Insights into the Adsorption of Copper/Zinc Ions over Aged Polyethylene and Polyethylene Terephthalate Microplastics

Mengyu Ma, Feihu Li*

School of Environmental Science and Engineering, Nanjing University of Information Science and Technology, 219 Ningliu Road, Nanjing 210044, China.

E-mail: <u>fhli@nuist.edu.cn</u> ORCID: <u>https://orcid.org/0000-0002-2969-8276</u>

Abstract: Microplastics (MPs) have aroused growing environmental concerns due to their biotoxicity and vital roles in accelerating the spread of toxic elements. Illuminating the interactions between MPs and heavy metals (HMs) is crucial for understanding the transport and fate of HM-loaded MPs in specific environmentally relevant scenarios. Herein, the adsorption of copper (Cu^{2+}) and zinc (Zn^{2+}) ions over polyethylene (PE) and polyethylene terephthalate (PET) particulates before and after heat persulfate oxidation (HPO) treatment was comprehensively evaluated in simulated swine wastewater. The effects of intrinsic properties (i.e., degree of weathering, size, type) of MPs and environmental factors (i.e., pH, ionic strength, and co-occurring species) on adsorption were investigated thoroughly. It was observed that HPO treatment expedites the fragmentation of pristine MPs, and renders MPs with a variety of oxygen-rich functional groups, which are likely to act as new active sites for binding both HMs. The adsorption of both HMs is pH- and ionic strength-dependent at a pH of 4 to 6. Co-occurring species such as humic acid (HA) and tetracycline (TC) appear to enhance the affinity of both aged MPs for Cu^{2+} and Zn^{2+} ions via bridging complexation. However, co-occurring nutrient species (e.g., phosphate and ammonia) demonstrate different impacts on the adsorption, improving uptake of Cu^{2+} by precipitation while lowering affinity for Zn^{2+} owing to the formation of soluble zinc-ammonia complex. Spectroscopic analysis indicates that the dominant adsorption mechanism mainly involves electrostatic interactions and surface complexation. These findings provided fundamental insights into the interactions between aged MPs and HMs in an environmentally relevant scenario (i.e., simulated swine wastewater).

1. Introduction

Plastic debris wastes, in particular microplastics (MPs, < 5 mm in diameter) are omnipresent in both the terrestrial and the aquatic environments 1-3. Nearly 2.41 million metric tons of microplastics enter the ocean from rivers annually, and the amount is believed to increase in the future $\frac{4}{2}$. A recent projection suggests that approximately 12 billion metric tons of plastic waste will be disposed of or released into the natural environment by 2050 if no interventions are implemented in the current plastic production and waste management policies $\frac{5}{2}$. Such a staggering emission of plastic waste has been posing significant threats and disruptions to the ecosystems and habitats of our planet for decades due to the biotoxicity and the crucial roles of MPs in spreading and enriching toxic substances (e.g., heavy metals (HMs) and organic pollutants), particularly into the food web 6-7. Specifically, the ability to bind such toxics of MPs endows them with a potential carrier for transporting these pollutants upward the food chain, leading to health concerns of bioaccumulation and biomagnification, in particular for human beings.

A growing body of evidence indicates that MPs from livestock farms or fallow lands to natural areas were often consumed as food by livestock and wide animals $\frac{8\cdot11}{1}$, rendering livestock meat and prey meat a critical exposure pathway of microplastics $\frac{12}{12}$. This is particularly concerning given that many toxic contaminants, such as antibiotic resistance genes (ARGs), HMs, and organic toxins, accompanied frequently with MPs in livestock farms $\frac{10\cdot11}{13}$, and that MPs can act as a vector of spreading such pollutants to our food web $\frac{12\cdot13}{12}$. Microplastics have been detected in various poultry and livestock meats $\frac{12}{14}$, raising biotoxicity concerns beyond microplastics themselves. The binding between MPs and heavy metals under a wide range of environmentally relevant conditions has been extensively explored so far $\frac{15\cdot23}{12}$. Apart from many environmental factors (e.g., pH, natural organic matter (NOM), and salinity), the inherent properties of MPs, such as small size, hydrophobicity, high surface area, and abundant surface functional groups, are believed to facilitate the adsorption of heavy metals on MPs 15-16.22.

Natural and anthropogenic weathering or degradation can greatly alter the surface properties of MPs, thereby affecting their affinity toward HMs 17-21. For instance, it was found that the adsorption potential of MPs for cadmium ions (Cd2+) was significantly improved after being biodegraded in a traditional wastewater treatment process 17. Besides, biofilms formed on MPs can promote their uptake of heavy meals due to the much greater abundance of functional groups (e.g., carboxyl, amino, and phenyl-OH) within the biofilms, which often show higher affinity for heavy metals $\frac{18}{24}$. It was also reported that the adsorption capacity of four aged MPs for copper (Cu²⁺) and Cd²⁺ ions from seawater was remarkedly enhanced after being weathered by Ultraviolet (UV) irradiation for 3 months $\frac{25}{25}$. However, most of the above studies focused on marine environments or sewage treatment scenarios $\frac{26}{2}$. Few works involved in the interaction between aged MPs and HMs in environmentally relevant scenarios, e.g., swine or poultry wastewater, which contains a wide variety of contaminants including ARGs, HMs, tetracycline (TC), dissolved organic matters (DOMs), ammonia, and phosphate 13, 27. Swine and poultry effluents are rich in nutrients and thus often applied as a crucial secondary source for phosphorus recovery through struvite crystallization $\frac{28-29}{28}$. However, the interactions between aged MPs and HMs in the complex swine wastewater remain poorly understood, which is of significance to elucidate the transport and fate of the HM-MP complexes in the effluents, particularly during the struvite recovery from swine wastewater $\frac{30}{2}$

This study aims to gain insights into the specific interactions between aged MPs and HM ions (i.e., Cu^{2+} and Zn^{2+}), with emphasis on the impacts of the intrinsic properties of MPs and the cooccurring species on the adsorption. We chose two common mi-



Fig. 1. (a) Schematic illustration of the accelerated weathering treatment of pristine PE and PET pellets by heat persulfate oxidation; (b) FT-IR spectra of pristine and aged PE and PET as a function of weathering time; (c-f) Digital images of 20-day-aged PE and PET with different sizes (scale bar = 1 cm).

croplastics, polyethylene (PE) and polyethylene terephthalate (PET), as model adsorbents to study their adsorption of Cu^{2+} and Zn^{2+} in simulated swine wastewater. To investigate the effects of anthropogenic weathering or aging time on the adsorption of HMs, microplastics with different sizes (1 mm and 50 µm) were aged for 5 and 20 days by the heat persulfate oxidation method before adsorption. The adsorption kinetics and isotherms of heavy metal ions over both pristine and aged microplastics were investigated to illuminate the possible mechanisms controlling the adsorption behavior of both HMs on MPs. The effects of pH, ionic strength, co-occurring tetracycline and humic acid, and ionic competition were also evaluated. This work could provide a fundamental understanding of the roles of aged microplastics in the capture and transport of HMs in nutrient-rich wastewater.

2. Materials and Methods

2.1. Chemicals

All chemicals are of analytical grade or higher purity. Potassium persulfate ($K_2S_2O_8$, $\geq 99.5\%$), copper chloride dihydrate (CuCl₂·2H₂O, $\geq 99.0\%$), and zinc chloride (ZnCl₂, $\geq 98.0\%$) were purchased from Sinopharm Chemical Reagent C o., Ltd. (Shanghai, China). Sodium chloride (NaCl, $\geq 99.5\%$), humic acid (HA), tetracycline (TC, $\geq 98.0\%$), and magnesium ammonium phosphate hexahydrate (MgNH₄PO₄·6H₂O, $\geq 98.0\%$) were obtained from Aladdin Biochemical Technology Co., Ltd. (Shanghai, China). Pristine polyethylene (PE) and polyethylene terephthalate (PET) of *ca*. 1 mm and 50 µm in size were purchased from Wangda Plastic Material Co. (Dongguan, China). All chemicals were used as received, without further purification. Deionized (DI) water was used in the preparation of the solutions. The pH of all solutions was adjusted using sodium hydroxide or hydrochloric acid solutions.

2.2. Weathering of pristine PE and PET microplastics

To attain aged microplastics, a facile artificially accelerated weathering treatment based on the heat persulfate oxidation (HPO) method $\frac{31}{31}$ was employed to treat both pristine PE and PET. As depicted in Fig. 1a, the pristine PE and PET microplastics were aged in a three-neck flask within a thermostatic water bath at a constant temperature of 70 °C to achieve the optimal oxidation efficiency of K₂S₂O₈. An electric stirrer was used to disperse the MP particulates in 100 mM freshly prepared K₂S₂O₈ solution (pH 7.0) at a constant speed of 60 RPM, and a Graham condenser was used to prevent the loss of water during the HPO process. The $K_2S_2O_8$ solution was replaced by fresh K₂S₂O₈ solution every 12 h due to depletion of the oxidant. The MP samples were separated from the suspension every 2 days and washed 3 times with deionized water before the next cycle of oxidation to avoid the accumulation of K₂SO₄ in the mixture. After being treated consecutively for 5 or 20 days, the aged microplastics (denoted as 'MP-size-weathering time', e.g., PE-50µm-20d) were collected and washed with excessive DI water, followed by freeze-drying and storage in a glass desiccator for further tests.



Fig. 2. SEM images of (**a**) pristine PE of 50 µm, (**b**) PE-50µm-5d, (**c**) PE-50µm-20d, (**d**) pristine PET of 50 µm, (**e**) PET-50µm-5d, and (**f**) PET-50µm-20d; (**g**) schematic illustration of the morphological evolution of microplastics derived from the above SEM images.

2.3. Characterization

Fourier transform infrared spectroscopy (FT-IR) was performed by the KBr pellet method using a Nicolet iS5 spectrometer (Thermo Fisher, USA). Scanning electron microscopy (SEM) was performed using a SU1510 microscope (Hitachi, Japan) at an accelerating voltage of 1.5 kV. The zeta potential of microplastics at different pH was determined using a Zetasizer Nano ZS90 meter (Malvern Instruments Ltd., UK). X-ray fluorescence spectroscopy (XRF) analysis was performed on a DELTA DC 4000 analyzer (Olympus, USA) with soil mode. The three-dimensional (3D) excitation-emission matrix (EEM) fluorescence spectroscopy was performed on a Cary Eclipse fluorescence spectrophotometer (Agilent Technologies, Inc., USA).

2.4. Batch adsorption experiments

Adsorption experiments were performed in brown glass vials (20 mL) to avoid the effect of light on the experiments. The stock solutions (100 mg L⁻¹) of Cu²⁺ or Zn²⁺ ions were prepared individually by dissolving the desired amount of copper chloride dihydrate and zinc chloride in deionized water. All adsorption experiments were performed in triplicate at standard atmospheric pressure and ambient temperature (~20°C). The effects of microplastic type (i.e., pristine and aged PE and PET), size (1 mm and 50 µm), weathering time (0, 5, and 20 days) on adsorption were performed by adding a desired amount of MPs in 20 mL clean brawn glass

bottles containing 10 mL of 5 mg L⁻¹ Cu²⁺ or Zn²⁺ at pH 6.0±0.1 with an adsorbent dose of 1 g L⁻¹, followed by capping and mixing on a Labquake tube rotator (Thermo Scientific, USA) at 80 RPM for 48 h. Then, the microplastics were recovered by filtering through a 0.22 μ m filter, and the supernatant solution was analyzed to determine the Cu²⁺ or Zn²⁺ concentrations on a ZEEnit 700P flame atomic absorption spectrophotometer (AAS, Analytik Jena GmbH, Germany).

The adsorption capacity of these MPs toward Cu^{2+} or Zn^{2+} ions can be calculated using eq. 1:

$$q_e = \frac{(C_0 - C_e) \times V}{m} \tag{1}$$

where q_e is the adsorption capacity (mg g⁻¹), *m* is the mass of the adsorbent (g), C_0 is the initial Cu²⁺ or Zn²⁺ concentration (mg L⁻¹), C_e is the heavy metal ion concentration after 48 h of adsorption assuming equilibrium is reached, and *V* is the total volume of the solution (L).

Likewise, the effects of solution pH (3–6) and ionic strength (0.1 and 1.0 M), co-occurring species including humic acid (HA, 0–100 mg L⁻¹), tetracycline (TC, 0–20 mg L⁻¹), and magnesium ammonium phosphate (MAP, 0–150 mg L⁻¹) on adsorption of Cu²⁺ or Zn²⁺ over two representative MPs (i.e., PE-50µm-20d and PET-50µm-20d) were also investigated in the same manner described

above. Additionally, the adsorption kinetic experiments were conducted with the same adsorbent dosage over a contact time ranging from 1.0 to 144 h. The experimental data were fitted with both the pseudo-first and the pseudo-second-order models given in eqs. 2 and 3:

$$ln(q_e - q_t) = lnq_e - k_1 t \tag{2}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{3}$$

where q_1 is the adsorption capacity (mg g⁻¹) at contact time t (h), and k_1 and k_2 are the pseudo-first- and second-order rate constants, respectively. Similarly, the adsorption isotherm tests were carried out over initial Cu²⁺ or Zn²⁺ ion concentrations from 0.1 to 10 mg L⁻¹, at 20, 30, and 40 °C (i.e., 293, 303, and 313 K), respectively. The experimental data were fitted using both the Freundlich and the Langmuir models formulated in eqs. 4 and 5:

$$q_e = k_F C_e^{1/n} \tag{4}$$

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

where $\mathbf{k}_{\rm F}$ (in (mg¹⁻ⁿ Lⁿ) g⁻¹) and \mathbf{n} are the Friedrich constants, $\mathbf{k}_{\rm L}$ is the Langmuir adsorption energy constant in L mg⁻¹, and $\mathbf{q}_{\rm m}$ is the theoretical maximum adsorption in mg g⁻¹.

2.5. Mechanism study

To elucidate the mechanism underlying Cu^{2+} or Zn^{2+} ion adsorption over these aged MPs, XRF and FTIR analysis of both the 20-day-aged and the Cu2+/Zn2+-loaded MPs were performed in sequence. Besides, as three-dimensional fluorescence excitationemission matrix (3D-EEM) spectroscopy is a powerful tool for distinguishing the fluorescence characteristics of organic matter in the aqueous environment, and therefore was used here to evaluate the impact of both HA and TC on the adsorption of Cu2+ or Zn2+ ions under environmentally relevant conditions. Briefly, the supernatant from adsorption isotherm testing using PE-50µm-20d or PET-50µm-20d as the adsorbent was employed for EEM testing on a Cary Eclipse fluorescence spectrophotometer. The excitation and emission slits were fixed at 10 nm. The excitation wavelength ranges from 200 to 500 nm versus the emission wavelength from 250 to 600 nm. The scanning speed was 1200 nm/min with a wavelength increment of 5 nm. For comparison, the EEM spectrum data of dilute HA and TC solution in the presence or absence of minor Cu²⁺ or Zn²⁺ ions were also collected and analyzed.

3. Results and Discussions

3.1. Characterization of pristine and aged MPs

FT-IR analysis is often used to examine the surface functional groups and properties of MPs. Fig. 1b depicts the FT-IR spectra of PE and PET microplastics before and after HPO treatment for different periods. The characteristic FT-IR absorption bands of the pristine PE at 2923, 2853, and 718 cm⁻¹ are attributable to the C-H stretching vibration, which was also observed at 2970, 2923, and 718 cm⁻¹ for the pristine PET ³². Besides, the C-H bending vibration of both MPs was also detected at 1468 cm⁻¹. Note that the intensity of these absorption bands shows a distinct positive correlation with the weathering time, with the same bands of greater intensity upon weathering for a longer period. This is indicative of fragmentation of the pristine PE by the HPO treatment, which has also been observed earlier $\frac{31}{2}$. Interestingly, a new carbonyl absorption peak at 1713 cm⁻¹ (vc=o) occurred on the aged PE with the same trend of the C-H bonds, indicating that the PE microplastics were oxidized and grafted with oxygen-containing Both pristine PE and PET microplastics are plain white (data not shown), regardless of their particle size. However, the aged MPs, particularly those of 50 µm in size, became slightly pale yellow after a continuous HPO treatment for 20 days (Fig. 1c-f), indicative of changes in the microscopic morphology and structure of these MPs upon HPO treatment. Such structural changes have also been demonstrated by the SEM images shown in Fig. 2. Note that both the pristine PE and PET particulates are nearly spherical with very smooth surfaces (Figs. 2a, d). Upon a consecutive HPO treatment for 5 days, however, both MPs were fragmented into smaller pieces with more irregular surface defects and holes (highlighted by the yellow arrows in Figs. 2b, e). As expected, further increasing the HPO treatment time up to 20 days has resulted in more and finer MP fragments with more abundant surface defects (e.g., cracks, holes, and wrinkles in Figs. 2c, f), which not only verified the above FT-IR results but also greatly increased the specific surface area of these MPs, thereby their affinity for heavy metals 19-21. Based on the SEM observations and the relevant analyses, the morphological evolution (fragmentation process) of microplastics upon HPO treatment is likely to occur in the manner illustrated in Fig. 2g.

The surface charges of MPs play a defining role in their interaction with heavy metals $\frac{20}{22-23}$. The zeta potential (ζ) of both pristine and aged microplastics were measured in different types of background electrolytes (i.e., NaCl, CuCl₂, ZnCl₂) and the results are shown in Fig. S1 (Supplementary materials). The results showed that the zeta potential of both microplastics decreased with increasing pH, and the pHPZC (point of zero charge) of these microplastics appeared between 3.0 and 4.2, which is consistent with previous report $\frac{34}{2}$. Note that weathering by HOP decreased the pH_{PZC} of the two pristine MPs by 0.3-0.8 unit of pH, which is likely due to the introduction of new negatively charged groups to the microplastic surface, i.e., grafting of oxygen-containing groups, thereby shifting the pHpzc of pristine microplastics toward lower pH regions $\frac{35}{2}$. The pH_{PZC} of both the pristine and the aged PET are slightly lower than those of PE (Table S1), indicating that the PET surfaces are more likely to be negatively charged under the same conditions.

3.2. Effects of type, size, and weathering time of MPs on adsorption

To understand the effects of microplastic type, particle size and weathering time on adsorption, the adsorption of Cu²⁺ and Zn²⁺ over two types of MPs, i.e., PE and PET, with particle sizes of 1 mm and 50 µm and weathering time of 5 and 20 days, respectively were investigated comprehensively, and the results are shown in Fig. 3. Obviously, there is little difference in the adsorption capacities of Cu²⁺ and Zn²⁺ of the two MPs of 1 mm under the same conditions regardless of the aging time (the white shading regions in Fig. 3), indicating that the type of MP has little impact on the adsorption affinity in the case of MP of 1 mm in size. With regards to MPs of 50 µm (yellow shading regions), however, both pristine PE and PET demonstrate a slightly higher affinity for Cu²⁺ over Zn^{2+} , with 0.62 mg Cu²⁺ g⁻¹ versus 0.57 mg Zn²⁺ g⁻¹ for PE, and 0.63 mg $Cu^{2+} g^{-1}$ versus 0.57 mg $Zn^{2+} g^{-1}$ for PET, respectively. Interestingly, as weathering time increased from 5 to 20 days, PE and PET showed different affinities for Zn²⁺ and Cu²⁺, respectively,



Fig. 3. Effects of microplastic type, size, and weathering time on Cu^{2+} and Zn^{2+} adsorption. (a) Cu^{2+} adsorption over PE, (b) Zn^{2+} adsorption over PE, (c) Cu^{2+} adsorption over PET, and (d) Zn^{2+} adsorption over PET.

with PE adsorbing more Zn^{2+} than Cu^{2+} and PET capturing more Cu^{2+} under the same conditions. This observation is in agreement with a previous report $\frac{36}{2}$ and is likely attributed in part to the much greater abundance of carbonyl groups (-C=O) in aged PET relative to aged PE (Fig. 1b). This functional group tends to form coordination bonds with Cu^{2+} ions preferentially. However, aged PE is rich in polar or charged sites that interact more favorably with Zn^{2+} ions $\frac{36}{2}$.

Moreover, it was noted that MPs of 50 µm demonstrated much greater adsorption capacities for both heavy metals than their counterparts of 1 mm under the same conditions, which is because the smaller the particle size, the larger its specific surface area, and therefore the more active sites for bonding heavy metal ions. This observation is in good agreement with those reported elsewhere ²². 24, 27. Besides, it was found that the longer the weathering time, the greater the adsorption capacities of the aged MPs for both heavy metals. This is as expected since the longer the weathering time, the higher the degree of fragmentation and the more defectrich MP fragments produced, thereby offering more sites (e.g., oxygen-containing functional groups) for the adsorption of heavy metals. In light of the adsorption capacity, PE-50µm-20d and PET-50µm-20d with the maximum adsorption capacities for both heavy metals, i.e., 0.84 and 0.92 mg Cu^{2+} g⁻¹ for PE (Fig. 3a, c) and 0.94 mg g^{-1} and 0.87 mg $Zn^{2+} g^{-1}$ for PET (Fig. 3b, d), were selected for the subsequent batch adsorption experiments.

3.3. Effects of pH and ionic strength

It is well-known that electrostatic interactions play an important role in the adsorption of heavy metal ions on MP adsorbents $\frac{36-37}{2}$. Fig. 4 shows the effects of solution pH and ionic strength on the adsorption of Cu²⁺ and Zn²⁺ over the two aged MPs, PE-50µm-20d and PET-50µm-20d. The adsorption of both Cu²⁺ and Zn²⁺ over the two aged MPs showed a gradual increase as the solution pH increased from 3 to 4, followed by a steep increase at pH 4 – 6. This observation is reasonable and expected since the surfaces of PE and PET are positively charged when the solution pH is less than their pH_{PZC} (Fig. S1), leading to relatively lower adsorption of



Fig. 4. Effects of pH and ionic strength (*I*) on Cu^{2+} and Zn^{2+} adsorption over the two aged MPs. (**a**) Cu^{2+} adsorption over PE-50 μ m-20d, (**b**) Zn^{2+} adsorption over PE-50 μ m-20d, (**c**) Cu^{2+} adsorption over PET-50 μ m-20d, (**d**) Zn^{2+} adsorption over PET-50 μ m-20d.

Cu²⁺ and Zn²⁺ due to the Coulomb repulsion between the adsorbents and the adsorbates. As the pH rises beyond their pH_{PZC} (i.e., pH >4, Table. S1), the PE and PET surfaces are negatively charged with increasing pH (Fig. S1), which is more favorable for the adsorption of positively charged heavy metal ions via the Coulomb attraction. This also explains the rapid increase in adsorption capacity at pH 4–6. Similar trends have also been observed for the adsorption of metal ions on other MPs $\frac{22}{29}$. 38 as well as nanomaterials $\frac{39}{29}$.

Ionic strength (I) dependence of adsorption has been widely used, in conjunction with the pH effect, to indirectly deduce the underlying adsorption mechanisms between the adsorbents and the adsorbates 40. Strong inner-sphere surface complexes were believed to form for ions with little ionic strength dependence; weak outer-sphere surface complexes were deemed to form for ions showing marked ionic strength dependence. Note that the adsorption of Cu2+ on both MP adsorbents demonstrated little ionic strength dependence over the pH ranging from 3 to 4 (Fig. 4a, c), indicating the probable formation of inner-sphere surface complexes between Cu²⁺ and the surface carboxyl groups of both aged MPs. As pH rises beyond 4, the Cu²⁺ adsorption on both aged MPs was dependent on the ionic strength, with relatively lower adsorption capacities at higher ionic strength (1.0 NaCl) due to the remarked competition from sodium ions (Na⁺) in solution. This phenomenon is indicative of the formation of weak outer-sphere surface complexes of Cu²⁺ on both aged MPs surfaces over the pH range of 4-6. In other words, the Coulomb attraction is the dominant mechanism responsible for Cu²⁺ uptake over pH 4-6. Similar results were found in a previous study $\frac{41}{2}$.

Likewise, the competition from Na⁺ ions in a solution of higher ionic strength with Zn²⁺ for adsorption is remarkable, leading to a great recession in the adsorption capacity of Zn²⁺. For example, the adsorption of Zn²⁺ on PE decreased from 0.93 mg g⁻¹ with I =0.1 M NaCl to 0.72 mg g⁻¹ with I = 1.0 M and from 0.87 mg g⁻¹ to 0.69 mg g⁻¹ on PET at pH 6. Such a distinct ionic strength dependence of Zn²⁺ adsorption on both aged MPs over the pH range



Fig. 5. Effects of co-occurring species on Cu^{2+} and Zn^{2+} adsorption over the two aged MPs. (a) Cu^{2+} adsorption, (b) Zn^{2+} adsorption over MPs in the presence of HA; (c) Cu^{2+} adsorption, (d) Zn^{2+} adsorption over MPs in the presence of TC; (e) Cu^{2+} adsorption, and (f) Zn^{2+} adsorption over MPs in the presence of MAP ions.

of 3-6 suggests the formation of weak out-sphere surface complexes of Zn^{2+} on both aged MPs surfaces. Furthermore, according to the DLVO theory, increasing the ionic strength of the solution could compress the bilayer over the adsorbent surface and thereby decrease the corresponding electrostatic repulsion, leading to increased aggregation of microplastics and a decrease in accessible adsorption sites, which further reduces the adsorption somewhat $\frac{42-43}{2}$.

3.4. Effects of co-occurring species

Recall that swine and poultry effluents are complex and rich in DOMs, antibiotics, and nutrient components (e.g., ammonia, and phosphate). Therefore, the following section focuses on evaluating the impacts of these co-occurring species on the adsorption of both Cu^{2+} and Zn^{2+} over the two aged MPs by employing HA as model DOM, TC as model antibiotic, and magnesium ammonia phosphate (MAP) ions as model nutrient components.

3.4.1 Effect of HA

DOMs are widespread in livestock effluents and inevitably interact with MPs, which is believed to influence the adsorption of heavy metals $\frac{34}{2}$ and other co-occurring contaminants $\frac{44}{2}$. HA has been reported to account for 50-75% of DOM in the natural environment $\frac{45}{2}$ and therefore was chosen as model DOM to explore its impact on the adsorption of heavy metals over the two aged MPs (Fig. 5a, b). As HA contents increased from 0 to 100 mg L⁻¹, the adsorption of both heavy metals on the two aged MPs increased obviously. For instance, the adsorption of Cu²⁺ on PE-50µm-20d was improved by 112.5%, from 0.8 to 1.7 mg g⁻¹, in the presence of 100 mg L⁻¹ of HA as compared to that without HA (Fig. 5a). Similar enhancements in the adsorption potential of heavy metals were also observed for Pb²⁺ adsorption on polystyrene (PS) in either a simulated effluent ⁴⁶ or in a real sewage scenario ¹⁷.

3.4.2 Effect of TC

TC is a common veterinary antibiotic that is widely used on livestock farms. It is well-defined that the interactions between TC and MPs can significantly alter the surface of MPs, which in turn changes the bioavailability, bioaccumulation, and fate of TC in aquatic environments $\frac{48-49}{2}$. The effect of co-occurring tetracycline (TC) on the adsorption of heavy metals over the two aged MPs (PE-50um-20d, and PET-50um-20d) was investigated and the results are given in Fig. 5c, d. Note that the adsorption of Zn^{2+} on both MPs did not increase so much as the TC concentration increased from 0 to 20 mg L^{-1} (Fig. 5d), while the adsorption of Cu^{2+} on aged PET increased profoundly with increasing TC (yellow shaded region in Fig. 5c), with a 2.3-fold increase in the adsorption capacity of Cu²⁺ in the presence of 20 mg L⁻¹ TC relative to that without TC. This observation indicates that a high concentration of TC significantly promotes Cu2+ adsorption over aged PET, which is likely due to the strong complexation reaction between Cu^{2+} and TC $\frac{50}{2}$ and the bridging ability of TC to bind up the resulting Cu-TC complexes with the aged PET 51. Similar observations have also been reported elsewhere $\frac{52-53}{52-53}$. It was also found that the presence of TC remarkedly improved the adsorption of Cu²⁺ on MPs while demonstrating almost no effect on the adsorption of Zn²⁺ on the same MPs due to the weak complexation between Zn²⁺ and TC $\frac{54}{2}$. The weak complexation affinity of Zn²⁺ with TC leads to a relatively small bridging enhancement and thus little increase in the adsorption of Zn^{2+} over the two aged MPs in the presence of TC.

3.4.3 Effect of MAP ions

Likewise, the effect of co-occurring MAP ions (i.e., Mg2+, NH4⁺, and PO4³⁻) on the adsorption of both heavy metals over the two aged MPs was studied in simulated effluents (Fig. 5e, f). Interestingly, MAP ions showed opposite effects on the adsorption of Cu^{2+} and Zn^{2+} on the two aged MPs, with the adsorption of Cu^{2+} increasing with MAP concentration and Zn2+ adsorption on the two aged MPs decreasing with MAP concentration. For example, the adsorption of Cu²⁺ on aged PET was improved by 200%, from 0.9 to 2.70 mg g⁻¹, in the presence of 10 mg L^{-1} MAP compared to that in the absence of MAP ions (yellow shaded region in Fig. 5e). This is likely to attribute to the reaction between Cu^{2+} and PO_4^{3-} to form sparingly-soluble copper phosphate (Cu₂(PO₄)₃) precipitates, resulting in a significant reduction in the content of dissolved Cu2+ in solution. Similar observation has also been reported previously $\frac{55}{2}$. However, in the case of Zn^{2+} , even zinc phosphate is also sparingly soluble in water, but the presence of NH4⁺ ions in the simulated solution is likely to boost the dissolution of such compound because of the formation of more soluble zinc ammine complexes $\frac{56}{2}$. Moreover, it is believed that the presence of Mg²⁺

appears to induce the agglomeration of both aged MPs via the cationic bridging $\frac{57-58}{5}$, which certainly reduces the abundance of active sites and consequently their adsorption capacity for Zn^{2+} .

3.5. Adsorption kinetics

To understand the adsorption behavior and the competition between the two heavy metals, adsorption kinetics were studied in both the unary and the binary adsorptive systems at an initial pH of 6 using both the pristine and the aged MPs as adsorbents. Intuitively, regardless of the type of adsorbent and adsorbate as well as the unary or binary adsorbate system, all adsorption kinetic data demonstrated a clear logarithmic relationship with the contact time (Fig. 6). Specifically, the adsorption of Cu^{2+} or Zn^{2+} ions on both the pristine and the aged MPs was highly rapid in the initial stage (within 0-25 min), followed by a slow adsorption stage (25-50 min) until an adsorption equilibrium was reached (>50 min). For example, after 25 min of adsorption, the adsorption capacity of Cu^{2+} on PET-50µm-20d attained 0.793 mg g^{-1}, accounting for 86% of the capacity (i.e., 0.922 mg g⁻¹) after adsorption for 2.5 h when an adsorption equilibrium was assumed to be reached. Concerning other adsorption processes, it was found that all the adsorption capacities of the initial stages have attained over 85% of the corresponding equilibrium capacity, indicating that the adsorption rates of Cu²⁺ and Zn²⁺ on these MPs were quite fast and that most of the adsorption was essentially accomplished in the initial rapid adsorption stage. Similar biphasic adsorption behavior was also observed in the case of Cu²⁺ captured by UV-aged PS particles ⁵⁹, and the initial rapid adsorption is believed to be ascribed to chemical reaction and film diffusion processes 60. Moreover, the high difference in concentration of Cu²⁺ or Zn²⁺ ions between the bulk solution and the adsorbent surface appears to boost a large mass transfer during the initial stage of adsorption, resulting in an initial rapid adsorption 61.



Fig. 6. Adsorption kinetics of Cu^{2+}/Zn^{2+} over both the pristine and the aged MPs in unary/binary adsorptive systems with Pseudo-1st-order kinetic modeling. (a) Cu^{2+} onto MPs in unary systems, (b) Cu^{2+} onto MPs in binary systems, (c) Zn^{2+} onto MPs in unary systems, and (d) Zn^{2+} onto MPs in binary systems (adsorbent dosage =1 g L^{-1} , pH = 6, T = 20 °C; in unary adsorptive systems, initial Cu^{2+} or Zn^{2+} (C_{0-Cu}/C_{0-Zn}) = 5 mg L^{-1} ; in binary adsorptive systems, $C_{0-Cu} = C_{0-Zn} = 5$ mg L^{-1}).



Fig. 7. Adsorption isotherms of Cu²⁺/Zn²⁺ over the aged MPs in unary/binary adsorptive systems with the Langmuir model fitting. (**a**) Cu²⁺ onto MPs in unary systems, (**b**) Cu²⁺ onto MPs in binary systems, (**c**) Zn²⁺ onto MPs in unary systems, and (**d**) Zn²⁺ onto MPs in binary systems (adsorbent dosage =1 g L⁻¹, pH = 6, contact time = 48 h; in unary adsorptive systems, $C_{0-Cu} = C_{0/2n} = 0-10 \text{ mg L}^{-1}$; in binary adsorptive systems, $C_{0-Cu} = C_{0-Zn} = 0-10 \text{ mg L}^{-1}$).

Interestingly, it is evident by comparing the adsorption in both the unitary and the binary adsorptive systems that there was a strong competition between Cu^{2+} and Zn^{2+} for binding sites, irrespective of the type of adsorbents and their degree of weathering. This phenomenon is indicative of the adsorption of both heavy metals over these MPs was governed by the same mechanism. In addition, the preference of both aged MPs toward different heavy metals, i.e., aged PE prefers to adsorb Zn^{2+} ions while aged PET prefers Cu^{2+} ions, was also observed in both unitary and binary adsorptive systems (Fig. 6), which is good agreement with the above results shown in Fig. 3.

Fitting of the kinetic data using both the pseudo-first-order (eq. 2) and the pseudo-second-order (eq. 3) models suggested that the best-fit kinetic parameters (Tables S2, and 3), particularly all the correlation coefficients (\mathbf{R}^2) are > 0.95, implying that both kinetic models are capable of well describing the adsorption behavior of both heavy metals on these MPs (Figs. 6, and S2). Further comparisons revealed that \mathbf{R}^2 values obtained from the pseudo-second-order model were a bit greater than those from the pseudo-first-order model for both heavy metals (Tables S2, and 3), indicating that the former is more suitable for describing all these adsorption kinetic data and that the adsorption of Cu²⁺ and Zn²⁺ over these MPs was governed by a chemisorption process ⁶⁰.

3.6. Adsorption isotherms

To evaluate the effect of temperature on Cu^{2+} and Zn^{2+} adsorption and estimate the theoretical maximum adsorption capacity (q_m) of these MPs, both the Freundlich (eq. 4) and the Langmuir (eq. 5) models are applied to the equilibrium adsorption data in both the unary and the binary adsorptive systems (Figs. 7, and S3). The best-fit isotherm parameters for both models are tabulated in Tables S4 and 5. Note that the best-fit R^2 values calculated from both the Langmuir model (0.994-0.999) and the Freundlich model



Fig. 8. (a) XRF and (b) FTIR spectra of 20-day-aged MPs (i.e., PE-50 μ m-20d and PET-50 μ m-20d) before and after adsorption of Cu²⁺ at pH 6; 3D-EEM spectra of (c) TC at pH 6, (d) TC + 0.08 mM Cu²⁺, and (e) TC + 0.08 mM Cu²⁺ + 0.1 g L⁻¹ PET; (f) the proposed adsorption mechanisms in the absence (left) or presence of HA and TC (right).

(0.981-0.997) are relatively close to 1, indicating that both models can accurately describe the adsorption process at different temperatures (i.e., 293, 303, and 313 K). However, R^2 values obtained from the Langmuir model were slightly greater than those from the Freundlich model for both the unary and the binary adsorptive systems, suggesting that the former model is better in defining these adsorption isotherm data and that both heavy metal ions were likely to occur in a monolayer manner based on the basic assumption of the Langmuir model $\frac{62}{2}$.

Additionally, the parameter *n* calculated from the Freundlich model is often used as an indicator of the easiness or likeliness of a specific adsorption process, with n > 1 indicative of a favorable adsorption process ⁶³. Note that all the *n* values are above 1, suggesting that the adsorption of Cu²⁺ and Zn²⁺ ions over both aged MPs are favorable and easy to proceed under the given conditions, in good agreement with previous reports ²², <u>36</u>, <u>59</u>, <u>64</u>. Moreover, the adsorption of both metal ions over these aged MPs was affected by temperature, with a higher adsorption capacity under high-temperature conditions (Table S4 and 5). Generally, the greater adsorption is an endothermic process, otherwise, the adsorption is exothermic.

The isotherm data at different temperatures suggest that the adsorption of both heavy metal ions on the two aged MPs was endothermic, in good agreement with the results of previous studies $\frac{21-22}{36}$. Consistent with the adsorption kinetic results, the adsorption of either Cu²⁺ or Zn²⁺ in the binary adsorptive systems was lower than that in the unary adsorptive systems under the same conditions (Figs. 7, and S3), indicating that competition between Cu²⁺ and Zn²⁺ ions occurred during the adsorption process, particularly in the binary adsorptive systems.

3.7. Adsorption mechanisms

To elucidate the mechanism responsible for Cu^{2+} and Zn^{2+} adsorption over both aged MPs, spectroscopic analysis was conducted on both MP samples (i.e., PE-50µm-20d and PET-50µm-20d) before and after adsorption (Figs. 8 and S4–6). Each heavy metal ion was successfully captured by both aged MPs after 48-h of contact at pH 6 (Figs. 8a, S4a), as indicated by the appearance of K_{a1}- and K_{a2}-shell emission lines of either Cu²⁺ or Zn²⁺ after adsorption. Besides, the intensity of absorption peaks at 1713 cm⁻¹ of both aged MPs and 3430 cm⁻¹ (attributable to the stretch vibration of surface hydroxyls) of the aged PET has changed apparently upon adsorption of either Cu²⁺ or Zn²⁺ ions (Figs. 8b, S4b), implying both the carboxyl and the surface hydroxyl groups are involved in the adsorption of both heavy metals, in good agreement with previous reports $\frac{36.65}{5}$. Such MPs-HMs interactions are most likely to be physical due to the absence of new peaks and no shifts in the above peaks $\frac{37.66}{5}$, which is also consistent with the above speculation about the dominant adsorption mechanism based on the results of ionic strength dependence (Fig. 4).

The 3D-EEM fluorescence spectra of TC and HA were studied respectively in the presence of HMs, and/or MPs to explore the impacts of both co-occurring species on adsorption (Figs. 8c-e, S5-6). The peak at Ex/Em = 375/526 nm (P1, Fig. 8c-e, S5) is the characteristic fluorescence spectrum of TC 67, whereas the peaks at Ex/Em = 260/464 nm (P1, Fig. S6), 295/532 nm (P2), and 235/450 nm (P3) are attributed to the humic-like compounds in HA 68-69. Note that the fluorescence intensity of TC or HA decreased obviously in the presence of individual HM or MP species (Figs. 8d, S5-6), indicative of fluorescence quenching due to the complexation between the fluorescers (i.e., HA, TC) and the quenchers (i.e., HMs and MPs) 69. The fluorescence quenching effect was quite remarkable in the ternary systems of TC-HMs-MPs and HA-HMs-MPs, with further reduction in the fluorescence intensity of either TC or HA (Figs. 8e, S5-6). This observation is likely due to the formation of new bridging complexes between TC or HA and HMs over the surface of MPs, in agreement with earlier reports 22, $\frac{43}{50}$. Collectively, the mechanisms of Cu²⁺ or Zn²⁺ adsorption over the surface of aged MPs are proposed (Figs. 8f), with Coulomb attraction and surface complexation dominated in the absence of either TC or HA (left), and with bridging complexation occurring in the presence of either TC or HA. However, further works to identify the molecular configuration and the fractions of such bridging complexes using X-ray absorption spectroscopy are needed to verify the mechanisms proposed above.

4. Conclusions

In summary, MPs have a great affinity toward heavy metals (e.g., Cu^{2+} and Zn^{2+} ions), thereof appear to accumulate and spread such contaminants in simulated swine wastewater at environmentally relevant concentrations. Weathering can significantly accelerate the fragmentation of pristine MPs and endow the aged MPs with a variety of oxygen-containing functional groups, which appear to act as new active sites for binding both Cu²⁺ and Zn²⁺ ions. In addition, co-occurring humic acid and tetracycline species seem to facilitate the adsorption of heavy metals over the aged MPs via bridging complexation, which in consequence increases the risk of combined contamination and co-exposure, particularly in the case of co-occurring tetracycline. The co-occurring nutrients (e.g., phosphate and ammonia), however, demonstrated different impacts on Cu²⁺ and Zn²⁺ ions, with improved sequestration of Cu²⁺ ions by precipitation but lower immobilization for Zn²⁺ due to the formation of soluble zinc ammine complexes. These findings provided important insights into the interactions between aged MPs and heavy metal ions in specific environmentally relevant scenarios, and how the interactions are impacted by the intrinsic features of MPs and the environmental factors (e.g., pH, ionic strength, cooccurring species). However, further studies to examine the transport and fate of these heavy metal-loaded MPs are needed in particular when a strategy of nutrient recovery (e.g., struvite crystallization) was applied to such nutrient-rich swine wastewater to elucidate the mediating role of MPs for spreading heavy metals and/or tetracycline to the reclaimed value-added products (e.g., fertilizer).

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Appendix A. Supporting Information

Supplementary data to this article can be found online.

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