Effects of virgin microplastics on the transport of Cd (II) in Xiangjiang River sediment

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Abstract

River sediments are considered as sinks of microplastics (MPs). Although numerous studies have been conducted on MPs pollution in river sediments, the impact of MPs on the environmental behavior of Cd (II) in river sediments is still unknown. In this work, the effects of six MPs (polyethylene, polypropylene, polystyrene, polyvinyl chloride, polymethyl methacrylate and polylactic acid) on the adsorption of Cd (II) by Xiangjiang River sediment and the transport of Cd (II) in sediment were studied. The results showed that the adsorption ability of sediment to Cd (II) decreased with the increase of the content of MPs in sediment. When the content of MPs in sediment increased to 10%, polypropylene had the greatest effect on the adsorption affinity of sediments to Cd (II). Moreover, the addition of MPs accelerated transport of Cd (II) in sediment, and the transport of Cd (II) in sediment increased with the increase of the content of MPs. The reason may be that after adding MPs, the adsorption capacity of sediment to Cd (II) decreases, and the mass transfer resistance of Cd (II) to sediment reduces, which leads to faster transport of Cd (II) in sediment. Especially, when the content of MPs in sediment increased to 10% (w/w), the saturation point of the breakthrough curve decreased by about 70 pore volumes. This work hopes to provide helpful views on the environmental behavior and risk assessment of Cd (II) in the presence of MPs.

Keywords: Microplastics; Cadmium; Adsorption; Transport; River sediment

1. Introduction

Plastics have been mass-produced in the consumer marketplace since their commercial development from the 1930s (Jambeck et al., 2015). Global plastic production in 2018 reached 359 million tons (Huang et al., 2021; Shen et al., 2020), which shows a 717% increase compared with that in 1950 (Li et al., 2019a), and the production is expected to double in the next 20 years (Jambeck et al., 2015). With the extensive production and application of plastics, it is inevitable that plastics are released into the natural environment (Ye et al., 2020; Shen et al., 2021a). The released plastics fragment in the environment may undergo ultraviolet radiation, wind erosion, wave action and abrasion (Law and Thompson, 2014; Shen et al., 2019a; Shen et al., 2019b). Furthermore, in combination with biological degradation, plastic fragments can be broken into microplastics (MPs) (Luo et al., 2021; Shen et al., 2021b; Thompson et al., 2004). Nowadays, as emerging contaminants, MPs are ubiquitous, and have been detected in oceans (Law, 2017), lakes (Driedger et al., 2015), rivers (Rochman, 2018), soil (Moller et al., 2020), air (Allen et al., 2019) and even arctic ice (Cozar et al., 2017; Peeken et al., 2018).

River sediment is an essential component of freshwater ecosystems and is under strong pollution pressure (Huang et al., 2018; Yang et al., 2020b). MPs contamination of sediment in rivers is being increasingly documented (Eo et al., 2019; Klein et al., 2015; Mani et al., 2019; Wen et al., 2018). For example, Klein et al. (2015) found that all their researched sediments contained MPs, and polyethylene, polypropylene, and polystyrene accounted for more than 75% of all polymer types after analyzing the river shore sediments of the Rhine and Main rivers in the Rhine-Main area in Germany. Eo et al. (2019) reported that the mean abundance of MPs in the Nakdong River was in the range of 1970 ±62 particles/kg in sediment. Furthermore, polypropylene and polyethylene accounted for approximately 50% of the MPs in sediment. Wen et al. (2018) investigated surface sediment samples from urban water area including the Xiangjiang River in Changsha, China. Their results showed that the average MP contents in the surface sediments ranged from 270.17 ± 48.23 items/kg to 866.59 ± 37.96 items/kg, and the polystyrene content was the most in the sediment samples.

Due to its property unlike sediment, MPs may affect sediment properties, such as the sediment structure and function. The influences of MPs on the soil structure and microbial functions have been recorded (Chen et al., 2020; Machado et al., 2019; Machado et al., 2018). For example, polyester fibers could increase water holding capacity of soil, decrease soil bulk density and microbial activity, and change the soil structure and function, which may further disturb the vital relationship between soil and water, as well as the microbial function (Machado et al., 2018). Biodegradable polylactic acid MPs had a legacy effect on soil bacterial communities and functions because they could trade off the priming effect of carbon source and affect the interactions among the species composition (Chen et al., 2020). Sediment provides a stable place for the accumulation of contaminants in rivers. Changes in sediment properties may affect environmental behavior of contaminants in river sediment. The effect of MPs on the adsorption of cadmium (Cd) by soil has been studied. For instance, Zhang et al. (2020) investigated the influences of MPs on adsorption and desorption of Cd in agricultural soils. They found that the adsorption ability of soils to Cd decreased, but the desorption ability increased after adding MPs. However, research on the impact of MPs on the environmental behavior of contaminants, especially on the transport of contaminants in river sediment, remains limited.

Owing to high toxicity, persistence, non-biodegradability and bioaccumulation, heavy metal has brought serious pollution worldwide (Liu et al., 2018; Yang et al., 2020a). Cadmium, considered as one of the major heavy metal pollutants in China and other regions of the earth, is widespread (including the Xiangjiang River) and has a higher bioavailability, toxicity and mobility (Huang et al., 2016; Huang et al., 2020; Liu et al., 2020). Moreover, the potential ecological risk index of Cd (II) was higher than other heavy metals (such as Cu, Cr, and Pb) in the study area (Xue et al., 2018). As the primary sink of contaminants, sediment plays a vital role in transport and fate of Cd (II) in aquatic ecosystems. However, the toxicity and bioavailability of Cd (II), and their fate, can be affected by sediment properties (e.g., cation exchange capacity and organic matter contents) (Du Laing et al., 2009). Considering that MPs are also present in Xiangjiang River sediment and have different properties from sediment, they are likely to affect the properties of sediment, thereby altering the environmental behavior of Cd (II) in sediment.

Based on the above, the existence of MPs may alter the adsorption of Cd (II) and the transport of Cd (II) in Xiangjiang River sediment. To validate this hypothesis, adsorption tests and column tests were performed to investigate the effects of MPs on the adsorption behavior and the transport characteristics of Cd (II) in Xiangjiang River sediment, respectively. Polyethylene (PE), polypropylene (PP), polystyrene (PS), polyvinyl chloride (PVC), polymethyl methacrylate (PMMA), polylactic acid (PLA) were used in this study, because these plastics are common in the aquatic environment and are of great environmental concern (Chen et al., 2020; Fu and Wang, 2019; Trifuoggi et al., 2019). The current study may provide evidence for assessing the environmental behavior and ecological risks of Cd (II) affected by MPs in the freshwater ecosystem.

2. Materials and methods

2.1 MPs and reagents

The virgin PE, PP and PVC MPs were obtained from Zhongcheng Plastic Co. Ltd, China. The virgin PS MPs were purchased from Kexinda High Polymer Material Co. Ltd, China. The virgin PMMA and PLA MPs were bought from Shanghai Aladdin Biochemical Technology Co. Ltd, China. All six types of plastic are in powder form, and they are made from large plastics by mechanical processing. The density of PE, PP, PS, PVC, PMMA and PLA are 0.94–0.96, 0.89–0.91, 1.05, 1.40, 1.20, and 1.20–1.30 g/cm^3, and the softening point of them are 92, 165, 240, 185–205, 150 and 155–185°C, respectively. The specific surface area of these MPs was measured using BET Surface Area and Pore Size Analyzer, and the particle size and zeta potential were measured using Zetasizer Nano. The MPs did not undergo any weathering processes before being used in the adsorption and column tests, and the as-received plastic materials were cleaned with 2% HNO3 and ultrapure water to remove potential heavy metals from their surface. Cd (II) stock solution (1000 mg/L) was prepared with the $CdCl_2 \cdot 2.5H_2O$ (analytical grade) in ultrapure water, and stored at 4 ℃.

2.2 Sediment collection and treatment

Xiangjiang River is the largest river in Hunan Province of China. In order to achieve an accurate and comprehensive understanding of the sediment in Changsha section of the Xiangjiang River, surface sediment (0–15 cm) samples were collected from six sites along the Changsha Section of the Xiangjiang River, as it frequently exchanges contaminants with the overlying water. Three parallel sediment samples were collected from each site and detailed sampling sites were provided in **Table S1** of the Supplementary Material. Then, all the sediments of the six samples were mixed and air-dried in a place with ventilation and no direct sunlight, and the leaves, roots and gravels were removed at the same time. After that, the samples were ground in a mortar and then sieved over a 0.5 mm mesh sieve. Finally, the samples were sealed and stored in a dry and dark place. Selected physicochemical properties of the sediment such as pH, organic carbon content and texture were determined by referring to the previous literature (Song et al., 2017). Besides, the Cd content in the sediment was measured by Inductively

Coupled Plasma Mass Spectrometry (ICP-MS).

2.3 Adsorption tests

Adsorption isotherm tests of Cd (II) adsorption by MPs, sediment, and sediment-MPs mixture (proportions of MPs in sediment, w/w: 0.05%, 0.5%, 5% and 10%) were performed in 50 mL conical flasks containing Cd (II) solutions of different concentrations on a shaker at 180 rpm for 24 h, 25 ± 1 ℃. The contents of MPs were selected based on previous relevant studies (Fuller and Gautam, 2016; Zhang et al., 2020). Moreover, given that our primary goal was to study the adsorption and transport characteristics of Cd (II) in sediment, although the MPs contents were high, they were fit for purpose. The choice of experimental period was based on preliminary adsorption tests. In order to study the adsorption mechanism of MPs to Cd, the adsorption isotherms of MPs to Cd were needed and different concentrations of Cd were also needed. The concentrations of Cd (II) were from 2 to 12 mg/L when using MPs as the sorbent, and were from 20 to 70 mg/L when using sediment and sediment-MPs mixture as the sorbent. Sorbent dosages of sediment, and sediment-MPs were both 10 g/L, while the dosages of MPs were 1 g/L. Each test consisted of three replicates and a blank treatment without sorbent. After adsorption equilibrium, the reaction system was permitted to statically settling for a moment, then supernatant was taken out and filtered with 0.22 μm syringe filter, and the concentrations of Cd (II) were analyzed by flame atomic absorption spectrometry (PAA 900F, PerkinElmer, U.S.A.).

2.4 Column tests

Column transport tests of Cd (II) in different sediment columns were conducted under saturated flow conditions, and the schematic diagram of apparatus for column test was shown in **Figure S1**. In this test, Perspex columns of 250 mm in length and 25 mm in inner diameter were used. The column packing adopted the technique formerly reported (Song et al., 2018). Concretely, nylon net with pore size of 0.15 mm was fixed at the bottom of the columns. A layer of 10 mm of quartz sand (25–50 mesh) was then added to supporting the sediment particles. Then, sediment was added to the columns bit by bit (4–5 mm increments). At the same time, the peristaltic pump (DDB-300, Zhisun Equipment Co., Ltd., Shanghai, China) was used to introduce the ultrapure water into the columns from the bottom to the top, until the columns were packed by sediment to a height of 42 mm. The flow direction here is bottom-up because it allows the sediment particles in the column to be more evenly distributed and prevents the formation of air bubbles during the column packing. In order to keep the pH range of the effluent consistent with the pH value of the influent, about 10 pore volumes (PVs) of ultrapure water were used to wash the columns. Finally, the Cd (II) solution, which prepared in advance, was slowly pumped into the sediment columns from the top until a constant hydraulic head was formed above the sediment particles, and the Cd (II) concentration was measured by collecting the effluent samples at specific leaching time intervals. The PVs of the packed columns were calculated by weight difference between the water-saturated column and the dry column. The calculated values of the sediment bulk density (ρ_b) and the porosity were 1.16 g/cm^3 and 0.54, respectively.

According to adsorption experiments, PP showed the most representative phenomenon under the same conditions when it dominated in sediment MPs, compared to other MPs. Therefore, PP was chosen as MPs representative in this column experiments. Specifically, 100 mg/L Cd (II) solutions were slowly introduced into the columns (from the top down) that contained sediment-PP mixture (proportions of PP in sediment, w/w: 0%, 0.05%, 0.5%, 5% and 10%) by the peristaltic pump. The experimental cycle of each test was 20 d. The choice of metal concentrations and experimental period were based on preliminary column transport test to obtain a good delineation of the breakthrough curves, and a manageable experimental time frame (Bianchi Janetti et al., 2013). During the column tests, an invariable water head of 100 mm was kept by pumping continuously and the effluent was collected periodically for the determination of Cd (II) concentrations.

To determinate the mass balance of the retained Cd (II), each column was divided equally into 6 segments after air-dried. Afterwards, Cd (II) concentrations were analyzed in these segments with the method previously reported (Zhang et al., 2020). In short, conical flasks containing sediment segments were filled with 50 mL NaCl solution (0.1M), and then shaken at 180 rpm at 25 ±1 ℃ for 24 h. Then, allowed the mixture of sediment and water to settle statically for a while. Subsequently, supernatant was taken out and filtered through with 0.22 μm syringe filter. Finally, Cd (II) concentrations were determined by FAAS.

2.5 Data processing

The obtained data of adsorption experiment was fitted with Freundlich isotherm model, which is given by the following equation (Song et al., 2017):

$$q_e = K_F c_e^{\frac{1}{n}} \tag{1}$$

where q_e (mg/g) is the amount of adsorbed Cd (II) at equilibrium, c_e (mg/L) is the equilibrium concentration of Cd (II), K_F (mg/g (mg/L)$^{-1/n}$) and n (dimensionless) are Freundlich parameters. K_F reflects the affinity of adsorbent to adsorbate and n is related to intensity of adsorption (Yan et al., 2017). Generally, the adsorption performances of adsorbents increase with the decrease of the value of $1/n$.

The distribution coefficient K_d was calculated to compare the adsorption affinity of Cd (II) between different sorbents (Yan et al., 2017). The equation is given by

$$K_d = \frac{q_e}{c_e} \tag{2}$$

The retardation factor, *R*, was calculated to assess the transport time of Cd (II) in sediment (Song et al., 2018). The equation is written as

$$R = 1 + \frac{\rho_b K_d}{\theta} \tag{3}$$

where θ is sediment porosity, and ρ_b is sediment bulk density.

Breakthrough curves (BTCs) are used to indicate the transport of Cd (II) through sediment columns. Concentrations of the effluent and influent of Cd (II) were defined as c and c_0, respectively. The safe point (SP_1) of the BTCs in this test was defined as the PVs corresponding to the previous test in which Cd (II) was first detected in effluent. The saturation point (SP_2) of the BTCs in this test was defined as the PVs corresponding to the concentrations of Cd (II) in effluent were approximately the same with that in influent and no longer change. The safe value (SV_1) and the saturation value (SV_2) were defined as Cd (II) content in sediment columns at SP_1 and at SP_2, respectively.

3. Results and discussions

3.1 Characterization of the MPs and sediment

The specific surface area of PE, PP, PS, PMMA, PVC and PLA are 4.75, 61.81, 3.52, 5.47, 7.74 and 0.59 m^2/g, respectively. The particle size of PE, PP, PS, PMMA, PVC and PLA are 9–14, 7–11, 7–13, 1–3, 0.8–1 and 9–13 μm, respectively. The zeta potential of PE, PP, PS, PMMA, PVC and PLA are 44.4 ± 6.1, –6.5 ± 0.5, –33.4 ± 0.7, –48.0 ± 0.7, –38.2 ± 0.5 and –24.1 ± 5.2 mV, respectively. The measured pH value, cation exchange capacity, organic matter content, and zeta potential of the sediment are 7.42, 16.6 cmol/kg, 1.63%, and –18.4 mV, respectively. The Cd content in the sediment is 9.35 mg/kg. Besides, the content of clay, silt and sand in the sediment sample is 29.2%, 34.3% and 36.5%, respectively.

MPs were also characterized by scanning electron microscope (SEM) and fourier transform infrared spectrometer (FTIR). The SEM images and the FTIR images of MPs are given in **Fig. 1** and **Fig S2**, respectively (please see Supplementary Material for more details).

3.2 Adsorption isotherms

3.2.1 Adsorption isotherms of Cd (II) onto MPs

The adsorption isotherms of Cd (II) onto MPs (**Fig. S3**) were obtained and the isotherm parameters for the Freundlich models were calculated (**Table S2**). Based on the good fitting effect of Freundlich model but poor fitting effect of Langmuir model (data not shown), it can be recognized that the adsorption process of Cd (II) by MPs is not a simple chemical adsorption, but a state of simultaneous physical and chemical adsorption (Lang et al., 2020). The microscopic understanding of it is that multiple interactions between MPs and Cd (II), such as electrostatic interaction and pore-filling, may be involved in the adsorption process (Torres et al., 2021). The results of Cd (II) adsorption by six MPs were similar to previous findings that the adsorption of Cd (II) by pristine MPs can be described by Freundlich models (Holmes et al., 2012; Li et al., 2019b; Turner and Holmes, 2015; Wang et al., 2019). The values of K_F and $1/n$ in these studies are different. These distinctions may come from the differences in plastic type, particle size and the reaction system. (Please see Supplementary Material for more details on Cd adsorption by MPs)

3.2.2 Adsorption isotherms of Cd (II) onto sediment and sediment-MPs mixture

The adsorption isotherms and their parameters of Cd (II) onto sediment and sediment-MPs mixture are exhibited in **Fig. 2** and **Table 1**. In **Table 1**, the R^2 values of Cd (II) adsorbed by sediments and sediment-MPs that calculated from the Freundlich model were more than 0.970. Therefore, Freundlich model was proper for describing the adsorption experimental data of Cd (II) onto sediments and sediments mixed with MPs. The results indicated that the adsorption of Cd (II) onto sediments and sediments mixed with MPs is multilayer adsorption. In **Table 1 and 2**, it can be seen that the addition of MPs would decrease the K_F values and increase the $1/n$ values of Cd (II) adsorption in sediment, and the K_F values decreased but the $1/n$ values increased with the increase of the content of MPs. The addition of MPs also decreased the K_d values of Cd (II) in sediment, and the K_d values decreased with the increase of the proportion of MPs. Taking PE MPs as an example, when the dosage of PE MPs increased from 0 to 0.5% to 10%, the values of K_F decreased from 1.843 to 1.625 to 1.252, the values of K_d decreased from 0.542 to 0.428 to 0.297, while the values of $1/n$ increased from 0.284 to 0.305 to 0.360. The results indicated that the adsorption ability of sediment to Cd (II) decreased with the increase of the content of MPs in sediment. Compared with those sediments which mixed with other MPs, the sediments that mixed with PP had the smallest values of K_F and K_d under the same experimental conditions, which showed that PP had the greatest effect on Cd (II) adsorption in sediments. Additionally, comparing the K_d values of Cd (II) adsorbed on sediment and on MPs, it could be found the value of K_d of sediments (K_d = 0.542) were higher than MPs (K_d = 0.198–0.288), which showed that the adsorption capacity of sediments to Cd (II) was better than that of MPs to Cd (II).

It has been widely accepted that sediment has a good adsorption capacity to heavy metals (Saeedi et al., 2010), and the fine adsorption effect for Cd (II) is found in our current test. MPs can also adsorb Cd (II), but their adsorption capacity is commonly lower compared to sediment (Besson et al., 2020). The reason may be that the sediment contains various organic and inorganic components such as organic matters and minerals, some of which possess fantastic adsorption capacity for Cd (II) (Namieśnik and Rabajczyk, 2015). For example, Cd (II) prefers to associate with organic binding phase in sediment and

Fe/Mn oxyhydroxide phase is one of the major binding phases for Cd (II) in the sediments (Chakraborty et al., 2016). Moreover, sediment organic matter content is the dominant factor influencing the partitioning of Cd (II) between the dissolved and particulate phase (Liu et al., 2019). When MPs enter into sediment, they might decrease water stable aggregates of sediment due to highly hydrophobic surface and comparatively simple surface properties, and reduce the accumulation of organic matter which due to organic matter was more likely to accumulate in large-sized soil aggregates (Chen et al., 2014; Gelaw et al., 2013; Huang et al., 2017; Machado et al., 2018). Moreover, the adsorption capacity of MPs to Cd (II) was weaker than that of sediment. The decrease of organic matter content in aggregates would result in the decrease of Cd (II) adsorption by sediment. Huang et al. (2019) have reported that Cd was more enriched in the macro-sized soil aggregates (> 0.25 mm) because of their higher organic matter content.

Although the types and sizes of the added MPs were different, they had similar effect on the Cd (II) adsorption in sediment except PMMA. The adsorption isotherm for PMMA at MPs/sediments ratio of 10% does not show a distinct difference with other five MPs. This may be that PMMA showed the least effects on the sediment adsorption behavior even though the MPs/sediments ratio was up to 10%. According to the measurement of zeta potential, PMMA has the greatest number of negative charges (–48.0 ± 0.7 mV) among the studied MPs. Besides, PP had the greatest effect on Cd (II) adsorption in sediments. The reason may be PP had the larger specific surface area (61.81 m^2/g) and could be easily adsorbed on the sediment matrix, then decreased water stable aggregates of sediment and reduced the adsorption of Cd (II) by organic matter in aggregates (Machado et al., 2018).

A previous study has found that addition of MPs decreases soil adsorption of Cd (II) (Zhang et al., 2020). This study got a similar result. However, the values of K_F in previous research on Cd (II) adsorption by soil were small (K_F = 0.4763). The reason may be that the soil type and property are different. In this study, the organic matter content of the sediment is 1.63%, which is higher than the soil (1.31%) used by Zhang et al. (2020), resulting in a higher adsorption capacity to Cd (II).

3.3 Transport of Cd (II) through sediment columns

3.3.1 Transport of Cd (II) through sediment columns with and without MPs

The BTCs of Cd (II) through sediment columns with and without MPs are shown in **Fig. 3**. On the whole, the concentration of Cd (II) in effluent continued to rise until reaching a stable plateau with the increase of the influent. When sediment columns had no MPs, SP_1 and SP_2 of the BTCs were 50 PVs and 240 PVs, respectively. There was almost no Cd (II) in the first 50 PVs, which was because sediment has a strong adsorption to Cd (II). After that, as the influent continued to increase, the concentration of Cd (II) in effluent would increase until it was approximately the same as the concentration in influent, that is, it was completely saturated. When the proportion of MPs in sediment columns were 0.05%, 0.5%, 5% and 10%, the SP_1 of the BTCs were 50, 40, 30 and 10 PVs, respectively. The addition of MPs lowered the SP_1 of BTCs of Cd (II) through sediment columns, which decreased by 0, 10, 20 and 40 PVs at the presence of 0.05%, 0.5%, 5% and 10% MPs, respectively. The transport of Cd (II) in the sediment with MPs was quicker than that without MPs. On the one hand, the upward trend of the BTCs became steep, and on the other hand, SP_2 of the BTCs was decreased. Moreover, with the increase of the MPs content in sediments, the experimental phenomenon was more obvious. When the contents of MPs in sediment columns reached to 0.05%, 0.5%, 5% and 10%, the SP_2 of the BTCs were 230, 220, 200 and 170 PVs, which decreased by about 10, 20, 40 and 70 PVs, respectively. The addition of MPs significantly shortened the saturation time of Cd (II) in sediment.

As a derived parameter, the retardation factor R is calculated with the value of K_d to quantify the slowing down of Cd (II) transport in sediments. The retention ability of Cd (II) in sediment increases and the migration ability decreases with the increase of the value of *R*. A higher value of *R* (2.164) was obtained when sediment had no MPs. However, the values of *R* decreased to 1.906, 1.722, 1.509 and 1.455, respectively, at the presence of 0.05%, 0.5%, 5% and 10% MPs in sediment. The results showed that the increase of the MPs content would reduce the retention ability of sediment, resulting in an increase of the migration ability of Cd (II). The safe values and saturation values of Cd (II) in sediment columns mixed with MPs in different ratios are illustrated in **Fig. 4**. As is shown in **Fig. 4**, the addition of MPs resulted in the decrease of the SV_1 and SV_2 of Cd (II) in sediment columns. When the proportions of MPs in sediment columns were 0.05%, 0.5%, 5% and 10%, the SV_1 of Cd (II) were 6, 4.8, 3.6 and 1.2 mg, which decreased by 0, 1.2, 2.4 and 4.8 mg, respectively, and the SV_2 of Cd (II) were 73.26, 69.27, 63.66 and 54.02 mg, which decreased by 0.86, 4.85, 10.46 and 20.1 mg, respectively. The addition of MPs lowered the retention of Cd (II) in sediment and the Cd (II) retained in sediment decreased with the increase of the content of MPs.

The fate of Cd (II) in natural systems is largely determined by its partitioning behavior between aqueous and immobile solid phases, as well as the factors that influence the partitioning. The transport of Cd (II) in sediment columns became faster with the increase of the contents of MPs. Especially, when the proportion of MPs in the sediment column increased to 10%, the breakthrough time of Cd (II) sharply reduced by about 70 PVs, which indicated that the affinity between Cd (II) and sediments was ever-reduced with the increase of MPs content. There are two major retardation mechanisms for the transport of Cd (II) in the column without MPs. First of all, Cd (II) may be retained by adsorption reactions involving the formation of either outer sphere or inner sphere complexes with the surfaces of mineral and organic constituents. Secondly, it may be retained by precipitation reactions leading to the formation of new secondary mineral phases (Evans, 1989). When MPs were added, the adsorption and precipitation of Cd (II) in sediment might be significantly decreased. The reason may be that the pristine MPs we used were highly hydrophobic on the surface and their surface properties were comparatively simple, which led to their adsorption capacity to Cd (II) was weak. When they enter into sediment, they might decrease water stable aggregates of sediment and reduce the accumulation of organic matter and mineral. The decrease of organic matter content and mineral content in aggregates results in reduced adsorption and precipitation of Cd (II) in sediment (Namieśnik and Rabajczyk, 2015), which will decrease the mass transfer resistance of Cd (II) to sediment. As a result, the transport of Cd (II) in sediment is accelerated, the saturation time is shortened, and the SV_1 and retention is reduced.

Additionally, a new study on MPs influence on the transport of contaminants (Nath et al., 2020) finds that the addition of aminated PS nanoparticles reduces the mobility of carboplatin in water-saturated natural soil. The difference in results may come from the size of the MPs they used is relatively smaller and they are pretreated before the column tests. As a consequence, mixing carboplatin with positively charged aminated PS nanoparticles (which can interact with the negatively charged soil matrix) results in interactions between the two components, causing a mobility reduction in soil owing to filtration and attachment of the carboplatin attached to the aminated PS nanoparticles to the soil matrix (Nath et al., 2020). In our study, the MPs used in the experiments showed poor adsorption capacity of Cd (II), thus they impeded the Cd (II) adsorption by sediment, resulting in accelerated transport of Cd (II) in sediment.

3.3.2 Spatial distribution of Cd (II)

The vertical spatial distribution of Cd (II) in sediment columns was illustrated in **Fig. 5**. In the sediment column without MPs, Cd (II) mainly distributed in the inlet and its spatial distribution showed an obvious downward trend with the increasing distance from inlet, which demonstrated that sediment has strong adsorption ability to Cd (II) and the migration ability of Cd (II) in sediment is weak. After adding the MPs, the spatial distribution of Cd (II) in sediment columns tended to be uniformed, and the trend became more obvious with the increase of the MPs content. The first three points were taken as the concentration of Cd (II) at inlet. The concentration of Cd (II) at the inlet was 14.09 mg/g without addition of MPs. However, when the MPs contents in sediment increased to 0.05%, 0.5%, 5% and 10%, the concentration of Cd (II) at the inlet decreased to 13.19, 12.57, 9.53 and 8.71 mg/g, which indicated that the accumulation of Cd (II) in the top sediment layer was reduced with the increase of the MPs content. In addition, the concentration of Cd (II) in outlet also changed when MPs added. When sediment column had no MPs, the concentration of Cd (II) in outlet was 2.23 mg/g. However, when the MPs contents soared to 5% and 10%, the concentrations of Cd (II) in outlet increased to 2.57 and 2.72 mg/g. The results showed that MPs in sediment facilitated the transport of Cd (II) into the deeper sediment layer. The reason may be that the addition of MPs reduces the Cd (II) adsorption by sediment and decreases the mass transfer resistance of Cd (II) to sediment, leading to the transport of Cd (II) into the deeper sediment layer.

3.4 Environmental implications

Bioavailability and fate of Cd (II) in freshwater ecosystem, to a great extent, is controlled by sediment adsorption (Du Laing et al., 2009). The release of MPs into sediment could significantly impact the adsorption of Cd (II) by sediment and the transport of Cd (II) in sediment. Furthermore, there was a dose-dependent effect on these processes. For example, with the increase of MPs content in sediment, the adsorption capacity of Cd (II) by sediment reduced and the transport of Cd (II) in sediment accelerated. When MPs are released into river sediment, on the one hand, they can reduce Cd (II) exposure to the upper sediment microbial community; on the other hand, can increase Cd (II) exposure to the deeper sediment microbial community and zooplankton, phytoplankton and bottom dweller. Moreover, the loss of Cd (II) retention in sediment facilitates the transport of Cd (II) into underground water, which presents additional environmental and health risks.

The findings have important implications for understanding the transport of Cd (II) in the presence of MPs, especially in “hot-spot” areas of MPs-contaminated sediments. These results also provide useful information for a worst-case scenario when evaluating potential risks of MPs in sediment. Additionally, from an environmental perspective, virgin MPs generally represent the MPs which are passively discharged or via accidental spillages into non-tidal rivers where flow is unidirectional and the scope for long-term deposition is limited (Turner and Holmes, 2015). By contrast, aged MPs are more probable to represent the MPs entering lentic environments where having longer residence time. Moreover, aging generally alters the hydrophobicity and polarity of MPs such as form oxygen-containing functional groups (OH, C=O and C-O) on their surface (Bandow et al., 2017). Therefore, aged MPs are probably having different particle shapes and surface properties, which may change not only their adsorption capacity to contaminants, but also their effects on sediment sorption ability, and finally influence the fate of contaminants in sediment. Further studies on the aged and secondary MPs in sediment should be conducted in future research.

4. Conclusions

The impacts of virgin MPs on the adsorption and transport of Cd (II) in Xiangjiang River sediment were studied in this work. Virgin MPs were found to reduce the adsorption ability of the sediment for Cd (II), and the adsorption ability of the sediment for Cd (II) decreased with the increase of the MPs contents.

The reason may be that MPs could decrease water stable aggregates of sediment due to highly hydrophobic surface and comparatively simple surface properties, and reduce the accumulation of organic matter. Moreover, the adsorption capacity of MPs to Cd (II) was weaker than that of sediment. The decrease of organic matter content in aggregates would result in the decrease of Cd (II) adsorption by sediment. Additionally, MPs could accelerate the transport of Cd (II) in sediment and the transport of Cd (II) in sediment increased with the increase of the contents of MPs, which because of the decrease of Cd (II) adsorption by sediment. The decrease of Cd (II) adsorption by sediment will decrease the mass transfer resistance of Cd (II) to sediment, accelerating the transport of Cd (II) in sediment. MPs were also found to reduce the safe value and retention of Cd (II) in sediment, and made the vertical spatial distribution of Cd (II) in sediment tend to be uniformed.

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