RESEARCH ARTICLE

Effects of soil environmental factors and UV aging on Cu^{2+} adsorption on microplastics

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Abstract

Microplastics (MPs) in natural environments have attracted lots of attention. Although the quantity of MPs present in terrene is much higher than that in aquatic environment, few studies have investigated the chemical behavior of MPs in terrestrial environment. This study investigate the Cu^{2+} (as a model heavy metal) adsorption capacity of six kinds of MPs (polyamide-6 (PA), polyethylene (PE), polystyrene (PS), polyethylene terephthalate (PET), polyvinyl chloride (PVC), polymethyl methacrylate (PMMA)) in batch adsorption experiments and the effects of different soil environmental factors, including pH and the presence of cations and low-molecular-weight organic acids (LMWOAs), as well as ultraviolet (UV) aging. The Cu^{2+} adsorption capacities of PA and PMMA were higher than those of other MPs and their maximum equilibrium adsorption capacities (estimated by the Langmuir adsorption equation) were 323.6 μg/g ± 38.2 and 41.03 ± 1.78 μg/g, respectively. The Cu^{2+} adsorption on MPs was affected by pH, and the greatest amount of Cu^{2+} adsorbed on PA and PMMA was observed at pH = 6 and pH = 7, respectively. The presence of Ca^{2+} or Mg^{2+} inhibited Cu^{2+} adsorption by MPs, due to competition for the adsorption sites. Moreover, Cu^{2+} adsorption by MPs was affected by various types of LMWOAs. The Cu^{2+} adsorption on PA was significantly reduced by citric acid, followed by oxalic acid, and oxalic acid was particularly evident for Cu^{2+} adsorption on PMMA. UV aging (200 h) had different effect on Cu^{2+} adsorption on MPs and it depends on the change of carbonyl index. Results demonstrate that soil environmental factors can change the ability of different MPs to adsorb Cu^{2+} and affect the transport of pollutants as carriers.

Keywords Microplastics · Adsorption · Copper · Environmental factors · Aging

Introduction

Plastic products are ubiquitous in our live, the annual production of plastics is drastically increasing, and it is expected to reach 33 billion tonnes by 2050 (Rochman et al., 2013). Plastics can be broken down through prolonged mechanical abrasion, ultraviolet (UV) radiation (Song et al., 2017), and

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microbial mineralization (Restrepo-Flórez et al., 2014) to form microplastics (MPs, size < 5 mm). MPs are widely spread across aquatic and terrestrial environments (Rios Mendoza and Balcer, 2018; He et al., 2018). As the main area where plastics are manufactured, terrestrial environments contain more MPs than aquatic environments. Previous studies reported that the annual amount of plastic released to land is 4–23 times higher than that released to oceans (Horton et al., 2017). Fuller and Gautam (2016) found that the concentrations of MPs widely varied (300–67,500 mg/kg) depend on the size in industrial soils from Sydney, Australia. Another study shows that average 55.5 mg/kg of MPs were found in 26 floodplain soil sites in Switzerland (Scheurer and Bigalke, 2018).

MPs are harmful to terrestrial life such as earthworms (Huerta-Lwanga et al., 2016; Rodriguez-Seijo et al., 2018), soil collembolans (Zhu et al., 2018), and other animals (Anbumani and Kakkar, 2018). In addition, MPs could reside in deeper soil or possibly arrive groundwater though transported by earthworms (Rillig et al., 2017) and pose severe threats to human health through their entry into foods

such as salt (Yang et al., 2015), seafood (Karami et al., 2018), and drinking water (Mintenig et al., 2019). Apart from their inherent toxicity, MPs serve as carriers that can transport different kinds of pollutants due to their electric charge, high-specific surface area, and hydrophobicity (Zhu et al., 2019). They have the ability to adsorb and transfer hazardous chemicals to organisms, thereby increasing the harm of such pollutants (Wang et al., 2018a). The adsorption of organic pollutants by MPs has been widely reported (Guo et al., 2018; Wang et al., 2018c), and the adsorptio

n of heavy metals by MPs in the marine environment is gradually gaining attention (Ashton et al., 2010; Holmes et al., 2012). Previous research showed that toxicity due to Ni in combination with PS-COOH (polystyrene with a carboxyl group) is higher than that observed in the case of acute Ni toxicity alone (Kim et al., 2017). Another study on Zn bio-availability revealed that high-density polyethylene (HDPE) fragments can adsorb Zn, and MPs can increase Zn bioavailability (Hodson et al., 2017). Therefore, it is imperative to investigate the adsorption of heavy metals on MPs to understand the transportation and toxicities of heavy metals coupled with MPs.

Despite the presence of huge quantities of MPs in adsorbed pollutants of total environment, most previous studies on the adsorption of MPs were mainly conducted in relation to the aquatic environment. Some attempts have been made to investigate the adsorption of organic pollutants in the terrestrial environment (Liu et al., 2018). However, little attention has been paid to the adsorption of heavy metals on MPs in the soil and the effects of different soil environmental factors on heavy metals adsorption. The soil environment can be affected by several factors and the extent of changes in soil environmental factors, such as soil pH ranging from 3 to 8 and high concentrations of inorganic cations and low-molecular-weight organic acids (LMWOAs), is far beyond what is found in an aqueous environment. Therefore, it is imperative to investigate the adsorption of pollutants on MPs under different soil environmental conditions. In addition, UV aging results in further accelerate fragmentation of plastic into smaller particles (MPs) (Briassoulis et al., 2015a; Song et al., 2017), changes in the functional groups on the plastic surface (Kelkar, 2017), and higher adsorbance of pollutants.

Copper (Cu) is one of the most common heavy metals in the environment. The contents of total and availability (DTPA-extractable) of Cu are 15–40 mg/kg and 0.1–10 mg/kg in soil, respectively (Ni et al., 2003). Although Cu is a trace element necessary for life, excessive amounts are harmful to organisms in terrestrial environments (Wang et al., 2018b). Thus, it will be used to model heavy metals in this paper. Study of the adsorption mechanism of Cu^{2+} on MPs is vital as the foundation for the investigation of the compound pollution of MPs and heavy metals. The present study endeavored to investigate Cu^{2+} adsorption on MPs upon variation of

various environmental factors including pH, the quantities of Ca^{2+}, Mg^{2+}, LMWOAs present, and UV aging. This study will highlight the important factors controlling Cu^{2+} adsorption on MPs, which will help to predict Cu^{2+} transport in the soil environment. In addition, the findings of this study will provide a basis for investigating the role of MPs as a carrier and transporter of heavy metals to soil organisms in the future.

Materials and methods

Materials

Six kinds of MPs (polyamide-6 (PA), polyethylene (PE), polystyrene (PS), polyethylene terephthalate (PET), polyvinyl chloride (PVC), and polymethyl methacrylate (PMMA)) were used in this study. PA and PVC were purchased from Aladdin Biochemical Polytron Technologies Inc. (Shanghai, China). PE, PET, and PS were purchased from Cheng Xinzhe Plastic Chemical Co. Ltd. (Suzhou, China). PMMA was purchased from Polymer Plastic Co. Ltd. (Dongguan, China). All chemical agents used were guaranteed reagent grade, and all solutions were prepared in high-purity Milli-Q water (Millipore Ltd., USA). The experimental vessel was soaked in 10% HNO_3 solution for 24 h and then washed with deionized water before the experiments.

Batch adsorption experiments

Adsorption isotherms

Adsorption isotherm experiments were conducted by adding 0.500 g of different MP particles to 25 mL solutions of different Cu^{2+} concentrations (0.05, 0.1, 0.5, 1, 2, 5, and 10 mg/L) consisting of a $Cu(NO_3)_2$ solution with 0.01 mol/L $NaNO_3$ as the background electrolyte in plastic centrifuge tubes. In order to better observe the adsorption characteristics, we selected the amount of microplastics higher than the environmental concentration. Based on the findings of kinetic experiments conducted in the present study (details in Fig. S1) and previous studies (Godjevargova and Mihova, 2003; Holmes et al., 2012), the adsorption time that the adsorption to reach equilibrium was identified as 24 h. After shaking at 200 rpm for 24 h, all samples were first centrifuged at 5000 rpm and then filtered through 0.45-μm polyethersulfone membrane filters (Germany). The control adsorption experiments containing $Cu(NO_3)_2$ and $NaNO_3$ without MPs were also simultaneously conducted, and this concentration of Cu^{2+} was referred as initial concentration (preliminary experiments found that the recovery of Cu^{2+} in control is 96.0–102.5%). The amount of Cu^{2+} adsorbed by MPs was calculated by the mass balance method (the difference between control and other treatment concentrations) (Hodson et al., 2017). All experiments were

performed in triplicate and the temperature was 25 °C. The filtered solution samples were acidified with 2% HNO_3 to determine the Cu concentration.

The Cu^{2+} adsorption isotherms of the MPs were described by the Langmuir Eq. (1) and the Freundlich Eq. (2):

$$Q_e = K_L Q_m C_e / (1 + K_L C_e) \qquad (1)$$

where Q_m (μg/g) is the maximum adsorption capacity of the MP, C_e (μg/L) is the equilibrium concentration of the solute, and K_L (L/g) is a Langmuir constant that characterizes the rate of the adsorption.

$$Q_e = K_F C_e^{\ b} \qquad (2)$$

where K_F (L/g) is the Freundlich adsorption coefficient, which relates to adsorption capacity, C_e (μg/L) is the equilibrium concentration of the solute, and b is the Freundlich isotherm exponent that indicates non-linearity.

Effects of pH, inorganic cations, and organic acids on the adsorption of Cu^{2+} by MPs

The effect of pH on the Cu^{2+} adsorption was examined by adjusting the pH of the solutions to 4–8 (at intervals of 1 unit) using NaOH or HNO_3 solutions. To examine the influence of other inorganic cations on Cu^{2+} adsorption, Ca^{2+} and Mg^{2+} were added to the suspensions with final concentrations of 7.7 mM and 6.5 mM, respectively. The concentrations used were equivalent to the values of their soil concentrations (1.54% and 0.78%, respectively) (Wei et al., 1991). Citric acid (CA), oxalic acid (OA), tartaric acid (TA), and malic acid (MA) were used to examine the influence of LMWOAs on Cu^{2+} adsorption. The molar ratios of Cu^{2+} to LMWOAs were set at 1:0.25, 1:0.5, 1:1, 1:2, and 1:4. The pH of all solutions (except in the pH experiment) was controlled at 6 by adding NaOH or HNO_3. 0.5 g of different MPs and 25 mL of solutions of different Cu^{2+} concentrations were added to plastic centrifuge tubes. The solution pH, inorganic cation concentration, and the LMWOA concentration were identified based on the above experimental design. After shaking at 200 rpm for 24 h, all samples were first centrifuged at 5000 rpm and then filtered through 0.45-μm polyethersulfone membrane filters. All filtered solution samples were acidified by HNO_3 and each treatment was repeated in triplicate.

Effects of UV aging on Cu^{2+} adsorption by MPs

The aging of plastics is a very long process; however, UV irradiation can accelerate the aging process. MPs were exposed to UVA-340 nm fluorescent lamps in the customized UV Illumination incubator (SANYO MLR-351H, Japan), and the UV irradiance applied to those MPs was 15.7 W/m², which was measured using a TM-213 light meter

(TENMARS, Taiwan). MPs were aged for 200 h with the humidity and the temperature at 60% and 30 °C, respectively. Afterward, the aged MPs were used to carry out Cu^{2+} adsorption isotherm experiments as described in the "Adsorption isotherms" section.

Analytical methods

The morphology of six kinds of MPs was observed using a scanning electron microscope (SEM, Hitachi S-4800, Japan) and selected a representative figure to show, while the specific surface areas were investigated by N_2/BET method (Autosorb-iQ, Quantachrome Instruments, USA). Attenuated total reflectance Fourier-transform infrared (ATR-FTIR) spectroscopy was used to analyze the MPs before the experiments. ATR-FTIR was carried out using OMNIC 8.0 (Thermo Nicolet, USA) to distinguish the surface groups via a Nicolet iS10 (USA) spectrophotometer. Zeta potentials of the MPs at pH 6 were determined using a zeta meter (Zetasizer Nano ZS90, Malvern Instruments Ltd., UK). Cu concentrations in the solutions were determined by a flame atomic absorption spectrophotometer (Hitachi Z-2000, Japan). The aging MPs were also analyzed by ATR-FTIR and SEM.
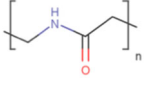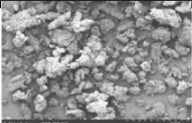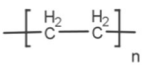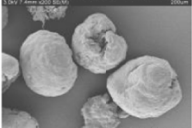
Statistical methods
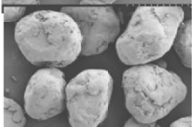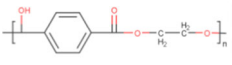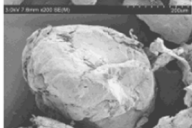
Cu speciation in different pH ($Cu(NO_3)_2 = 0.5$ mg/L, pH = 4, 5, 6, 7, 8) and the presence of LMWOAs (add components $Cu^{2+} = 0.5$ mg/L, $NO_3^- = 1.0$ mg/L and different concentrations LMWOAs, temperature was set to 25 °C and pH fixed at 6, the molar ratios of Cu^{2+} to LMWOAs were set at 1:0.25, 1:0.5, 1:1, 1:2, and 1:4.) was analyzed by using Visual MINTEQ 3.1. Statistical anal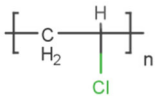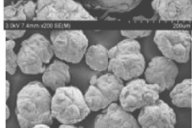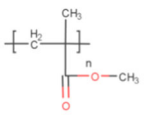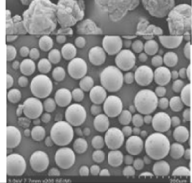ysis was performed using Excel 2010 (Microsoft, USA), SPSS 18.0 (IBM, USA), and comparisons among effects of inorganic cations treatments were performed by two independent one-way ANOVA and followed by Duncan's test at the $p < 0.05$. All figures were drawn by Origin 2017 (OriginLab, USA).

Results and discussion

Characteristics of different kinds of MPs

The different MPs had distinct morphologies, and their characteristics are shown in Table 1. PA particles were porous and PMMA particles were spherical, while other materials were of irregular shape. The particle sizes of MPs ranged from 70 to 350 μm. The zeta potentials of different kinds of MPs were determined at pH 6, PA had the smallest zeta potential (− 7.59 mV), followed by PVC (− 8.70 mV), while the zeta potentials of other materials were relatively close (− 15.2 mV∼− 16.1 mV). In contrast, the specific surface area of PA is much

Table 1 The basic properties of MPs

Name	Structural formula	Average diameter (μm)	Zeta potential (mV)	BET (m²/g)	morphology
PA		69.86	-7.59	8.710	
PE		204.7	-15.2	2.110	
PS		192.0	-16.1	<0.001	
PET		350.8	-16.7	0.475	
PVC		137.8	-8.70	0.556	
PMMA		74.76	-15.9	0.110	

larger than other MPs, up to 8.71 m²/g, scanning electron microscopy confirmed that the surface of PA has many micro-pores, and the order of the surface areas was PA > PE > PVC > PET > PMMA > PS. Meanwhile, FTIR spectra revealed different MPs have different structures and properties (Fig. S2). PA has an amide group (–CONH–) that is chromogenic, is strongly polar, and is susceptible to the effects of UV, water, temperature, and other environmental factors (Lu et al., 2005). PE only has carbon–carbon bonds (–C–C–) and a long carbon chain, while PVC and PS include a chlorine atom and benzene rings among the carbon–carbon bonds, respectively. PET has benzene rings and an ester group (–COO–) in the long-chain polymers, and PMMA has an ester group (–COO–) on the branched chain. Sorption of contaminants on microplastics was related to the physicochemical properties of the polymer (Alimi et al., 2018).

Cu²⁺ adsorption on different kinds of MPs

The Cu²⁺ adsorption capacities of PA and PMMA were significantly higher compared with the other MPs (PE,

PS, PET, PVC) (Fig. 1) and the equations of Langmuir and Freundlich were used to fit the adsorption isotherms (Table 2). Cu²⁺ adsorption on PA, PE, PET, and PVC was better described by the Freundlich equation while the adsorption on PS and PMMA was better fitted the Langmuir equation. The maximum adsorption capacities of PA and PMMA derived from the Langmuir equation were 324 ± 38.2 μg/g and 41.0 ± 1.78 μg/g, respectively. However, the maximum adsorption capacities of PE, PS, PET, and PVC were < 10 μg/g.

Ashton et al. (2010) investigated the Cu²⁺ adsorption capacity of PE MPs in the coastal zones of south England and found that the Cu²⁺ adsorption capacity of original PE plastic granules was only 0.28 ± 0.18 μg/g. In another study, conducted at four locations in south-west England, Holmes et al. (2012) found that the capacities of microplastic pellets to adsorb Cu²⁺ ranged from 0.064 to 1.32 μg/g. Maybe salts in seawater could affect their adsorption. Overall, the adsorption capacities of heavy metals on MPs are related to their surface properties, such as their functional groups, specific surface area, and zeta
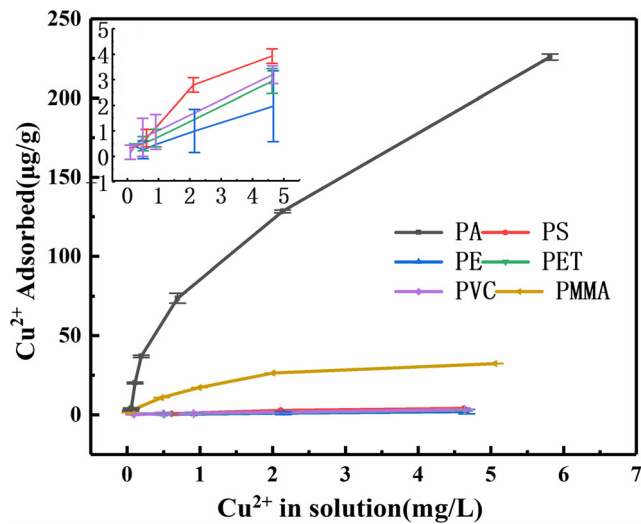
Fig. 1 The Cu^{2+} adsorption isotherms of different virgin MPs (PA (black), PS (red), PE (blue), PET (green), PVC (purple), PMMA (brown))

potential. Brennecke et al. (2016) showed that the Cu^{2+} (released from antifouling paint to water) adsorption capacity of PVC (1320 µg/g) was much higher than that of PS (1100 µg/g) due to the higher specific surface area and the polar functional groups (chlorine) of PVC. Furthermore, the type of MP could play a more important role in the adsorption of contaminants than its other characteristics. In the present study, the higher adsorption capacities of PA and PMMA compared with the other MPs was associated with the polar functional groups (–NHCO– and –COO–) of PA and PMMA, which made them more hydrophilic and allowed more Cu^{2+} to adsorb on their surfaces. In addition, PA may also increase its adsorption capacity through the formation of hydrogen bonds (Li et al., 2018). The adsorption capacity of other materials was attributed to their zeta potential, specific surface area, and hydrogen bonding or polar interactions. Owing to PA and PMMA has stronger adsorption abilities; they were selected as representative MPs to study the influence of various environmental factors on Cu^{2+} adsorption.

Effects of pH and inorganic cations on Cu^{2+} adsorption by MPs

The Cu^{2+} adsorption capacity on PA reached the maximum when the pH was 6. However, other pH conditions had no significant influence on the adsorption capacity (Fig. 2a). That could be hydrophilic groups (–NHCO–) in both ends of the molecular chain make the solution stable under acid-base conditions. Cu^{2+} adsorption by PMMA significant increased from pH 4 to 7 and then decreased with further increases in pH, the maximum adsorption amount was 13.8 ± 0.401 µg/g. The H^+ could compete with the Cu^{2+} for the adsorption site of PMMA, leading to a lower Cu^{2+} adsorption capacity when the pH is decreased. Our findings of a continuous increase in Cu^{2+} adsorption capacity for PMMA with increasing pH were in agreement with the findings of Demirata-Öztürk (1996), who also found that the Cu^{2+} adsorption capacity of PMMA increased when the pH increased from 4 to 7. The simulation of Cu morphology using Visual MINTEQ 3.1 showed that only Cu^{2+} and $CuNO_3^+$ exist in an acid solution (pH 4 and 5) (Fig. S3). When the pH ≥ 6, other dissolved Cu moieties ($CuOH^+$, $Cu_2(OH)_2^{2+}$) begin to appear; when the pH > 7, the Cu^{2+} concentration could drop rapidly; at a pH of 8, $Cu(OH)_2$ precipitate appears. The Cu^{2+} concentration is constantly reduced with increasing pH.

The presence of inorganic cations is deemed to affect Cu^{2+} adsorption on MPs. Ca^{2+} and Mg^{2+} are important cations in aquatic and terrestrial environments, and they affect the migration and adsorption of pollutants in both environments. As shown in Fig. 2b, in the presence of Ca^{2+} and Mg^{2+} (the concentrations of Ca^{2+} and Mg^{2+} all matched environmental concentrations and were higher than the Cu^{2+} concentration), Cu^{2+} adsorption on MPs was inhibited. In addition, Cu^{2+} adsorption on PMMA was more easily affected by Ca^{2+} and Mg^{2+} than that on PA, and Ca^{2+} had a greater inhibitory effect on Cu^{2+} adsorption than Mg^{2+}. When Ca^{2+} and Mg^{2+} exist, the amount of Cu^{2+} adsorbed by PMMA were 5.80 ± 0.568 µg/g and 6.93 ± 2.05 µg/g, compare with blank (13.2 ± 1.14 µg/g) (the amount of Cu^{2+} adsorbed by PA in the

Table 2 The Langmuir and Freundlich fitting parameters of the Cu^{2+} adsorption on virgin MPs

Materials	Langmuir adsorption equation			Freundlich adsorption equation		
	Q_m(µg/g)	K_L(L/µg)	R^2	K_F	b	R^2
PA	324 ± 38.2	0.369 ± 0.098	0.982	82.0 ± 4.70	0.580 ± 0.037	0.990
PS	8.28 ± 2.55	0.204 ± 0.105	0.969	1.34 ± 0.231	0.730 ± 0.128	0.947
PE	8.46 ± 13.4	0.064 ± 0.127	0.861	0.560 ± 0.151	0.805 ± 0.198	0.873
PET	8.71 ± 7.74	0.110 ± 0.142	0.940	0.892 ± 0.194	0.775 ± 0.149	0.951
PVC	6.29 ± 0.948	0.221 ± 0.060	0.993	1.08 ± 0.055	0.703 ± 0.035	0.996
PMMA	41.0 ± 1.78	0.785 ± 0.090	0.995	16.4 ± 1.40	0.459 ± 0.065	0.954

$p < 0.05$ in the two adsorption equations

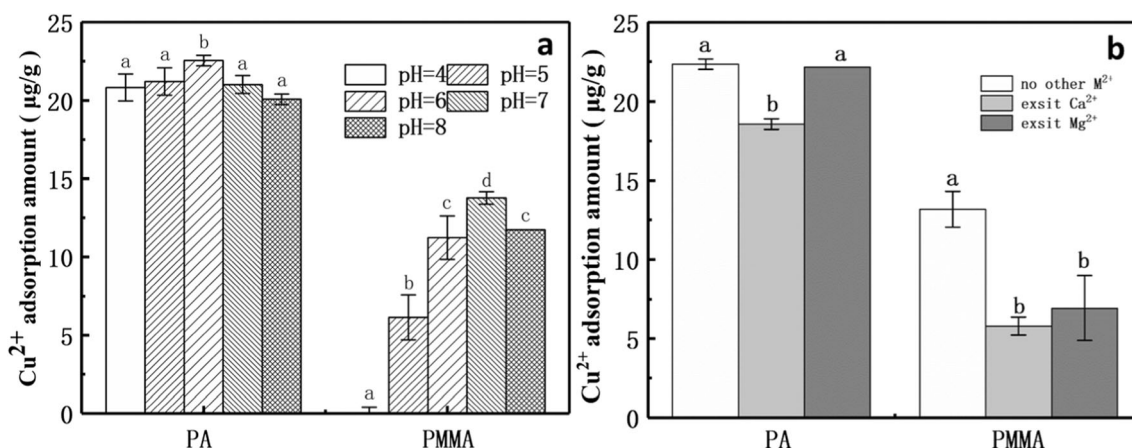**Fig. 2** Cu^{2+} adsorbed on virgin PA and PMMA under the effect of different pH (**a**) and the coexistence of metal cation (7.7 mM Ca^{2+} or 6.5 mM Mg^{2+}) (**b**) (Comparisons among treatments were performed by Duncan's test at the $p < 0.05$ and $n = 3$)

treatment of blank, Ca^{2+}, Mg^{2+} was 22.3 ± 0.328, 18.6 ± 0.328, 22.2 ± 0.000 μg/g). These cations compete with Cu^{2+} at the adsorption sites of the MP surface, which will in turn affect the Cu^{2+} adsorption. For instance, for PA modified with immobilized dead yeast cells, high concentrations of Ca^{2+} and Mg^{2+} reduced Cu^{2+} adsorption (Godjevargova and Mihova, 2003). It was also found that Ca^{2+} was more influential than Mg^{2+} when the concentrations of Ca^{2+} and Mg^{2+} reached 2000 mg/L, and the adsorption capacities of Cu^{2+} decreased by more than 50% and 10%, respectively.

Effects of organic acids on Cu^{2+} adsorption by MPs

Low-molecular-weight organic acids (LMWOAs) can complex with heavy metals in the soil and thus affect their behavior in the soil environment (Yang et al., 2006). Four common LMWOAs (citric acid, oxalic acid, tartaric acid, and malic acid) were selected as representatives to assess the effects of organic acids on Cu^{2+} adsorption by MPs.

Cu^{2+} adsorption by PA was significantly reduced in the presence of citric acid, followed by oxalic acid, while no substantial effects of tartaric acid and malic acid on Cu^{2+} adsorption were observed (Fig. 3). The capacity of organic acids to chelate with Cu^{2+} is positively correlated with log K (log K is complex stability constant), and Wang et al. (2009) found that the stronger the coordination of an organic acid with Cu^{2+}, the greater the decrease in Cu^{2+} adsorption onto the Hydroxyapatite. The log K values (25 °C, ionic strength = 0.1 M) of the organic ligands with Cu follow the order: citric acid > oxalic acid > malic acid > tartaric acid (Martell and Smith, 1977). Oxalic acid exhibited an obvious inhibiting effect on Cu^{2+} adsorption by PMMA. In contrast, low and high concentrations of citric acid (mole ratios of Cu citric acid > 1 and < 1) promoted and inhibited Cu^{2+} adsorption by PMMA, respectively. Citric acid could provide more adsorption sites for PMMA to adsorb Cu^{2+} when it adsorbed on PMMA. These results were similar with Cu^{2+}
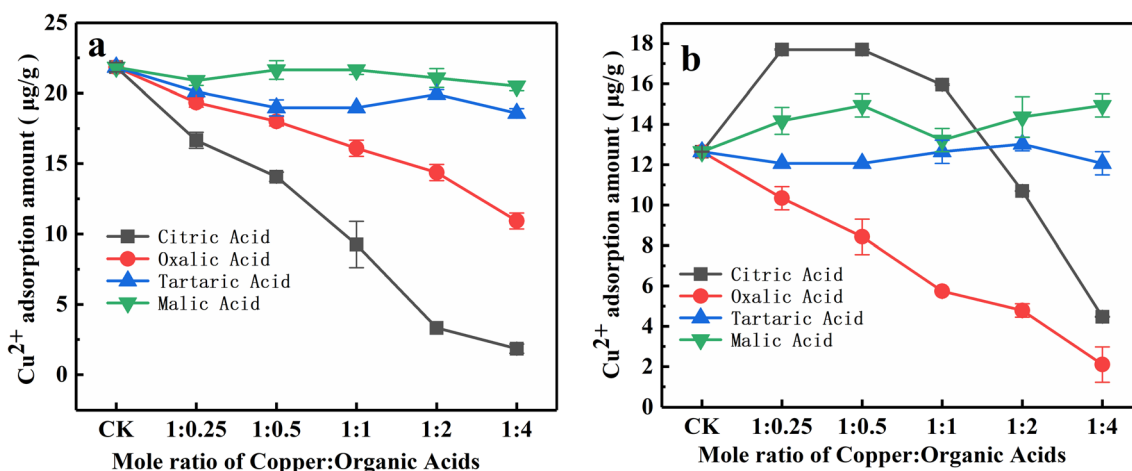

Fig. 3 Effects of different concentrations of LMWOAs on Cu^{2+} adsorption by PA (**a**) and PMMA (**b**)
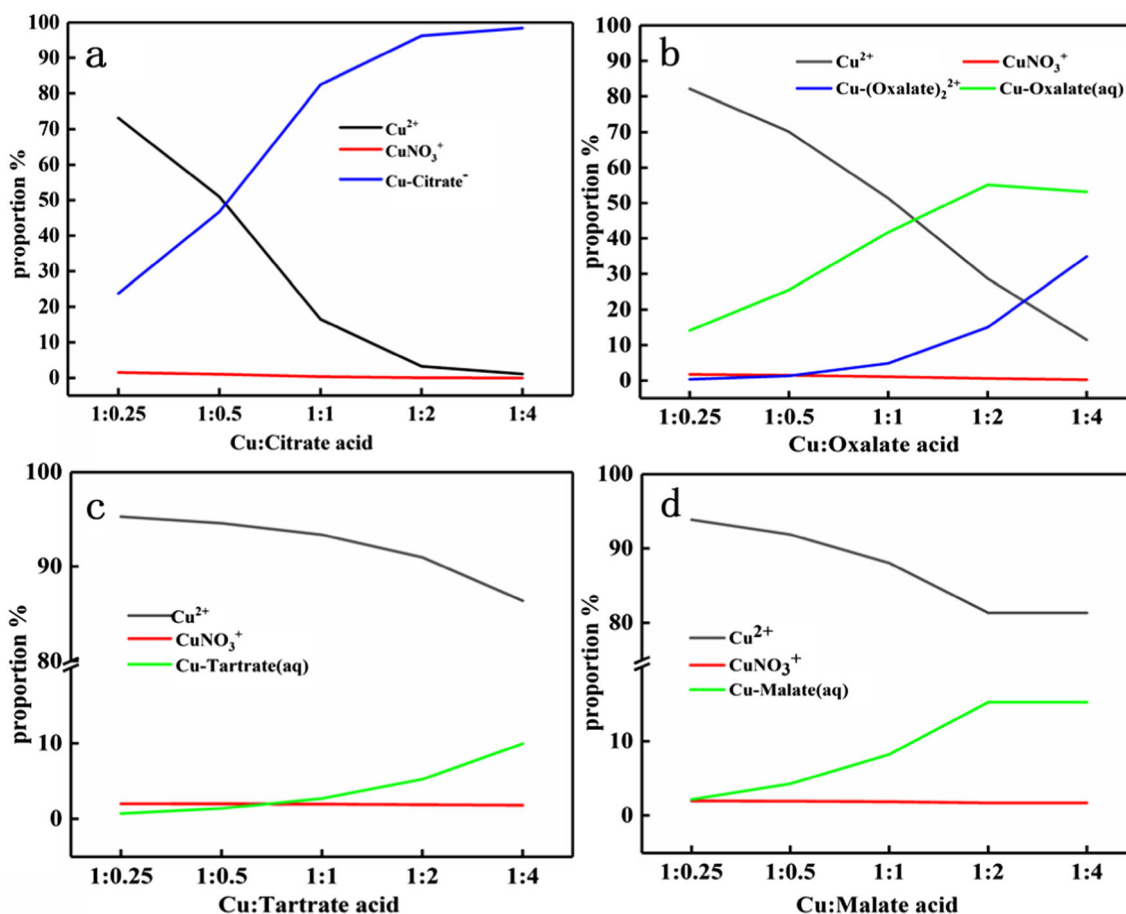
Fig. 4 Main Cu speciation in the solution under various molar ratio of Cu to organic acid (total Cu concentration 0.5 mg/L, pH = 6; simulated by Visual MINTEQ, the proportion less than 1% are excluded from diagram)

adsorption on biochar effected by citric acid and oxalic acid (Zhou et al., 2016). From Fig. 4a, when the mole ratios of Cu:citric acid > 1, the main Cu fraction was Cu^{2+} (positive charged), which was conductive to the Cu adsorption on PMMA. However, when the mole ratios of Cu:citric acid < 1, the main Cu fraction was Cu-citrate⁻ (negative charged), which was not conductive to the Cu adsorption on PMMA. Citric acid and oxalic acid are strong complexing agents for Cu^{2+}. The proportion of Cu^{2+} significantly decreased with increasing concentration of citric acid and oxalic acid. In contrast, tartaric acid and malic acid exhibited much weaker complexing abilities towards Cu^{2+} (Fig. 4).

It is possible that competitive adsorption sites on the plastic surface can reduce the adsorption of Cu^{2+} on the surface of MPs. Furthermore, low concentrations of citric acid can be used as complexing bridges to enhance the affinity of small-molecular organic acids for the MP surface, thus increasing Cu^{2+} adsorption on the surface of the MPs. Previous studies also revealed that organic acids can increase Cu^{2+} adsorption on the surface of hydroxyapatite and soil (Hu, 2005; Wang et al., 2009). Consequently, LMWOAs affect the Cu^{2+}

adsorption of MPs is via the complexation of it with Cu^{2+}. The presence of oxalic acid reduces the adsorbed Cu^{2+} on MPs, adsorption of Cu is almost not affected by tartaric acid and malic acid. In addition, the effect of citric acid on adsorption depends on MPs.

Effects of UV aging on Cu^{2+} adsorption by MPs

Figure 5 and Table S1 showed that Cu^{2+} adsorption on PA slightly decreased while it slightly increased on PMMA after UV aging. The adsorption capacities on aged PA and PMMA were 265 ± 25.7 μg/g and 79.4 ± 10.5 μg/g, respectively. ATR-FTIR spectra show that the absorption peaks of aged MPs are lower than those of the virgin MPs (Fig. S4), arising from the decomposition of the –C–C– chain, which could reduce molecular weights (Pushpadass et al., 2010). The carbonyl index of the spectra was defined as the ratio of the carbonyl absorption band to the optical density of the methylene absorption band. The carbonyl indexes could be obtained by calculating the magnitudes of the absorption peaks of virgin and aged MPs (Yousif et al., 2012; Briassoulis et al., 2015b). The absorption peaks of the carbonyl group and
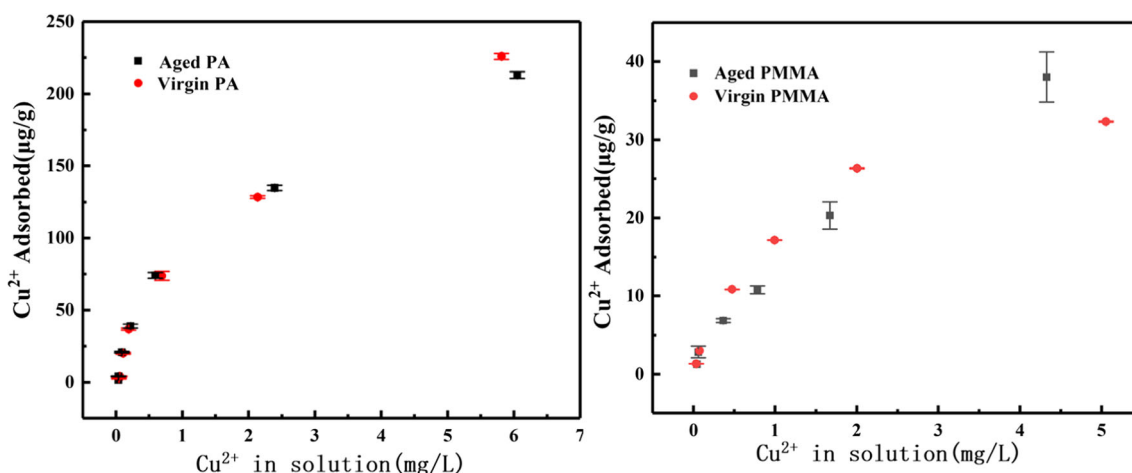
Fig. 5 Adsorption of Cu^{2+} on virgin and aged PA and PMMA (black is aged MPs, red is virgin MPs)

reference alkyl group in PA and PMMA were at 1634.9 cm^{-1} and 1439.6 cm^{-1} and 1721.2 cm^{-1} and 1434.3 cm^{-1}, respectively (Table 3). The carbonyl index of PA decreased from 13.6 to 9.04 while it increased from 2.79 to 4.94 for PMMA after UV aging. Müller et al. (2018) have found that PP (polypropylene) and PS weathered in UVA-340 nm fluorescent lamps (UV irradiance was 26 W/m^2) at 60 °C for 4 weeks. Carbonyl bands increased from 0.22 to 1.65 and from 0.33 to 1.24 (area unit), respectively. Hüffer et al. (2018) also found that UVC weathered PS MPs for 96 h make the carbonyl index increased from 0.36 to 1.61. (UVA and UVC are two types of ultraviolet light; UVA (320–420 nm) is generally used for aging test; UVC (200–275) is short-wave ultraviolet light is mainly used for sterilization.) The positive correlation between the Cu^{2+} adsorption capacities of the two MPs after aging and the number of carbonyl groups was consistent with previous studies. Godjevargova and Mihova (2003) have found that modified PA beads have more carbonyl groups than unmodified PA beads, and this makes the former adsorb more Cu^{2+}.

It has been previously reported that many types of polymers are susceptible to UV degradation because the energy of UV radiation exceeds that of all the strongest carbon bonds

(Murray et al., 2012). UV light can cause fracture of the polymer, a decrease in molecular weight, and the production of free radicals, or it may cause an increase in the length of the molecular chain and the crosslinking of the polymer (Yousif and Haddad, 2013). Different materials may require different aging conditions. Li et al. (2008) reported that carboxyl groups appeared in pure polypropylene after exposure for 80 days outdoors in Beijing, China. Degradation occurred and carbonyl peaks appeared after low-density polyethylene (LDPE) was exposed outdoors for 3000 h in Messina, Sicily (Italy) (Severini et al., 1993). Wavelengths less than 300 nm could lead to the generation of amide groups and breakage of N–C bonds in PA, while wavelengths ranging from 340 to 400 nm could lead to the production of free radicals in the polymer (Hu, 1998). The degradation of plastics might be affected by physical, chemical, and biological aspects of the comprehensive factors present under natural conditions, and cause an increase in the adsorption quantity when the number of oxygen functional groups increases. Generally, the adsorption capacity of aged MPs in the environment is greater than that of virgin MPs (Holmes et al., 2012; Mato et al., 2001; Turner and Holmes, 2015). The aging conditions need to be further optimized to determine the aging effects on the adsorption of heavy metals by MPs.

Table 3 Comparison of the peak area of different MPs before and after aging

Function group and vibration	Virgin PA			Aged PA			Functional groups changes
	Center	Area	Ratio	Center	Area	Ratio	
CH3 deformation absorptions	1439.6	1.615	13.6	1435.7	2.184	9.04	/
Acylamino C=O stretching	1634.8	21.96		1634.3	19.74		Decrease
Function group and vibration	Virgin PMMA			Aged PMMA			Functional groups changes
	Center	Area	Ratio	Center	Area	Ratio	
CH3 deformation absorptions	1434.3	3.887	2.79	1434.3	2.015	4.94	/
Acylamino C=O stretching	1721.2	10.82		1721.2	9.952		Increase

Conclusions

The results of this study reveal Cu^{2+} adsorption is greatly influenced by the type of MP. The Cu^{2+} adsorption capacities of PA and PMMA were higher than those of the other MPs (PE, PS, PET, PVC) and were affected by the surface area, chemical group, etc. The Cu^{2+} adsorption capacities of PA and PMMA reach the maximum when pH is at 6 and 7, respectively. The presence of Ca^{2+} and Mg^{2+} inhibited Cu^{2+} adsorption by MPs. Different concentrations and types of LMWOAs had different effects on Cu^{2+} adsorption. The presence of oxalic acid reduces the adsorbed Cu^{2+} on MPs, adsorption of Cu is almost not affected by tartaric acid and malic acid. In addition, the effect of citric acid on adsorption depends on MPs. In addition, UV aging (200 h) had a different effect on Cu^{2+} adsorption by MPs, which depends on the change of carbonyl index. Overall, different soil environmental factors could affect Cu^{2+} adsorption on MPs, and this provides important data that improve our understanding of the behavior of MPs in a terrestrial environment. Further studies are required and the focus should include (1) how different components of the soil compete with MPs to adsorb Cu^{2+}, (2) investigation of the adsorption capacity of aged MPs, and (3) investigation of the adsorption of other heavy metals on MPs in a terrestrial environment.

Compliance with ethical standards

Ethical approval All experiments comply with the current laws of China. This article does not contain any studies with human participants or animals performed by any of the authors.

Conflict of interest The authors declare that they have no conflicts of interest.

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