MPs: (a) PA MPs, and (b) PLA MPs

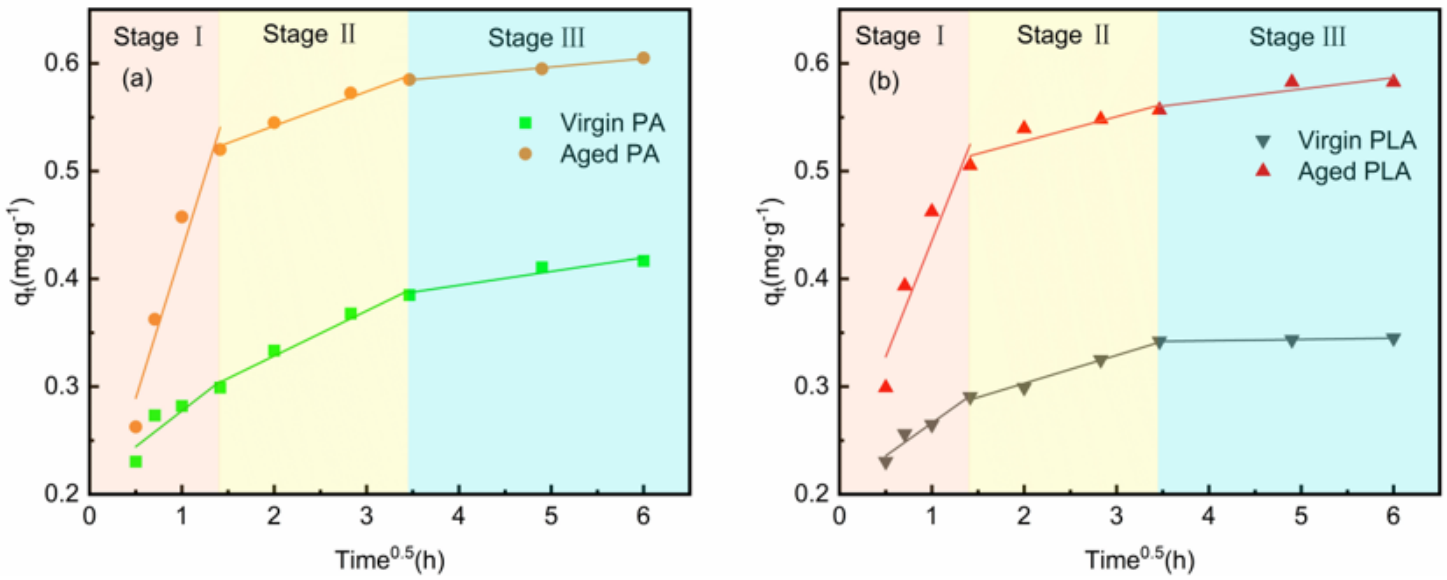


Figure 5

Intra-particle diffusion model of Cu(II) adsorption by virgin and aged MPs: (a) PA MPs, and (b) PLA MPs

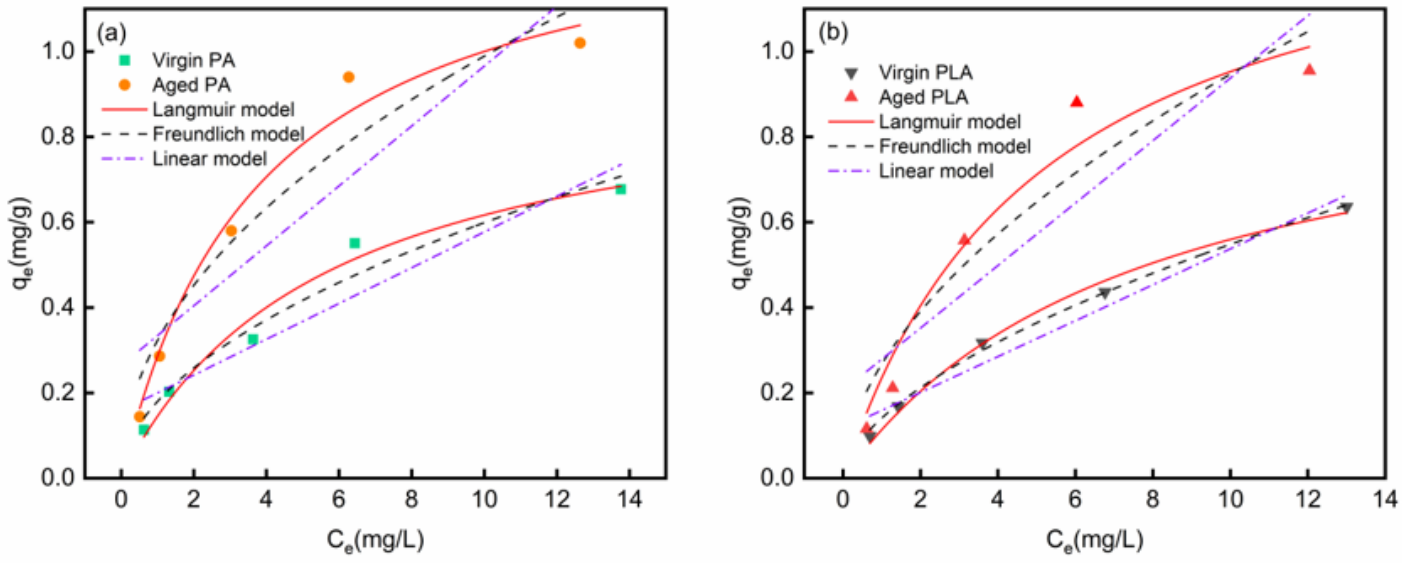


Figure 6

The adsorption isotherm of virgin and aged MPs: (a) PA MPs, and (b) PLA MPs

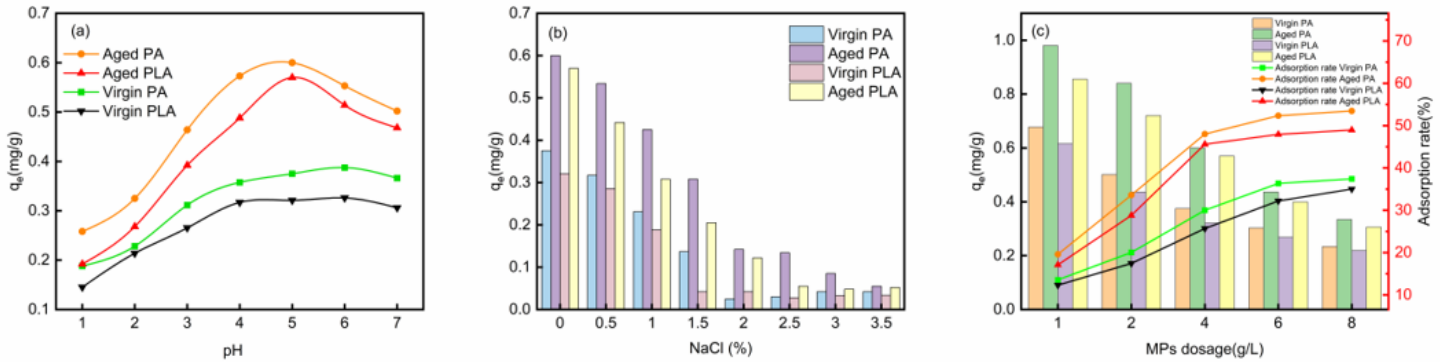


Figure 7

Influencing factors of Cu(II) adsorption by virgin and aged MPs: (a) pH, (b) salinity, and (c) MPs dosage