

Research Article

Coexistence and Adsorption Properties of Heavy Metals by Polypropylene Microplastics

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Plastic particles with a diameter of 5 mm or less are called microplastics. Microplastics are one of the primary sources of pollution in the environment. It has been proven that microplastics are also carriers of heavy metals, but there are few studies on their adsorption mechanism. In this study, the adsorption of Pb, Cu, Cd, and Zn by polypropylene (PP) microplastics was analyzed and discussed. The morphology of PP was observed by scanning electron microscopy (SEM), the surface elemental composition of PP was determined by X-ray photoelectron spectroscopy (XPS), and the functional groups of PP were analyzed by Fourier transform infrared spectroscopy (FTIR). The results showed that the adsorption behavior of microplastics to different heavy metals could be balanced in 32 hours. Kinetics experiments showed that the adsorption process could be fitted well by a two-stage dynamic model, and the adsorption of Pb and Cu by PP is greater than that of Cd and Zn. The Freundlich model has the best fitting effect on Pb for the adsorption isothermal results. The Langmuir model showed that the process is favorable for adsorption. The adsorption of mixed heavy metals by microplastics showed that when the concentration of the mixed adsorption mass was low, the presence of a coexistence system promoted the adsorption of Zn and Cu by microplastics. With an increasing concentration, the adsorption of 4 heavy metals by microplastics is inhibited.

1. Introduction

At present, plastic has unconsciously entered all aspects of life, from industry to agriculture and from technology to human life [1–4]. Because of its low cost, lightweight, durability, and extensibility, plastics are widely used all worldwide [5, 6]. The global consumption of plastics is estimated to reach 348 million tons in 2018 [7]. Although plastic products bring us much convenience, they can also enter into the environment and cause harm [3, 8, 9]. Plastic waste in the environment is decomposed into tiny plastics under physical and chemical actions. When the diameter of these plastics is no more than 5 mm, they can be defined as microplastics [10–12]. For example, in mining areas, there are many microplastics and heavy metals in subsidence areas due to

human activities or other factors [13], which have a great adverse impact on human, animal, and plant life. As a highly trophic organism, humans are one of the victims affected by pollution accumulating in the food chain, and we have begun to pay attention to microplastic pollution [13–15]. Therefore, it is imperative to study microplastics. Due to some properties of microplastics, such as physicochemical properties, surface properties, small particle size, large specific surface area, and hydrophobicity, they may adsorb other harmful pollutants in the surrounding environment, such as heavy metals [16, 17]. And studies have shown, in addition to the direct impact of microplastics on organisms, they are also potential carriers of heavy metals due to their stubbornness and high specific surface area [3, 18, 19]. The first report on the amount of metals in microplastics appeared in early

2010 at The Turner Laboratory [20], where the authors investigated the association between metals and plastic production particles in the Marine environment. Then, groundbreaking results by Holmes et al. [3] on metal adsorption on microplastics showed that the formation of biofilms on microplastics affects the adsorption of heavy metals. Since then, researchers have made the adsorption of heavy metals by microplastics more clear. Heavy metals generally refer to metals with a density greater than 4.5 grams per cubic centimeter. Heavy metals are persistent and toxic pollutants that are not easy to transfer and linger for a long time, causing serious harm to plants, animals, and even humans [4]. Heavy metals can be divided into two categories according to their toxic characteristics. One group is toxic at high concentrations but essential for plants and animals at low concentrations, including elements such as Cu, Zn, and Fe. The other group is toxic to organisms even at low concentrations, endangering the health of animals and plants, including elements such as Cd, Pb, and Hg [21].

Until recently, despite the awareness that heavy metals [22–25] and microplastics [26–30] would cause ecological risks, their combined effects on heavy metals are still poorly known, especially when many heavy metals coexist. Previous studies have used microplastics to adsorb various heavy metals, respectively. For example, Mao et al. [31] studied the adsorption mechanism of polystyrene (PS) for heavy metals and the effect of aging on the adsorption of heavy metals. Purwiyanto et al. [32] investigated the adsorption of Pb and Cu in microplastics in the Musi River and the environment effect. Taking polyethylene terephthalate (PET) fragments as typical micro plastics, Wang et al. [33] used ultraviolet radiation to simulate the photoaging of microplastics in the environment in the laboratory and studied the adsorption of Cu^{2+} and Zn^{2+} . And the results show that the adsorption capacity of aged microplastics for heavy metals is higher than that of original microplastics. However, there are few studies on the adsorption of microplastics in the environment of coexistence of heavy metals. And because heavy metals coexist in the actual environment, it is very necessary to simulate this coexistence environment to study microplastics and heavy metals. We selected several representative heavy metals (Pb, Zn, Cu, and Cd) to study their adsorption characteristics to microplastics to clarify the adsorption mechanism [15–17]. The adsorption kinetics and isothermal adsorption models were used to study the adsorption of heavy metals on microplastics. There are many kinds of microplastics on the market. We chose polypropylene (PP) as the research object because PP is one of the most widely used plastics and has good adsorption capacity [34, 35]. Thus, we combined a model of heavy metal coexistence and adsorption to systematically simulate the real environment (coexistence of multiple heavy metals). The adsorption effect of different concentrations of metal and whether there is mutual promotion or inhibition between heavy metals were studied. This work can provide a theoretical basis for the normal environmental behavior of microplastics and their interactions with heavy metals.

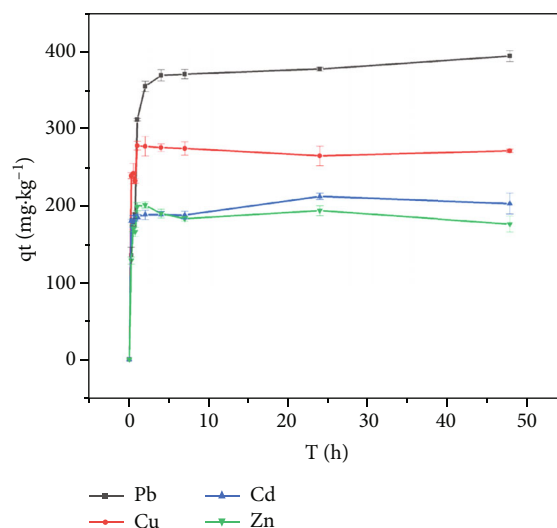


FIGURE 1: Adsorption curve of polypropylene microplastics ($C_e = 0.7 \text{ mg}\cdot\text{L}^{-1}$, $V = 20 \text{ mL}$, temperature at 298 K).

2. Materials and Methods

2.1. Materials and Characterization. Polypropylene (PP) was purchased from Sinopec Shanghai Chemical Co., Ltd. Lead (Pb), zinc (Zn), copper (Cu), and cadmium (Cd) standard solutions were purchased from National Nonferrous Metals and Electronic Materials Analysis and Testing Center. A crusher (800A) was purchased from Yongkang Azera Electric Appliance Co., Ltd. An atomic absorption spectrophotometer with specification A3 was purchased from Beijing General Instrument Co., Ltd. All analytically pure chemicals (anhydrous ethanol, hydrochloric acid, and potassium nitrate) for the adsorption experiments were purchased from Sinopharm Chemical Reagent Co., Ltd.

2.2. Sample Preparation. The purchased polypropylene plastic particles were crushed by the pulverizer, and then, the crushed plastic particles were passed through a 20-mesh sieve and kept in a beaker. Polypropylene is a hydrophobic substance, and ultrapure water and magnetic rotor were added to the beaker and stirred for 24 hours to wash it. Then, the samples were soaked in 10% hydrochloric acid (HCl) for 48 hours. Finally, ultrapure water and ethanol were used for cleaning it, and any heavy metals were removed using an ultrasonic cleaner. After cleaning, the plastic was placed into an electric constant temperature drying oven at 50°C for 72 hours. After drying, the microplastics were sealed in a polyethylene bag [16].

2.3. Adsorption Experiments and Data Analysis

2.3.1. Adsorption Kinetics. The experiment was conducted and analyzed with a flame atomic absorption spectrophotometer. Two groups of basic solutions without heavy metals and two groups of PP were used as controls. Then, the adsorption capacity of PP for heavy metals was calculated by the concentration dependence between the two experiments [36, 37].

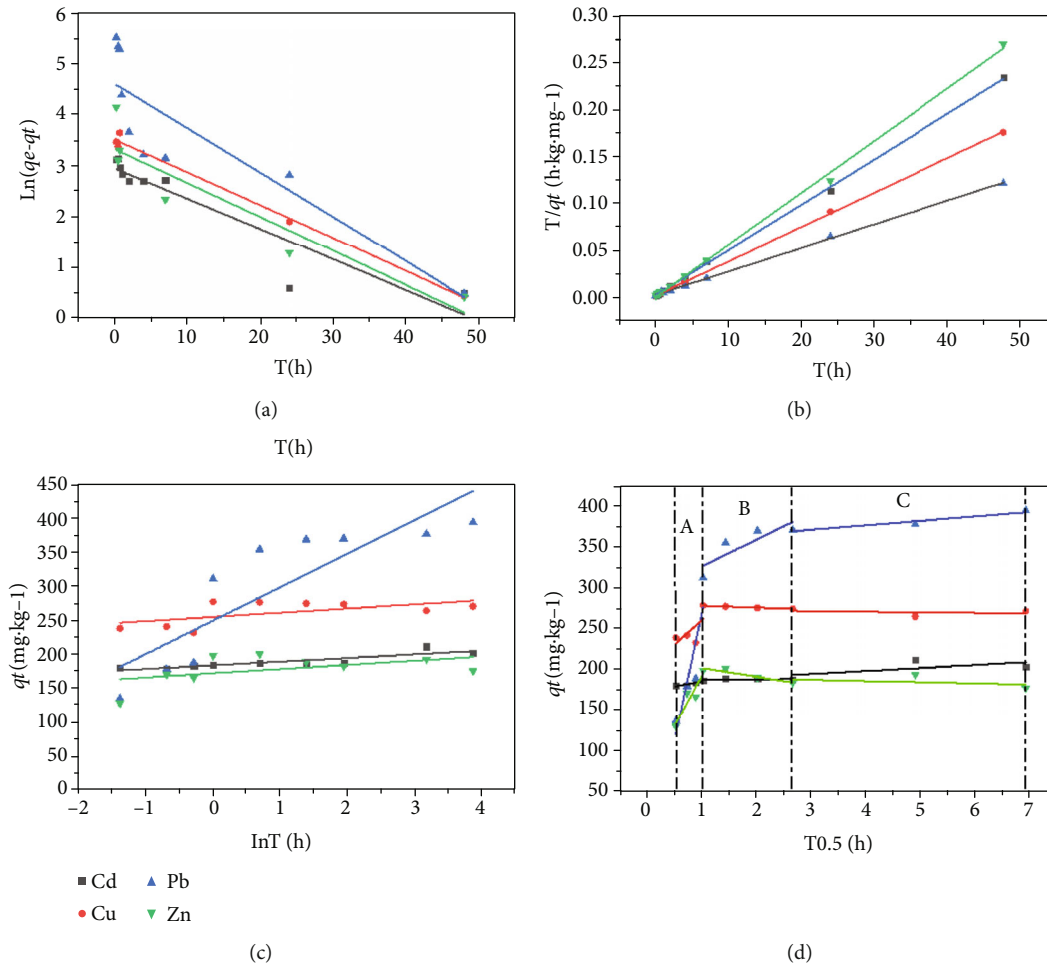


FIGURE 2: (a) First-order kinetics model, (b) second-order dynamic model, (c) Elovich model, and (d) intraparticle diffusion model ($C_e = 0.7$ mg·L⁻¹, $V = 20$ mL, temperature at 298 K).

The adsorption kinetics of the four kinds of heavy metals in microplastics can be described by the first-order and second-order kinetics models. The formula of each model is as follows: (1) the first-order kinetics adsorption model, (2) the second-order kinetics adsorption model, (3) the Elovich model, and (4) the intraparticle diffusion model:

$$\begin{aligned} \lg(q_e - q_t) &= \lg q_e - k_1 t, \\ \frac{t}{q_t} &= \frac{1}{K_2 q_e^2} + \frac{t}{q_e}, \\ q_t &= \frac{1}{\beta} \ln(\alpha \cdot \beta) + \frac{t}{\beta} \ln t, \\ q_t &= k_{\text{dif}} t^{1/2} + C, \end{aligned} \quad (1)$$

where q_e (mg·g⁻¹) represents the adsorption amount at adsorption equilibrium, q_t (mg·g⁻¹) represents the adsorption capacity at time t (min), K_1 (mg·min·g⁻¹) represents the adsorption reaction rate constant of the first-order kinetics adsorption model, K_2 (mg·min·g⁻¹) is the adsorption reaction rate constant of the second-order kinetics adsorption model, α (mmol·g⁻¹·min⁻¹) represents the initial adsorp-

tion rate constant of the reaction in Elovich model, β (g·mmol⁻¹) is the parameter related to the surface coverage degree of the adsorbent and the chemical adsorption activation energy, and K_{dif} (mg·g⁻¹·min^{-1/2}) is the intraparticle diffusion rate constant.

2.3.2. Adsorption Isotherm. A standard solution of heavy metals (Pb, Zn, Cu, and Cd) was used for this experiment. The determination method was the same as for the adsorption kinetics.

The equation of Henry's model used in this study is as follows:

$$q_e = K_H C_e, \quad (2)$$

where q_e (mg·g⁻¹) represents the adsorption capacity of a unit adsorbate, K_H (L·g⁻¹) represents Henry's coefficients, and C_e (mg·L⁻¹) represents the mass concentration of adsorbate in the liquid phase.

The adsorption process of Pb, Cu, and other heavy metals on the microplastics was simulated by a one-dimensional model (Freundlich and Langmuir models) [23, 38]. The

TABLE 1: Fitting parameters of adsorption kinetics of heavy metals by microplastics.

Adsorbate	First-order kinetic			Second order dynamic			Intraparticle diffusion		
	K_1	q_e	R^2	K_2	q_e	R^2	A	R^2 B	C
Pb	0.0885	395.62	0.7790	0.0063	396.83	0.9995	0.7896	0.7235	0.9277
Cd	0.0606	203.32	0.8650	0.0419	205.34	0.9994	0.7641	0.3798	0.1109
Cu	0.0656	271.99	0.9934	0.0824	271.00	0.9998	0.3889	0.9819	1.0000
Zn	0.0677	193.72	0.8638	0.0320	178.89	0.9983	0.8645	0.8742	0.1341

Freundlich model uses the assumption of a heterogeneous surface, and the equation is [23, 39–41]

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e, \quad (3)$$

where q_e ($\text{mg}\cdot\text{L}^{-1}$) represents the equilibrium adsorption capacity of adsorbate in the solid phase, C_e ($\text{mg}\cdot\text{g}^{-1}$) represents the equilibrium concentration of the adsorbate in the liquid phase, K_F ($\text{mg}\cdot\text{g}^{-1}$) is the partition coefficient of the Freundlich model and represents the adsorption capacity, and n is dimensionless and represents the nonlinear degree of the adsorption isotherm model.

The Langmuir model assumes that adsorption takes place in a single layer and is uniform, and adsorption arises only once on each side [39]. The equation is

$$\frac{1}{q_e} = \frac{1}{bq_m} \cdot \frac{1}{C_e} + \frac{1}{q_m}, \quad (4)$$

where q_m ($\text{mg}\cdot\text{g}^{-1}$) represents the saturated adsorption capacity on the adsorbent and b ($\text{L}\cdot\text{mg}^{-1}$) represents the adsorption constant of the Langmuir model.

The linear equation of the Temkin model is [42]

$$q_e = \frac{RT}{b_T} \ln C_e + \frac{RT}{b_T} \ln A_T, \quad (5)$$

where $B = RT/b_T$, b_T ($\text{J}\cdot\text{mol}^{-1}$) is the Temkin constant related to the heat of adsorption, A_T ($\text{L}\cdot\text{mg}^{-1}$) is the Temkin isotherm equilibrium binding constant, R is the gas constant, and T is the absolute temperature at 303 K.

2.3.3. Coexistence of Adsorption. Microplastics can adsorb heavy metals, and organic pollutants due to their large specific surface area and hydrophobicity. Microplastics have different adsorption capacities when adsorbing different heavy metals. In the coexistence adsorption experiment, a standard solution of heavy metals (Pb, Zn, Cu, and Cd) was used for detection, and the determination method was performed with a flame atomic absorption spectrophotometer.

2.4. Material Characterization. Scanning electron microscopy (SEM) (Flexsem1000, Hitachi, Japan) was used to examine the morphology of PP. A small sample was fixed on a metal platform, and the sample surface was sprayed with platinum. The magnification of SEM was selected as 100 times, and the acceleration voltage was 15 kV. The func-

TABLE 2: Fitting parameters of Elovich model.

Adsorbate	α	β	R^2
Cd	3.4828×10^{15}	0.1845	0.7919
Cu	5.3942×10^{18}	0.1613	0.3535
Pb	7.9035×10^3	0.0202	0.7466
Zn	8.2402×10^{12}	0.1615	0.2413

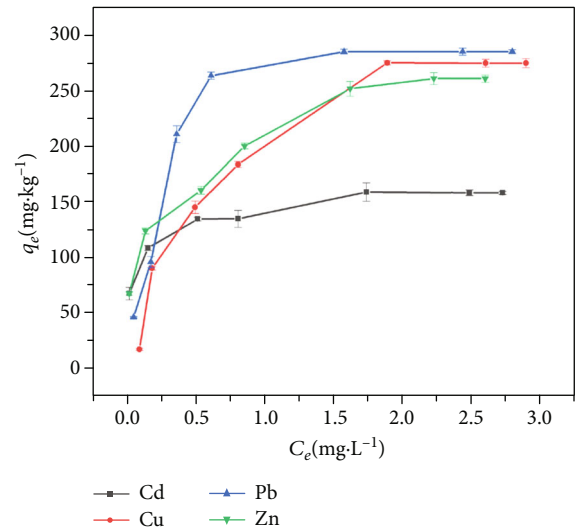


FIGURE 3: Adsorption isotherm on the original polypropylene ($V = 20$ mL, temperature at 298 K, $t = 48$ h).

tional groups of PP were analyzed by Fourier transform infrared transmission (FTIR) spectroscopy (Nicolet IS50, Thermo Fisher Scientific, USA). After the interference light formed by the transmission and reflection of the light source penetrates the sample, the optical signal is processed by Fourier transform, and the infrared absorption spectrum of transmittance is obtained. The surface element composition of PP was determined by X-ray photoelectron spectroscopy (XPS) (Escalab 250XI, Thermo Fisher Scientific, USA) [43].

3. Results and Discussion

3.1. Adsorption Kinetics Analysis. To evaluate the effect of timing on the adsorption of heavy metals on PP, four kinds of heavy metals were selected to test the adsorption capacity of PP for heavy metals over different periods [31]. It can be

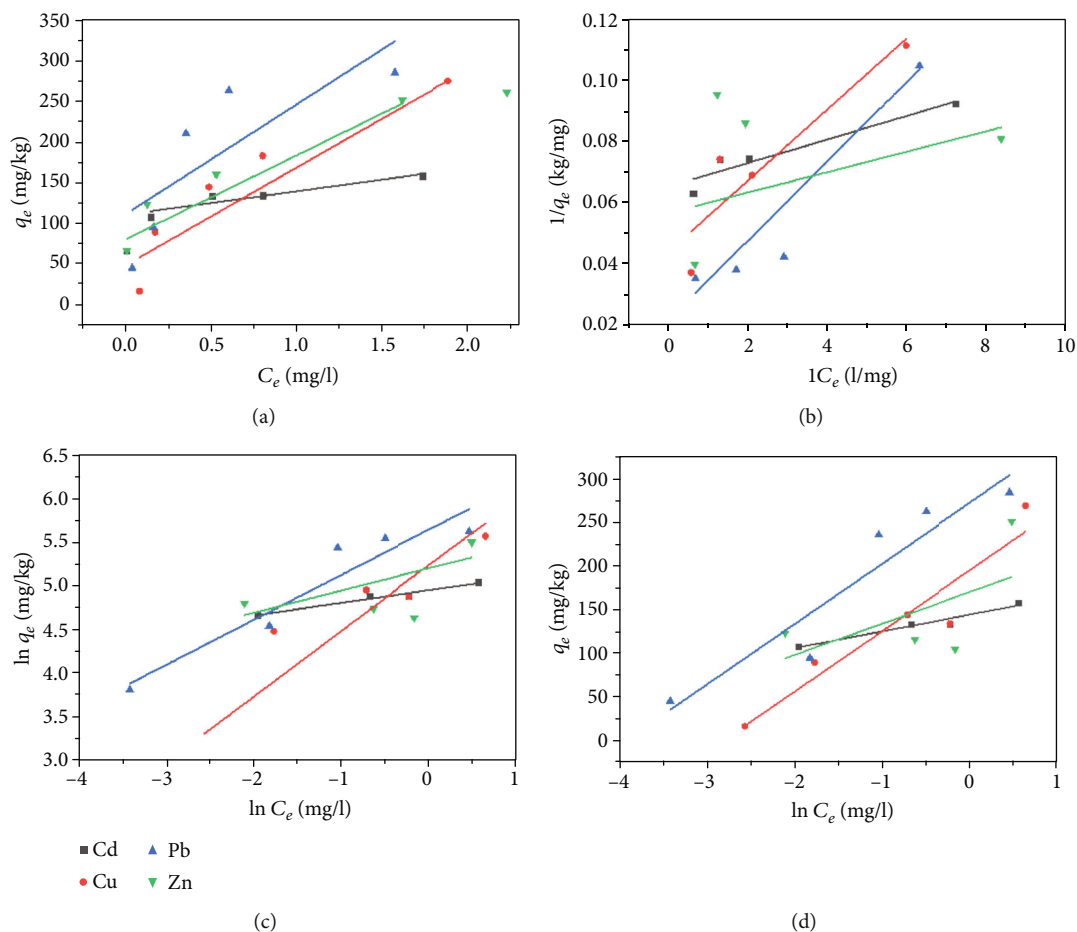


FIGURE 4: (a) Henry model, (b) Langmuir model, (c) Freundlich model, and (d) Temkin model ($V = 20$ mL, temperature at 298 K, $t = 48$ h).

TABLE 3: Regression parameters of Henry and Langmuir models for adsorption isotherms of heavy metals on microplastics.

Absorbate	Henry model		Langmuir model		
	K_H	R^2	b	q_m	R^2
Cd	28.650	0.8971	0.002	152.672	0.9091
Cu	119.790	0.8924	3.836	224.719	0.8493
Pb	134.798	0.5897	1.713	452.489	0.9820
Zn	102.993	0.9202	17.212	176.056	0.2983

TABLE 4: Regression parameters of Freundlich and Temkin models for adsorption isotherms of heavy metals on microplastics.

Absorbate	Freundlich model			Temkin model		
	K_F	n	R^2	RT/b_T	A_T	R^2
Cd	144.496	6.840	0.9672	19.074	2005.992	0.9569
Cu	194.340	1.318	0.8391	69.331	16.993	0.9039
Pb	293.081	1.921	0.9066	69.372	52.118	0.8921
Zn	186.810	3.894	0.61048	35.919	114.544	0.3333

seen from the adsorption curve in Figure 1 that different heavy metals have different adsorption characteristics, and the order of adsorption capacity is $Pb^{2+} > Cu^{2+} > Cd^{2+} > Zn^{2+}$. The maximum adsorption capacity of Pb^{2+} was $395.62 \text{ mg}\cdot\text{kg}^{-1}$, followed by Cu^{2+} ($271.99 \text{ mg}\cdot\text{kg}^{-1}$) and Cd^{2+} ($203.32 \text{ mg}\cdot\text{kg}^{-1}$), and the minimum adsorption capacity of Zn^{2+} was $193.73 \text{ mg}\cdot\text{kg}^{-1}$. At the same time, the research results of Godoy et al. [44] showed that Pb is the heavy metal most readily adsorbed by microplastic polypropylene. In the adsorption process of this study, the adsorption was fast in the first 4 hours, was slow between 4 and 32 hours, and finally reached equilibrium. To further clarify the adsorption characteristics, we processed the data with origin 2018 and used a first-order kinetics model, second-

order kinetics model, intraparticle diffusion model, and Elovich model to describe the adsorption capacity of lead (Pb), zinc (Zn), cadmium (Cd), and copper (Cu) on polypropylene microplastics.

Figures 2(a) and 2(b) show the first-order and second-order kinetics fitting diagrams, respectively. The R -square of the first-order model is between 0.92 and 0.98, and that of the second-order model is between 0.996 and 0.999, which indicates that the adsorption process of heavy metals by PP is more in line with a second-order kinetics model. When Lang et al. studied the adsorption of heavy metals on polystyrene microplastics, they also considered that the adsorption was more in line with a pseudo-second-order kinetics model than a first-order kinetics model [45].

Figure 2(d) shows the intraparticle diffusion model, which shows that the adsorption can be divided into three stages of A, B, and C, and the adsorption occurs powerfully in stage A, then becomes milder in stage B and by stage C; the adsorption almost stops and reaches the saturation state. Moreover, the linear graph does not pass through the origin, indicating that the adsorption process involves intraparticle diffusion, but is not unique. The kinetics fitting parameters are shown in Tables 1 and 2.

In this study, the concentration of adsorbate was constant, and PP had a greater specific surface area and more micropores, which led to more adsorption sites on the surface of PP, and the corresponding maximum adsorption capacity was larger. However, the adsorption capacity for Pb and Cu was stronger.

3.2. Adsorption Isotherm Analysis. Figure 3 shows the adsorption isotherms of four heavy metals on the original PP. It can be seen from the isotherm diagram that each heavy metal has a different adsorption capacity. In the initial stage, q_e increased rapidly with increasing adsorbent concentration. When the adsorbent concentration increases to a certain degree, q_e increases slowly and gradually tends to become stable. At the same time, it can be seen from the q_e and the slope of the image when the microplastic polypropylene tends to be stable that the adsorption amount of heavy metals Pb and Cu is greater than that of Cd and Zn, which is consistent with the results of the adsorption kinetics experiment.

To better study the adsorption characteristics of heavy metals, we used the Henry, Langmuir, Freundlich, and Temkin models to fit them [46, 47], as shown in Figures 4(a)–4(d), and the regression parameters are listed in Tables 3 and 4. From the fitting results, we can see that the Freundlich model has the best fitting effect for the heavy metals Pb, Cu, Cd, and Zn, where n is greater than 1; it shows that PP adsorption of heavy metals is multilayer adsorption, and the adsorption is favorable. Fasfous et al. studied tetrabromobisphenol. An adsorption experiment on multiwalled carbon nanotubes, also showed that the adsorption is favorable when n is between 1 and 10 [48, 49].

According to the above research, Tables 3 and 4 show that the Freundlich coefficient (K_F) of heavy metal adsorption by microplastics meets the order of $Pb^{2+} > Cu^{2+} > Zn^{2+} > Cd^{2+}$. The maximum adsorption capacity of Pb^{2+} was $452.489 \text{ mg}\cdot\text{kg}^{-1}$, the maximum adsorption capacity of Cd^{2+} was $152.672 \text{ mg}\cdot\text{kg}^{-1}$, Cu^{2+} was $224.719 \text{ mg}\cdot\text{kg}^{-1}$, and Zn^{2+} was $176.056 \text{ mg}\cdot\text{kg}^{-1}$. The results also show that among the four heavy metals, PP has the highest adsorption affinity for Pb^{2+} , Cu^{2+} , and Zn^{2+} which have similar affinities, and PP has the lowest affinity for Cd^{2+} .

3.3. Coexistence Adsorption. The above studies show that polypropylene microplastics have different adsorption capacities for lead, zinc, copper, and cadmium. Obviously, it can be seen that the maximum adsorption capacity of Pb is higher than that of the other heavy metals. To describe the adsorption characteristics of each heavy metal more clearly, we used Origin 2018 to draw Figures 5 and 6 to show

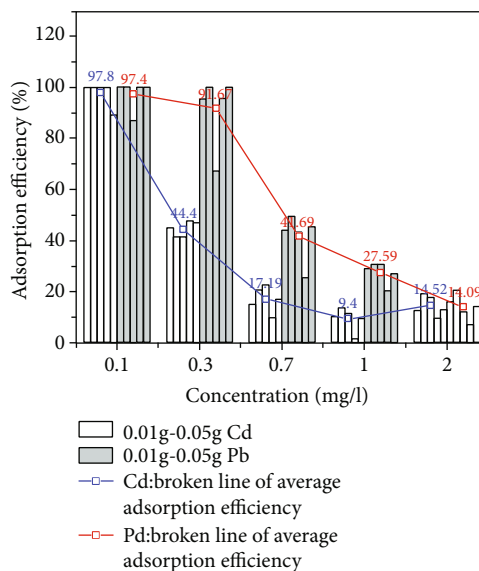


FIGURE 5: Adsorption efficiency of microplastics to Cadmium (Cd) and lead (Pb) ($V = 20 \text{ mL}$, temperature at 298 K , $t = 48 \text{ h}$).

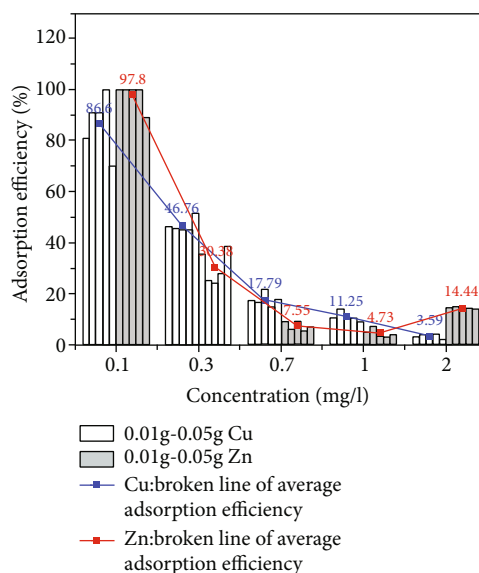


FIGURE 6: Adsorption efficiency of microplastics to copper (Cu) and Zinc (Zn) ($V = 20 \text{ mL}$, temperature at 298 K , $t = 48 \text{ h}$).

the adsorption efficiency of the four heavy metals under coexisting adsorption. Figure 5 shows the adsorption efficiency of Cd and Pb, and Figure 6 shows the adsorption efficiency of Cu and Zn.

As we can see from Figures 5 and 6, the adsorption efficiency of microplastics for Pb, Cu, Zn, and Cd is the highest when the concentration of mixed adsorbent is 0.1 mg/L , and the adsorption efficiency of heavy metals all slows down with the increase of adsorbate concentration. Accordingly, when the concentration of adsorbate is low, the adsorption effect of microplastics on 4 kinds of heavy metals can almost be regarded as saturated state, and with the increase of the concentration of mixed adsorbents, the removal effect was

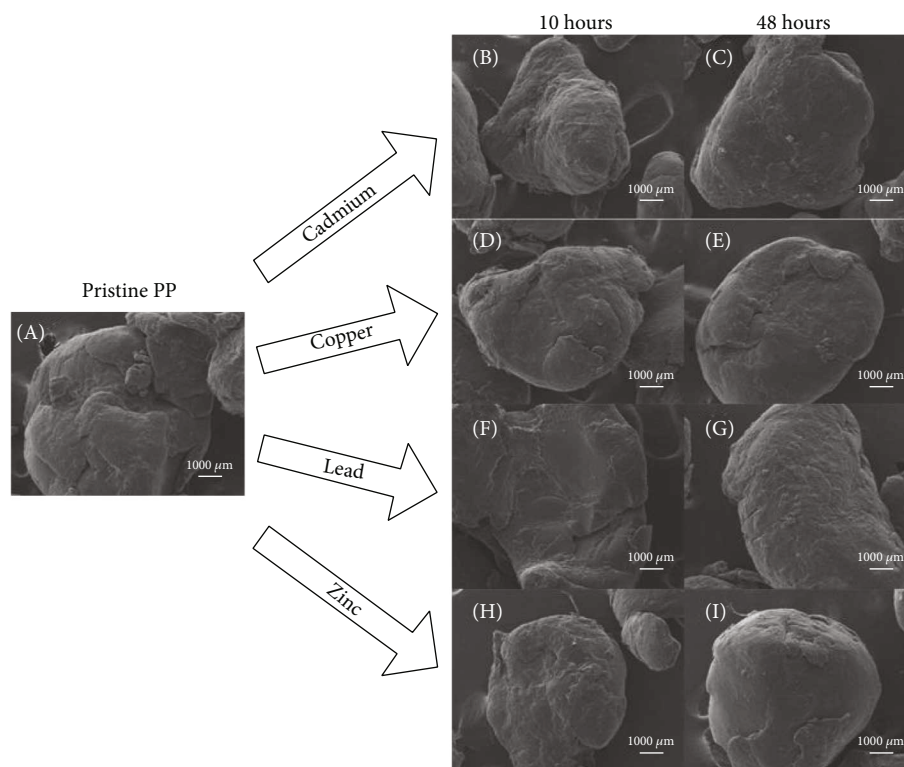


FIGURE 7: Scanning electron microscopy of polypropylene adsorption of different heavy metals ($C_e = 0.7 \text{ mg}\cdot\text{L}^{-1}$, $V = 20 \text{ mL}$, temperature at 298 K).

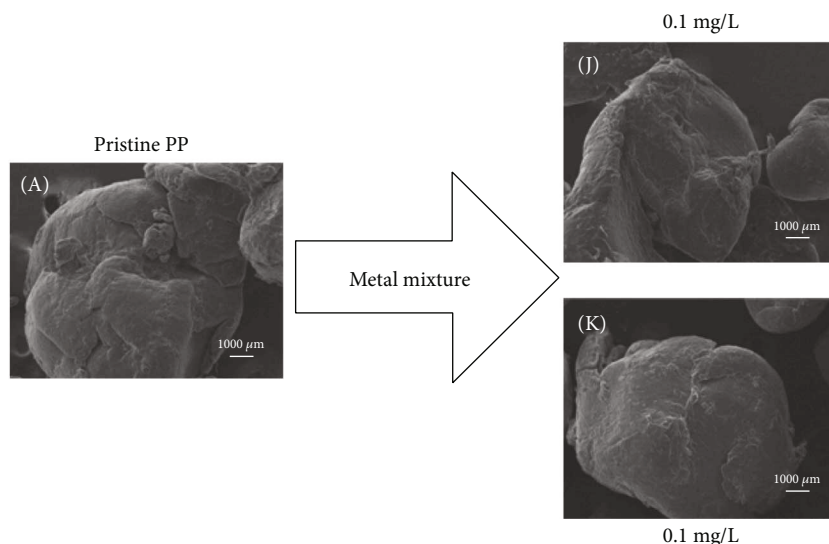


FIGURE 8: Scanning electron microscopy of polypropylene adsorption of various heavy metals ($V = 20 \text{ mL}$, temperature at 298 K, $t = 48 \text{ h}$).

inhibited. Chen et al. studied the adsorption characteristics of Pb, Zn, Cd, and Cr in the incineration process. They described several adsorption mechanisms: for metals with high volatility such as Cd, physical molecular adsorption and particle growth are the main adsorption mechanisms; for heavy metals (medium to high volatility), such as Pb, physical and chemical adsorption mechanisms are crucial; and for metals with low volatility, such as Cu and Cr, chemical reactions are the main adsorption mechanism [50].

In this study, when the concentration of adsorbate is low, in the range of 0.1-0.3 mg/L, the coexistence of various metals can promote the adsorption of Pb and Cu, and then with an increase in the concentration of adsorbate, a coexistence system can inhibit the adsorption of microplastics. Overall, the adsorption rates of Pb, Cu, Zn, and Cd are significantly different when the concentration of the adsorbate is the same, which indicates that there is competitive adsorption in the coexisting adsorption system [51]. In the

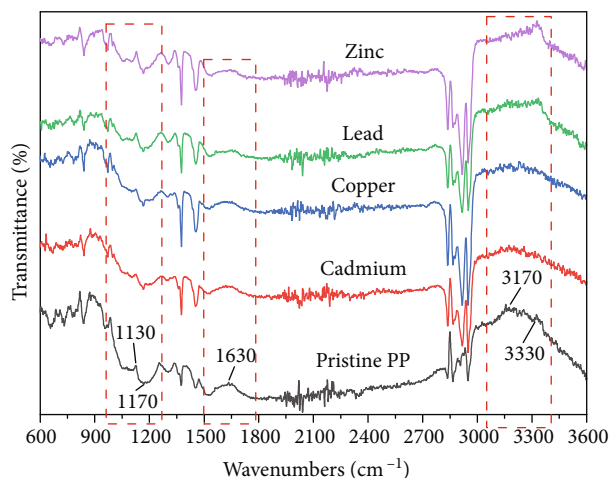


FIGURE 9: FTIR diagram of PP after adsorption of heavy metals with different concentrations ($C_e = 0.7 \text{ mg}\cdot\text{L}^{-1}$, $V = 20 \text{ mL}$, temperature at 298 K).

multicomponent adsorption of Pb, Cd, and Ni by microwave functionalized cellulose, Taha et al. mentioned that the coexistence of Cd and Ni can significantly slow down the absorption of Pb, and Pb has the most obvious effect on the adsorption capacity [52], which is similar to the finding of our study. This may also be related to the adsorption mechanism of different heavy metals, and different adsorption mechanisms and reaction conditions will affect the adsorption of different metals by microplastics, showing different results.

3.4. Characterization Analysis

3.4.1. SEM Characterization Analysis. The surface morphology of PP was studied by SEM, and the results of adsorption of different heavy metals by PP are shown in Figure 7. At 100 \times magnification, 20-mesh polypropylene particles can be observed with irregular shapes and compact structures. As time passes, the surface of the PP becomes regular. With increasing of adsorption time, the surface voids of the PP decreased, probably because the absorption of heavy metals became regular. The phenomenon of PP adsorption of Zn was very obvious. The results of the coexistence adsorption experiment are shown in Figure 8. The surface shape was more regular when the heavy metal concentration was 0.3 mg/L than when the heavy metal concentration was 0.1 mg/L. This provides for a reference for us to better understand the adsorption properties of heavy metals to plastics.

3.4.2. FTIR Characterization Analysis. As shown in Figure 9, after adsorption of different heavy metals, the change trend of the FTIR absorption peak of PP was basically the same. As shown in Figure 10, the absorption peak strength of FTIR decreased significantly before and after the adsorption of various heavy metals by PP, but there was no significant change in the absorption peaks after the adsorption of different concentrations of heavy metals.

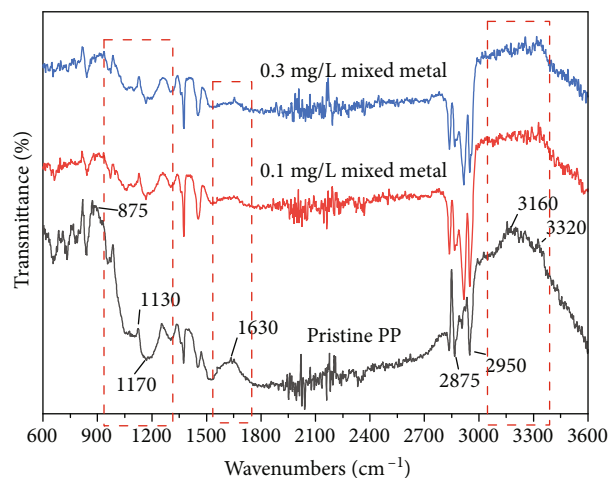
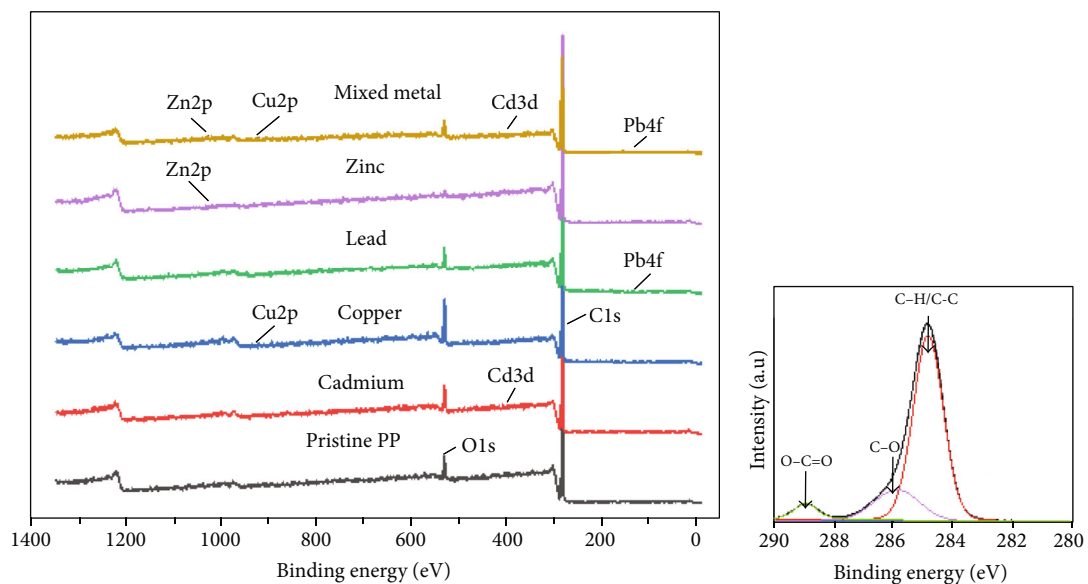


FIGURE 10: FTIR diagram of PP after adsorption of different kinds of heavy metals ($V = 20 \text{ mL}$, temperature at 298 K, $t = 48 \text{ h}$).

As shown in both Figures 9 and 10, the absorption band at 875 cm^{-1} can be attributed to the plane deformation of C-H (-CH) monosubstituted benzene, and skeleton vibration is observed. The peaks were observed at 1130, 1375, and 1666 cm^{-1} , which were caused by the tensile vibration of phenolic hydroxyl groups (C-OH) and carbonyl groups (C=O). The absorption band at 1630 cm^{-1} is attributed to aromatic carbon-carbon (C-C) skeleton vibrations.

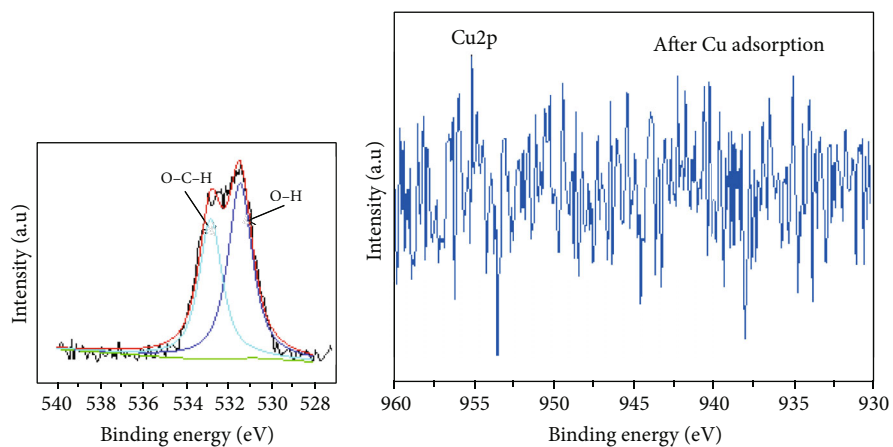
3.4.3. XPS Characterization Analysis. Figure 11(a) shows the XPS characterization of microplastics before and after adsorbing heavy metals, making the positions of C1s, O1s, Pb4f, Cd3d, Zn2p, and Cu2p peaks. By fitting the peaks of high-resolution XPS spectra in the C1s and O1s regions, the chemical states of elements C and O can be identified (Figures 11(b) and 11(c)), and the peaks of different binding energy can also be seen corresponding to different groups from the graph. XPS analysis of the original microplastics PP has C1s peaks at 288.5 eV, 286.0 eV, and 284.8 eV, representing C-H/C-C, C-O-C, and O-C=O, respectively. For the spectrum of O1s, the peaks at junction of 531.4 eV and 532.9 eV are C-O and H-O-C, respectively. No other new peaks have been observed in the XPS spectrum, indicating that the mainly adsorption of heavy metals of PP is physical adsorption. Lin et al. studied the XPS spectrum before and after microplastics adsorbing Pb, indicating that there are no bonds between microplastics and Pb (II), and physical adsorption is the main driving force of microplastics adsorption [53].

As shown in the XPS high-resolution spectra of each heavy metal region in Figures 11(d)–11(f), peaks of Pb4f, Cd3d, Zn2p, and Cu2p can be observed from the XPS survey of microplastics after adsorbing heavy metals, indicating the heavy metals were surely adsorbed on the surface of microplastics. But the results in the full spectrum map can not be obviously observed. It may be due to the heavy metals were mainly adsorbed into the interior of microplastics, so there is less surface adsorption [54].



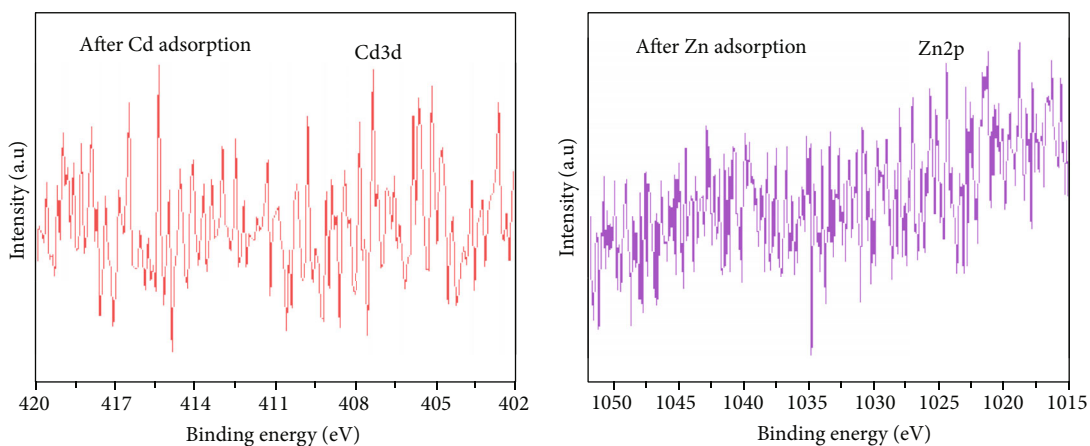
(a)

(b)



(c)

(d)



(e)

(f)

FIGURE 11: Continued.

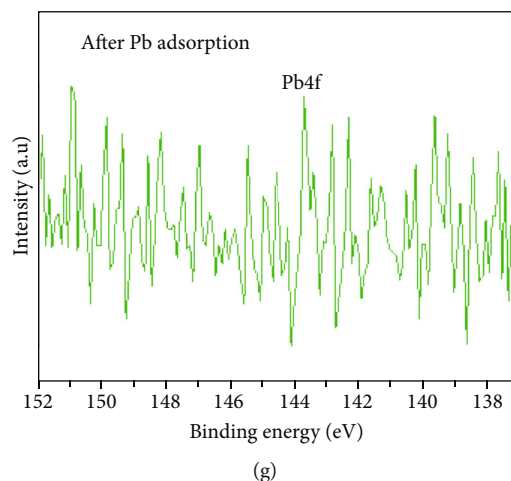


FIGURE 11: (a) XPS characterization before and after microplastics adsorption of heavy metals, (b) C1s spectrum of the original PP, (c) O1s spectrum of the original PP, (d) microplastic adsorption of Cu^{2+} , (e) microplastic adsorption of Cd^{2+} , (f) microplastic adsorption of Zn^{2+} , and (g) microplastic adsorption of Pb^{2+} ($V = 20 \text{ mL}$, temperature at 298 K , $t = 48 \text{ h}$).

4. Conclusion

The adsorption mechanism of 4 kinds of heavy metals (Pb, Cu, Cd, and Zn) on PP over different time periods was studied to improve our understanding of the heavy metal adsorption characteristics of microplastics. Compared with previous studies, our kinetics model showed that different heavy metals have different adsorption characteristics, and the adsorption capacity of these 4 heavy metals is $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Cd}^{2+} > \text{Zn}^{2+}$. The adsorption is more consistent with the secondary kinetics and the adsorption has been proven to be multilayer and beneficial. In addition, we also studied the coexistence adsorption experiments of 4 kinds of heavy metals and found that there was competitive adsorption among the heavy metals, which was mainly related to the types and volatility of the adsorbates.

From the SEM characterization diagram, we can observe that the polypropylene particles before the adsorption of heavy metals are irregular in shape and have gaps on their surface. With the passage of adsorption time, the shape of PP tends to become regular. The FTIR characterization results showed that the change trend of the absorption peak of PP was basically the same before and after single adsorption of different heavy metals. When a variety of metals coexist for adsorption, the absorption peak strength of PP before and after adsorption slows down obviously at $900\text{--}1200 \text{ cm}^{-1}$. In the future, we will focus on the adsorption characteristics and adsorption processes of other heavy metals.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon reasonable request to 953481783@qq.com.

Additional Points

Highlights. (1) The coexistent adsorption of four heavy metals (Pb, Cu, Cd, and Zn) by microplastics was consid-

ered. (2) There was competitive adsorption between heavy metal adsorption, which was mainly related to the type and volatility of the adsorbed substance. (3) The adsorption characteristics depended on different types of heavy metals, and microplastics had the highest adsorption capacity for Pb.

Conflicts of Interest

The authors declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

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