

Original Research

Root Exudates Alter the Adsorption and Desorption Capacities of Aged MPs for Cd²⁺

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Abstract

Microplastics (MPs) and Cd widely coexist in the soil environment. However, how root exudates (REs) affect the interactions between MPs and Cd²⁺ remains poorly understood. In this study, we investigated the effects of simulated and real REs on the adsorption of Cd²⁺ by and desorption of Cd²⁺ from aged MPs (polystyrene, PS; polylactic acid, PLA). Results showed that simulated single root exudate (SSRE) significantly decreased the adsorption capacities of the two aged MPs for Cd²⁺, especially citric acid (CA). Simulated mixed REs (SMREs) and real mixed REs (RMREs) showed inhibitory trends, where the Cd²⁺ adsorption capacity of MPs declined as RE concentrations increased. With regard to Cd²⁺ desorption, CA dramatically boosted desorption rates by 228% for aged PS-MPs and 489% for aged PLA-MPs compared with the control group. In contrast, individual serine and glucose reduced Cd²⁺ desorption efficiency. SMREs and RMREs generally facilitated Cd²⁺ desorption, except at high RMRE concentrations, but these promoting effects did not show a linear correlation with RE concentrations. Cd²⁺ adsorption by the two aged MPs in the presence of SSRE was well fitted by the quasi-secondary kinetic model. These findings highlight that the environmental fate of heavy metals in rhizosphere soil containing MPs deserves greater research attention.

Keywords: aged microplastics, root exudates, cadmium, adsorption, desorption

Introduction

Pollution by microplastics (MPs) is a global environmental problem, as their particles can be transported in terrestrial, aquatic, and atmospheric ecosystems through wind, surface and subsurface runoff, and infiltration [1]. The terrestrial environment, especially agricultural soil, is the main source and sink of MPs due to the extensive use of mulching film. Mulching

film can form MPs of various sizes under the effects of weathering, abrasion, oxidation, and degradation [2, 3]. Owing to their small size, strong hydrophobicity, aging and surface functional groups, and large specific surface area, MPs can easily act as carriers to adsorb contaminants and change their environmental behaviors [4, 5]. This phenomenon is more pronounced in aged MPs, as they have abundant pores, cracks, fractures, and pits as well as oxygen-containing functional groups (–OH, C=O, =CH, –C=O, and –COOH) and a large surface area [6, 7]. These structural and chemical alterations collectively enhance the pollutant adsorption affinity of MPs. Previous studies have confirmed that the adsorption

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capacity of MPs toward contaminants rises progressively with the degree of aging [6, 8]. Heavy metals (HMs) are among the most common contaminants adsorbed by MPs because of their widespread occurrence in various environments, including agricultural soil. Hou et al. [9] estimated that 14-17% of cropland exceeds agricultural thresholds for at least one toxic metal based on 796084 sampling points from 1493 regional studies worldwide. The adsorption of HMs by MPs is primarily governed by sole electrostatic attraction and the combined effects of electrostatic interaction and surface complexation, such as the hydrophilicity of MPs induced by surface groups [10, 11]. Nevertheless, such adsorption processes are susceptible to multiple variables, including MP type and characteristics, the chemical characteristics of HMs and environmental factors, such as pH, ionic strength, organic matter, and microbes [12, 13]. Bi et al. [14] investigated the adsorption behavior and mechanism of HMs onto MPs based on meta-analysis assisted by machine learning of 134 publications, and found that MP/HM concentrations, specific surface area of MPs, and pH significantly affected the adsorption of HMs by MPs. Lu et al. [15] found that humic acid (HA) promoted the adsorption of Pb^{2+} on PS-MPs, and the higher the HA concentration was, the greater the adsorption of Pb^{2+} by MPs.

The rhizosphere is a special microzone that is widely present in soil, particularly farmland, where abundant root-derived compounds accumulate. These secretions include phenols, mucilage, sugar, organic acids, lipids, proteins, and amino acids [16]. Root exudates (REs) can release H^+ , bear abundant polar functional groups, and exhibit surfactant properties and thus may change the adsorption and desorption of HMs by MPs. Low-molecular-weight organic acids, such as acetic, citric, oxalic, tartaric, and malic acids, may facilitate HM mobilization in the rhizosphere [17]. Luo et al. [18] found that aged polypropylene microplastics (PP-MPs) interacted more strongly with HA, and there was a higher affinity between them. Their work also demonstrated that fulvic acid (FA) increased oxygen-containing functional groups on the surface of polystyrene microplastics (PS-MPs) [19]. Meanwhile, MP exposure stimulates the biosynthesis and exudation of amino acids by plant roots [20]. These processes may cause more complicated interactions between MPs and HMs in the rhizosphere than in the non-rhizosphere. However, relevant research remains limited. Abbasi et al. [21] reported that PET particles could act as a vector in transferring heavy metals to the rhizosphere zone. Jędruchiewicz et al. [12] pretreated artificial MPs via microwave-assisted HNO_3 digestion to investigate how simulated root exudates affect HM leaching from MPs and found that HM leaching efficiency followed the order: soil solution > root exudate solution > distilled water. Liu et al. [22] found that low-molecular-weight organic acids induced by aged MPs and As-Cd exert critical controls over As-Cd bioavailability and microrhizosphere environment.

In this study, aged MPs-PS and aged MPs-PLA were chosen to investigate the effects of simulated and real root exudates on the adsorption and desorption of Cd^{2+} by the two aged MPs. Polystyrene is widely used because of its versatility in applications, such as insulation foam, packaging, medical supplies, and biaxially oriented film for food packaging. Over the past decade, PS waste has accounted for approximately 10% of global plastic debris [23]. Polylactic acid is a biodegradable polymer with the largest production among all bioplastics [24]. Driven by the sustainable environmental development strategy, the application of degradable polymers has been expanding rapidly [25]. Nevertheless, both PS and PLA are prone to fragment into microplastics (MPs) once released into the environment and subjected to long-term weathering, regardless of their inherent biodegradability [26]. Given that the adsorption of HMs by MPs may be affected by organic matter and organic acids, we hypothesized that root exudates could change the adsorption and desorption capacities of aged MPs for Cd^{2+} by competing for adsorption sites and changing the polarity of MPs, but the effects depend on the components and concentrations of root exudates.

Materials and Methods

Materials

Pure 100-mesh (150 μm in diameter) MPs-PS and MPs-PLA were purchased from Huachuang Plasticising Co., Ltd. (China). All other chemicals were purchased from Beijing Chemical Reagents Company (China), and they were of analytical grade.

Preparation of Aged MPs

MPs were treated by Fenton oxidation according to the procedure of Velo-Gala et al. [27]. Briefly, 1.2 mL of 30% H_2O_2 and 77.6 mL of deionized water were mixed in a 200 mL conical flask, and then 1.2 mL of 200 mmol/L $FeSO_4$ solution and 2.00 g of MPs (PS or PLA) were added. The mixture was shaken at 25°C and 180 rpm. After the aging treatment, the suspension was filtered using a 0.22 μm membrane filter to collect aged MPs. The characteristics of the two aged MPs are shown in Supplementary Material 1.

Preparation of Aged MPs with Cd^{2+} (MPs-Cd)

This experiment aimed to prepare Cd^{2+} -loaded aged MPs (MPs-Cd) for subsequent Cd^{2+} desorption experiments under RE exposure. Twenty grams of aged MPs (PS or PLA) and 20 mL of 1.0 mg/L Cd^{2+} solution were added to a 250 mL conical flask. The conical flask was shaken at 180 rpm and 25°C until the aqueous Cd^{2+} concentration reached equilibrium. The suspension was filtered through a 0.45 μm membrane, and the filtrate was used to determine Cd^{2+} concentration. Based on

the Cd^{2+} concentration difference in solution, the adsorption capacity of aged MPs for Cd^{2+} was calculated. Aged MPs-Cd included aged MPs-PS-Cd and aged MPs-PLA-Cd.

Effects of Root Exudates on the Adsorption and Desorption of Aged MPs for Cd^{2+}

Simulated Single Root Exudate (SSRE)

Glucose, serine, and citric acid (CA) are the primary components of root exudates, and they were chosen as representatives of SSRE in this study [28].

Experiment on the adsorption of Cd^{2+} by aged MPs in the presence of SSRE: This experiment had four factors, which included two types of aged MPs (MPs-PS and MPs-PLA), one Cd^{2+} level (1.00 mg/L), three SSREs (glucose 10.0 mmol/L, serine 12.5 mmol/L, and CA 25.0 mmol/L), and seven sampling time points (0.5, 1.0, 3.0, 5.0, 12, 24, and 36 h). There were 42 treatments in total, and each treatment had three replicates. The corresponding SSRE solution, 20 mL of 1.0 mg/L Cd^{2+} solution, and 20 mg of aged MPs were added to a 100 mL conical flask. In the control treatment, SSRE was replaced with deionized water while all other experimental conditions remained identical. All flasks were shaken at 180 rpm and 25°C. Aqueous samples were taken at predetermined time intervals and filtered through 0.45 μm membrane filters. The residual Cd^{2+} concentration in the filtrate was quantified, and the Cd^{2+} adsorption capacity of aged MPs under SSRE exposure was calculated from the variation in aqueous Cd^{2+} concentrations.

Experiment on the Cd^{2+} desorption from Cd^{2+} -loaded aged MPs in the presence of SSRE: Twenty milligrams of Cd^{2+} -loaded aged MPs (MPs-PS-Cd or MPs-PLA-Cd) were added to a 100 mL conical flask, and then 40 mL of SSRE solution (10.0 mmol/L glucose, 12.5 mmol/L serine, or 25 mmol/L citric acid) was added. In the control treatment, the SSRE solution was replaced with an equal volume of deionized water, while all other experimental parameters remained consistent. All conical flasks were shaken at 180 rpm and 25°C for 24 h. At the end of the experiment, an aqueous sample was filtered through a 0.45 μm membrane. The filtrate was used to determine the dissolved Cd^{2+} concentration. Based on the Cd^{2+} concentration difference in solution, the Cd^{2+} desorption capacity of aged MPs under SSRE exposure was calculated from the variation in aqueous Cd^{2+} concentrations.

Simulated Mixed Root Exudates (SMREs)

Experiment on Cd^{2+} adsorption by aged MPs in the presence of SMREs: The experiment had four factors, which included two types of aged MPs (MPs-PS and MPs-PLA), one Cd^{2+} level (1.00 mg/L), three SMRE concentrations (low, medium, and high), and one sampling time point (36 h). There were 6 treatments in

total, and each treatment had three replicates. The low SMREs contained 2.67 mmol/L glucose, 2.67 mmol/L fructose, 1.33 mmol/L sucrose, 2.67 mmol/L tartaric acid, 1.98 mmol/L oxalic acid, 1.3 mmol/L citric acid, 1.33 mmol/L histidine, 1.33 mmol/L serine, and 0.78 mmol/L glutamic acid. The medium and high concentrations of SMREs were twofold and threefold the low SMRE concentration, respectively. All experimental procedures were consistent with those adopted in the SSRE experiments.

Experiments on Cd^{2+} desorption from Cd^{2+} -loaded aged MPs in the presence of SMREs: Twenty milligrams of Cd^{2+} -loaded aged MPs (MPs-PS-Cd or MPs-PLA-Cd) were added to a 100 mL conical flask, and then 40 mL of SMRE solution (low, medium, and high) was added. All other experimental procedures were identical to those used for the SSRE experiments.

Real Mixed Root Exudates (RMREs)

RMREs were collected from rice seedlings according to the method described by Williams et al. [29]. Briefly, 15 rice plants (at the five-leaf stage) were selected and rinsed with sterile deionized water. The seedlings were suspended in a 500 mL conical flask that contained 300 mL of sterile deionized water. The conical flask was placed on ice to prevent RMRE biodegradation during collection. The collection process lasted 18 h in an artificial climate chamber at 25°C. Finally, the RMRE solution was filtered through a 0.22 μm membrane. The original RMRE solution was diluted with deionized water at dilution ratios of 1.0 $\times$, 2.0 $\times$, and 5.0 $\times$ to obtain high, medium, and low RMRE concentrations, respectively.

Experiment on the adsorption of Cd^{2+} by aged MPs in the presence of RMREs: Three concentrations of RMREs were used, and all other experimental procedures were consistent with the SSRE adsorption experiment described in the Section of simulated single root exudate (SSRE).

Experiments on Cd^{2+} desorption from Cd^{2+} -loaded aged MPs in the presence of RMREs: This experiment was conducted in 250 mL conical flasks, and each conical flask contained 200 mL of 10% sterile Hoagland solution and 200 mg of MPs-PS-Cd or MPs-PLA-Cd (prepared in the Section of preparation of aged MPs with Cd^{2+} (MPs-Cd)). One, three, and six rice seedlings (10 cm in height) were cultivated in individual flasks to produce low, medium, and high RMRE concentrations, respectively. The nutrient solution was replenished every three days to maintain a constant volume throughout the incubation. All seedlings were grown in an artificial climate chamber with a 10 h light/14 h dark photoperiod, a light intensity of 480 $\mu\text{mol}/(\text{m}^2\cdot\text{s})$, day/night temperatures of 20-25°C and 15-20°C, and a relative humidity of 50-85%. The experiment lasted 21 days. At the end of the incubation, aqueous samples were collected and filtered through a 0.45 μm membrane. The filtrates were analyzed to determine dissolved Cd^{2+} concentrations.

The Cd^{2+} desorption capacity of aged MPs under RMRE exposure was calculated based on the variation in solution Cd^{2+} concentrations before and after the experiment.

Adsorption Kinetics

The kinetics of Cd^{2+} adsorption by the two aged MPs were modeled using two kinetic models: Quasi-primary kinetics (QPK) and Quasi-secondary kinetics (QSK) [30].

$$\text{QPK: } q_t = q_e(1 - e^{-k_1 t})$$

$$\text{QSK: } q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t}$$

where k_1 is the quasi-primary kinetic reaction rate constant, i.e., the physical adsorption rate (min^{-1}); and k_2 represents the quasi-secondary kinetic reaction rate constant, i.e., chemisorption rate ($\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$). q_e (mg/g) is the adsorption capacity at equilibrium, and q_t (mg/g) is the adsorption capacity at time t .

Effect Of Citric Acid on The Two-Dimensional Correlation Spectroscopy (2D-COS) Spectra of Two Aged MPs

To further elucidate the structural variations of aged MPs induced by REs, citric acid was selected as a representative root exudate to investigate its effects on 2D-COS spectra. Three CA concentrations were set: 0, 25.0, and 50.0 mmol/L. The experimental procedures were identical to those described for the SSRE-mediated Cd^{2+} adsorption experiment on aged MPs, with a fixed adsorption duration of 24 h.

Determination and Characterization

Cd^{2+} Concentration in Solution

Cd^{2+} concentration in solution was determined using inductively coupled plasma optical emission spectrometry (ICP-OES) with an Avio 200 instrument (PerkinElmer, USA). The adsorption capacity (Q_e) of aged MPs for Cd^{2+} was calculated according to the following equation:

$$Q_e = \frac{(C_0 - C_e) \cdot V}{m}$$

where C_0 is the initial Cd^{2+} concentration in solution before the adsorption process; C_e is the Cd^{2+} concentration when adsorption is in equilibrium (mg/L); V is the volume of the solution (L); and m is the mass of aged MPs (mg).

The desorption capacity (Q_m) of Cd^{2+} from aged MPs-Cd was calculated according to the following equation:

$$Q_m = \frac{(C_i - C_0) \times V}{m}$$

where C_0 is the initial Cd^{2+} concentration in solution before the desorption process; C_i is the Cd^{2+} concentration in solution when Cd^{2+} desorption is in equilibrium (mg/L); V is the volume of the solution (L); and m is the mass of the adsorbent (mg).

Characterization of Aged MPs

The infrared spectra of aged MPs were analyzed using an FTIR spectrophotometer (Nicolet iS5, Thermo Fisher Scientific, USA) over the wavenumber range from 4000 to 400 cm^{-1} . 2D-COS analysis of the infrared spectrum was conducted using the 2D Shige software [31].

Statistical Analysis

Statistical significance ($P < 0.05$) was evaluated via one-way ANOVA and post-hoc LSD tests using SPSS 26. Linear and nonlinear least-squares fitting were applied to match adsorption kinetic and isotherm curves and derive relevant model parameters.

Results and Discussion

Effects of Root Exudates on Cd^{2+} Adsorption by Aged MPs

Simulated Single Root Exudate (SSRE)

Compared with the deionized water control, three SSREs significantly decreased the adsorption capacity of MPs-PS for Cd^{2+} (Fig. 1). Among them, CA exhibited the strongest inhibitory effect with an adsorption reduction rate of 88.5%, whereas glucose showed the weakest inhibition (21.4%). As a ternary organic acid, CA contains three -COOH groups and an -OH group. In aqueous solution, CA-released H^+ competes with Cd^{2+} for available adsorption sites on the surface of aged MPs-PS [32], which reduces the surface electronegativity of aged MPs, alters the protonation state of the MP surface, and changes the speciation of dissolved Cd^{2+} , thereby reducing the adsorption capacity of aged MPs for Cd^{2+} [33]. In addition, the deprotonated citrate ions can form stable complexes with aqueous Cd^{2+} [34] and lower the concentration of free Cd^{2+} in solution. Complexation and electrostatic interactions are regarded as the main forces for heavy metal adsorption by MPs-PS [35]. Therefore, CA produces the largest effect on Cd^{2+} adsorption by aged MPs-PS. This finding is consistent with the result of Cheng et al. [7] who found that fulvic acid inhibited Cu^{2+} adsorption by competing for adsorption sites and forming complexes with Cu^{2+} on the polyamide (PA) and PLA MPs. In contrast, glucose is a monosaccharide with

five -OH groups and rarely forms complexes with Cd^{2+} or releases H^+ . These properties weaken its inhibitory effect on Cd^{2+} adsorption. Serine has a -COOH group, a -NH₂ group, and an -OH group and can release a small amount of H^+ and chelate Cd^{2+} [33]. However, the -NH₂ group is mostly protonated to -NH₃⁺ under aqueous conditions, generating electrostatic repulsion toward cationic Cd^{2+} . Furthermore, Cd^{2+} binding near serine residues increases the hydrophobicity of the local microenvironment [36]. These effects are unfavorable for further Cd^{2+} adsorption. Consequently, serine shows a moderate inhibitory effect, with a reduction magnitude lower than that of CA but higher than that of glucose. Similar inhibitory trends of SSREs on Cd^{2+} adsorption were also observed for aged MPs-PLA (Fig. 1).

In terms of MP type, aged PLA-MPs exhibited markedly lower Cd^{2+} adsorption capacities than aged PS-MPs in deionized water. This may be related to the following facts: (i) Due to their high density, the specific surface area of aged MPs-PLA is lower than that of aged MPs-PS when the same weight of MPs is used [37]; (ii) Aged MPs-PS have more groups that can adsorb Cd^{2+} [38]. In the presence of serine or CA, however, the opposite trend was observed. This is possibly because (i) aged MPs-PLA are more hydrophilic (water contact angle is about 80 degrees) than aged MPs-PS (water contact angle is about 96 degrees) and easily adsorb or react with hydrophilic serine and CA. A larger water contact angle corresponds to stronger surface hydrophobicity, which hinders PS-MPs from capturing hydrophilic Cd^{2+} . Ding et al. [39] found that the water contact angles were consistent with the relative adsorption capacities of PS particles for organic pollutants. (ii) Aged MPs-PLA have more oxygen-containing functional groups during the cleavage of ester bonds (-COO-), such as hydroxyl (-OH) and carboxyl (-COOH), and they may form complexes with Cd^{2+} . By contrast, glucose only slightly suppressed Cd^{2+} adsorption onto aged

PLA-MPs (a decrease of 1.46%). This weak inhibitory effect is possibly because glucose cannot dissociate H^+ and barely interferes with surface adsorption sites or forms complexes with dissolved Cd^{2+} .

In summary, root exudates with -COOH groups impose a stronger inhibitory effect on HM adsorption by MPs than root exudates lacking -COOH groups, such as proteins, lipids, and sugars. Some plants, such as rice, wheat, bean, corn, and tobacco, secrete abundant low-molecular-weight organic acids, including tartaric acid, oxalic acid, citric acid, and propionic acid [40], and HM adsorption by MPs in their rhizosphere is low. Certainly, if HM-loaded MPs migrate into the rhizosphere, adsorbed metals may desorb into the surrounding environment, elevating HM exposure risks to soil matrices and terrestrial plants. In addition, it should be pointed out that root exudates differ across plant developmental stages and diurnal time points and under abiotic and biotic stresses [41], and the presence of HMs can also affect root exudates [42]. These variables make the interactions among root exudates, MPs, and HMs highly complex.

Simulated Mixed Root Exudates (SMREs)

Mixed root exudates are more prevalent than single root exudates in the rhizosphere. In this study, we investigated the effects of SMREs on the adsorption capacities of the two aged MPs for Cd^{2+} . Compared with deionized water, SMREs significantly decreased the adsorption capacities of the two aged MPs for Cd^{2+} regardless of SMRE concentration (Fig. 2). The higher the SMRE concentration was, the lower the adsorption capacity of aged MPs for Cd^{2+} was. SMREs contain more organic acids and amino acids than SSREs, such as tartaric acid, oxalic acid, citric acid, glutamic acid, histidine, and serine. These compounds release abundant H^+ and promote the generation of Cd^{2+} complexes. As a result, the two aged MPs exhibit weaker Cd^{2+} adsorption capacities under SMRE treatment than under SSRE treatment.

In terms of MP type, the adsorption capacity of aged MPs-PS for Cd^{2+} was significantly higher than that of aged MPs-PLA regardless of SMRE concentration. This finding differs from the effects of serine and citric acid on Cd^{2+} adsorption by the two aged MPs. The possible reason is that SMREs consist of a greater variety of hydrophilic components that have a greater impact on hydrophilic MPs-PLA. Li et al. [43] found that the existence of different adsorbates affected their adsorption behavior on adsorbents. The detailed impact mechanisms need to be studied in the future.

Real Mixed Root Exudates (RMREs)

The above results have confirmed that SMREs can significantly decrease the adsorption capacities of the two aged MPs for Cd^{2+} (Fig. 2). However, it is unclear whether RMREs can produce similar inhibitory effects.

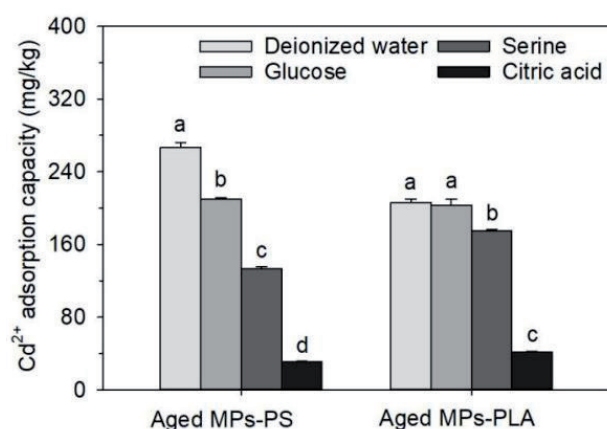


Fig. 1. Effects of SSRE on Cd^{2+} adsorption by the two aged MPs. Different lowercase letters for each aged MP indicate significant differences among four treatments at $p < 0.05$. Data are presented as mean $\pm$ standard deviation (SD, $n = 3$). The same applies below.

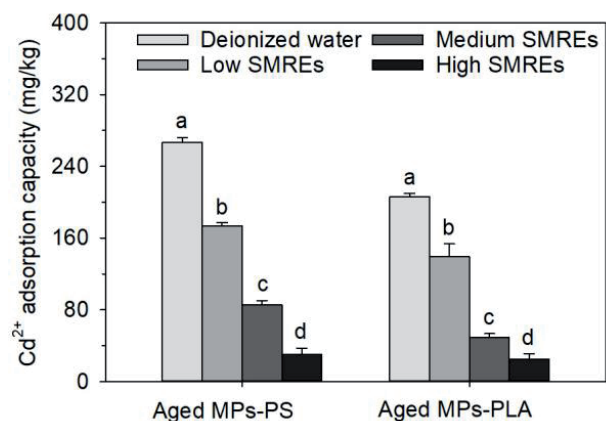


Fig. 2. Effects of SMREs on Cd²⁺ adsorption by the two aged MPs

RMREs are widely present in the soil environment, and their effects on MPs and HMs have attracted much attention [44, 45]. Herein, RMREs were secreted by rice plants. As shown in Fig. 3, compared with deionized water, the adsorption capacities of the two aged MPs for Cd²⁺ decreased with increasing RMRE concentration regardless of aged MP type, indicating that the higher the RMRE concentration was, the lower the adsorption capacity of aged MPs for Cd²⁺ was. This is consistent with the trend induced by SMREs.

In terms of MP type, the adsorption capacity of aged MPs-PS for Cd²⁺ was significantly higher than that of aged MPs-PLA regardless of RMRE concentration, which was consistent with the trend induced by SMREs. RMREs are more complex than SMREs, and their abundant components exert pronounced effects on the interaction between aged MPs and Cd²⁺.

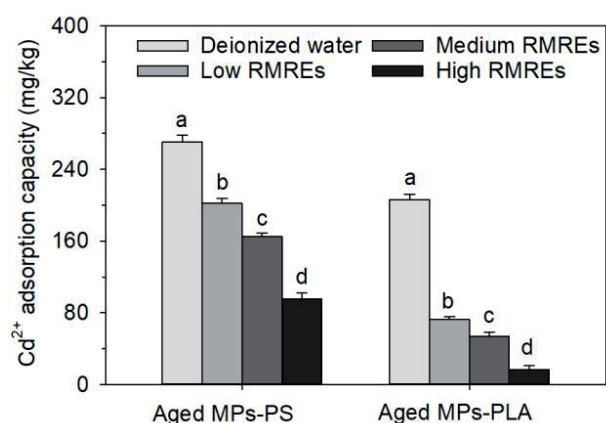


Fig. 3. Effects of RMREs on Cd²⁺ adsorption by the two aged MPs.

Effects of Root Exudates on Cd²⁺ Desorption from Aged MPs-Cd

Simulated Single Root Exudate (SSRE)

Compared with deionized water, CA significantly boosted Cd²⁺ desorption from aged MPs-PS-Cd and MPs-PLA-Cd by 252% and 490%, respectively, whereas serine and glucose exerted the opposite effects (Fig. 4). The large amount of H⁺ released by CA may be a key factor influencing Cd²⁺ release [46]. These hydrogen ions compete with surface-bound Cd²⁺ on aged MPs and facilitate Cd²⁺ desorption [47]. Moreover, the carboxyl groups of CA can form complexes with Cd²⁺ adsorbed by aged MPs, further accelerating Cd²⁺ desorption [48]. In theory, serine is expected to induce a similar effect, yet the results contradicted this speculation. This may be related to the following facts: (i) less H⁺ is released by serine due to its lower isoelectric point (5.68) relative to the natural water pH value [49]; (ii) Serine is a weak chelating agent that cannot readily remove Cd²⁺ from aged MPs; (iii) The positive charges of serine compress the electric double layer and stabilize the solid-liquid interface, hindering the release of adsorbed Cd²⁺ from aged MPs [50]. These factors cause serine to suppress Cd²⁺ desorption. Glucose exerts an identical inhibitory effect via comparable pathways.

In terms of MP type, Cd²⁺ desorption from aged MPs-PS-Cd was higher than that from aged MPs-PLA-Cd in deionized water, whereas the opposite trend emerged in the presence of CA. In deionized water, Cd²⁺ desorption is largely governed by the intrinsic Cd²⁺ adsorption capacity of MPs. The larger the adsorption capacity of MPs for Cd²⁺ is, the larger the desorption capacity for Cd²⁺ from MPs is. However, Cd²⁺ desorption capacity is controlled by CA's solubilizing effect and MP properties in the presence of CA. For example, MPs-PLA adsorb Cd²⁺ through weak forces and Cd²⁺ is readily desorbed from MPs, while MPs-PS adsorb Cd²⁺ through strong forces that hinder Cd²⁺ desorption [51]. Previous studies have verified that the adsorption of Cd²⁺ by aged

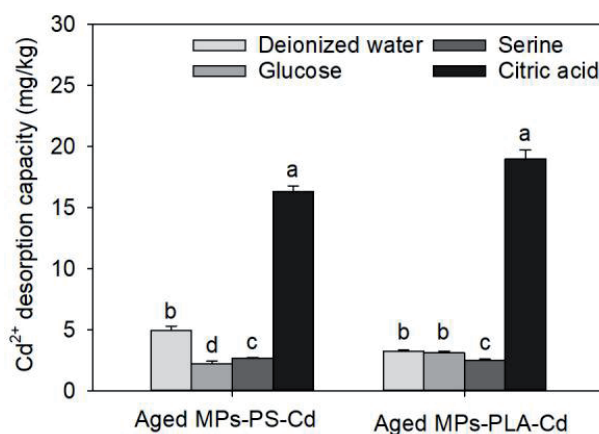


Fig. 4. Effects of SSRE on Cd²⁺ desorption from the two Cd-loaded aged MPs.

MPs-PS occurs mainly through covalent bonds [52], which substantially impedes Cd^{2+} detachment.

Simulated Mixed Root Exudates (SMREs)

Due to their widespread presence in the environment, we investigated the effects of SMRE concentrations on Cd^{2+} desorption. Compared with deionized water, SMREs significantly increased Cd^{2+} desorption from aged MPs-Cd regardless of MP concentration and type (Fig. 5). Among them, a low concentration of SMREs caused the largest increase in Cd^{2+} desorption, whereas medium and high concentrations of SMREs yielded weaker promoting effects. This is possibly because abundant components in medium and high concentrations of SMREs preferentially bind free aqueous Cd^{2+} to form soluble metal complexes [42]. These Cd-complexes can be removed from solution by a microporous membrane when determining Cd^{2+} concentration, lowering the concentration of free Cd^{2+} in solution. Theoretically, medium and high SMRE concentrations should trigger larger Cd^{2+} desorption than low SMRE concentration, but this phenomenon is masked by the interaction between root exudates and free Cd^{2+} in the aqueous phase. This speculation needs to be confirmed in future studies.

Real Mixed Root Exudates (RMREs)

To clearly confirm the effects of RMREs on Cd^{2+} desorption from aged MPs-Cd, we conducted an experiment in which root exudates were continuously secreted by rice plants in solution for 21 days. As shown in Fig. 6, compared with deionized water, low and medium RMRE concentrations significantly increased Cd^{2+} desorption from aged MPs-Cd regardless of MP type, which was consistent with the promoting effects induced by SMREs. In contrast, high RMRE concentration significantly decreased Cd^{2+} desorption compared with deionized water. This is contrary to the effect induced by high SMRE concentration.

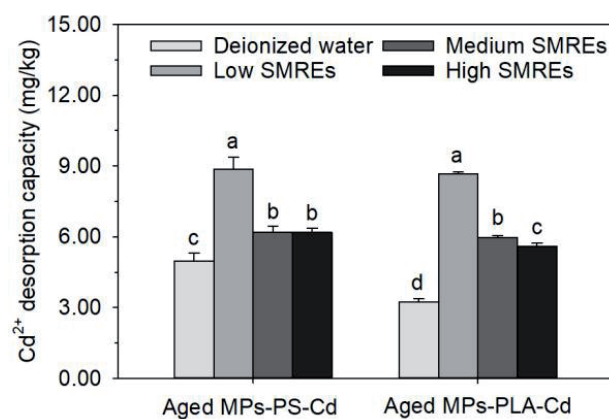


Fig. 5. Effects of SMREs on Cd^{2+} desorption from the two Cd-loaded aged MPs.

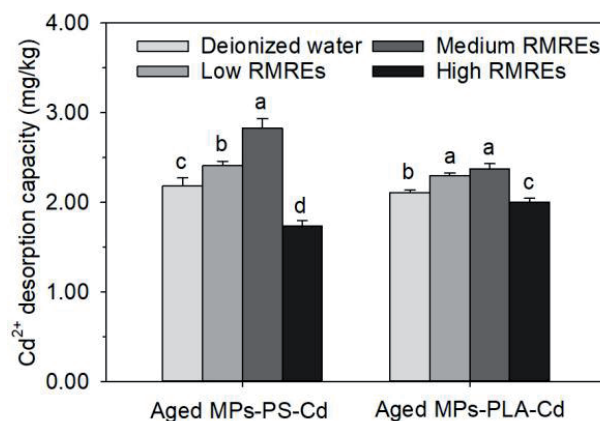


Fig. 6. Effects of RMREs on Cd^{2+} desorption from the two Cd-loaded aged MPs.

The possible reason is that desorbed Cd^{2+} is absorbed by rice plants. A high concentration of RMREs was produced by six rice plants, which accumulated more dissolved Cd^{2+} from the solution than the systems containing only one or three seedlings. Accordingly, the apparent reduction in measured Cd^{2+} desorption at a high RMRE level does not reflect the true desorption capacity of MPs. Theoretically, high RMRE concentration should trigger greater Cd^{2+} desorption than low and medium concentrations. This hypothesis could have been verified by quantifying Cd^{2+} accumulation within rice tissues, yet we omitted this measurement in the original trial. A supplementary experiment has recently been completed to validate the above inference.

In terms of MP type, Cd^{2+} desorption from the two Cd-loaded aged MPs did not show an obvious difference between deionized water and the low RMRE concentration. At the medium RMRE concentration, aged MPs-PS-Cd showed greater Cd^{2+} desorption than aged MPs-PLA-Cd, whereas the opposite trend was found at high RMRE concentration. This material-specific variation in Cd^{2+} desorption behavior is analogous to the patterns induced by SSRE and SMREs.

Adsorption Kinetics of Aged MPs for Cd^{2+} in the Presence of SSRE

Adsorption of Cd^{2+} by aged MPs in solution showed three stages regardless of MP type and the presence of SSRE (Fig. 7). At the initial stage (0-5 h), the adsorption increased rapidly, followed by a slight increase within 5-12 h. The slowest adsorption occurred at the last stage (12-36 h), until the adsorption equilibrium was attained. This pattern is consistent with the results of most studies on HM adsorption by MPs [14, 53]. At the beginning of the reaction, more vacant binding sites are available for Cd^{2+} capture. As sites are gradually saturated, electrostatic repulsion between adsorbed Cd^{2+} and the diminishing number of vacant sites hinders further adsorption.

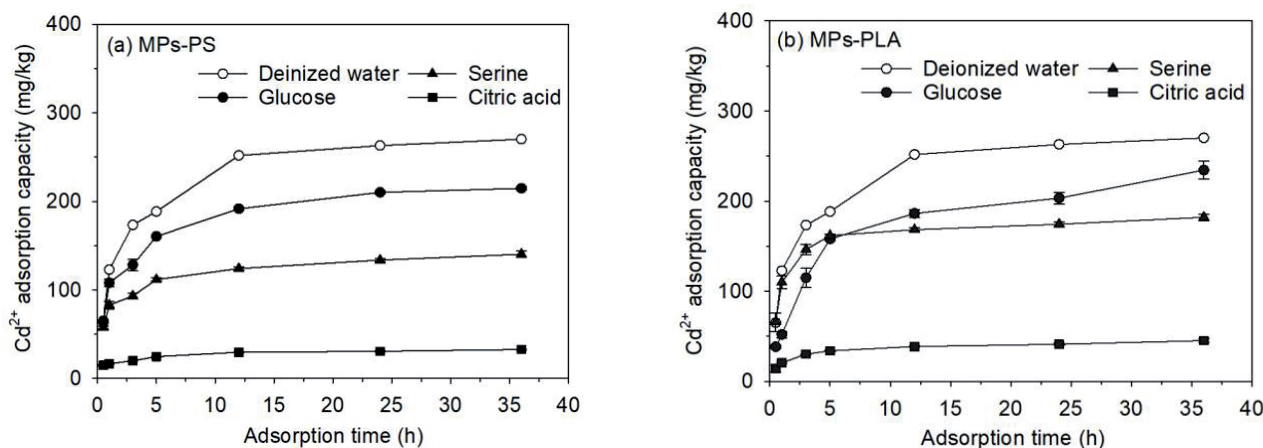


Fig. 7. Effects of SSRE on the kinetics of Cd^{2+} adsorption by the two aged MPs.

Adsorption kinetic models are widely used to evaluate adsorbent performance and reveal the mass transfer mechanism during adsorption [54]. In this study, the quasi-primary and quasi-secondary kinetic models were fitted. The kinetics of Cd^{2+} adsorption by the two aged MPs in the presence of SSRE were summarized in Table 1. Both kinetic models predicted that compared with deionized water, $Q_{e,\text{cal}}$ was lower in the presence of SSRE regardless of SSRE type (Table 1). CA caused the largest $Q_{e,\text{cal}}$ decrease of 87.9%–88.2% in aged MPs-PS and 78.8%–79.1% in aged MPs-PLA. These results are consistent with the changes in $Q_{e,\text{exp}}$, confirming that REs can decrease Cd^{2+} adsorption by aged MPs in the experimental and simulation studies. Such phenomena can be explained by three main mechanisms: (i) REs preferentially coordinate with Cd^{2+} to generate metal–organic complexes, thereby lowering the concentration of free Cd^{2+} in solution; (ii) RE species deposit onto the MP surface, provide more adsorption sites, and strengthen electrostatic repulsion toward Cd^{2+} ; (iii) REs modulate solution pH and ionic strength, which mitigate the electrostatic attraction between MPs and Cd^{2+} .

All the R^2 values of the quasi-primary and quasi-secondary kinetics were higher than 0.8 except for the Cd^{2+} adsorption by aged MPs-PS in the presence of CA ($R^2 = 0.64$). Relatively, the quasi-secondary kinetics better fitted Cd^{2+} adsorption by the two aged MPs than the quasi-primary kinetics regardless of the presence of SSRE, as R_2^2 was always higher than R_1^2 . Moreover, the adsorption capacities at equilibrium ($Q_{e,\text{cal}}$) predicted by the quasi-secondary kinetics were closer to the experimental results ($Q_{e,\text{exp}}$) than those predicted by the quasi-primary kinetics regardless of the presence of SSRE. This is consistent with most previous results. Revellame et al. [55] reported that about 87% of the adsorption systems in the surveyed literature in the past two decades were better fitted by the pseudo-second-order model.

The parameter k_2 of the quasi-secondary kinetics is often used to describe the rate of adsorption equilibrium, and a larger k_2 value represents a faster adsorption

rate. Compared with deionized water, the presence of SSRE increased the k_2 values for Cd^{2+} adsorption on both aged MPs. In particular, CA exerted the most prominent promoting effect, raising k_2 10-fold for aged PS-MPs and 5.33-fold for aged PLA-MPs, respectively (Table 1). These results indicate that SSRE accelerates the attainment of Cd^{2+} adsorption equilibrium, possibly because (i) SSRE improves ion exchange, which is one of the main factors affecting HM adsorption by MPs [56]; (ii) SSRE or its dissociated ions compete for adsorption sites on aged MPs, and decrease the adsorption capacity of aged MPs for Cd^{2+} [57]; (iii) SSRE changes structural groups on the surface of aged MPs, further modulating the equilibrium time.

Effects of Root Exudates on the Functional Groups of Aged MPs

To characterize structural alterations in the two aged MPs induced by SSRE, FT-IR spectroscopy was employed. Representative bands of the two aged MPs were identified in their FT-IR spectra. For the aged PS-MPs (Fig. 8a), diagnostic peaks assigned to C–H bending and skeletal vibrations appeared at 1451/1492 cm^{-1} , alongside out-of-plane C–H bending vibrations of monosubstituted benzene rings at 698/758 cm^{-1} , consistent with previous literature [39]. In contrast, aged PLA-MPs exhibited prominent bands at 1750 cm^{-1} (C=O stretching vibration), 1210 cm^{-1} (asymmetric C–O–C stretching vibration), and 1180 cm^{-1} (C–O stretching vibration) (Fig. 8b). The peaks of 1750 cm^{-1} and 1180 cm^{-1} are intrinsic to both CA and aged MPs-PLA [58]. Nevertheless, relative to deionized water, CA addition does not evidently change the shifting tendency or intensity of the characteristic FT-IR peaks of the two aged MPs. This indicates that adsorption interactions are unlikely to dominate the interfacial association between CA and aged MPs. Song et al. [59] also found that MPs-PS adsorbed HA poorly due to the presence of only –CH₃ and –CH₂ groups. The present result is similar to the report of Chen et al. [60] that the effects of HA on

Table 1. Kinetic parameters of Cd²⁺ adsorption by aged MPs in the presence of different SSREs.

MP type	Root exudate	$Q_{c,exp}$ ($\mu\text{g}\cdot\text{g}^{-1}$)	Quasi-primary kinetics			Quasi-secondary kinetics		
			$Q_{c,cal}$ ($\mu\text{g}\cdot\text{g}^{-1}$)	k_1 (h^{-1})	R_1^2	$Q_{c,cal}$ ($\mu\text{g}\cdot\text{g}^{-1}$)	k_2 ($\text{g}\cdot(\mu\text{g}\cdot\text{h})^{-1}$)	R_2^2
Aged MPs-PS	Deionized water	270	255	0.423	0.90	278	0.002	0.97
	Glucose	215	198	0.497	0.82	215	0.003	0.95
	Serine	140	121	1.227	0.88	132	0.011	0.97
	Citric acid	32.6	30.8	0.405	0.64	32.7	0.022	0.85
Aged MPs-PLA	Deionized water	206	190	0.473	0.91	210	0.003	0.98
	Glucose	235	213	0.255	0.97	244	0.004	0.99
	Serine	182	169	1.046	0.93	182	0.008	0.97
	Citric acid	45.3	40.2	0.609	0.88	43.9	0.019	0.98

MPs-PS spectra decreased with increasing MP size, and almost no spectral change was observed for HA with 6 and 20 μm PS-MPs. In this study, MP size is about 150 μm . However, the present result is contrary to the findings of Luo et al. [18, 19] that HA and FA increased oxygen-containing functional groups on the surface of PP-MPs and PS-MPs, and also obviously changed the FT-IR characteristic peaks. Such discrepancies may originate from variations in experimental conditions, including the type, particle size and degree of aging of MPs, as well as solution properties (pH and ionic strength) and the type and concentration of organic acids.

Conventional one-dimensional FTIR spectroscopy alone cannot resolve the sequential variation of surface functional groups on the two aged microplastics. To further elucidate the temporal evolution of chemical bonds on the two aged MPs in the presence of different CA concentrations, a 2D-COS analysis was employed. This technique effectively deconvolutes complex overlapping absorption bands inherent to one-dimensional FTIR spectra.

For aged MPs-PS, five autopeaks centered at 697/756 cm^{-1} (C–H out-of-plane bending of a monosubstituted benzene ring), 1028 cm^{-1} (C–H in-plane bending vibration of a monosubstituted benzene ring), and 1452/1493 cm^{-1} (C=C skeletal vibration of the benzene ring) appeared in the synchronous map along the diagonal line (Fig. 9a). Among these peaks, the peak at 697 cm^{-1} exhibited the weakest intensity, indicating that it was insensitive to CA treatment, whereas the other autopeaks displayed comparable intensities. This phenomenon is possibly because MPs-PS have fewer functional groups, rendering them weakly responsive to CA. The asynchronous maps explained the sequential change of aged MPs-PS functional groups with increasing CA concentrations (Fig. 9b)). Table 2 summarizes the assignments and cross-peak signs extracted from synchronous and asynchronous maps of aged MPs-PS. According to Noda's rule, the sequence of peak changes was as follows: 756 cm^{-1} (C–H) > 1452 cm^{-1} (C=C) > 1493 cm^{-1} (C=C) > 1028 cm^{-1} (C–H) > 697 cm^{-1} (C–H). These functional groups are on the benzene ring.

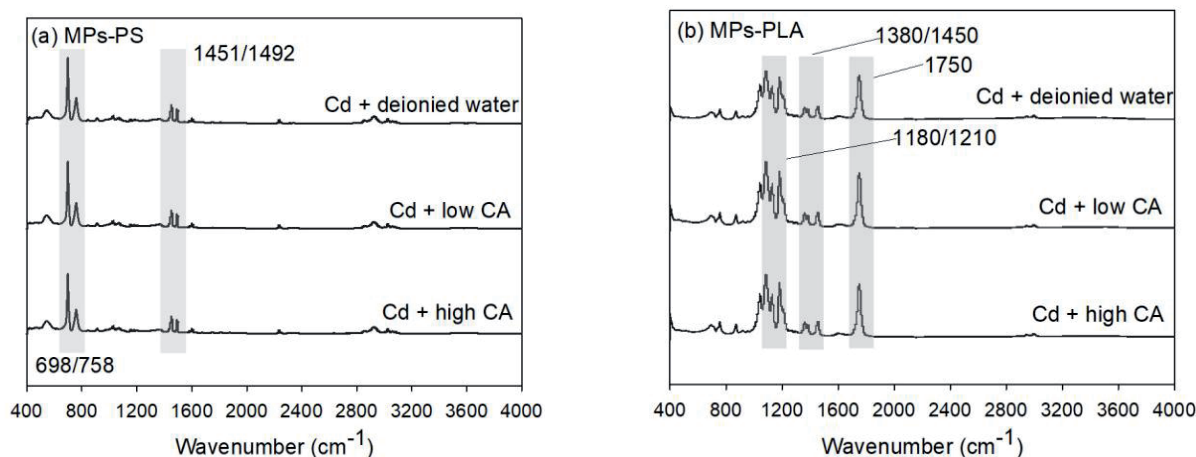


Fig. 8. Effects of SSRE on functional groups of two aged MPs.

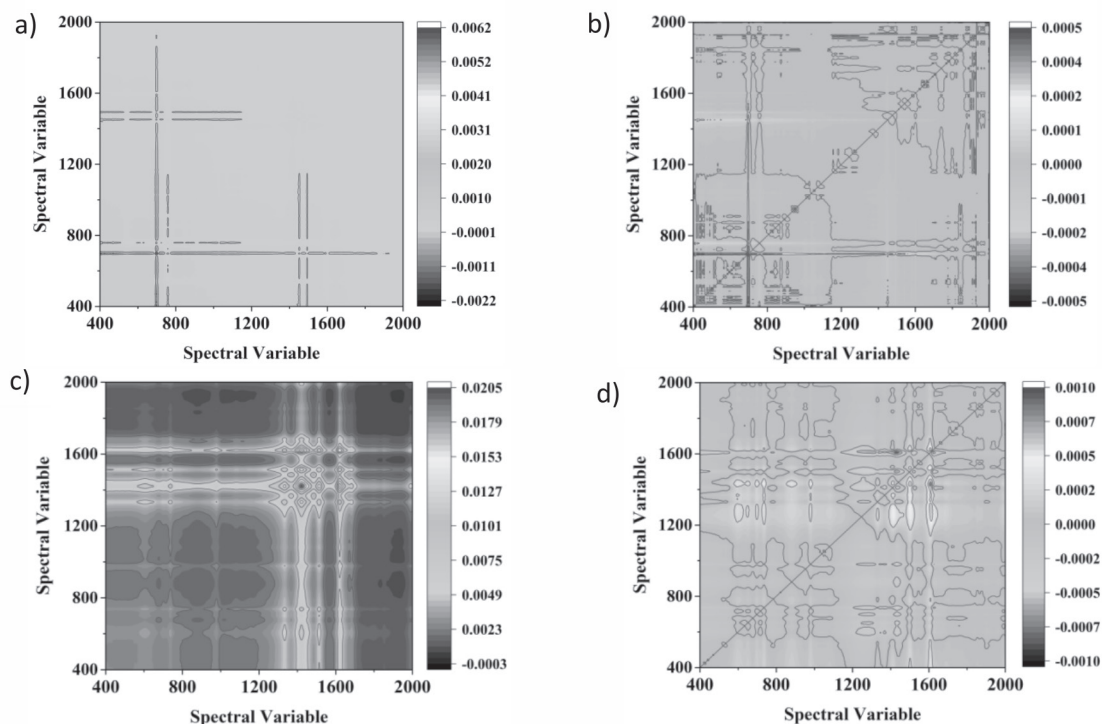


Fig. 9. Synchronous and asynchronous 2D correlation maps of MPs-PS (a, b) and MPs-PLA (c, d) in the presence of citric acid (CA). Red colors denote positive correlation, and blue colors denote negative correlation; darker colors indicate higher intensity.

For aged MPs-PLA, the identified autopeaks at 1330 cm^{-1} (methyl C–H bending vibration), 1360 cm^{-1} (methyl C–H symmetric bending vibration), 1420 cm^{-1} (CH_3 symmetric bending), 1480 cm^{-1} (methyl C–H bending vibration), 1510 cm^{-1} (conjugated C=C stretching vibration), 1620 cm^{-1} (C=C produced by aging) appeared in the synchronous map along the diagonal line (Fig. 9c)). Among all bands, the intensity of 1420 cm^{-1} was the strongest, followed by the peak at 1620 cm^{-1} , while the intensity at 1927 cm^{-1} was the weakest. This result indicates that the vibrational band at 1420 cm^{-1} undergoes the most prominent variation, implying that methylene ($-\text{CH}_2-$) groups are most susceptible to shifts in CA concentration. The cross-peaks in the synchronous map were positive, which indicated that all functional groups of aged MPs-PLA changed simultaneously with increasing CA concentration.

The corresponding asynchronous map was shown in Fig. 9d). Table S1 outlines the vibrational assignments and cross-peak signs extracted from the synchronous and asynchronous maps of aged MPs-PLA. According to Noda's rule, the sequence of peak changes was as follows: 1360 cm^{-1} (methyl C–H) $> 1330\text{ cm}^{-1}$ (methyl C–H) $> 1510\text{ cm}^{-1}$ (C=C) $> 1480\text{ cm}^{-1}$ (methyl C–H) $> 1420\text{ cm}^{-1}$ ($-\text{CH}_3$) $> 1620\text{ cm}^{-1}$ (C=C).

For both aged MPs-PS and MPs-PLA, the initial functional groups responding to CA exposure were C–H (PS) and C–H (PLA), respectively. As a representative DOM, CA can generate reactive oxygen species (ROS), such as hydroxyl radicals ($\cdot\text{OH}$), which accelerate the oxidative degradation of MPs [61]. Detailed mechanisms need to be studied in the future. In addition, the autopeaks of aged MPs-PLA had significantly greater peak intensities than those of aged MPs-PS,

Table 2. The assignments and signs of the cross-peaks in the synchronous and asynchronous maps (as shown in brackets) of aged MPs-PS in the presence of citric acid (signs were obtained in the lower-right corner of the maps, +, positive; -, negative).

Peak (cm^{-1})	Band assignments	Sign				
		697	756	1028	1452	1493
697	C–H out-of-plane bending of a monosubstituted benzene ring	+	+(+)	-(-)	+(+)	+(+)
756	C–H out-of-plane bending of a monosubstituted benzene ring		+	-(+)	+(-)	+(-)
1028	C–H in-plane bending vibration of a monosubstituted benzene ring			+	-(-)	-(-)
1452	C=C skeletal vibration of the benzene ring				+	+(-)
1493	C=C skeletal vibration of the benzene ring					+

indicating that aged MPs-PLA were more susceptible to chemical modification by CA. This is possibly because aged MPs-PLA have more functional groups (such as $-OH$ and $-COO^-$) that can interact with CA groups (such as $-COOH$ and $-OH$) via esterification and transesterification. Moreover, CA regulates adsorption by forming soluble Cd-citrate complexes and competing for hydrogen bonding with PLA's ester groups. These dual effects weaken direct interfacial binding between PLA and Cd^{2+} while modifying surface polarity, collectively amplifying the overall impact of CA on aged PLA-MPs.

The adsorption and desorption capacities of MPs for HMs are influenced by many factors, such as ionic hydration radius, electronegativity, and affinity between metal ions and functional groups on the MP surface, MP type, and MP size [14, 62]. Moreover, the interactions between MPs and HMs are affected by environmental factors and vary with different soil properties (pH, particle size, dissolved organic matter, number of humic-like substances, and microorganisms) [63] and water properties (pH, salinity, temperature, redox potential, and dissolved organic matter) [64]. The rhizosphere represents a unique microhabitat within the soil system and is widely distributed in agricultural and forest soils. Root exudates released in this zone alter the interactions between MPs and HMs and reshape the geochemical mobility of HMs. These changes may further modulate HM bioaccumulation in crops and pose potential risks to food safety [65, 66]. Accordingly, it is necessary and important to consider the effects of MPs on heavy metal behaviour in the rhizosphere.

Conclusions

This study investigated the effects of simulated and real root exudates on the adsorption and desorption capacities of two aged MPs for Cd^{2+} . The aims were to clarify how root exudates modulate the interactions between Cd^{2+} and MPs in the rhizosphere as well as the subsequent implications for soil environmental quality and crop safety. Both single and mixed root exudates were also evaluated. Overall, root exudates significantly decreased Cd^{2+} adsorption by MPs and increased Cd^{2+} desorption from Cd-loaded aged MPs, indicating that root exudates may elevate the ecological risk of Cd in the rhizosphere. Among the tested root exudates, the components with one or more $-COOH$ groups exerted dominant effects on Cd behaviour. Notably, exudate components with more carboxyl groups corresponded to higher potential Cd risk. Two primary mechanisms accounted for these variations: root exudates alter the surface functional group composition of aged MPs to modify their inherent Cd^{2+} adsorption capacity, and the released H^+ competes with Cd^{2+} for adsorption sites on the MP surface. In comparison, glucose exhibited the weakest influence on Cd^{2+} adsorption and desorption processes, whereas mixed root exudates induced more

pronounced effects than single exudates, with their regulatory efficiency highly dependent on exudate concentration. In summary, the rhizosphere may pose a high HM risk to soil health and plant safety due to the root exudate-mediated modulation of MPs-HMs interactions. It needs to be pointed out that the interactions between MPs and HMs are affected by multiple factors, including MP characteristics and HM species, plant type and growth stage, and environmental conditions. Therefore, further comprehensive investigations are required to elucidate complex interaction mechanisms under diverse field conditions.

AI Usage Disclosure Statement

The authors used the AI tool Doubao for minor grammar and expression refinement. No AI tools were involved in experimental design, data acquisition, data analysis or conclusion drawing. All AI-modified contents were fully reviewed, validated and revised by all authors, who take full responsibility for the entire manuscript.

Conflict of Interest

The authors declare no conflict of interest.

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Supplementary Materials

Table S1. The assignment and sign of each cross-peak in synchronous and asynchronous (in the brackets) maps of aged MPs-PLA in the presence of citric acid (signs were obtained in the lower-right corner of the maps, +, positive, - negative)

Peak (cm ⁻¹)	Band assignments	Sign*					
		1330	1360	1420	1480	1510	1620
1330	Methyl C-H bending vibratio	+	+(+)	+(-)	+(-)	+(-)	+(-)
1360	Methyl C-H bending vibration		+	+(-)	+(-)	+(-)	+(-)
1420	Aromatic ring C=C stretching vibration			+	+(+)	+(+)	+(-)
1480	Methyl C-H bending vibration				+	+(+)	+(-)
1510	Conjugated C=C stretching vibration					+	+(-)
1620	C=C produced by aging						+

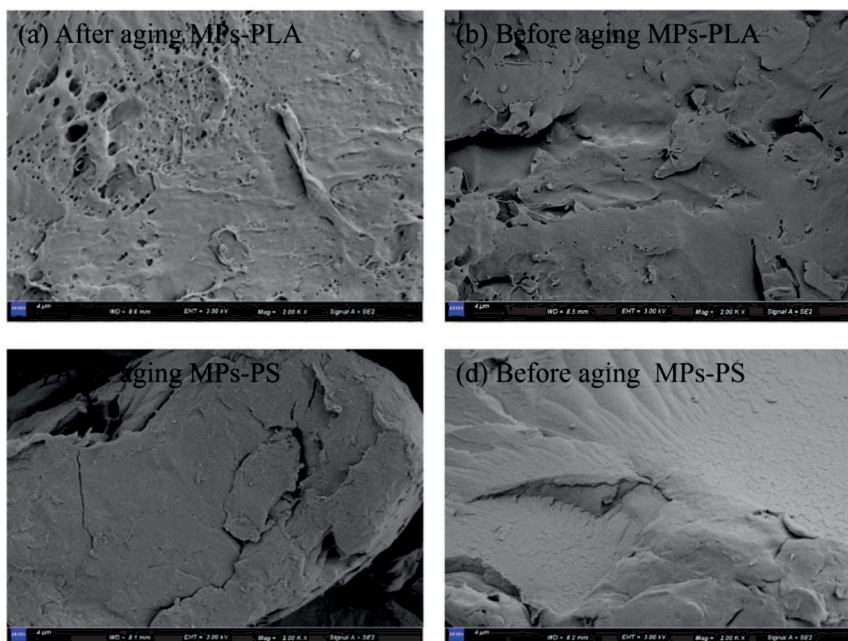


Fig. S1. SEM images of the two MPs before and after aging.

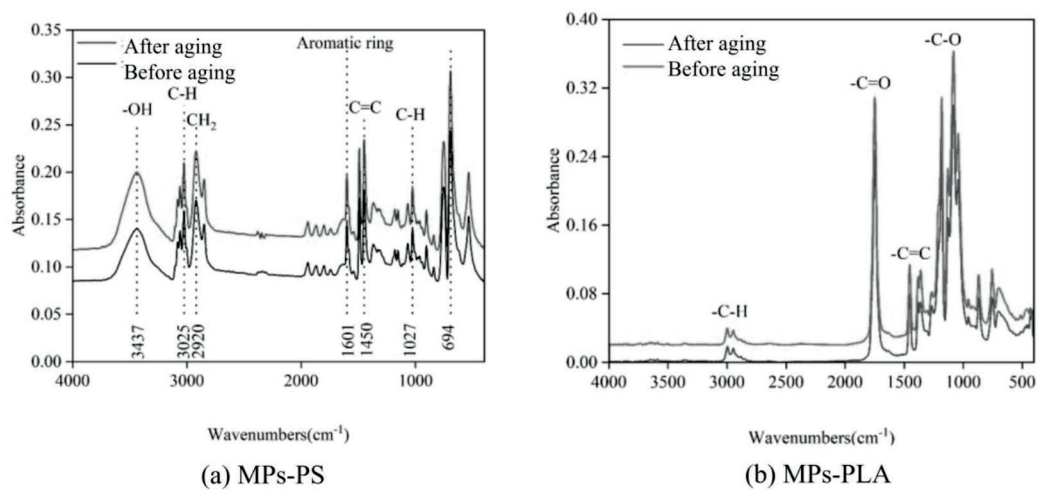


Fig. S2. Functional groups of the two MPs before and after aging.