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Enhancement in adsorption potential of microplastics in sewage sludge for metal pollutants after the wastewater treatment process

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ABSTRACT

Microplastics (MPs) as new pollutants of environmental concern have been widely detected in sewage sludge, and may act as significant vectors for metal pollutants due to their adsorption property. Our findings show that Cd, Pb, and Co, but not Ni, contents in sewage sludge are lower than that of corresponding metal irons adsorbed on sludge-based MPs, indicating that the MPs accumulate such metal pollutants as Cd in the sludge samples. In contrast to virgin MPs, sludge-based MPs are one order of magnitude higher adsorption capacity for Cd, which reaches up to 2.523 mg g^{-1}, implying that there is a considerable enhancement in adsorption potential of the MPs for metals after the wastewater treatment process. SEM analysis shows that sludge-based MPs have rougher and more porous surface than virgin MPs, and FTIR spectra reveal that functional groups such as C—O and O—H are found on sludge-based MPs. Further, two-dimensional FTIR correlation spectroscopy indicates that C—O and N—H functional groups play a vital role in the process that sludge-based MPs adsorb Cd, which are not found in virgin MPs. The results imply that increased adsorption potentials of the sludge-based MPs to Cd are attributed to changes in the MP physicochemical properties during wastewater treatment process. In addition, such factors as pH value, and sludge inorganic and organic components also have an effect on the MP adsorption to Cd. Principal component analysis shows that the MPs could be divided into three categories, i.e. polyamide, rubbery MPs (polyethylene and polypropylene) and glassy MPs (polyvinyl chloride and polystyrene). Their adsorption potentials to Cd follow the decreasing order: polyamide > rubbery MPs > glassy MPs. In summary, these findings indicate that MPs may exert an important influence on fate and transport of metal pollutants during sewage sludge treatment process, which deserves to be further concerned.

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1. Introduction

Many researchers have found that wastewater treatment plants (WWTPs) are important sources of microplastics (MPs) (Murphy et al., 2016). The number of MPs decreases gradually during the different treatment stages, such that less than 3% of the MPs are released into effluent (Lares et al., 2018; Talvitie et al., 2017). Thus, most MPs are retained in sewage sludge (Lares et al., 2018; Mahon et al., 2017; Mason et al., 2016; Talvitie et al., 2017). In our previous work, an average of $22.7 \pm 12.1 \times 10^3$ MP particles per kilogram of sewage sludge dry weight were detected (Li et al., 2018c). Using the sludge for agricultural applications means placing MPs directly into the soil, and researchers have estimated that 63 000–430 000 and 44 000–300 000 tons of MPs enter into the soil system annually when sewage sludge is applied to land in Europe and North America, respectively (Nizzetto et al., 2016), exceeding the estimated 93 000–236 000 tons of MPs present in surface water (Sebille, 2015). In China, approximately 1.56×10^{14} particles of sludge-based MPs are discharged into the soil or other natural environments in 2015 (Li et al., 2018c). However, fate and behavior of the MPs in sewage sludge have yet not to be clarified.

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MPs act as vectors for pollutants due to their large specific surface area, and pose a potential threat to the environment (Koelmans et al., 2016). Field studies have indicated that persistent organic pollutants (POPs) and metal pollutants adhere to the MPs (Chen et al., 2018a; Koukina et al., 2016; Wang et al., 2017). Organic pollutants adsorbed on the MPs include dichlorodiphenyltrichloroethane, and phenylalanine 17 alpha ethinyl estradiol, etc. (Wang et al., 2015; Wang and Wang, 2018; Xu and Liu, 2018). Not only can MPs adsorb organic pollutants, but they can adsorb metal pollutants as well. Adsorption of copper (Cu) and zinc (Zn) by polyethylene (PE) and polyvinyl chloride (PVC) has been investigated (Brennecke et al., 2016). Researchers found that MPs derived from sediment have greater adsorption capacities for metal ions than do virgin plastics, likely because the functional groups generated on plastics during the weathering process effectively adsorb metal ions (Holmes et al., 2014).

In contrast to unmanaged natural environments (Song et al., 2017; Ter Halle et al., 2016), managed man-made environments such as anaerobic digestion and composting can lead to higher biodegradation of plastics such as polylactic acid and polycaprolactone (Narancic et al., 2018). Thus, intensive mechanical abrasion and microbial function during the treatment processes in WWTPs might cause an enhanced effect on physicochemical properties of the MPs, compared to marine and freshwater environment. Mahon et al. (2017) showed that physicochemical properties of MPs in sewage sludge are changed during the treatment processes, for example, the MPs are sheared into smaller sizes in lime stabilization, thermal drying causes their surface to melt and blister, and the MP abundance decreases in anaerobic digestion. However, it is unclear whether these changes affect their potentials to adsorb pollutants.

One of the challenges of applying sludge to land is the presence of some metal pollutants such as Pb, Cd, Ni, etc. Owing to their long-term accumulation in soil, humans are exposed to these metal pollutants through food chain (Giller and E.W, 1998; Smith, 2009). Hence, we hypothesize that significant changes on physicochemical properties of MPs during the treatment processes may enhance their adsorption potential for metal pollutants. The formation of MP-contaminant combination is potentially harmful to organisms, because the pollutants adsorbed on MPs would desorb in different organ sites (Bakir et al., 2014; Khan et al. 2015, 2017; Kim et al., 2017) and may have additional negative effects on the organism, such as, changes in biological activity of enzyme (Hodson et al., 2017; Kim et al., 2017; Luis et al., 2015). Koelmans et al. (2016) suggested that MP ingestion is unlikely to increase the exposure to and thus risks of hydrophobic organic chemicals in marine environment, but Hodson et al. (2017) reported that the existence of MPs could increase the metal exposure in earthworms and enhance the pollutants bioavailability, indicating that MPs can act as vectors of pollutants and increase their risks in the terrestrial environment.

Fourier transform infrared (FTIR) spectroscopy is a sensitive tool for exploring chemical structure of MPs, and has been widely applied to characterize them (Cabernard et al., 2018; Hendrickson, 2018; Wang et al., 2017). However, it is difficult to detect significant changes in MP spectra during adsorption process of MPs to pollutants using conventional one-dimensional method. Two-dimensional FTIR correlation spectroscopy (2D FTIR COS), as a potential method, can be used to resolve the overlapped peak problems of conventional FTIR spectroscopy, and elucidate the interaction mechanism between MPs and pollutants. By distributing spectral intensity trends within a data set collected as a function of the perturbation sequence (e.g. adsorption time) over a second dimension, one can get cross-correlations that define structural relations (Li et al., 2014). The relative direction and sequencing/ordering of band intensity changes can be determined by synchronous and asynchronous spectra generated with 2D FTIR COS (Chen et al., 2018b; Li et al., 2014). The auto-peaks in the synchronous spectrum denote overall susceptibility of the corresponding spectral region to change in spectral intensity as an external perturbation is used to the system. The cross-peaks in asynchronous spectrum probe the specific sequencing/ordering of spectral intensity changes through asynchronous analysis (Noda and Ozaki, 2005). In this study, 2D FTIR COS is used to determine order and degree of these changes in main functional groups on the MP surfaces during the adsorption to metal pollutants.

The objectives of this study are to: 1) investigate the contents of metals in sewage sludge and those adsorbed on the sludge-based MPs; and 2) compare the adsorption and physicochemical characteristics of virgin and sludge-based MPs for Cd using various techniques, such as adsorption isotherms, X-ray photoelectron spectroscopy, scanning electron microscopy (SEM), microscope FTIR spectroscopy, and two-dimensional FTIR correlation spectroscopy; and 3) explore the effect of such factors as pH value, sludge inorganic matter (silica sand, SS) and organic matter (protein and humic substances) on adsorption potentials of MPs to Cd.

2. Materials and methods

2.1. Materials and reagents

Three sewage sludge samples were collected from three WWTPs, respectively. The S1 and S2 sludge samples were obtained from the W1 and W2 WWTPs, respectively, in Shenzhen in December 2016, while the S3 sample was collected from the W3 WWTP in Shanghai in September 2017. Physicochemical properties of the sludge samples including pH value, total solids (TS) content, volatile solids (VS)/TS, elemental composition (C, H, N and S), and metal contents were analyzed. Detailed methods for the parameters are provided in the Supporting Information (SI), and the results are shown in Table 1. Table S1 of the SI shows the detailed characteristics of the WWTPs.

Virgin MPs including polyamide (PA), polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), and polystyrene (PS) were purchased from the Micro Powders Inc., Shanghai, China. Cadmium chloride ($CdCl_2 \cdot 2.5H_2O$), lead nitrate [$Pb(NO_3)_2$], nickel nitrate hexahydrate [$Ni(NO_3)_2 \cdot 6H_2O$], cobalt nitrate hexahydrate [$Co(NO_3)_2 \cdot 6H_2O$], zinc chloride ($ZnCl_2$) and copper sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$) all are 99.0% pure and obtained from the Sinopharm Group Corp. Shanghai, China. Metal stock solutions of 1000 mg L^{-1} were prepared using deionized water. All metal standard solutions, standard bovine serum albumin, and commercial humic substances were purchased from the Aladdin Industrial Corp., Shanghai, China.

2.2. MP extraction

The methods used to extract MPs in sewage sludge have been reported in our previous work (Li et al., 2018c). In brief, 100 g of sludge was added to an Erlenmeyer flask with 1000 mL saturated sodium chloride (1.2 g mL^{-1} NaCl). After stirring for 30 min, the mixture was allowed to settle for 5 h. Then, the top water was filtered via a vacuum filtration unit using a 37-μm sieve. The extraction was carried out in triplicate, and all the MP extracts were collected in the sieve. The sieve in the vacuum filtration unit was then washed with more than 600 mL distilled water to remove any salt residues. The MP particles were hand-sorted from the filters with fine-tip tweezers under the stereomicroscope, and then carefully rinsed with deionized water to eliminate the attached organic matter (Leslie et al., 2017). After air-drying, the rinsed particles were used for the following adsorption experiment and analysis.

Table 1
Properties of sewage sludge samples derived from three wastewater treatment plants (WWTPs).

Parameters		Sludge samples		
		S1	S2	S3
pH		7.29	6.88	7.38
TS (%)		15.42 ± 0.1	15.42 ± 0.1	16.60 ± 0.5
VS/TS (%)		58.66 ± 0.2	64.15 ± 0.3	59.61 ± 0.2
Elemental composition (%)	C	32.13 ± 0.16	32.89 ± 0.63	33.84 ± 0.28
	H	5.53 ± 0.0265	5.90 ± 0.29	5.15 ± 0.14
	N	4.78 ± 0.025	4.45 ± 0.08	6.02 ± 0.08
	S	0.94 ± 0.007	1.14 ± 0.15	0.85 ± 0.02
Abundance of MPs (particles kg^{-1} dry sludge)		13787	15080	37463

2.3. Batch adsorption experiment

In this experiment, five virgin MPs, i.e., PA, PE, PP, PVC and PS were used to evaluate adsorption property of MPs for metal pollutants, such as Pb, Cd, Zn, Cu, Co and Ni. All metal solutions were prepared by diluting stock solutions with deionized water and adjusting the pH with 0.1 M HCl and 0.1 M NaOH. The adsorption was conducted in centrifuge tubes, each of which contained 0.1 g MP particles and 10 mL aqua of 10 mg L^{-1} metal solution. The tubes were placed on an end-over-end shaker at 30 rpm at room temperature for 24 h. Preliminary test showed that 24 h was sufficient to reach adsorption equilibrium (SI Fig. S1). The control group was carried out in the same metal solution using the same procedure but without MP particles. Each test including the control, was run in triplicate.

Cd was used to compare adsorption capacities of the virgin and sludge-based MPs and investigate the influence of pH value, and sludge components on adsorption capacities of the virgin MPs. Cd solution concentrations used for the virgin MPs were 2, 4, 6, 8, 10 and 15 mg L^{-1}, while 2, 4, 6, 8, 10, 15, 20, 40, 60, 80 and 100 mg L^{-1} metal were used for the sludge-based MPs. The pH values ranged from 5.0 to 9.0. Sludge components included inorganic matter (IOM) and organic matter (OM). 0.1 g SS was added to 10 mL aqua of 10 mg L^{-1} Cd solution with 0.1 g MP, to study the IOM influence on MP adsorption. To analyze the OM influence, protein solutions ranging from 0 to 40 mg L^{-1} were prepared, while humic substance solutions were used with the contents from 0 to 80 mg L^{-1}. After 24 h of sorption, the MP particles were extracted, and the solutions were filtered using 0.45 μm membrane filter. The metal concentrations in the filtrates were measured using inductively coupled plasma optical emission spectrometer (ICP-OES) as described in the SI, and the metal contents adsorbed on the MPs were calculated by determining the difference between the control and sample filtrate. The MP particles from the tubes were air-dried for the following analysis.

2.4. MP analysis

Chemical composition of the sludge-based MP particles were identified by Microscope Fourier Transform infrared spectrometer (FTIR, IR/NicoletiN10 MX, Thermo Fisher Scientific Inc., USA) according to our previous study (Li et al., 2018c). Thermo Scientific Hummel Polymer and Additives FTIR Library and Synthetic Fibers by Microscope FTIR Library were used to analyze the spectra, and then the MP types were determined and percentage of MP in potential MP particles for each WWTP was estimated. The contents of such metals as Cd, Pb, Ni and Co adsorbed on the sludge-based MPs were analyzed as the following method shown in the SI. Shortly, the metals were firstly desorbed into 10% aqua regia from the MP surfaces and then measured by the ICP-OES. SEM analyses was conducted in order to determine the surface structures of the virgin and sludge-based MPs using Hitachi SU-1500 scanning electron microscopy (SEM, Hitachi High Technologies Corp., Japan) according to the previous studies as reported by Mahon et al. (2017). X-ray photoelectron spectroscopy (XPS) was applied to measure the Cd content on the surface of MP particles before and after the Cd adsorption experiment using X−ray photoelectron spectrometer (ESCALAB 250, Thermo Fisher Scientific Inc., USA) (Li et al., 2017). FTIR spectra of the virgin and sludge-based MPs were gained through a Nico 380 MX FTIR spectrometer using attenuated total reflectance module (Thermo Fisher Scientific Inc., USA). pH values at the point of zero charge (pH_{PZC}) of the virgin MPs were estimated according to the pH drift method (Yang and Chun, 2004). Specific surface areas of the virgin and sludge-based MPs were determined by N_2 adsorption-desorption at 77 K with an Autosorb-IQ2 surface area analyzer (Quantachrome Corp., USA).

2.5. Two-dimensional FTIR correlation spectroscopy (2D FTIR COS)

FTIR spectra of the MPs were analyzed using 2D COS according to the references (Li et al. 2014, 2015), to further reveal subtle structural variations of the virgin and sludge-based MPs after their interaction with different contents of Cd. The FTIR spectra were normalized by summing the absorbance from 4000 to 400 cm^{-1}, and multiplying by 1000. Subsequently, the normalized data set were transformed into a new spectral matrix using principal component analysis (PCA) in Matlab R2012b (The Mathworks, USA) to reduce the level of noise (Babamoradi et al., 2013), and then 2D FTIR COS maps were conducted using 2D Shige software (Kwansei Gakuin University, Japan) and re-plotted by Origin 9.0 software (OriginLab Corp., USA).

2.6. Data analysis

Langmuir, Freundlich and Dubbin-Radushkevich models were applied to fit adsorption isotherms of Cd on the virgin and sludge-based MPs. The three models can be described by Equations (1)–(3), respectively.

$$\frac{Ce}{q_e} = \frac{1}{k_L q_{\max}} + \frac{Ce}{q_{\max}} \tag{1}$$

$$\ln q_e = \ln k_F + \frac{1}{n} \ln Ce \tag{2}$$

$$q_e = q_{DR} \exp(-B_{DR}\varepsilon_{DR}^2) \tag{3}$$

In which C_e (mg L^{-1}) is the Cd concentration remaining in the solution at equilibrium, q_e (μg g^{-1}) is the amount of Cd adsorbed per mass unit of adsorbent at equilibrium, $q_{\max}$ (μg g^{-1}) is the maximum adsorption capacity, k_L (L mg^{-1}) is the Langmuir binding constant, k_F (mg^{1-n} L^n g^{-1}) and n are Freundlich constants related

to the adsorption capacity and the adsorption intensity, q_{DR} (μg g^{-1}) and B_{DR} (mol^2 J^{-2}) are the D-R isotherm constants and ε_{DR} is the Polanyi potential that is equal to $RT\ln(1+\frac{1}{C_e})$, where R is the gas constant (8.314 J mol^{-1} K^{-1}) and T is the absolute temperature (K).

Different types of MPs were categorized using PCA according to their adsorption properties to Cd in presence of such factors as pH, SS, protein, and humic substances. The data were normalized prior to analysis, to obtain standardized values on the ordination scores. PCA was carried out with the SPSS 13.0 software.

3. Results and discussion

3.1. Metal contents adsorbed on the sludge-based MPs

As shown in Fig. 1, the contents of Cd, Pb and Co adsorbed on the sludge-based MPs are higher than those of the corresponding metal irons in sewage sludge, but the Ni content is lower. This indicates that the MPs accumulate some metals in the sludge samples, in accordance to the previous results from the sea and river water. Brennecke et al. (2016) found that metal concentrations on plastics are higher than in the surrounding seawater, indicating that the MPs act as vectors for metal pollutants. Analysis of energy dispersive X-ray spectroscopy showed that the metals carried by MPs are not inherent but are instead derived from the environment, implying that the metal accumulation on the MPs in surface sediment from the Beijiang River (Wang et al., 2017).

MP particles extracted from the sewage sludge were identified using microscope FTIR, and the results are shown in Fig. S2 of the SI. Primarily, PA, PE, polyolefin (olefin), PS, and alkyd resin (AR) are found in the sludge. To investigate the effect of MP type on metal accumulation, PA, PE, PP, PVC, and PS were used to adsorb Pb, Cd, Zn, Cu, Co, and Ni which are often found in the sewage sludge. In general, the metal contents adsorbed on the MPs decrease in the following order: Pb > Cd > Zn > Cu > Co > Ni. The potential capacities of different MPs for metal adsorption present the following descending order: PA > PE > PP > PVC > PS. Kołodyńska et al. (2012) and Rocha et al. (2009) reported similar results based on the biochar with the following order: Pb > Cd > Cu. Other researchers found the order of organic substances adsorbed on different types of plastics to be PA ≥ PE ≥ PP > PVC > PS (Li et al., 2018a; O'Connor et al., 2016; Wang et al., 2018), consistent with the adsorption results of MPs and metals in this study. Thus, the results imply that the MP type has a significant effect on the adsorption of metal pollutants on MP.

3.2. Comparison of adsorption capacity between virgin and sludge-based MPs

Mahon et al. (2017) found that MPs have the characteristics of melting and blistering after thermal treatment, and shredding and flaking after lime stabilization. These changes in MP physicochemical properties during sludge treatments might cause a significant variation in adsorption potentials of the MPs for metal pollutants. Therefore, adsorption and physicochemical features of the virgin and sludge-based MPs are systematically investigated and compared in this study.

As show in Fig. 1, high contents of Cd are adsorbed on the virgin and sludge-based MPs. Meanwhile, Cd is one of the most toxic metals due to its solubility, mobility, and biological accumulation potential (Nies, 1991), and can be transported into cells, where it

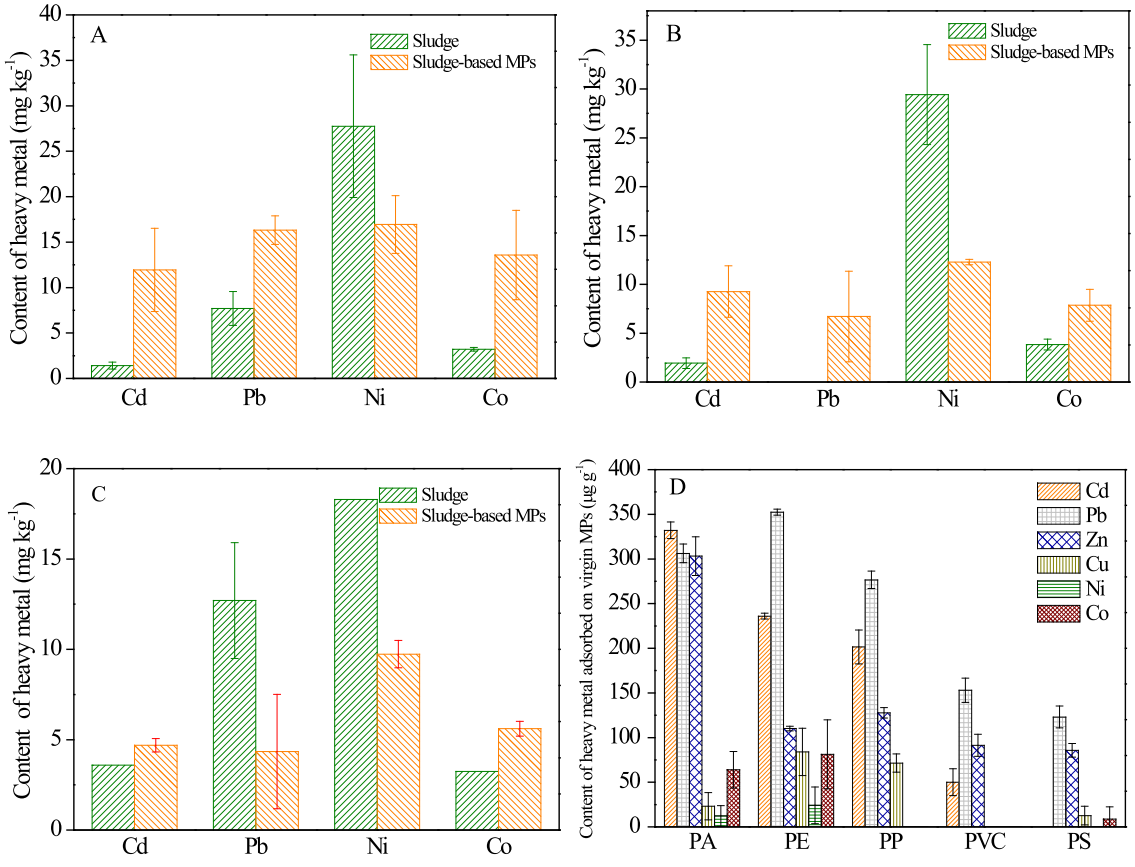


Fig. 1. The content of metals in sewage sludge and adsorbed on the sludge-based MPs (A–C) and virgin MPs (D) (mean value ± SD, n = 3).

can disrupt protein structure and function (Belhalfaoui et al., 2009; Xu et al., 2017). Therefore, Cd is used as a representative metal to evaluate the difference in adsorption of the virgin and sludge-based MPs to metals in this study.

XPS analysis shows that two additional Cd3d (405 eV and 411 eV) peaks are observed in XPS spectra of the MPs after the adsorption process (SI Fig. S3), compared with the virgin MPs, indicating that Cd is indeed adsorbed on the MPs. Cd adsorption isotherms of the virgin and sludge-based MPs are shown in Fig. 2. The isotherms of virgin PA, PE, PP and PS, and sludge-based MP fit the Langmuir model well (Tables 2 and SI Fig. S4), implying that the adsorptions are monolayer adsorption. The isotherm of PVC fits Freundlich model well, revealing that the adsorption belongs to multilayer adsorption. According to the Langmuir model, Cd adsorption capacity of the sludge-based MPs reaches a maximum of 2.523 mg g^{-1}, which is one order of magnitude higher than that of the virgin MPs (Table 2), corresponding to the previous results from the comparison of virgin and aged MPs from the nature environment (Holmes et al., 2014; Turner and Holmes, 2015; Wijesekara et al., 2018). Holmes et al. (2014) reported greater adsorption of metals on beached (aged) plastics than on virgin plastics. In another study, modified microbeads that were incubated for several days in soils, sediments and biosolids are found to adsorb more Cu than untreated microbeads (Wijesekara et al., 2018).

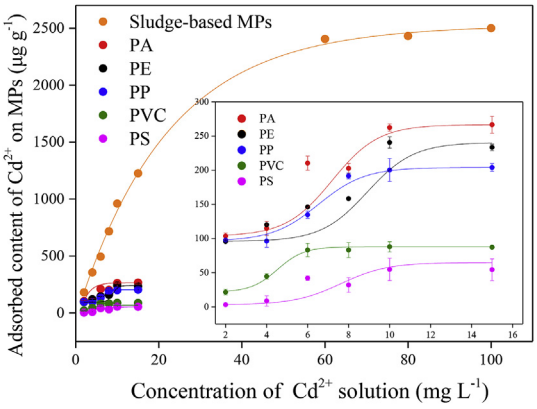


Fig. 2. Sorption isotherms of Cd on the virgin and sludge-based MPs. (mean value ± SD, n = 3).

SEM analysis reveals that the surfaces of sludge-based MPs exhibit wrinkled and aggregated structures (Fig. 3), in contrast to smooth surfaces of the virgin MPs (Mahon et al., 2017; Wijesekara et al., 2018). Specific surface area of the sludge-based MPs is higher than that of the virgin MPs except for PS (SI Table S2), indicating that more potential adsorption sites exist on the sludge-based MPs. FTIR spectra of the sludge-based MP present some characteristic peaks, distinct from the virgin MPs (SI Fig. S5). Compared with virgin PE, the corresponding sludge-based MP shows stronger peaks at 1000–1100 cm^{-1} to the C–O stretching of primary and secondary alcohols, and at 1370–1376 cm^{-1} to the C–H and O–H deformation of alcohol and phenolic groups. The result implies the presence of O-containing (C–O and O–H) groups on the sludge-based MPs, which is possibly attributed to oxidative degradation and erosion of the MPs (Ceccarini et al., 2018), and the attachment of organic matter on them (Wijesekara et al., 2018). Turner and Holmes (2015) showed that the attachment of organic matter to MPs during the weathering process affects the adsorption of metal. Hence, these results indicate that the emergence of O-containing functional groups may play an important role in enhancing metal adsorption potential of the sludge-based MPs.

To further understand the role of the functional groups during the MP adsorption to Cd, 2D COS was used to analyze the FTIR spectra. Significant spectral variations are found in the ranges of 900–1300 cm^{-1} and 1350–1600 cm^{-1}, which contain the bands corresponding to amides, carboxylic acids, esters, aliphatic group, and carbohydrates (Li et al. 2014, 2015). As shown in Fig. 4, four major auto-peaks in synchronous map of the sludge-based MPs follow in the decreasing order: 1580 > 1440 cm^{-1}, implying that N–H functional group plays a greater role in adsorbing metals,

Table 2
Constants defining Cd adsorption on the virgin and sludge-based MPs according to the isotherm models.

MPs	Langmuir	Freundlich	Dubbin-Radushkevich
PE	$k_L = 0.414$ L μg^{-1} $q_{max} = 234.5$ μg g^{-1} $R^2 = 0.92$ $p = 0.000$	$k_F = 4.53$ μ$g^{1-1/n}$ g^{-1} $L^{1/n}$ $n = 3.7$ $R^2 = 0.89$ $p = 0.001$	$q_{DR} = 202.6$ μg g^{-1} $R^2 = 0.79$ $p = 0.006$
PA	$k_L = 0.320$ L μg^{-1} $q_{max} = 339.6$ μg g^{-1} $R^2 = 0.89$ $p = 0.005$	$k_F = 5.28$ μ$g^{1-1/n}$ g^{-1} $L^{1/n}$ $n = 2.58$ $R^2 = 0.83$ $p = 0.011$	$q_{DR} = 214.4$ μg g^{-1} $R^2 = 0.56$ $p = 0.006$
PP	$k_L = 0.675$ L μg^{-1} $q_{max} = 199.2$ μg g^{-1} $R^2 = 0.91$ $p = 0.003$	$k_F = 4.71$ μ$g^{1-1/n}$ g^{-1} $L^{1/n}$ $n = 3.67$ $R^2 = 0.67$ $p = 0.047$	$q_{DR} = 201.5$ μg g^{-1} $R^2 = 0.84$ $p = 0.029$
PS	$k_L = 0.516$ L μg^{-1} $q_{max} = 69.9$ μg g^{-1} $R^2 = 0.81$ p = 0.037	$k_F = 1.11$ μ$g^{1-1/n}$ g^{-1} $L^{1/n}$ $n = 2.23$ $R^2 = 0.662$ $p = 0.094$	$q_{DR} = 103.7$ μg g^{-1} $R^2 = 0.83$ $p = 0.029$
PVC	$k_L = 0.845$ L μg^{-1} $q_{max} = 222.2$ μg g^{-1} $R^2 = 0.64$ $p = 0.012$	$k_F = 0.813$ μ$g^{1-1/n}$ g^{-1} $L^{1/n}$ $n = 1.24$ $R^2 = 0.94$ $p = 0.007$	$q_{DR} = 67.6$ μg g^{-1} $R^2 = 0.03$ $p = 0.784$
Sludge-based MPs	$k_L = 0.547$ L μg^{-1} $q_{max} = 2.52$ mg g^{-1} $R^2 = 0.98$ $p = 0.000$	$k_F = 50.6$ μ$g^{1-1/n}$ g^{-1} $L^{1/n}$ $n = 4.67$ $R^2 = 0.91$ $p = 0.000$	$q_{DR} = 1.67$ mg g^{-1} $R^2 = 0.70$ $p = 0.784$

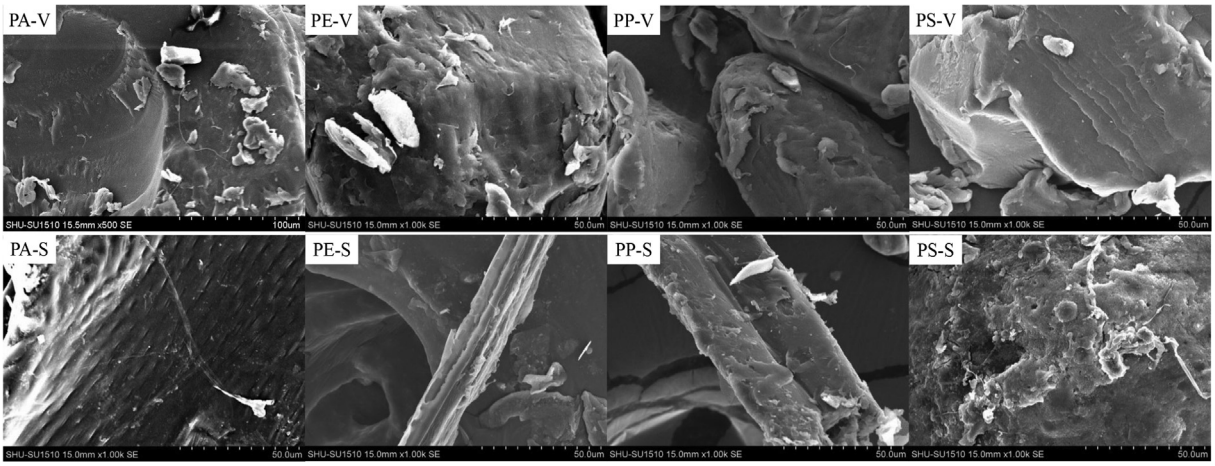


Fig. 3. SEM graphs of the virgin and sludge-based MPs (V, virgin MPs; S, sludge-based MPs).

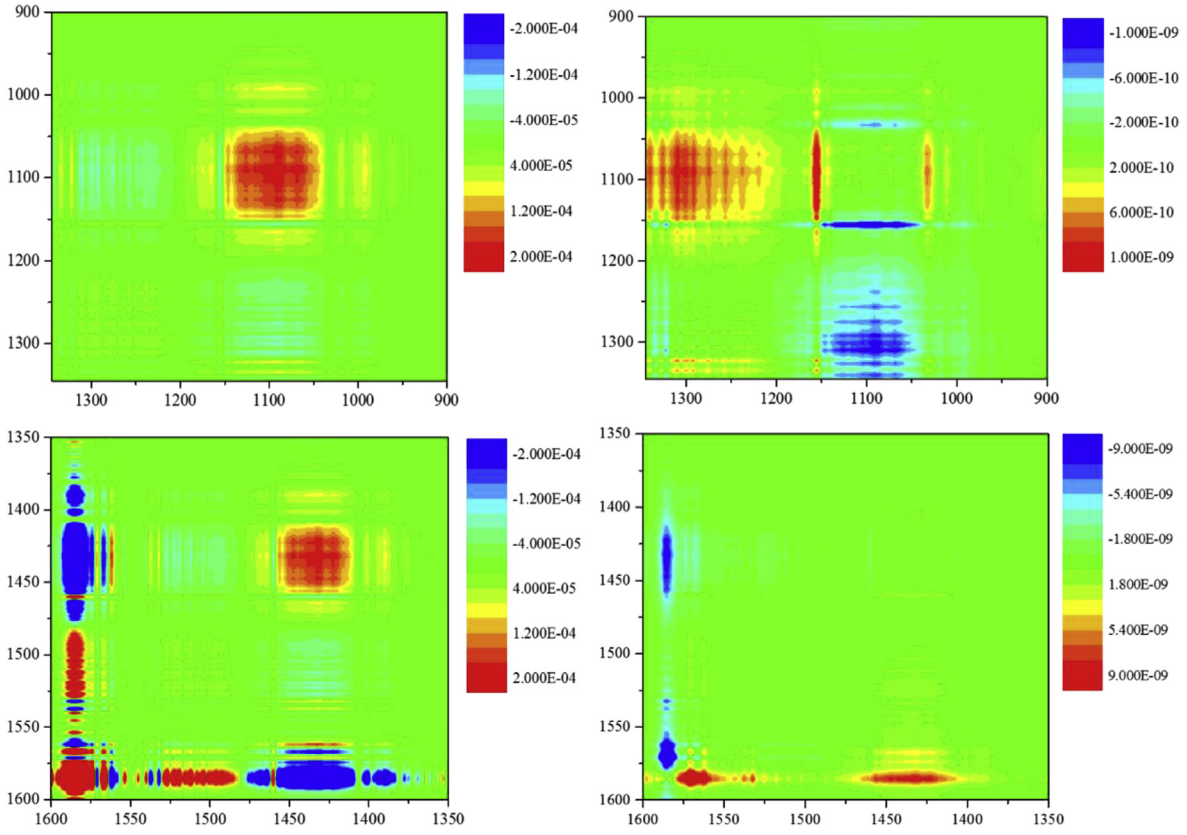


Fig. 4. Synchronous (left) and asynchronous (right) 2D correlation maps generated from 900 to 1300 cm^{-1} (above) and 1350–1600 cm^{-1} (below) regions of FTIR spectra of the sludge-based MPs adsorbing increasing contents of Cd.

compared with C–H functional group. Off-diagonal peaks (cross-peaks) in the synchronous map show correlated signals, implying simultaneous or coincidental changes in spectral intensities at two different spectral variables (Li et al. 2014, 2015). Two main cross-peaks at (1460, 1580) and (1520, 1580) cm^{-1} are positively correlated in the sludge-based MPs, suggesting the simultaneous changes. Three cross-peaks at (1390, 1580), (1440, 1580) and (1540, 1580) cm^{-1} show that the bands are correlated negatively, implying that the functional-group changes are not simultaneous. In contrast to synchronous maps of the virgin MPs (SI Figs. S6–S9), specific C–O group at 1100 cm^{-1} is observed in that of the sludge-based MPs, complementing and confirming the finding of important role of C–O functional group in metal adsorption on the sludge-based MPs based on FTIR analysis. In the asynchronous map, cross-peaks can provide useful information about sequential order of the changes of different organic functional groups. According to Noda's rule (Noda and Ozaki, 2005), the band changes follow the order: 1050 → 1250 cm^{-1} and 1580 → 1440 cm^{-1}. The structural variation sequence in the adsorption process could be proposed as follows: C–O→C–H and N–H→C–H. The results indicate that the C–O and N–H functional groups are combined preferentially with Cd during the adsorption, compared with C–H group. The results

complement and confirm the findings from FTIR spectra that physicochemical changes of the sludge-based MPs such as generation of O-contain groups result in the enhancement of MP adsorption capacity.

Fragmentation of MPs weathered by environment factors like wind, sunlight, and mechanical abrasion in natural environments has been reported widely (Song et al., 2017; Ter Halle et al., 2016). However, these processes often require long periods of time (Ceccarini et al., 2018). In contrast to the natural environment, WWTPs are artificial ecosystems in which intensive physical, chemical, and biological processes occur in the presence of high contents of organic matter and various active microbes. MP surface may be abraded by shearing effect attributable to mechanical mixing at "grit & grease" removal stage and/or the aeration at activated sludge tank. Elevated pH in lime stabilization can fragment plastics, resulting in larger quantities and smaller size classes of plastics (Mahon et al., 2017; Zubris and Richards, 2005). Microorganisms are critical community during biological treatment process in WWTPs. The MPs are colonized by microbe, leading to the formation of biofilm. PE-degrading bacteria have been found in the biofilm (De Tender et al., 2017), and can cause chain scission and oxidation of PE (Restrepo-Flórez et al., 2014). Therefore, the polymer-degrading bacteria in the biofilms can lead to changes in the MP surface during secondary wastewater treatment processes. Researchers suggested a decrease in MP abundance after sludge anaerobic digestion attributable to the biological breakdown of polymers (Shah et al., 2008; Yoshida, 2016). Therefore, wastewater treatment processes cause changes in physicochemical properties of MPs, and thus can enhance their capacity to adsorb such pollutants as metals.

3.3. Factors affecting the Cd adsorption by virgin MPs

Sewage sludge has a broad pH range, and it contains high contents of complex inorganic and organic matter, such as protein and humic substances. Enhancing our knowledge about the influences of environmental factors (e.g., pH value) and sludge components (e.g., inorganic and organic matter) is vital to understand adsorption potential of MPs in sewage sludge to metals.

3.3.1. Effect of pH value

The adsorption of metal ions depends on pH value of solution because it affects both surface charge of the adsorbent and the speciation of metal ions (Melo and Neto, 2013). Fig. 5A shows that the adsorbed Cd contents on the MPs first increase, then decrease in the range of pH 5–9. The adsorption of Cd on MPs increases as the pH due to the enhancement of the anionic surface, indicating the significance of electrostatic interactions (Wang et al., 2015). A decrease in the adsorption at higher pH is attributed to the formation of precipitation competing with Cd iron for active sites of the MPs, which reduces metal retention (Kołodyńska et al., 2012; Vimala and Das, 2009). The highest adsorbed Cd contents are found at pH 7.7, 7.4, 7.1, 6.0 and 6.0 for PA, PE, PP, PVC and PS, respectively (Fig. 5A), indicating that pH value has different influence on different types of MPs for Cd adsorption. The pH_{PZC} (the point of zero charge) is the pH at which the surface of the MP has a net zero

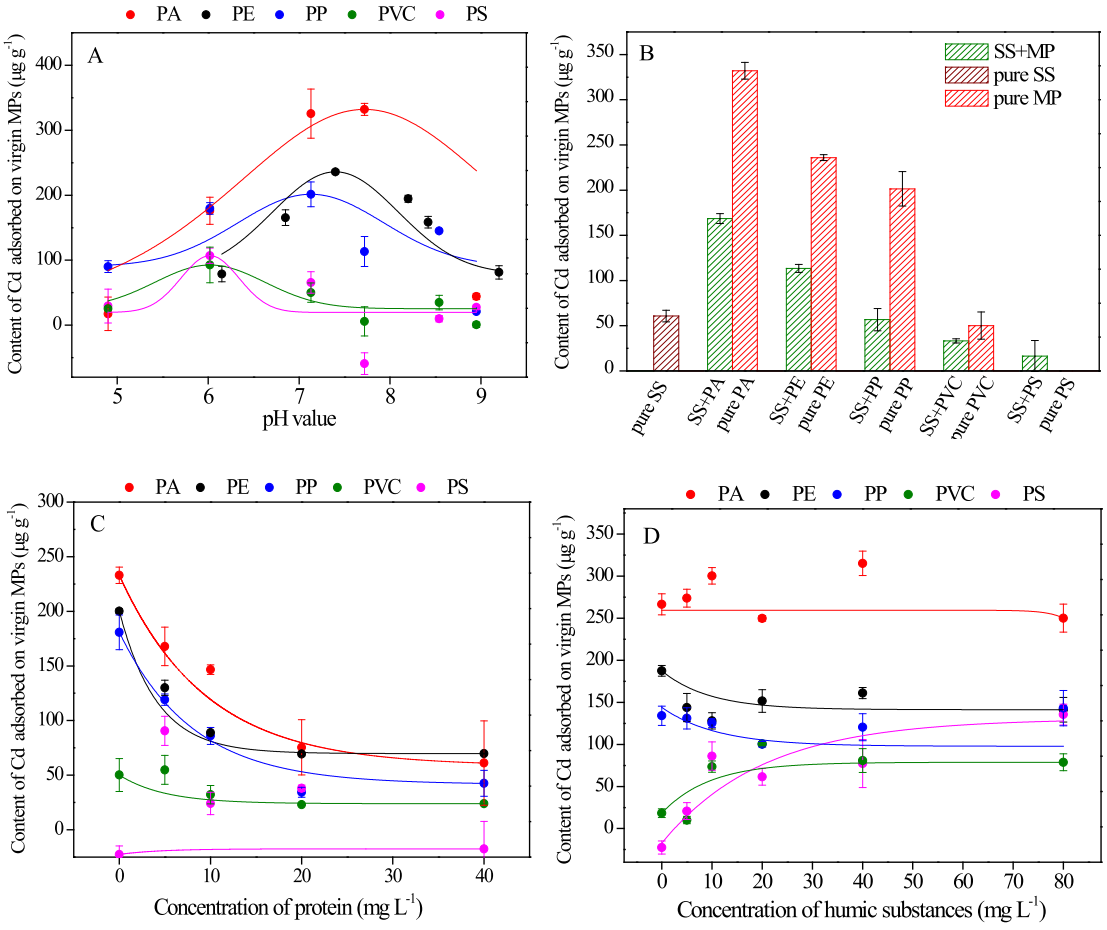


Fig. 5. The influence of pH value, silica sand (SS), protein, and humic substances on adsorption of Cd on the MPs (mean value ± SD, n = 3).

charge. At pH > pH_{PZC}, the MP surface has a net negative charge and cations can be adsorbed. Table S2 of the SI shows that pH_{PZC} values of the five MPs are 5.59–5.85, and less than the pH at which the highest adsorbed Cd contents are found. The result implies that adsorption of Cd on the MPs belongs to chemical adsorption. The negative charge on the MPs are attributed to negatively charged groups that are bonded chemically to the microsphere during polymerization (Dong, 2005; Lu et al., 2018). In this study, pH values of the sewage sludge range from 6.88 to 7.38 (Table 1), indicating that adsorption potentials of the sludge-based MPs shows a high level for metals in terms of pH value.

3.3.2. Effect of sludge components

Sewage sludge are composed of inorganic particles and organic matter (Wei et al., 2018). The percentage of sand in sludge inorganic matter reaches up to 78.9% in China (Zhao, 2015), and thus SS was selected as a representative of sludge inorganic component (Duan and Dai, 2016) in the study. Sludge organic matter including protein and humic substances might affect adsorption of the MPs to metals (Wei et al., 2016). Organic matter can readily adsorb metals, so it has a potential role in metal transport into the environment and metal sorption to bacterial cells (Hu et al., 2007; Joshi and Juwarkar, 2009). Many OM functional groups, such as carboxyl, phosphoric, sulfhydryl, phenolic, and hydroxyl groups, all can complex with metals (Sheng et al., 2010). However, there is little information about the influence of sludge IOM and OM components on the adsorption of metal on MPs.

Content of Cd adsorbed on the MPs in SS + MP group is lower than that in the corresponding pure MP group except for PS (Fig. 5B). These results imply that inorganic matter in sewage sludge affects metal adsorption of the MPs adversely. Fig. 5C shows that Cd content adsorbed on the MPs decreases with the protein concentration, except for PS. Research reported that protein has a net positive charge at pH 7.5 (Matsui et al., 2015). Positively charged protein molecules are attracted to negatively charged surface of the MPs, and thus compete with Cd for adsorption sites on the MPs. As shown in Fig. 5D, with the concentration of humic substances, the Cd contents adsorbed on PA, PE, and PP decrease, and on PVC and PS increase. It is well-known that humic substances as common natural organic matter are often negatively charged, and can adsorb cations, causing a decrease in available Cd content for sorption of the MPs. Therefore, the adsorption potentials of PA, PE and PP to Cd reduce as the content of humic substances increases. Researchers also reported that concentrations of adsorbed tetracycline on PS, PP, and PE decreased with an increase in humic substance concentrations (Xu and Liu, 2018). On the other hand, humic substances can adhere to the MP surfaces, causing an increase in zeta potentials and negative charge on the MPs surfaces (Li et al., 2018b; Lu et al., 2018), and increasing electrostatic interactions between Cd and the MPs. Chen et al. (2018b) found that the interaction between humic substances and MPs results in formation of the co-polymer. The interaction increases negative surface charges on MPs and enhances their stability (Alimi et al., 2018; Lu et al., 2018). Therefore, the adsorbed Cd contents on PVC and PS increase with humic substances concentration.

PCA was used to classify the five MPs, i.e. PA, PE, PP, PVC and PS, according to their maximum Cd adsorption amount and changing characteristics of adsorbed Cd content under the influence of pH, and sludge IOM and OM components. As Fig. 6 shows, the five MPs are divided into three main categories, Category 1 (PA), Category 2 (PE and PP), and Category 3 (PVC and PS). The above results show that adsorption potentials of the three categories of MPs follow the decreasing order: Category 1 > Category 2 > Category 3. The presence of polar amide functional group (–CO–NH–) and hydrogen bonding on the PA surface might cause its high adsorption capacity

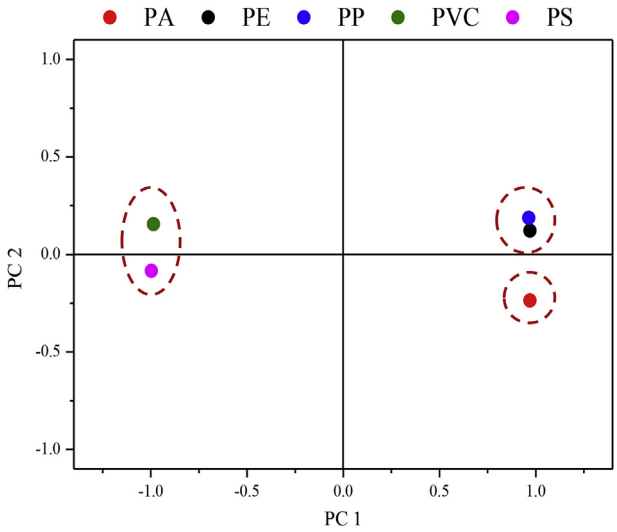


Fig. 6. Principal component analysis (PCA) of different types of MPs according to their maximum Cd adsorption amount and changing characteristics of adsorbed Cd content under the influence of pH, and sludge IOM and OM components.

to Cd (Li et al., 2018a). According to the glass transition temperatures (T_g), the plastics are divided into two categories, rubbery plastics (PE and PP) and glassy plastics (PVC and PS) (Alimi et al., 2018; Teuten et al., 2009). Rubbery plastics have a large amount of free volume between the molecules, while glassy polymers have a dense structure and closed internal nanoscale pores (Teuten et al., 2009). Therefore, the structure of glassy plastics leads to lower pollutant mobility and slower diffusivity rates than those observed in rubbery plastics, resulting in lower adsorption capacity (Pascall et al., 2005). These results complement and confirm that the MP type has a significant effect on the metal adsorption.

3.4. Implications and limitations of this study

Our results show that MPs can act as vectors for metals in sewage sludge and potentially influence on metal fate and transport when sewage sludge is applied to land. Tons of the MPs enter the soil system annually during sludge land application (Li et al., 2018c; Nizzetto et al., 2016). Organisms take up the metal pollutants adsorbed on the MPs, resulting in the partial accumulation of metal pollutants and increasing their potentials risks. Adsorption capacity of the sludge-based MPs for such metal as Cd is one order of magnitude higher than that on virgin MPs, implying a considerable increase in MP adsorption capacity on the metal after the wastewater treatment process, and thus the sludge-based MPs might produce higher effect to the metal transport than the virgin MPs. The results are attributed to changes in physicochemical characteristics of the MPs during wastewater treatment processes. The MPs are oxidized and/or coated by organic matter, causing an increase in potential adsorption sites and the generation of O-containing group on their surfaces, and thus enhancing their adsorption to metal pollutants. In addition, biofilm formation on the MPs also possibly contributes to the changes. Wu et al. (2017) showed that the presence of plastic colonization could influence transport and transformation of the pollutants. In summary, it requires more attention to the potential risks resulted from metal accumulation on the MPs in sewage sludge.

Limitations of this study are that the MPs were gained from the sewage sludge samples through hand picking, and limited amounts were available for experiments. Thus, adsorption properties of different types of the sludge-based MPs to metal pollutants is lack

of investigation, and physicochemical changes in the MPs during simulated wastewater treatment processes need to further investigate. Such study will allow us to obtain a profound understanding of the mechanism related to enhanced adsorption of the MPs to metal after the wastewater treatment process. In addition, it is significant to further explore the influence of wastewater treatment processes, both individually and collectively, on the MP adsorption to other pollutants such as other metals and organic pollutants.

4. Conclusions

MPs can accumulate the metals in sewage sludge, although the adsorption capacity might differ for different metal irons and plastics types. Adsorption potentials of the MPs to such metal as Cd increase by about ten times during entering into sewage sludge after wastewater treatment processes, compared with virgin MPs. They are resulted from physicochemical changes of the sludge-based MPs during the treatment processes, such as the emergence of rough and porous structures, and the presence of C–O and O–H groups on the MP surfaces. It needs further investigation to understand how wastewater treatment processes to affect MP physicochemical properties in controlled experiments. Analyses of factors affecting the MP adsorption indicate that sludge inorganic and organic components have an adverse effect on metal adsorption potentials on the MPs. However, the influence differs for different MP types, e.g. humic substances seem to enhance adsorption of the glassy MPs to Cd. In sum, ecological risk of metal accumulation on the MPs needs to further investigate during sludge land application.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.watres.2019.03.069.

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