Study on the Adsorption Behavior and Mechanism of Heavy Metals in Aquatic Environment before and after the Aging of Typical Microplastics

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Abstract: As a new type of pollutant, microplastics can be used as carriers of heavy metals in the water environment, which can have an impact on the migration and transformation of heavy metals and toxic effects. Microplastics can age in the environment and adsorb heavy metals, causing significant impacts on the environment. Therefore, understanding the interactions between aging microplastics and coexisting heavy metal ions is essential to assess the environmental impact of microplastics. This experiment mainly studies the adsorption kinetics, adsorption isotherms, and environmental factors of heavy metal Cu (II) between microplastics PA and PLA. Conduct research on microplastics before and after aging to further explore the adsorption mechanism of heavy metals by microplastics before and after aging.

Key Words: Microplastics; Heavy metal ions; Aged adsorption

1 Introduction

In 2004, Professor Thompson from the UK first proposed the concept of microplastics (MPs) in an article published in Science[1]. In terms of definition, it is generally classified as a solid plastic particle with a thickness of less than 5mm, which is a synthetic polymer that is neither soluble in water nor biodegradable[2]. Because microplastics have a relatively stable chemical structure and are not easily biodegradable, they can be transported over long distances with wind and water flow, and a large amount of microplastics can be detected in aquatic environments. In seawater, these microplastics can not only be ingested by organisms, but also have a serious impact on pollutants in the food chain. They can also become a new ecological niche, laying a solid foundation for the survival and development of microorganisms[3].

Microplastics are small in size, low in density, easy to float on the water, brightly colored, and abundant in the environment, so they are likely to be ingested by low nutrient level animals and subsequently transferred from low to high nutrient levels in the food chain [4]. In the early stages of ingestion, particles are mainly concentrated in the digestive system. It has been found that the gills, intestines, digestive tract, and stomach of Indian Ocean tail fish all contain particles [5].

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Microplastics have the ability to absorb heavy metals in the environment, has a large specific surface area, there have been reports on the growth inhibition and reduced reproductive ability caused by the release of some substances in them, such as brominated flame retardants and plasticizers [6]. And high specific surface area and porosity can enable microplastics to have strong adsorption effects on heavy metals, POPs, antibiotics, etc. [7]. Therefore, the harm it causes to the environment is even greater than the harm it causes itself.

On May 24, 2022, the General Office of the State Council of the People's Republic of China issued a notice on the issuance of a new pollution control action plan, proposing that microplastics have become one of the four new pollutants. The article pointed out that strengthening the collaborative management of new pollutants with multiple environmental media, conducting key technology research on environmental risk assessment and control of toxic and harmful chemicals, and strengthening the theoretical and mechanism research on the ecological and environmental hazards of new pollutants such as microplastics, Increase technological support.

Microplastics enter the living environment of aquatic organisms through liquid transmission, and the pollutants they contain are important components that cause water pollution. Microplastics mainly exist in the water environment and are easily ingested by aquatic organisms, thereby affecting their health. Microplastics can adsorb heavy metals in the environment, serving as adsorption carriers for heavy metals, resulting in more serious environmental pollution. In view of this, this article intends to analyze the adsorption properties of different types of microplastics in water based on existing relevant literature.

2 Study on the adsorption behavior of PA and PLA on Cu (II) before and after aging

2.1 Experimental materials and instruments

Experimental materials used are shown in Table 1.

Table 1 Experimental Materials

The Name Of The Material	Specification	Manufacturers
Polyamide (PA)	200 Mesh	Ruixiang Plasticizing Co., Ltd
Polylactic Acid (PLA)	200 Mesh	Ruixiang Plasticizing Co., Ltd
Nitric Acid (HNO_3)	Analytical Pure	Sinopharm Chemical Reagent Co., Ltd
Sulphuric Acid(H_2SO_4)	Analytical Pure	Sinopharm Chemical Reagent Co., Ltd
Copper Sulphate Pentahydrate ($Cuso_4 \cdot 5H_2O$)	Analytical Pure	Sinopharm Chemical Reagent Co., Ltd

The main instrument names/models and manufacturers during the experimental process are shown in Table 2.

Table 2 Experimental instruments

Instrument Name	Model	Manufacturer
Electronic Balances	AL204	METTLER TOLEDO Technology (China) Co., Ltd
Benchtop Thermostatic Oscillator	THZ—C	Taicang Huamei Biochemical Instrument Factory
Organic Nylon 6 Vacuum Filter Head	0.22MM	Tianjin Jinteng Experimental Equipment Co., Ltd
Circulating Water Vacuum Pump	SHZ—D (III)	Gongyi Zihua Instrument Co., Ltd
Benchtop Ultrapure Water System	Milli-Q®IQ7000	Merck Millipore Group, Germany
Atomic Absorption Spectrophotometer	AA320N	Shanghai INESA Analytical Instrument Co., Ltd

2.2 Experimental content

2.2.1 Adsorption isotherm

Take the dilution ratio of Cu (II) standard stock solution, set the experimental concentration gradient at 1mg/L, 2mg/L, 5mg/L, 10mg/L, 20mg/L, and the solution volume is 50ml. Take 0.20g of microplastic original PA, aged PLA, original PLA, and aged PLA each, and shake them in a 50ml dark brown bottle at 25 ℃ and 200r/min using a constant temperature oscillator. After shaking for 24 hours, take samples, as above. Set up three parallel samples for the adsorption experiment.

2.2.2 Adsorption kinetics

Dilute the standard reserve solution of Cu (II) with a concentration of 5mg/L and a solution volume of 50ml. Take 0.20g each of the original PA, aged PLA, original PLA, and aged PLA microplastics and shake them in a 50ml shaded brown bottle at 25 ℃ and 200r/min using a constant temperature oscillator. The sampling time is set at 0.25h, 0.5h, 1h, 2h, 4h, 8h, 12h, 24h, 36h, and 0.22 for sampling μ M organic nylon 6 vacuum filter head was used to filter microplastics to obtain Cu ion solution, and three sets of parallel samples were set up for adsorption experiments.

2.2.3 Setting of ion strength

Dilute the standard reserve solution of Cu (II) with a concentration of 5mg/L and a solution volume of 50ml. Take 0.20g of raw PA, aged PLA, raw PLA, and aged PLA from microplastics, and weigh 0.016, 0.08, 0.16, 0.32, 0.48, and 0.8g of sodium chloride respectively. Prepare a series of sodium chloride solutions with constant volume, each containing a specific concentration of 0, 1, 5, 10, 20, 30, and 50 parts per thousand (‰). Shake it in a 50ml shaded brown bottle at 25 ℃ and 200r/min using a constant temperature oscillator, After shaking for 24 hours, samples were taken as above, and three sets of parallel samples were set up for the adsorption experiment.

2.2.4 Desorb

After the adsorption experiment is completed. The saturated microplastics, including original PA, aged PLA, original PLA, and aged PLA, are placed in an oven for drying. 50ml of pure water is then added, and a constant temperature oscillator is used to oscillate at 25 ℃ and 200r/min. The sampling time is set to 0.1h, 0.25h, 0.5h, 1h, 2h, 4h, and 8h. The microplastics are filtered with a vacuum filter head to obtain a Cu (II) desorption solution, and the desorption amount of heavy metal Cu is calculated[8]. For the desorption experiment, three sets of parallel samples were established.

2.3 Results and discussion

2.3.1 The adsorption kinetics characteristics of PA and PLA on Cu (II) before and after aging

The adsorption and adsorption experiments of Cu (II) on the surfaces of original microplastics PA, PLA, and aged PA, PLA were conducted using a Cu (II) solution with a concentration of 5mg/L. The adsorption of Cu (II) on both the original microplastics and aged microplastics was examined at various concentrations.The data in Figure 1 were obtained. It can be found that within 8 hours before the experiment, There is a strong adsorption between microplastics and Cu (II), which is due to the abundant adsorption sites provided by microplastics for heavy metals, promoting the adsorption of Cu (II) on the surface of microplastics. As the adsorption progresses, the adsorption effect between microplastics and Cu significantly decreases after 8 hours.This is because the adsorption sites on the surface of microplastics decrease[9], resulting in a decrease in the solubility of Cu (II) in the solution. After 24 hours, the adsorption rate reaches a plateau, indicating that the adsorption sites on the microplastics are saturated. At this point, the interaction force between the microplastics and Cu (II) decreases, leading to a decrease in the overall adsorption capacity between the two. The adsorption equilibrium is reached within 24-36 hours.

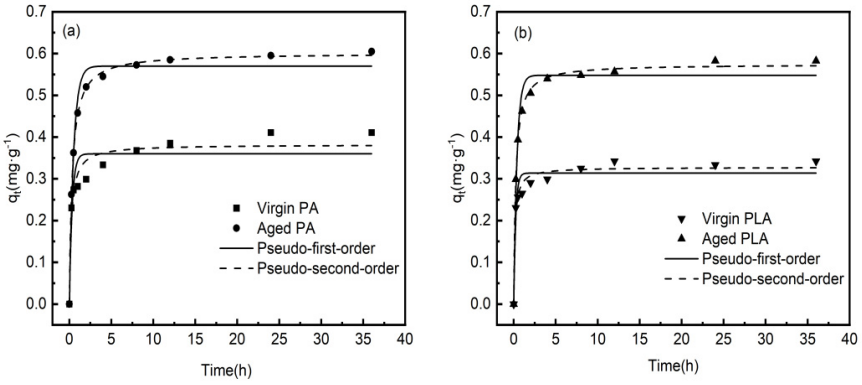

Figure 1 Cu (II) adsorption kinetic fitting curves: (a) Cu and PA; (b) Cu and PLA

By comparing the correlation coefficient R2, it can be seen that its specific parameters are shown in Table 3.From these results, it can be inferred that the quasi second-order adsorption

kinetic model provides a better fit to the data.When Cu (II) concentration is 5mg/L, the adsorption capacity of original PA and PLA is 0.3820mg/g and 0.326mg/g, respectively. The adsorption capacity of aged PA and PLA is 0.650mg/g and 0.575mg/g, respectively. After aging, the adsorption capacity of microplastics has increased.

Table 3 Adsorption kinetic fitting parameters of Cu(II) on original PA\PLA and Aged PA\PLA

Subjects And Microplastics	Heavy Metal Concentration (mg/L)	Quasi-Primary Adsorption Kinetic Model $q_t=q_e(1-e^{-K_1 t})$			Quasi-Secondary Adsorption Kinetic Model $\frac{t}{q_t}=\frac{1}{K_2 q_e^2}+\frac{1}{q_e}t$		
		K_1 (h^{-1})	q_e (mg/g)	R^2	K_2 ($g\cdot mg^{-1}\cdot h^{-1}$)	q_e (mg/g)	R^2
PA	5	1.967	0.359	0.884	4.641	0.3820	0.943
Aged PA	5	3.109	0.573	0.971	11.945	0.605	0.997
PLA	5	3.336	0.314	0.954	7.723	0.326	0.982
Aged PLA	5	2.620	0.548	0.974	16.372	0.575	0.998

2.3.2 Isothermal adsorption characteristics of PA and PLA on Cu (II) before and after aging

In the adsorption experiment, Cu (II) solutions with concentration gradients of 1mg/L, 2mg/L, 5mg/L, and 10mg/L and 20mg/L to determine the changes in equilibrium adsorption capacity of Cu (II) on the surface of microplastics under four different conditions: original PA, aged PA, original PLA, and aged PLA. The adsorption scatter plot was fitted using the Langumir isotherm adsorption model, Freundlich isotherm adsorption model, and Linear isotherm adsorption model, as shown in Figure 2.

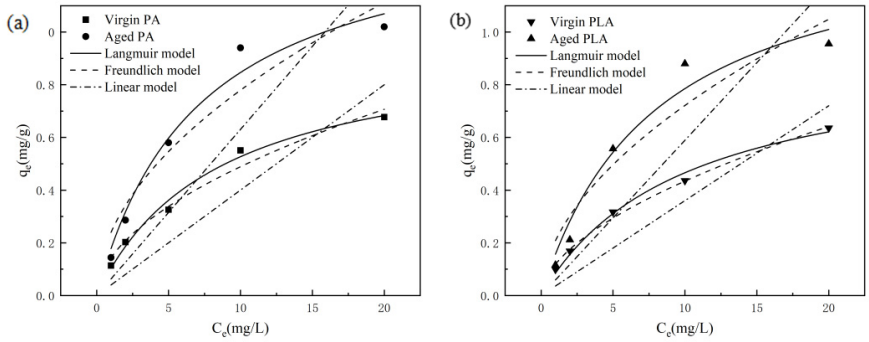

Figure 2 (a) PA adsorption isotherms; (b) PLA adsorption isotherms

From Table 4, it can be seen that the qm of PA and PLA after UV aging is 1.433mg/g and 1.414mg/g, which is about 1.47 and 1.42 times that of the original PA and PLA, indicating that aging can enhance the adsorption capacity of microplastics. This may be due to the surface morphology of PA and PLA after aging (cracks and grooves)[10] thereby improving the binding ability of microplastics to Cu.

Table 4 Cu (II)adsorbs isotherm fitting parameters on PA and PLA

Subjects And Microplastics	Sampling Time (h)	Langmuir Adsorption Model $q_e = q_m \frac{K_L C_e}{1 + K_L C_e}$			Freundlich Adsorption Model $q_e = K_F C_e^{1/n}$			Linear Adsorption Model $q_e = K_d C_e$	
		KL (L/mg)	qm (mg/g)	R2	KF (L/mg)	n	R2	Kd	R2
PA	24	0.1185	0.971	0.989	0.143	1.87	0.974	0.040	0.667
Aged PA	24	0.1366	1.433	0.991	0.232	1.93	0.944	0.061	0.603
PLA	24	0.0904	0.993	0.989	0.115	1.72	0.975	0.036	0.788
Aged PLA	24	0.1249	1.414	0.967	0.208	1.85	0.9054	0.058	0.625

2.3.3 The Impact of Ion Strength on the Adsorption of Cu (II) by PA and PLA

The adsorption behavior of microplastics PA and PLA on Cu (II) is shown in Figure 3(a). Two types of microplastics exhibit different adsorption abilities for heavy metals at different ionic strengths. When the ion strength is 5 ‰, the microplastic PLA reaches its minimum value, and when the ion strength is 10 ‰, the microplastic PA reaches its minimum value. Afterwards, as the ion strength increases, the adsorption capacity of microplastics remains stable at a minimum value. The ion strength reduces the adsorption effect of microplastics, which may be due to the abundance of Na^+in the solution. Na^+will become a competitor to Cu (II), competing with the adsorption sites of microplastics, thereby reducing the adsorption of heavy metal copper by microplastics[11]. When the ion strength is less than 10 ‰, the adsorption capacity of PA is greater than that of PLA. When the ion strength is 5 ‰, this difference reaches its maximum value. When the ion strength is greater than 10 ‰, the adsorption capacity of the two types of microplastics PA and PLA is similar to that of PA ≈ PLA. As the ion strength increases, a large number of anions such as Cl - will form anionic complexes with metal copper ions, thereby reducing the adsorption capacity of microplastics for heavy metals. When the ion concentration increases, the double layer between the microplastics is compressed, resulting in a reduction in the repulsive force between the microplastics, thus triggering the aggregation effect of the microplastics. At the same time, it reduces the specific surface area of microplastics, thereby reducing their adsorption performance.

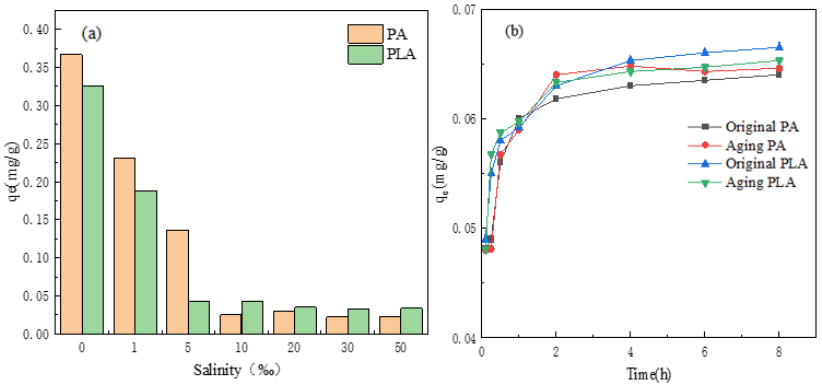

Figure 3 (a)Effect of salinity (NaCl) on the adsorption of Cu(II) by PA and PLA;(b) Desorption amount of Cu(II) on PA and PLA

2.3.4 Desorption characteristics of PA and PLA on Cu (II) before and after aging

The desorption amount of Cu (II) on PA and PLA is shown in Figure 3(b). The desorption ability of four types of microplastics is primitive PLA>aged PLA>aged PA>primitive PA. The desorption rate is relatively fast from 0 to 0.5 hours, and remains slow at 0.5 to 2 hours. However, the adsorption and desorption rates reach consistency at 4 hours, achieving dynamic equilibrium. The desorption rates of original PA, aged PA, original PLA, and aged PLA were 54.1%, 47.2%, 73.5%, and 52%, respectively.

3 Conclusions and Prospest

3.1 Conclusions

(1) Through relevant research, it has been found that the surface morphology changes of aged microplastics PA and PLA provide more adsorption sites for heavy metals. After UV aging, the qm of PA is 1.433mg/g, which is 1.57 times that of the original PA, and the qm of PLA is 1.414mg/g, which is 1.42 times that of the original PLA. This suggests that the increased age of microplastics amplifies their ability to adsorb pollutants and heavy metals, leading to heightened environmental pollution. Consequently, this has substantial implications for environmental safety and health, posing a certain level of risk to human well-being.

(2) The adsorption capacity of Cu (II) on PA and PLA surfaces is different. The adsorption capacity of microplastics to the same heavy metal ions is aging PA>PA>aging PLA>PLA. Environmental factors such as pH, ion strength, and aging can also significantly affect the ability of microplastics to adsorb heavy metals, resulting in a very complex adsorption effect of microplastics on heavy metals. When the ion strength of microplastics for Cu (II) adsorption is 10% lower, the adsorption capacity of PA is greater than that of PLA. When the ion strength is 5%, the difference reaches its maximum value. When the ion strength is greater than 10%, the adsorption capacity of the two types of microplastics PA and PLA is similar to that of PA $\approx$ PLA.

(3) Desorption capacity: Original PLA>Aging PLA>Aging PA>Original PA. The adsorption of Cu (II) by the original PA in an aqueous environment is relatively stable and difficult to desorb. The presence of PA has a significant fixation effect on the free state of Cu (II) in the environment. When saturated microplastics enter a new environment, copper is not easily desorbed and re-enters the environment, greatly reducing the risk of secondary pollution. Significantly inhibited the migration of Cu (II) in the environment.

3.2 Prospect

Although research on microplastics is receiving increasing attention both domestically and internationally, people's understanding of their mechanisms of action is very limited. Although there are more and more characterization methods for microplastics, and people's understanding of their structure and properties is becoming more profound, Because of the impact of diverse environmental factors in the natural surroundings, the numerous physical properties and characteristics of microplastics undergo continuous alterations. making it difficult for people to comprehensively regulate them. Based on the above results, this project aims to establish a

more accurate pollution model for microplastic particles under actual environmental conditions by analyzing the effects of different environmental factors (such as weathering, temperature, microorganisms, etc.) on the structure and performance of microplastic particles. In terms of degradation pathways, there is relatively little research on environmentally friendly and efficient plastic degradation methods, and further exploration is needed in future research.

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