Water Air Soil Pollut (2023) 234:198
https://doi.org/10.1007/s11270-023-06201-2

Study on Copper Desorption Behavior from Microplastic Particles in Different Media

Ruixin Zhang · Zhaoying Li · Xi Gao ·
Silu Chang · Bo Yan · Guangbi Li

Received: 7 January 2023 / Accepted: 26 February 2023

Abstract Microplastics can act as carriers of pollutants in the aquatic environment and have the potential to absorb and release heavy metal pollutants. In this study, copper (Cu(II)) was chosen as the classical pollutant, mainly investigated the desorption behavior of the heavy metal Cu(II) from polystyrene (PS) microplastics in Milli-Q water, artificial seawater, and simulated gastric fluid. The results showed that the desorption occurred rapidly, within a few hours or even minutes in different media. The desorption of copper was consistent with pseudo-second-order model and the Freundlich isothermal model. The desorption amounts were in the order of simulated gastric fluid > artificial seawater > Milli-Q water. In addition, hysteresis was obviously detected in the adsorption/desorption of Cu(II) in the three environments media. Moreover, the influence of adsorption medium is greater than the desorption medium on desorption. Increasing the temperature would improve the desorption ability. There was a higher risk of exposure in warm-blooded organisms than in cold-blooded organisms. In addition, the presence of sediment particles had a significant effect on desorption, which would reduce the desorption ratio. This study reveals the migration behavior of heavy metals carried by microplastics, which provides a scientific basis for assessing ecological risks and studying the migration and transformation patterns of contaminants.

Keywords PS microplastics · Cu(II) · Desorption · Simulated gastric fluid · Temperature

1 Introduction

The problem of microplastic pollution has received attention widely around the world. Thompson et al. (2004) first introduced the concept of microplastics and defined them as plastic debris and particles less than 5mm in diameter (Law &Thompson 2014). Due to its strong plasticity, chemical stability, multifunctional, durable, lightweight, cheap, and other characteristics have been widely used in the world (Rios et al. 2007). Previous research investigations have

---

R. Zhang · Z. Li · X. Gao · S. Chang · B. Yan
College of Marine and Environmental Sciences, Tianjin
University of Science and Technology, Tianjin 300457,
People's Republic of China

B. Yan
Key Laboratory of Marine Resource Chemistry
and Food Technology (TUST), Ministry of Education,
Tianjin 300457, People's Republic of China

B. Yan (✉)
Tianjin Marine Environmental Protection and Restoration
Technology Engineering Center, Tianjin 300457,
People's Republic of China
e-mail: yanbo@tust.edu.cn

G. Li
College of Chemical Engineering and Materials
Sciences, Tianjin University of Science & Technology,
Tianjin 300457, People's Republic of China

found that microplastics are ubiquitous in aquatic environments, mainly discharged from urban wastewater treatment plants into freshwater systems and transported from rivers to the ocean (Iyare et al. 2020, Kay et al. 2018, Zhang et al. 2020). So far, microplastics have been detected in freshwater, seawater, and sediments all over the world (Eerkes-Medrano et al. 2015, Law &Thompson 2014, van Sebille et al. 2015).

Due to their small size and widespread existence, micro/nano plastics are highly likely to be ingested by aquatic animals (Galloway et al. 2017, Scherer et al. 2018, Steer et al. 2017).Atamanalp et al. (2021) reported that microplastics were detected in the brain, gastrointestinal tract, gills, and muscles of Marine fish. In addition, microplastics have been reported to be present in the digestive tracts of many wild aquatic animals, such as molluscs, fish, bivalves, birds, pinnipeds, and even zooplankton (Botterell et al. 2019, Holland et al. 2016, Hurley et al. 2017, Sanchez et al. 2014). Studies have shown that the ingestion of microplastics will harm the health of organisms, affect the normal physiological function of organisms, may affect the structure of intestinal microorganisms (Jin et al. 2018), cause tissue inflammation (von Moos et al. 2012), and even destroy cell membranes (Ding et al. 2021) and lead to oxidative stress (Hu &Palic 2020). In addition, microplastics can be passed and accumulated along the food chain, eventually endangering human health (Cole et al. 2013, Nelms et al. 2018). In recent years, microplastics have been found in the human body (Schwabl et al. 2019), which demonstrated the presence of microplastics in the human gastrointestinal tract.

In addition to their own toxicity (Min et al. 2020), microplastics are more likely to adsorb and accumulate various pollutants in aquatic environment, such as persistent organic matter heavy metal ions and antibiotics, due to their unique surface characteristics, such as large specific surface area, high porosity, strong hydrophobicity, and multi-spatial structure (Ashton et al. 2010, Atugoda et al. 2020, Ogata et al. 2009). The adsorption properties of microplastics make them become carriers, carrying pollutants to migrate in the water environment, and then enter the living organisms through biological ingestion, resulting in combined toxicity (Rochman et al. 2013, Rochman et al. 2014). Moreover, the adsorption and desorption effect of microplastics on typical pollutants can change their concentration distribution, medium distribution law, and environmental behavior, thus affecting the toxic effect of pollutants (Allen et al. 2019). Studies indicate that microplastics can alter Ag pathways, uptake and increase Zn and Cd bioavailability under appropriate conditions (Hodson et al. 2017, Lu et al. 2018). It also found that the association of microplastics and Cd increased Cd accumulation in zebrafish liver, viscera, and gills (Lu et al. 2018).

Desorption, as an interface process, plays an important role in determining the fate and ecological risk of toxic pollutants adsorbed by microplastics in water environment (Zhang et al. 2020). However, at present, a large number of studies are mainly focused on the desorption of organic pollutants by microplastics, such as polycyclic aromatic hydrocarbons (Voparil &Mayer 2000), phenylalanine (Teuten et al. 2009) and drugs (Fan et al. 2021). Previous studies have found that pollutants have a lower desorption capacity in aqueous environments than in the gastrointestinal tract. The low desorption of drugs by polyamide and polyethylene microplastics in rivers suggest that adsorbed drugs can be transported over considerable distances (McDougall et al. 2022, Wagstaff et al. 2022). Bakir et al. (2014a) found that polyvinyl chloride (PVC) and polyethylene (PE) microplastics desorbed persistent organic pollutants more than 30 times as much in intestinal conditions as in seawater, indicating that the presence of intestinal surfactants enhances pollutant desorption. In addition, temperature and pH are considered to be important factors affecting desorption (Bakir et al. 2014a, Bakir et al. 2014b). Liu et al. (2020) found that high temperature slightly enhanced the desorption of antihyperlipidemia atorvastatin (ATV) and antihypertensive amlodipine (AML) in gastric and intestinal fluid, and increasing pH could promote the dissolution of ATV but inhibit the dissolution of AML. McDougall et al. (2022) showed that the pH of the solution affected the morphology of the drug and the amount of surface charge of microplastics. At low pH, maximal desorption of cationic drugs in gastric fluid was observed due to the decrease in surface charge of microplastics.

Due to the desorption mechanism of metals, microplastics can be used as point sources of heavy metals in the environment (Munier &Bendell 2018). Similarly, the interaction between heavy metals and microplastics, i.e. their adsorption and desorption mechanisms, has also attracted attention. Chen et al. (2022) found that PVC microplastics have high adsorption and low desorption capacity for heavy metals, which can effectively accumulate heavy metals in the heavy metal–polluted aquatic environment, and then migrate and release them into the human digestive system. What is more, Wang et al. (2019) reported that microplastics had a very high desorption rate of cadmium ions (up to 92.9%). Zhou et al. (2020) observed a high desorption rate in the simulated intestinal environment. Hodson et al. (2017) also found that the high desorption rate (59.5%) of Zn ions adsorbed by polyethylene microplastics in the intestinal tract of synthetic earthworms means that adsorbed metal ions are likely to be re-released, thus metal-contaminated microplastics pose a higher ecological risk. However, the desorption behavior of microplastics in carrying heavy metal pollutants into various environments (fresh water, seawater, gastric fluid) is not clear. Therefore, further studies are needed to accurately assess the migration and transformation behavior of heavy metals carried by microplastics in natural environments (Zhou et al. 2020).

Copper (Cu(II)) is widely used in production and life. Improper discharge of wastewater containing copper in smelting, metal processing, machinery manufacturing, organic synthesis, and other industries, makes it become a heavy metal pollutant in the environment. In addition, copper is an essential trace element for aquatic animals (Linder &Hazegh-Azam 1996), but excess copper can have toxic effects on organisms (Craig et al. 2007, Liu et al. 2010). According to previous studies, copper can be adsorbed by microplastics (Ashton et al. 2010, Godoy et al. 2019; Tang et al. 2021b), and microplastics-copper composite has higher toxicity than copper alone, suggesting that microplastics may play an important role in the bioavailability and toxicity of copper in the environment (Santos et al. 2021). Polystyrene (PS) has become a major source of plastic pollution worldwide (Kwon et al. 2018), which is widely used in cosmetics, personal care, and other applications (Andrady &Neal 2009) for its stability and cost-effective properties. The high consumption of polystyrene has caused some environmental problems and has become a common type of microplastic in the water environment (Liu et al. 2019). The desorption behavior of polystyrene microplastics on Cu(II) in different media (fresh water, seawater, and gastric fluid) was investigated by laboratory simulation. The main research objectives of this paper include the following: (i) to study the kinetics of desorption of PS microplastics and the isotherms of copper desorption in fresh water, seawater, and gastric fluid; (ii) investigate the effect of temperature on desorption; and (iii) to explore the influence of the existence of sediment particles on desorption.

2 Materials and Methods

2.1 Materials and Reagents

Copper (solid power, purity > 99.9%) was obtained from Shanghai Meyer Co., Ltd., China. The sea salt used to simulate seawater was purchased from China Academy of salt Engineering and Technology Co., Ltd. Pepsin A (≥ 250 units/mg solid) was bought from Hefei Qiansheng Biotechnology Co., Ltd., China. PS microplastics (average particle size of 180 μm) was purchased from Dongguan Hua Chuang Plastic Chemical Raw Materials Co., Ltd., China. Copper quantitation was performed using an inductively coupled plasma mass spectrometer (ICP-MS, Thermo Scientific, US) measurement.

2.2 Adsorption Experiments

Adsorption kinetics experiment was conducted in fresh water at 27°C. Milli-Q water was used to simulate fresh water. 60 mg PS sample and 30 mL Cu(II) solution with initial concentration of 1 mg/L were mixed in 250 mL conical flask and sealed the bottle with a sealing film, and then, the bottles were shaken in temperature-controlled shaking incubator (ZWYR-2102C, China) at 27°C, and 180 rpm. Samples were collected in sequence at 15, 30, 60, 120, 180, 300, 420, 540, 720, 1080, and 1440 min. The sample was filtered with 0.45 μm membrane to obtain the supernatant and the adsorption amount of Cu(II) was detected.

Adsorption isothermal experiments were carried out in Milli-Q water and artificial seawater respectively. Artificial sea water was prepared according to the manufacturer instructions, 30 g sea salt was dissolved in 1L of pure water to simulate natural seawater. In this experiment, 60 mg of PS was added to 30 mL Cu(II) solutions with different initial concentrations (0.1 ~ 1 mg/L). The mixtures were subsequently placed in temperature-controlled shaking incubator and shaken at a fixed speed of 180 rpm at 18°C, 27°C, and 37°C respectively. The shaking time was specified based on previous kinetic experiments to reach adsorption equilibrium. In the present study, each experiment was conducted in triplicate.

The formula for calculatiing the adsorption amount of copper on microplastics is shown as Eq. 1:

$$q_t = \frac{(C_0 - C_t)V}{m} \tag{1}$$

where q_t (mg/g) is the adsorption amount of Cu(II) adsorped at time t (min); C_0 (mg/L) reflects the initial adsorption concentration of Cu(II) in solution; C_t (mg/L) is the concentration of Cu(II) in solution after adsorption; V (mL) is the volume of adsorption solution; m (g) is the mass of microplastics.

2.3 Desorption Experiments

Cu(II) laden solid particles were prepared for the desorption experiment. The preparation process followed the above adsorption experiment. After adsorption equilibrium, the microplastics were collected via vacuum filtration, air-dried for 48 h, and then used for desorption experiment. Simulated gastric fluid was prepared by dissolve 2.0 g of sodium chloride and 3.2 g of pepsin A in water to a final volume of 1000 mL. The pH of simulated gastric fluid was adjusted to 2.0 by hydrochloric acid to mimic the acidic stomach (Convention 2013). Simulated fresh water (pH ≈ 7.0) and artificial seawater (pH ≈ 8.0) were prepared for comparison. For desorption kinetic experiments, 30 mL background solutions of different media were spiked into conical flasks containing 60 mg Cu-loaded PS microplastics, respectively, and then were oscillated in temperature-controlled shaking incubator at 180 rpm. The temperatures were kept at 18°C and 37°C to mimic the digestive conditions of cold- and warm-blooded aquatic organisms, respectively (Tanaka et al. 2015). The desorption kinetics experiments of Milli-Q water and artificial seawater mediums were explored under 18°C, 27°C, and 37°C.

Desorption isotherms were conducted for Cu-laden PS microplastics from the adsorption processes with initial concentrations of 0.1~1.0 mg/L. The weighing method was adopted in desorption isotherms experiments. The specific operation method is as follows: The conical flasks with microplastics (M_0) were weighed before adsorption isothermal experiment. After the adsorption isothermal experiment, all the supernatant were removed as far as possible using the needle tube (the loss ratio of microplastic was < 0.1%, which was negligible), and the conical flasks with the supernatant removed (M_1) were weighed again. Thereafter, the same volume of background solution was added, the weight was recorded as M_2. The sample bottles were then shaken under the same conditions for another 720 min. The isothermal desorption of simulated gastric fluid was completed with Milli-Q water medium as adsorption medium. All of the experiments were conducted in triplicate. Considering the density of the background solution, the quantity of the desorption was calculated by mass balance. The calculation formula is shown in Eq. 2:

$$q_e^d = \frac{\frac{C_e^d \times (M_2 - M_1)}{\rho_2} - \frac{C_e \times (M_1 - M_0)}{\rho_1}}{m} \tag{2}$$

where ${q_e}^d$ (mg/g) is the desorption amount of Cu(II) under desorption equilibrium; C_e (mg/L) and ${C_e}^d$ (mg/L) reflect the adsorption and desorption equilibrium concentration of Cu(II) in solution, respectively; m (g) is the mass of PS microplastic added; ρ_1 (g/cm^3) and ρ_2 (g/cm^3) are the density of Cu(II) solution and the density of background solution, respectively.

2.4 Effect of Sediment Particles on Desorption in the Presence

The effects of sediment (S) particles on desorption were investigated in the system with Milli-Q water, artificial seawater, and simulated gastric fluid as background solutions. The sediment used in this study comes from the intertidal zone of Gaoshaling, which has a high content of sand and belongs to silty sand. The retrieved sediment is air-dried, ground, and sieved to remove large particulate matter and residual organisms. Ultimately, the particles intercepted between 60 mesh and 100 mesh screens were selected for this experiment. The solid-liquid ratio of the experiment was 2 g/L, and the experimental setups were as follows: (i) only PS-Cu(II) microplastics were added, that is, 60 mg PS-Cu(II) + 30 mL background solution; (ii) sediment particles were added, namely, 30 mg PS-Cu(II) + 30 mg S + 30 mL background solution. Similarly, the samples were put in temperature-controlled shaking incubator for 720 min at a constant temperature of 27°C and a rotational speed of 180 rpm. Since most organisms are in a warm blood state, thus, an extra set of 37℃ simulated gastric fluid desorption experiments was added to the experimental setup.

2.5 Date Analysis

The uptake kinetics was fitted using the pseudo-first-order model (Eq. 3) and the pseudo-second-order model (Eq. 4):

$$q_t = q_e\left(1 - e^{-k_1 t}\right) \tag{3}$$

$$q_t = \frac{q_e^2 k_2 t}{1 + k_2 q_e t} \tag{4}$$

where q_t (mg/g) and q_e (mg/g) are the adsorption amount of Cu(II) adsorbed at any time and under equilibrium. k_1 (1/min) and k_2 (g·mg^{-1}·min^{-1}) represent the rate constants of pseudo-first-order and pseudo-second-order adsorption kinetics, respectively. In desorption experiment, $q_t{}^d$ and $q_e{}^d$ are used to represent the desorption amount of Cu(II) desorbed at any time and under equilibrium, respectively.

Langmuir model (Eq. 5) and Freundlich model (Eq. 6) were applied by the isotherm experimental data:

$$q_e = q_m \frac{K_L C_e}{1 + K_L C_e} \tag{5}$$

$$q_e = K_F C_e^{1/n} \tag{6}$$

where C_e (mg/L) reflects the adsorption equilibrium concentration of Cu(II) in solution; K_L (g/mg) and K_F (mg$^{-1/n}$·L$^{-1/n}$g^{-1}) are the affinity constants of the Langmuir and Freundlich; q_m (mg/g) is the theoretical maximum adsorption capacity of microplastics; $1/n$ is the Freundlich constants.

The desorption degree during desorption were quantified by the desorption hysteresis index (HI) (Liu et al. 2018), which was calculated according to the formula below (Eq. 7) (Wu &Sun 2010):

$$\text{Hysteresis index } (HI) = \left.\frac{q_e^d - q_e^s}{q_e^s}\right|_{T,C_e} \tag{7}$$

where $q_e{}^d$ and $q_e{}^s$ referred to the equilibrium concentrations in the solid phase in the absorption and desorption experiments, respectively. And the bracket subscripts T and C_e specify conditions held constant. HI suggests whether the reversibility of the adsorption process, with a higher value for more irreversible adsorption and the value of 0 for completely reversible adsorption.

The kinetics and isotherms models were fitted by using Origin 2018 software.

3 Results and Discussion

3.1 Adsorption Kinetics and Isotherms of Cu(II) onto PS

In order to determine the adsorption equilibrium time and better prepare copper-loaded microplastics, the adsorption of Cu(II) onto PS microplastics in Milli-Q water was studied firstly. The adsorption kinetics of Cu(II) to PS are given in Fig. 1. In this study, the amount adsorption of PS to Cu(II) increased rapidly in the first 15 min, following the adsorption quantity hardly increases and ending to dynamic equilibrium. The results showed that the adsorption process was divided into two stages: the first stage was the rapid adsorption stage, and the second stage was the slow equilibrium stage. The reason for this phenomenon was that in the early stage of adsorption, Cu^{2+} ions were rapidly adsorbed by the adsorption active sites in microplastics, resulting in less and less adsorption sites, and finally reaching saturation and entering dynamic equilibrium (Ma et al. 2019). Fitted parameters based on pseudo-first-order and pseudo-second-order models are summarized in Table 1. The fitted results indicated that the pseudo-second-order kinetic model could better

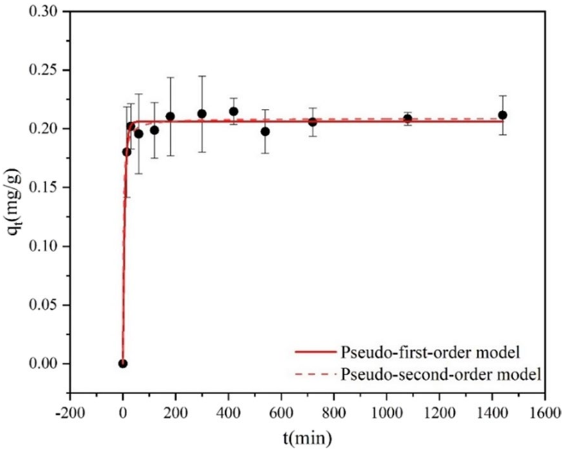

Fig. 1 The pseudo-first-order model and the pseudo-second-order model fitting curve of Cu(II) onto PS microplastics in Milli-Q water

Table 1 Parameters of the kinetics models for sorption experimental date of Cu(II) on PS microplastics (temperature = 27°C)

Model	q_e/(mg•g^{-1})	K/(min^{-1})	R^2
Pseudo-first order	0.206	0.1371	0.9884
Pseudo-second order	0.209	2.1852	0.9900

describe the adsorption (R^2: 0.9900 > 0.9884). It was speculated that the adsorption of Cu^{2+} by PS is a complex process, which is not determined by a single factor, but the result of the joint action of many factors. This adsorption process was not only affected by the concentration of adsorbent itself, but also affected by the active adsorption site on the surface of the adsorbent and electrostatic force. It may include both physical adsorption and chemical adsorption (Liu et al. 2019; Yin and Peng 2018).

In order to better understand the adsorption capacity between adsorbate and adsorbent, isothermal adsorption experiments of PS to Cu(II) were carried out in Milli-Q water and artificial seawater medium respectively. On the basis of the results above, in order to ensure that the adsorption of Cu^{2+} on microplastics can completely achieve adsorption equilibrium, 720 min was chosen as the shake time for the adsorption isotherm study. Figure 2 illustrates the modeling results of Cu(II) on PS microplastics based on Langmuir and Freundlich isotherms, and the parameters of isotherm models are given in Table 2. As shown in Fig. 2, the adsorption quantity of Cu(II) on the PS surface also increases gradually with the increase of Cu(II) concentration in solution, but the slope of the curve was decreasing, that is, the adsorption rate showed a decreasing trend. This may be due to the fact that the adsorption sites on the surface of PS microplastics are less occupied and more in the exposed state in the solution with lower copper concentration. With the increase of Cu(II) concentration, more adsorption sites were occupied by Cu^{2+}. When the amount of Cu^{2+} ions exceeds the adsorption point on the PS microplastic surface, the adsorption mainly

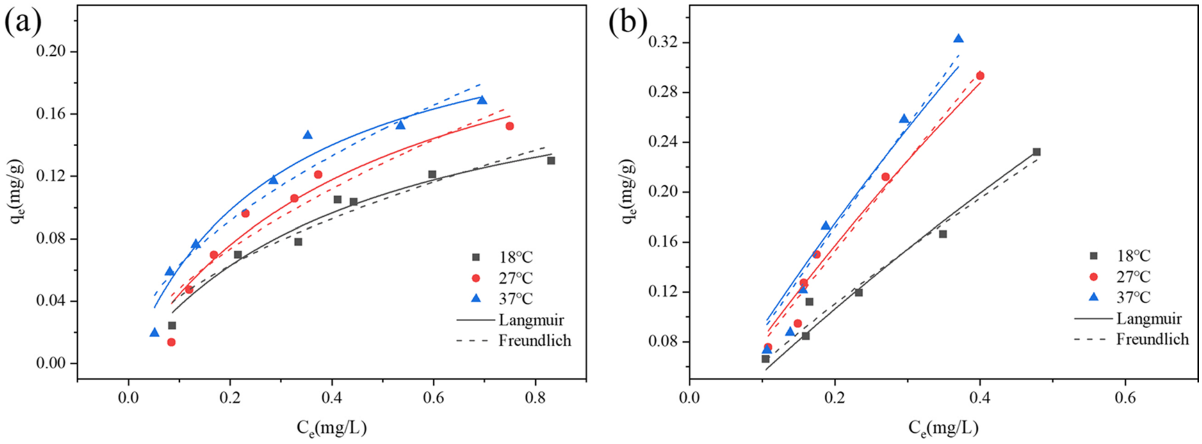

Fig. 2 Adsorption isotherms of Cu(II) on PS microplastics in **a** Milli-Q water and **b** artificial seawater

Table 2 Isotherm parameters for the adsorption of Cu(II) on PS microplastics in Milli-Q water and artificial seawater

Model	Parameter	Milli-Q water			Artificial seawater		
		18°C	27°C	37°C	18°C	27°C	37°C
Langmuir	K_L(g/mg)	2.0029	2.0295	2.8356	0.3549	0.5046	0.4939
	q_m(mg/g)	0.2154	0.2627	0.2437	1.6110	1.7115	1.9443
	R^2	0.9608	0.9171	0.9655	0.9596	0.9687	0.9412
Freundlich	K_F(mg$^{-1/n}$·L$^{-1/n}$g^{-1})	0.1556	0.1961	0.2183	0.4143	0.7163	0.8034
	1/n	0.5712	0.6111	0.5396	0.8223	0.9608	0.9595
	R^2	0.9192	0.8548	0.9180	0.9643	0.9729	0.9582

occurs on the surface of the PS microplastic would be close to saturation, thus affecting the subsequent adsorption rate.

According to the isotherm curves, the Langmuir model and Freundlich model can describe the adsorption of copper on PS well. However, the data of the fitting parameters indicated that the adsorption of Cu(II) on PS in Milli-Q water was well matched by Langmuir curve (R^2: 0.9171~0.9613). For artificial seawater medium, the fitting coefficient of Freundlich model is higher than Langmuir model, indicating that the adsorption in artificial seawater conforms to the Freundlich model (R^2: 0.9282~0.9716). Other studies of the adsorption in microplastics have confirmed this result. Godoy et al. (2019) found that the adsorption of copper by five types of microplastics, in Mill-Q, including PS, followed the Langmuir model. Wang et al. (2022) study showed that the Freundlich model was more suitable to describe the adsorption of copper by PS and PET microplastics in simulated seawater. It indicates that monolayer adsorption may be the main adsorption mechanism in Milli-Q water and the main adsorption mechanism was multilayer adsorption in artificial seawater medium, which was mainly affected by van der Waals force and electrostatic force.

The estimated q_m values of Langmuir model indicated that PS microplastics of the adsorption capacity for copper in artificial seawater is higher than that in Milli-Q water. On the other hand, the values of $1/n < 1$ from Freundlich modeling, indicating that the adsorption is favorable. This means that the increase of concentrations of metals in the solution as the adsorption will be enhanced (Guo et al. 2018a, Guo et al. 2018b, Hameed &Rahman 2008, Wu et al. 2019). Another important parameter in the Freundlich model, the value of K_F can reflect the adsorption capacity of the adsorbent. The higher the value of K_F, the higher the affinity to the adsorbate (Tang et al. 2021a). The order of K_F (artificial seawater) > K_F (Milli-Q water), indicating the binding ability of PS and copper in artificial seawater is stronger than that in Milli-Q water. Similar results were found by Godoy et al. (2019) in their study about the potential of microplastic as carriers of metals. They reported that possibly due to new molecules were formed for cations bind to microplastics, resulting better adsorbed of chromium and copper onto polyvinyl chloride (PVC) and polypropylene (PP), respectively in seawater than Distilled water. On the whole, the results showed that the adsorption of Cu(II) on PS microplastic is beneficial in water with high ionic strength. The adsorption of Cu(II) by PS exist monolayer adsorption and multilayer adsorption process and it is a complex process, in which physical adsorption and chemical adsorption coexist (Lang et al. 2020). It was consistent with the results of adsorption kinetics.

Furthermore, increasing temperature will promote adsorption. Langmuir isotherm model showed that in the same background solution medium, the maximum adsorption amount q_m value showed an increasing trend with the arise of temperature. In this study, the K_F value increased with the elevated of temperature, indicating that the temperature increase enhanced the affinity of PS microplastics for Cu(II).

3.2 Desorption Kinetics and Isotherms in Different Media

3.2.1 Desorption Kinetics of Cu(II) from PS Microplastics

Based on the above results, to ensure that the adsorption state could fully achieve dynamic equilibrium, Cu-loaded PS was prepared in batches at 24 h in Milli-Q water. Cu(II) laden PS microplastics of the adsorption concentrations were in the range of 0.093–0.150 mg/g. The desorption kinetics experiments were carried out in a solid-liquid ratio of 5 g/L. Fig. 3 summarizes the desorption kinetics behaviors under the conditions of Milli-Q water, artificial seawater, and simulated gastric fluid environments at different temperatures. The results showed that the desorption occurred of Cu(II) from PS microplastics is a rapidly process. Previous studies have found that the rapid desorption of Cu(II) by triethylenetetramine-functionalized polymeric adsorbents can be completed in a matter of minutes (Liu et al. 2012). As can be seen from Fig. 3, the desorption capacity of Cu(II) by microplastics in Milli-Q water and artificial seawater environments increased rapidly in the first 120 min and then tended to desorption dynamic equilibrium. It was noteworthy that desorption reached to dynamic equilibrate at 15 min in simulated gastric fluid medium. The fitting results are listed in Table 3. Compared to pseudo-first-order model, for simulated gastric fluid environment, the desorption of copper from PS microplastics was more consistent with the pseudo-second order kinetic model. According to the correlation coefficient R^2, both the pseudo first-order model and the

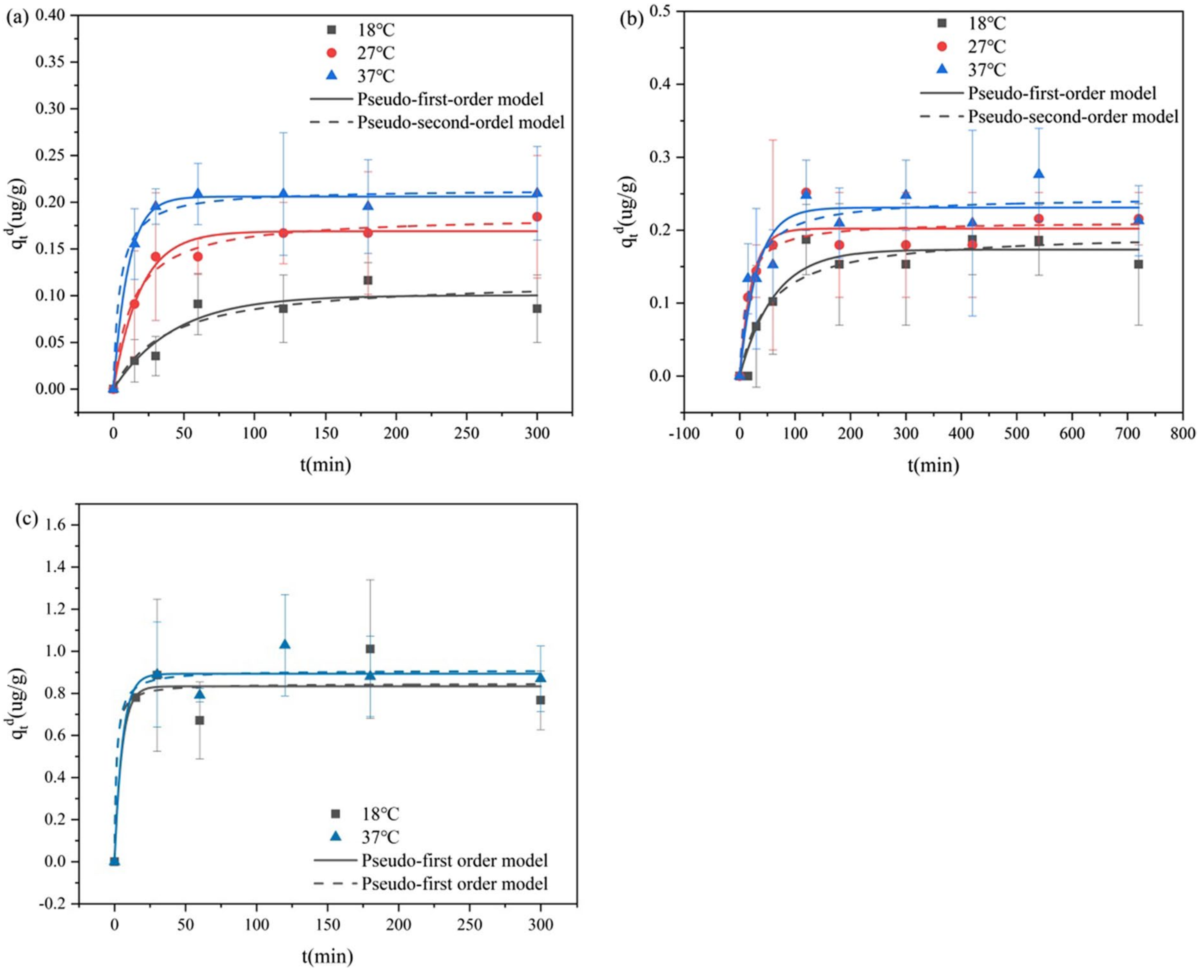

Fig. 3 Desorbed Cu(II) concentrations (μg/g) from PS microplastics in **a** Milli-Q water, **b** artificial seawater, and **c** simulated gastric fluid at different temperatures. Data is fitted using the pseudo-first order and pseudo-second order kinetics models

Table 3 Desorption kinetics fitting parameters in three environmental media at different temperatures

Model	Parameter	Milli-Q water			Artificial seawater			Simulated gastric fluid	
		18°C	27°C	37°C	18°C	27°C	37°C	18°C	37°C
Pseudo-first order	q_e^d(μg·g $^{-1}$)	0.1002	0.1688	0.2060	0.1734	0.2022	0.2310	0.8331	0.8927
	K_1(min^{-1})	0.0232	0.0517	0.0946	0.0161	0.0453	0.0314	0.1917	0.1799
	R^2	0.8803	0.9651	0.9949	0.9033	0.8836	0.8442	0.8713	0.9467
Pseudo-second order	q_e^d(μg·g^{-1})	0.1177	0.1858	0.2138	0.1970	0.2117	0.2455	0.8465	0.9096
	K_2(min^{-1})	0.2246	0.3927	1.0234	0.0958	0.3814	0.2126	1.0163	0.7320
	R^2	0.8441	0.9800	0.9843	0.8659	0.8637	0.8728	0.8717	0.9484

pseudo-second-order model could better fit the desorption of copper in Milli-Q water and artificial seawater, but combined with the fitting graph and fitting parameters, it was found that the theoretical equilibrium desorption amounts of the pseudo-second order model were closer to the real equilibrium desorption amounts and the fitting curves were closer to the experimental date points, which can better describe desorption.

Through comparing the value of desorption velocity constant k_2 values (Table 3), the desorption velocity in different media were evaluated more accurately. It was obvious that the desorption velocity of copper on PS microplastics follows that simulated gastric fluid > Milli-Q water > artificial seawater on a whole. The findings were consistent with previous research results (Bakir et al. 2014a) that the desorption rates of HOCs were faster under physiological conditions than in water without organic matters.

Moreover, the equilibrium desorption q_e^d values (Table 3) displayed that at the same temperature, compared with other substrates, PS microplastic for copper have the highest desorption quantity and desorption ratio in simulated gastric fluid. The results showed that heavy metals were released more in simulated gastric fluid medium due to the carrier effect of PS microplastics. Many previous studies have also found this phenomenon. Previous studies had shown that PS microplastics can adsorb pepsin, thus, which may also depend on pepsin competing for adsorption sites through π-π and hydrophobic interactions, resulting in enhanced desorption (Liu et al. 2020). In addition, this can be attributed to low pH reduced the surface charge of microplastic, thus reduce the adsorption strength of microplastic heavy metal ions adsorption (Wagstaff et al. 2022). On the other hand, the desorption amounts of copper in Milli-Q water and artificial seawater were 0.1858 μg/g and 0.2117 μg/g at 27°C, respectively. The corresponding desorption ratio was 0.198% and 0.228%. It is observed that the desorption ratio of copper in artificial seawater was higher than that in fresh water. This result was also arisen in previous desorption studies of pharmaceutical desorption on microplastics, mainly attributed to the effect of surface electrostatic interaction (Wagstaff and Petrie 2022). It was reported that electrostatic interaction is generally treated as the mechanisms effecting of the adsorption process of heavy ions (Kabbashi et al. 2009). Since the high concentration of Na^+ ions in seawater had a charge shielding effect on the surface of microplastics, a low zeta potential was detected (Wagstaff & Petrie 2022). It means that the surface of microplastic particles was reduced the electronegativity, thereby weakening the adsorption of positively charged copper ions (Zou et al. 2020).

The desorption capacity of Cu(II) in artificial seawater was stronger than in Milli-Q water. Therefore, after adsorbing copper ions to PS microplastics, the potential for transport of PS microplastics for Cu(II) in simulated fresh water is considerable. Cu^{2+} ions adsorbed by microplastics will migrate with the migration of microplastics. When Cu-loaded PS is transported from freshwater to seawater, more of the adsorbed copper may be released, resulting in the accumulation of copper in the Marine environment, thus posing a potential risk to Marine life. Moreover, as the adsorption results above show that the stronger adsorption capacity of PS microplastics on copper in seawater, the initial adsorption amount was larger, so the bioavailability may be increased after being ingested by organisms, which will bring greater toxicity to Marine organisms.

3.2.2 The Effect of Temperature on Desorption

According to the desorption velocity constant *k* value, the desorption velocity was all accelerated with the increase of temperature in the three media. The results showed that the increasing temperature accelerates the desorption of copper, means, the copper desorption amount per unit time increases. Table 3 shows that the desorption amount of simulated gastric fluid at 37°C (0.9096 μg/g) was higher than that at 18°C (0.8465 μg/g). In other words, the exposure risk of desorption of PS microplastics carrying Cu(II) in warm-blooded organisms was higher than that in cold-blooded organisms. However, compared with the water environment, the effect of temperature on simulated gastric fluid desorption was very small. The desorption quantity increased by about two times from 0.1177 to 0.2138 μg/g in Milli-Q water with the temperature increasing from 18°C to 37°C, while that in artificial seawater was less than double. The results showed that the effect of temperature on the desorption in fresh water was greater than that in seawater. This study confirmed the effect of temperature on desorption, that is, increasing temperature is beneficial to enhance desorption. These results were similar to a previous study where it was found high temperature slightly enhanced the desorption of pharmaceuticals in gastric and intestinal fluid (Fan et al. 2021).

3.2.3 Desorption Isotherms of Cu(II) from PS Microplastics

In order to better explore the desorption, the desorption isothermal experiments were carried out and fitted by Langmuir and Freundlich isotherm models. The fitting diagrams and parameters of all these models are shown in Fig. 4 and Table 4, respectively. The correlation coefficient R^2 of the Freundlich model range from 0.8654 to 0.9758 in Milli-Q water, from 0.5516 to 0.8117 in artificial seawater, and from 0.6441 to 0.9249 in simulated gastric fluid, and these values are higher than the Langmuir model fitting values, indicating that there is a multilayer desorption process of copper on PS microplastics.

The desorption isotherm experiment of Cu(II) from PS microplastics in Milli-Q water and simulated gastric fluid were conducted after the adsorption isotherm experiment in Milli-Q water medium. Artificial seawater prepared with sea salt was used as the background solution in the simulated seawater medium adsorption and desorption experiments. Through the Freundlich model, it can be found that the $K_F{}^d$ value in Milli-Q water was larger than the corresponding value in simulated gastric fluid, which possibly because of the high affinity of Cu(II) and PS microplastics in Milli-Q water than that of simulated gastric fluid, that is, the desorption degree of Cu(II) from PS microplastics in Milli-Q water was relatively lower. According to the desorption concentration $C_e{}^d$,

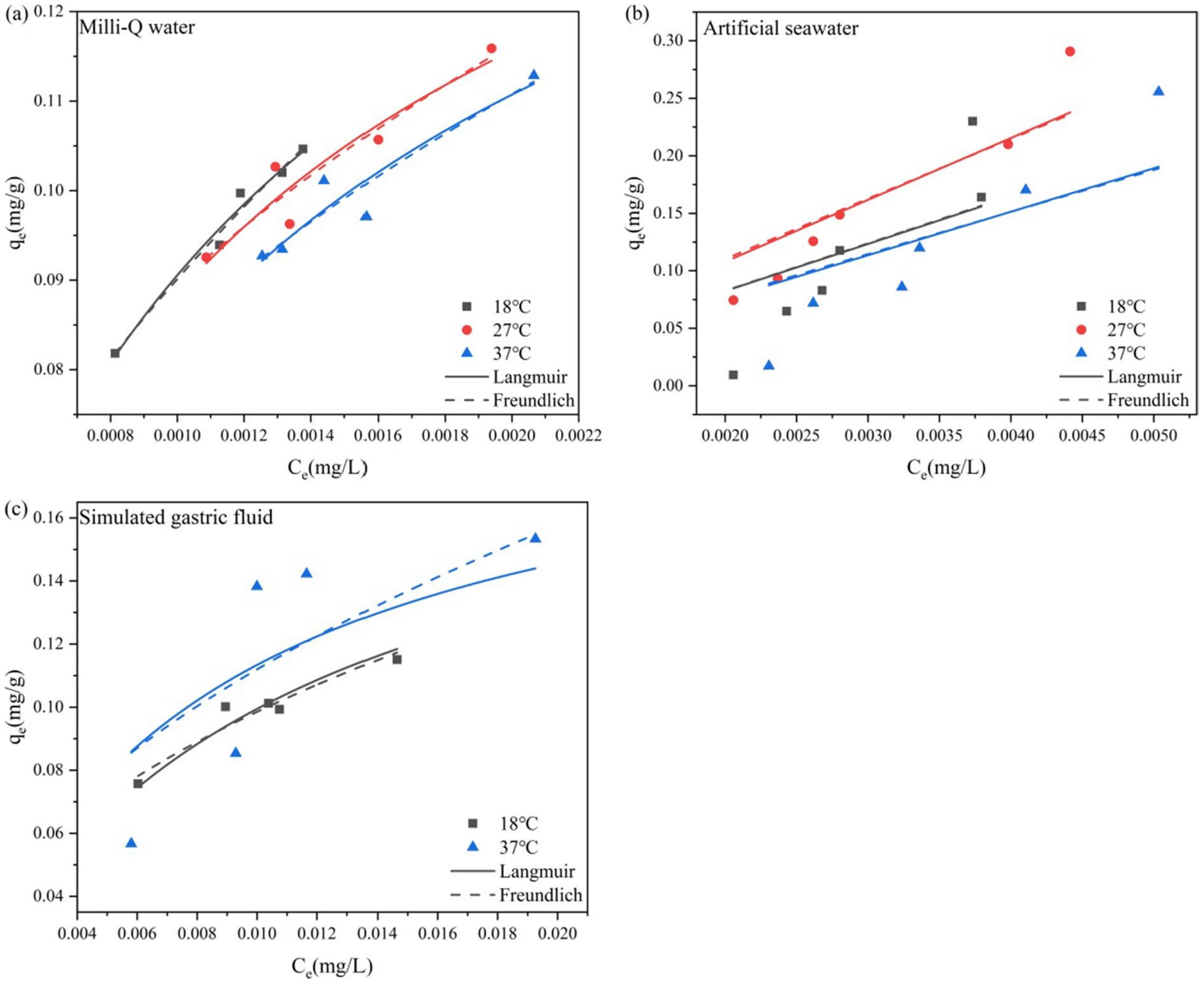

Fig. 4 Desorption isotherm of Cu(II) by PS at different temperatures in **a** Milli-Q water, **b** artificial seawater, and **c** simulated gastric fluid at different temperatures

Table 4 Desorption isothermal fitting parameters in three environmental media at different temperatures

Model	Parameter	Milli-Q water			Artificial seawater			Simulated gastric fluid	
		18°C	27°C	37°C	18°C	27°C	37°C	18°C	37°C
Langmuir	$K_L{}^d$(g/mg)	1065.91	1125.81	975.545	0.5669	0.8366	0.4048	122.078	126.239
	$q_m{}^d$(mg/g)	0.1754	0.1669	0.1674	72.670	64.587	93.635	0.2011	0.2032
	R^2	0.9745	0.8577	0.8549	0.4386	0.7852	0.5875	0.9181	0.6294
Freundlich	$K_F{}^d$(mg$^{-1/n}$·L$^{-1/n}$g^{-1})	2.3202	1.2103	1.2250	41.240	43.539	31.3008	0.8097	1.0894
	1/n	0.4702	0.3768	0.3866	0.9998	0.9621	0.9657	0.4573	0.5940
	R^2	0.9758	0.8717	0.8654	0.5516	0.8117	0.6537	0.9249	0.6441

it was found that the copper concentration of desorption in artificial seawater was greater than that of Milli-Q water, which was consistent with the above desorption kinetic results. However, the values of $K_F{}^d$ showed that $K_F{}^d$ (artificial seawater) > $K_F{}^d$ (Milli-Q water), it suggests that the desorption intensity in artificial seawater is weaker than that in Milli-Q water (Wu et al. 2020). It may be the result that the affinity of PS microplastics after adsorption of copper ions in artificial seawater is stronger than that in Milli-Q water (as described in "Section 3.1"). Therefore, in addition to the influence of initial desorption medium, desorption may also be related to the initial adsorption medium. Moreover, the influence of adsorption medium is greater than the desorption medium on desorption. In addition, at the same temperature $K_F{}^d$ (Milli-Q water) > $K_F{}^d$ (simulated gastric fluid) > K_F (Milli-Q water), and $K_F{}^d$ (artificial seawater) > K_F (artificial seawater), indicating the existence of desorption hysteresis in Milli-Q water, simulated gastric fluid, and artificial seawater environments (Wu et al. 2020).

3.3 Hysteresis Analysis

The desorption hysteresis of PS microplastics to copper was observed in three environmental media. The desorption hysteresis coefficient (HI) for the desorption isotherms of Cu(II) from the microplastics was calculated using the Freundlich model (Ma et al. 2017). Theoretically, HI > 0 means that the adsorption is irreversible and hysteresis occurs; if HI < 0 indicates that adsorption is completely reversible and there is no desorption hysteresis (Zuo et al. 2019). As shown in Table 5, the values of HI > 0 in Milli-Q water, artificial seawater, and simulated gastric fluid environmental media. What's more, the HI values of in three environments were large than 1. It means that Cu(II) was greatly affected by desorption hysteresis, which occurred significant irreversible hysteresis during the desorption processes all in Milli-Q water, simulated gastric fluid, and artificial seawater environments. The desorption capacity of PS microplastics as a carrier for copper is very low. Additionally, the HI values in artificial seawater > Milli-Q water > simulated gastric fluid mean that the desorption hysteresis exists obviously in artificial seawater. This is inconsistent with the results of desorption kinetics, which may be due to the fact that the influence of adsorption medium is greater than the desorption medium on desorption. What's more, in the same desorption background solution, it was found that the values of HI decreased with the temperature rising, suggesting the desorption ability was enhanced by high temperature. This result was also illustrated in the desorption kinetics.

Table 5 Desorption hysteresis index (HI) in three environmental media at different temperatures

	Milli-Q water	Artificial seawater	Simulated gastric fluid
18°C	13.9	98.5	4.20
27°C	5.17	59.8	-
37°C	4.61	38.0	3.99

3.4 Effect of Sediment Particles on Desorption

Besides microplastic particles, sediment particles can also act as the carrier of contaminant, producing in adsorption-desorption effect on contaminant

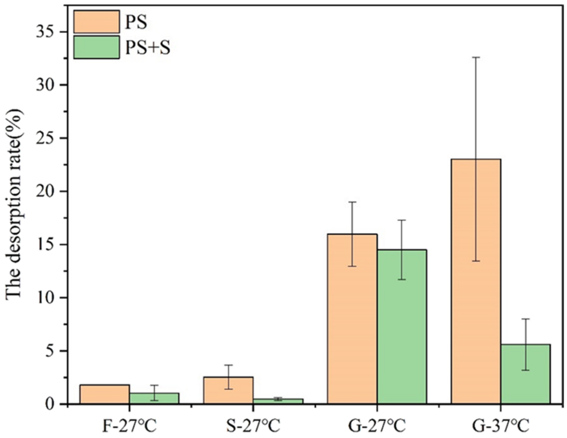

Fig. 5 Desorption rates of copper in Milli-Q water at 27°C (F-27°C), artificial seawater at 27°C (S-27°C), simulated gastric fluid at 27°C (G-27°C), and simulated gastric fluid at 37°C (G-37°C) under coexistence of PS, PS + S

(Kaeseberg et al. 2018; Yu et al. 2022). In addition, the co-existence of the two can also be swallowed by organisms with sediment filter feeding, into the organism (Van Cauwenberghe et al. 2015). In this study, the effect of sediment particles on microplastic desorption in Milli-Q water, artificial seawater, and simulated gastric fluid was explored by adding sediment particles to copper-laden microplastics. The results are shown in Fig. 5. The desorption percentage of Cu(II) after the addition of sediment particles was significantly reduced in all media, possibly due to the sediment contains various organic and inorganic components, which have strong adsorption capacity for metal ions, resulting in a higher adsorption velocity than the desorption velocity, so that part of the desorption copper in the solution is adsorbed on the sediment particles. It showed that the copper on the microplastics was transferred to the sediment, increasing the accumulation of pollutants in the sediment. The presence of a large number of sediment particles reduced the bioavailability and toxic effects of metals in microplastics, but posed additional risks to the sediment system.

What's more, with the addition of sediment particles, the desorption percentage in different environmental media were relatively decreased by 42.1% (Milli-Q at 27°C), 81.3% (artificial seawater at 27°C), 9.2% (simulated gastric fluid at 27°C), and 75.7% (simulated gastric fluid at 37°C), respectively. It was observed that the effect of sediment particles on the desorption of copper from PS microplastics in artificial seawater was greater than that in Milli-Q water and simulated gastric fluid. Furthermore, the influence of sediment particles on desorption increased with the rise of temperature in simulated gastric fluid medium. Therefore, compared to cold-blooded organisms, the sediment particles possibly have a significant effect on the desorption of copper from microplastics in the simulated gastric fluid of warm-blooded organisms. In addition, at the same temperature, the relatively decreased of desorption percentages in artificial seawater is higher than Milli-Q water. Therefore, it was speculated that when contaminated microplastics migrate from freshwater sediments to Marine sediment environments, they will increase the migration of pollutants of Marine sediments and bring greater risks to the Marine environment.

4 Conclusions

Microplastics are carriers of pollutants because of their unique surface properties. In this study, the desorption behavior of PS microplastics for copper in different environments was mainly explored. The results of batch experiments showed that the desorption of Cu(II) from PS microplastics was rapid and occurred within 120 min in Milli-Q water and artificial seawater. Specially, the simulated gastric fluid reached equilibrium in 15 min. Cu(II) desorption from the PS microplastics could be well fitted by the pseudo-second-order kinetics and the Freundlich isotherm models. The desorption velocity of copper on PS follows: simulate simulated gastric fluid > Milli-Q water > artificial seawater. Desorption quantity in the following order: simulated gastric fluid > artificial seawater > Milli-Q water. The desorption capacity of PS microplastics as a carrier for copper is very low in water environment, indicating that Cu^{2+} ions can be transported over long distances with microplastics, increasing the migration of metal pollutants. Desorption hysteresis phenomena occurred in all three environments matrices. Moreover, the influence of adsorption medium is greater than the desorption medium on desorption. More copper ions were released in gastric fluid, which leads to greater biotoxicity. What's more, temperature increase was beneficial to improve the desorption of copper by PS, and the exposure risk of Cu(II) in warm-blooded animals was higher than that in cold-blooded animals. In addition, the presence of sediment particles had a significant effect on desorption, which would reduce the desorption ratio.

Author Contribution All authors contributed to the study conception and design. Ruixin Zhang: investigation, material preparation, data collection and analysis, writing—original draft, writing review and editing. Zhaoyin Li: investigation, material preparation, formal analysis. Xi Gao: investigation, material preparation, formal analysis. Silu Chang: investigation, material preparation. Bo Yan: methodology, resources, writing—review and editing, supervision, project administration, funding acquisition. Guangbi Li: methodology, resources, funding acquisition.

Data Availability All data generated or analyzed during this study are included in this published article.

Declarations

Ethical Approval Not applicable.

Consent to Participate Not applicable.

Consent to Publish Not applicable.

Competing Interests The authors declare no competing interests.

References

Allen, S., Allen, D., Phoenix, V. R., Le Roux, G., Durántez Jiménez, P., Simonneau, A., Binet, S., & Galop, D. (2019). Atmospheric transport and deposition of microplastics in a remote mountain catchment. *Nature Geoscience, 12*, 339–344. https://doi.org/10.1038/s41561-019-0335-5

Andrady, A. L., & Neal, M. A. (2009). Applications and societal benefits of plastics. *Philosophical Transactions of the Royal Society B: Biological Sciences, 364*, 1977–1984. https://doi.org/10.1098/rstb.2008.0304

Ashton, K., Holmes, L., & Turner, A. (2010). Association of metals with plastic production pellets in the marine environment. *Marine Pollution Bulletin, 60*, 2050–2055. https://doi.org/10.1016/j.marpolbul.2010.07.014

Atamanalp, M., Kokturk, M., Ucar, A., Duyar, H. A., Ozdemir, S., Parlak, V., Esenbuga, N., & Alak, G. (2021). Microplastics in tissues (brain, gill, muscle and gastrointestinal) of Mullus barbatus and Alosa immaculata. *Archives of Environmental Contamination and Toxicology, 81*, 460–469. https://doi.org/10.1007/s00244-021-00885-5

Atugoda, T., Wijesekara, H., Werellagama, D. R. I. B., Jinadasa, K. B. S. N., Bolan, N. S., & Vithanage, M. (2020). Adsorptive interaction of antibiotic ciprofloxacin on polyethylene microplastics: Implications for vector transport in water. *Environmental Technology & Innovation, 19*, 100971. https://doi.org/10.1016/j.eti.2020.100971

Bakir, A., Rowland, S. J., & Thompson, R. C. (2014a). Enhanced desorption of persistent organic pollutants from microplastics under simulated physiological conditions. *Environmental Pollution, 185*, 16–23. https://doi.org/10.1016/j.envpol.2013.10.007

Bakir, A., Rowland, S. J., & Thompson, R. C. (2014b). Transport of persistent organic pollutants by microplastics in estuarine conditions. *Estuarine, Coastal and Shelf Science, 140*, 14–21. https://doi.org/10.1016/j.ecss.2014.01.004

Botterell, Z. L. R., Beaumont, N., Dorrington, T., Steinke, M., Thompson, R. C., & Lindeque, P. K. (2019). Bioavailability and effects of microplastics on marine zooplankton: A review. *Environmental Pollution, 245*, 98–110. https://doi.org/10.1016/j.envpol.2018.10.065

Chen, X. J., Ma, J. J., Yu, R. L., Hu, G. R., & Yan, Y. (2022). Bioaccessibility of microplastic-associated heavy metals using an in vitro digestion model and its implications for human health risk assessment. *Environmental Science and Pollution Research, 29*, 76983–76991. https://doi.org/10.1007/s11356-022-20983-8

Cole, M., Lindeque, P., Fileman, E., Halsband, C., Goodhead, R., Moger, J., & Galloway, T. S. (2013). Microplastic ingestion by zooplankton. *Environmental Science & Technology, 47*, 6646–6655. https://doi.org/10.1021/es400663f

Convention EP. (2013). Gastric juice, artificial. *European Pharmacopoeia 11.0, Europe, 555*, 1039900.

Craig, P. M., Wood, C. M., & McClelland, G. B. (2007). Oxidative stress response and gene expression with acute copper exposure in zebrafish (Danio rerio). *American Journal of Physiology-Regulatory, Integrative and Comparative Physiology, 293*, R1882–R1892. https://doi.org/10.1152/ajpregu.00383.2007

Ding, Y., Zhang, R., Li, B., Du, Y., Li, J., Tong, X., Wu, Y., Ji, X., & Zhang, Y. (2021). Tissue distribution of polystyrene nanoplastics in mice and their entry, transport, and cytotoxicity to GES-1 cells. *Environmental Pollution, 280*, 116974. https://doi.org/10.1016/j.envpol.2021.116974

Eerkes-Medrano, D., Thompson, R. C., & Aldridge, D. C. (2015). Microplastics in freshwater systems: a review of the emerging threats, identification of knowledge gaps and prioritisation of research needs. *Water Research, 75*, 63–82. https://doi.org/10.1016/j.watres.2015.02.012

Fan, X., Gan, R., Liu, J., Xie, Y., Xu, D., Xiang, Y., Su, J., Teng, Z., & Hou, J. (2021). Adsorption and desorption behaviors of antibiotics by tire wear particles and polyethylene microplastics with or without aging processes. *Science of the Total Environment, 771*, 145451. https://doi.org/10.1016/j.scitotenv.2021.145451

Galloway, T. S., Cole, M., & Lewis, C. (2017). Interactions of microplastic debris throughout the marine ecosystem. *Nature Ecology and Evolution, 1*, 116. https://doi.org/10.1038/s41559-017-0116

Godoy, V., Blazquez, G., Calero, M., Quesada, L., & Martin-Lara, M. A. (2019). The potential of microplastics as carriers of metals. *Environmental Pollution, 255*, 113363. https://doi.org/10.1016/j.envpol.2019.113363

Guo, X., Pang, J., Chen, S., & Jia, H. (2018a). Sorption properties of tylosin on four different microplastics. *Chemosphere, 209*, 240–245. https://doi.org/10.1016/j.chemosphere.2018.06.100

Guo, X. T., Pang, J. W., Chen, S. Y., & Jia, H. Z. (2018b). Sorption properties of tylosin on four different microplastics.

Chemosphere, 209, 240–245. https://doi.org/10.1016/j.chemosphere.2018.06.100

Hameed, B. H., & Rahman, A. A. (2008). Removal of phenol from aqueous solutions by adsorption onto activated carbon prepared from biomass material. *Journal of Hazardous Materials, 160*, 576–581. https://doi.org/10.1016/j.jhazmat.2008.03.028

Hodson, M. E., Duffus-Hodson, C. A., Clark, A., Prendergast-Miller, M. T., & Thorpe, K. L. (2017). Plastic bag derived-microplastics as a vector for metal exposure in terrestrial invertebrates. *Environmental Science & Technology, 51*, 4714–4721. https://doi.org/10.1021/acs.est.7b00635

Holland, E. R., Mallory, M. L., & Shutler, D. (2016). Plastics and other anthropogenic debris in freshwater birds from Canada. *Science of the Total Environment, 571*, 251–258. https://doi.org/10.1016/j.scitotenv.2016.07.158

Hu, M., & Palic, D. (2020). Micro- and nano-plastics activation of oxidative and inflammatory adverse outcome pathways. *Redox Biology, 37*, 101620. https://doi.org/10.1016/j.redox.2020.101620

Hurley, R. R., Woodward, J. C., & Rothwell, J. J. (2017). Ingestion of microplastics by freshwater tubifex worms. *Environmental Science & Technology, 51*, 12844–12851. https://doi.org/10.1021/acs.est.7b03567

Iyare, P. U., Ouki, S. K., & Bond, T. (2020). Microplastics removal in wastewater treatment plants: A critical review. *Environmental Science: Water Research & Technology, 6*, 2664–2675. https://doi.org/10.1039/d0ew00397b

Jin, Y., Xia, J., Pan, Z., Yang, J., Wang, W., & Fu, Z. (2018). Polystyrene microplastics induce microbiota dysbiosis and inflammation in the gut of adult zebrafish. *Environmental Pollution, 235*, 322–329. https://doi.org/10.1016/j.envpol.2017.12.088

Kabbashi, N. A., Atieh, M. A., Al-Mamun, A., Mirghami, M. E. S., Alam, M. D. Z., & Yahya, N. (2009). Kinetic adsorption of application of carbon nanotubes for Pb(II) removal from aqueous solution. *Journal of Environmental Sciences, 21*, 539–544. https://doi.org/10.1016/s1001-0742(08)62305-0

Kaeseberg, T. Z. J., Schubert, S., et al. (2018). Sewer sediment-bound antibiotics as a potential environmental risk: Adsorption and desorption affinity of 14 antibiotics and one metabolite. *Environmental pollution, 239*, 638–647. https://doi.org/10.1016/j.envpol.2018.04.075

Kay, P., Hiscoe, R., Moberley, I., Bajic, L., & McKenna, N. (2018). Wastewater treatment plants as a source of microplastics in river catchments. *Environmental Science and Pollution Research, 25*, 20264–20267. https://doi.org/10.1007/s11356-018-2070-7

Kwon, B. G., Chung, S. Y., Park, S. S., & Saido, K. (2018). Qualitative assessment to determine internal and external factors influencing the origin of styrene oligomers pollution by polystyrene plastic in coastal marine environments. *Environmental Pollution, 234*, 167–173. https://doi.org/10.1016/j.envpol.2017.11.046

Lang, M., Yu, X., Liu, J., Xia, T., Wang, T., Jia, H., & Guo, X. (2020). Fenton aging significantly affects the heavy metal adsorption capacity of polystyrene microplastics. *Science of the Total Environment, 722*, 137762. https://doi.org/10.1016/j.scitotenv.2020.137762

Law, K. L., & Thompson, R. C. (2014). Oceans. Microplastics in the seas. *Science, 345*, 144–145. https://doi.org/10.1126/science.1254065

Linder, M. C., & Hazegh-Azam, M. (1996). Copper biochemistry and molecular biology. *American Journal of Clinical Nutrition, 63*, 797S–811S. https://doi.org/10.1093/ajcn/63.5.797

Liu, C. K., Zhao, X. X., Fang, L., & Yue, X. F. (2012). Copper ion desorption performance from triethylenetetramine-functionalized polymeric adsorbents. *Advanced Materials Research, 518-523*, 709–714. https://doi.org/10.4028/www.scientific.net/AMR.518-523.709

Liu, G., Zhu, Z., Yang, Y., Sun, Y., Yu, F., & Ma, J. (2019). Sorption behavior and mechanism of hydrophilic organic chemicals to virgin and aged microplastics in freshwater and seawater. *Environmental Pollution, 246*, 26–33. https://doi.org/10.1016/j.envpol.2018.11.100

Liu, J., Ma, Y., Zhu, D., Xia, T., Qi, Y., Yao, Y., Guo, X., Ji, R., & Chen, W. (2018). Polystyrene nanoplastics-enhanced contaminant transport: role of irreversible adsorption in glassy polymeric domain. *Environmental Science & Technology, 52*, 2677–2685. https://doi.org/10.1021/acs.est.7b05211

Liu, J., Zhang, T., Tian, L., Liu, X., Qi, Z., Ma, Y., Ji, R., & Chen, W. (2019). Aging significantly affects mobility and contaminant-mobilizing ability of nanoplastics in saturated loamy sand. *Environmental Science & Technology, 53*, 5805–5815. https://doi.org/10.1021/acs.est.9b00787

Liu, P., Wu, X., Liu, H., Wang, H., Lu, K., & Gao, S. (2020). Desorption of pharmaceuticals from pristine and aged polystyrene microplastics under simulated gastrointestinal conditions. *Journal of Hazardous Materials, 392*, 122346. https://doi.org/10.1016/j.jhazmat.2020.122346

Liu, X. J., Luo, Z., Xiong, B. X., Liu, X., Zhao, Y. H., Hu, G. F., & Lv, G. J. (2010). Effect of waterborne copper exposure on growth, hepatic enzymatic activities and histology in Synechogobius hasta. *Ecotoxicology and Environmental Safety, 73*, 1286–1291. https://doi.org/10.1016/j.ecoenv.2010.06.019

Lu, K., Qiao, R., An, H., & Zhang, Y. (2018). Influence of microplastics on the accumulation and chronic toxic effects of cadmium in zebrafish (Danio rerio). *Chemosphere, 202*, 514–520. https://doi.org/10.1016/j.chemosphere.2018.03.145

Ma, J., Zhao, J., Zhu, Z., Li, L., & Yu, F. (2019). Effect of microplastic size on the adsorption behavior and mechanism of triclosan on polyvinyl chloride. *Environmental Pollution, 254*, 113104. https://doi.org/10.1016/j.envpol.2019.113104

Ma, L., Southwick, L. M., Willis, G. H., & Selim, H. M. (2017). Hysteretic characteristics of atrazine adsorption-desorption by a sharkey soil. *Weed Science, 41*, 627–633. https://doi.org/10.1017/s0043174500076438

McDougall, L., Thomson, L., Brand, S., Wagstaff, A., Lawton, L. A., & Petrie, B. (2022). Adsorption of a diverse range of pharmaceuticals to polyethylene microplastics in wastewater and their desorption in environmental matrices. *Science of the Total Environment, 808*, 152071. https://doi.org/10.1016/j.scitotenv.2021.152071

Min, K., Cuiffi, J. D., & Mathers, R. T. (2020). Ranking environmental degradation trends of plastic marine debris based on physical properties and molecular structure. *Nature Communications, 11*, 727. https://doi.org/10.1038/s41467-020-14538-z

Munier, B., & Bendell, L. I. (2018). Macro and micro plastics sorb and desorb metals and act as a point source of trace metals to coastal ecosystems. *PLoS One, 13*, e0191759. https://doi.org/10.1371/journal.pone.0191759

Nelms, S. E., Galloway, T. S., Godley, B. J., Jarvis, D. S., & Lindeque, P. K. (2018). Investigating microplastic trophic transfer in marine top predators. *Environmental Pollution, 238*, 999–1007. https://doi.org/10.1016/j.envpol.2018.02.016

Ogata, Y., et al. (2009). International Pellet Watch: Global monitoring of persistent organic pollutants (POPs) in coastal waters. 1. Initial phase data on PCBs, DDTs, and HCHs. *Marine Pollution Bulletin, 58*, 1437–1446. https://doi.org/10.1016/j.marpolbul.2009.06.014

Rios, L. M., Moore, C., & Jones, P. R. (2007). Persistent organic pollutants carried by synthetic polymers in the ocean environment. *Marine Pollution Bulletin, 54*, 1230–1237. https://doi.org/10.1016/j.marpolbul.2007.03.022

Rochman, C. M., Hoh, E., Kurobe, T., & Teh, S. J. (2013). Ingested plastic transfers hazardous chemicals to fish and induces hepatic stress. *Scientific Reports, 3*, 3263. https://doi.org/10.1038/srep03263

Rochman, C. M., Kurobe, T., Flores, I., & Teh, S. J. (2014). Early warning signs of endocrine disruption in adult fish from the ingestion of polyethylene with and without sorbed chemical pollutants from the marine environment. *Science of the Total Environment, 493*, 656–661. https://doi.org/10.1016/j.scitotenv.2014.06.051

Sanchez, W., Bender, C., & Porcher, J. M. (2014). Wild gudgeons (Gobio gobio) from French rivers are contaminated by microplastics: preliminary study and first evidence. *Environmental Research, 128*, 98–100. https://doi.org/10.1016/j.envres.2013.11.004

Santos, D., Felix, L., Luzio, A., Parra, S., Bellas, J., & Monteiro, S. M. (2021). Single and combined acute and subchronic toxic effects of microplastics and copper in zebrafish (Danio rerio) early life stages. *Chemosphere, 277*, 130262. https://doi.org/10.1016/j.chemosphere.2021.130262

Scherer, C., Weber, A., Lambert, S., & Wagner, M. (2018). Interactions of microplastics with freshwater biota, freshwater microplastics. In *The Handbook of Environmental Chemistry* (pp. 153–180). Springer. https://doi.org/10.1007/978-3-319-61615-5_8

Schwabl, P., Koppel, S., Konigshofer, P., Bucsics, T., Trauner, M., Reiberger, T., & Liebmann, B. (2019). Detection of various microplastics in human stool: A prospective case series. *Annals of Internal Medicine, 171*, 453–457. https://doi.org/10.7326/M19-0618

Steer, M., Cole, M., Thompson, R. C., & Lindeque, P. K. (2017). Microplastic ingestion in fish larvae in the western English Channel. *Environmental Pollution, 226*, 250–259. https://doi.org/10.1016/j.envpol.2017.03.062

Tanaka, K., Takada, H., Yamashita, R., Mizukawa, K., Fukuwaka, M. A., & Watanuki, Y. (2015). Facilitated leaching of additive-derived PBDEs from plastic by seabirds' stomach oil and accumulation in tissues. *Environmental Science & Technology, 49*, 11799–11807. https://doi.org/10.1021/acs.est.5b01376

Tang, S., Lin, L., Wang, X., Sun, X., & Yu, A. (2021a). Adsorption of fulvic acid onto polyamide 6 microplastics: Influencing factors, kinetics modeling, site energy distribution and interaction mechanisms. *Chemosphere, 272*, 129638. https://doi.org/10.1016/j.chemosphere.2021.129638

Tang, S., Lin, L., Wang, X., Yu, A., & Sun, X. (2021b). Interfacial interactions between collected nylon microplastics and three divalent metal ions (Cu(II), Ni(II), Zn(II)) in aqueous solutions. *Journal of Hazardous Materials, 403*, 123548. https://doi.org/10.1016/j.jhazmat.2020.123548

Teuten, E. L., et al. (2009). Transport and release of chemicals from plastics to the environment and to wildlife. *Philosophical Transactions of the Royal Society B: Biological Sciences, 364*, 2027–2045. https://doi.org/10.1098/rstb.2008.0284

Thompson, R. C., Olsen, Y., Mitchell, R. P., Davis, A., Rowland, S. J., John, A. W., McGonigle, D., & Russell, A. E. (2004). Lost at sea: where is all the plastic? *Science, 304*, 838. https://doi.org/10.1126/science.1094559

Van Cauwenberghe, L., Claessens, M., Vandegehuchte, M. B., Janssen, C. R., et al. (2015). Microplastics are taken up by mussels (Mytilus edulis) and lugworms (Arenicola marina) living in natural habitats. *Environmental pollution, 199*, 10–17. https://doi.org/10.1016/j.envpol.2015.01.008

van Sebille, E., Wilcox, C., Lebreton, L., Maximenko, N., Hardesty, B. D., van Franeker, J. A., Eriksen, M., Siegel, D., Galgani, F., & Law, K. L. (2015). A global inventory of small floating plastic debris. *Environmental Research Letters, 10*, 124006. https://doi.org/10.1088/1748-9326/10/12/124006

von Moos, N., Burkhardt-Holm, P., & Kohler, A. (2012). Uptake and effects of microplastics on cells and tissue of the blue mussel Mytilus edulis L. after an experimental exposure. *Environmental Science & Technology, 46*, 11327–11335. https://doi.org/10.1021/es302332w

Voparil, I. M., & Mayer, L. M. (2000). Dissolution of sedimentary polycyclic aromatic hydrocarbons into the lugworm's (Arenicola marina) digestive fluids. *Environmental Science & Technology, 34*, 1221–1228. https://doi.org/10.1021/es990885i

Wagstaff, A., Lawton, L. A., & Petrie, B. (2022). Polyamide microplastics in wastewater as vectors of cationic pharmaceutical drugs. *Chemosphere, 288*, 132578. https://doi.org/10.1016/j.chemosphere.2021.132578

Wagstaff, A., & Petrie, B. (2022). Enhanced desorption of fluoxetine from polyethylene terephthalate microplastics in gastric fluid and sea water. *Environmental Chemistry Letters, 20*, 975–982. https://doi.org/10.1007/s10311-022-01405-0

Wang, F., Yang, W., Cheng, P., Zhang, S., Zhang, S., Jiao, W., & Sun, Y. (2019). Adsorption characteristics of cadmium onto microplastics from aqueous solutions. *Chemosphere, 235*, 1073–1080. https://doi.org/10.1016/j.chemosphere.2019.06.196

Wang, X., Zhang, R., Li, Z., & Yan, B. (2022). Adsorption properties and influencing factors of Cu(II) on polystyrene and polyethylene terephthalate microplastics in seawater.

Science of the Total Environment, 812, 152573. https://doi.org/10.1016/j.scitotenv.2021.152573

Wu, P., Cai, Z., Jin, H., & Tang, Y. (2019). Adsorption mechanisms of five bisphenol analogues on PVC microplastics. *Science of the Total Environment, 650*, 671–678. https://doi.org/10.1016/j.scitotenv.2018.09.049

Wu, P., Tang, Y., Jin, H., Song, Y., Liu, Y., & Cai, Z. (2020). Consequential fate of bisphenol-attached PVC microplastics in water and simulated intestinal fluids. *Environmental Science and Ecotechnology, 2*, 100027. https://doi.org/10.1016/j.ese.2020.100027

Wu, W., & Sun, H. (2010). Sorption-desorption hysteresis of phenanthrene--effect of nanopores, solute concentration, and salinity. *Chemosphere, 81*, 961–967. https://doi.org/10.1016/j.chemosphere.2010.07.051

Yin, Y. G. X., & Peng, D. (2018). Iron and manganese oxides modified maize straw to remove tylosin from aqueous solutions. *Chemosphere, 205*, 156–165. https://doi.org/10.1016/j.chemosphere.2018.04.108

Yu, P., Cui, H., Bai, J., Chen, G., Liu, H., Liu, Z., & Xia, J. (2022). Adsorption and desorption of Cu, Zn, Pb, and Cd on surface sediments from a shallow lake, North China. *Ecohydrology & Hydrobiology*. https://doi.org/10.1016/j.ecohyd.2022.01.002

Zhang, S., Han, B., Sun, Y., & Wang, F. (2020). Microplastics influence the adsorption and desorption characteristics of Cd in an agricultural soil. *Journal of Hazardous Materials, 388*, 121775. https://doi.org/10.1016/j.jhazmat.2019.121775

Zhang, X., Chen, J., & Li, J. (2020). The removal of microplastics in the wastewater treatment process and their potential impact on anaerobic digestion due to pollutants association. *Chemosphere, 251*, 126360. https://doi.org/10.1016/j.chemosphere.2020.126360

Zhou, Y., Yang, Y., Liu, G., He, G., & Liu, W. (2020). Adsorption mechanism of cadmium on microplastics and their desorption behavior in sediment and gut environments: The roles of water pH, lead ions, natural organic matter and phenanthrene. *Water Research, 184*, 116209. https://doi.org/10.1016/j.watres.2020.116209

Zou, J., Liu, X., Zhang, D., & Yuan, X. (2020). Adsorption of three bivalent metals by four chemical distinct microplastics. *Chemosphere, 248*, 126064. https://doi.org/10.1016/j.chemosphere.2020.126064

Zuo, L. Z., Li, H. X., Lin, L., Sun, Y. X., Diao, Z. H., Liu, S., Zhang, Z. Y., & Xu, X. R. (2019). Sorption and desorption of phenanthrene on biodegradable poly(butylene adipate co-terephtalate) microplastics. *Chemosphere, 215*, 25–32. https://doi.org/10.1016/j.chemosphere.2018.09.173