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RESEARCH ARTICLE

Occurrence and migration of microplastics and plasticizers in different wastewater and sludge treatment units in municipal wastewater treatment plant

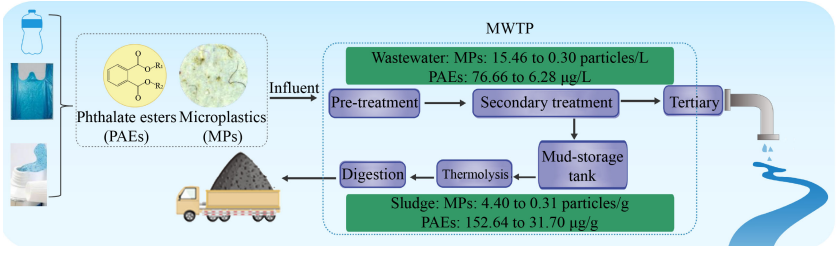
Sen Dong, Peng Gao, Benhang Li, Li Feng (✉), Yongze Liu, Ziwen Du, Liqiu Zhang (✉)

Beijing Key Laboratory for Source Control Technology of Water Pollution, Engineering Research Center for Water Pollution Source Control and Eco-remediation, Beijing Forestry University, Beijing 100083, China

HIGHLIGHTS

- Reduce the quantifying MPs time by using Nile red staining.
- The removal rate of MPs and PAEs in wastewater and sludge were investigated.
- MPs and PAEs were firstly analyzed during thermal hydrolysis treatment.
- The removal of PAEs from wastewater and sludge was mainly biodegradation.

GRAPHIC ABSTRACT



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ABSTRACT

Microplastics (MPs) and plasticizers, such as phthalate esters (PAEs), were frequently detected in municipal wastewater treatment plants (MWTP). Previous research mainly studied the removal of MPs and PAEs in wastewater. However, the occurrence of MPs and PAEs in the sludge was generally ignored. To comprehensively investigate the occurrence and the migration behaviors of MPs and PAEs in MWTP, a series of representative parameters including the number, size, color, shape of MPs, and the concentrations of PAEs in wastewater and sludge were systematically investigated. In this study, the concentrations of MPs in the influent and effluent were 15.46±0.37 and 0.30±0.14 particles/L. The MP removal efficiency of 98.1% was achieved and about 73.8% of MPs were accumulated in the sludge in the MWTP. The numbers of MPs in the sludge before and after digestion were 4.40±0.14 and 0.31±0.01 particles/g (dry sludge), respectively. Fourier Transform Infrared Spectroscopy (ATR FT-IR) analysis showed that the main types of MPs were polyethylene terephthalate (PET), polypropylene (PP), polyethylene (PE), and polystyrene (PS). Six PAEs, including phthalate (DMP), diethyl phthalate (DEP), diisobutyl phthalate (DIBP), ortho dibutyl phthalate (DBP), butyl benzyl phthalate (BBP), and bis(2-ethyl) hexyl phthalate (DEHP), were detected in the MWTP. The concentrations of total PAEs (ΣPAEs) in the influent and effluent were 76.66 and 6.28 μg/L, respectively. The concentrations of ΣPAEs in the sludge before and after digestion were 152.64 and 31.70 μg/g, respectively. In the process of thermal hydrolysis, the number and size of MPs decreased accompanied by the increase of the plasticizer concentration.

1 Introduction

Plastic products are widely used in daily life and industrial production. Because of the lack of effective recycling and treatment, a large number of plastic products eventually became plastic waste. Microplastics (MPs) and plasticizers were two typical pollutants related to plastic waste. They inevitably enter the environment with ecological and health risks (Lee and Kim, 2018).

MPs were defined as plastic particles < 5 mm in size (Huerta Lwanga et al., 2016). Microplastics have become a new type of global pollutant because of their extensive sources, difficult to be removed, long-term accumulation, and adverse effects on ecosystems and human health (Nel et al., 2021). Some MPs are originated from the fragments of large plastic products, and other MPs come

✉ Corresponding authors
E-mails: fengli_hit@163.com (L. Feng);
zhangliqiu@bjfu.edu.cn (L. Zhang)

from personal care products, such as toothpaste and facial cleansers (Ustabasi and Baysal, 2019). In the past few years, MPs had been widely detected in environments such as oceans (Auta et al., 2017), freshwater (Eerkes-Medrano et al., 2015), sediments (He et al., 2020), and soils (Li et al., 2021). In China, about 209 trillion plastic microbeads (about 3.069 million tons) were discharged into the water environment every year (Cheung and Fok, 2017). Phthalate esters (PAEs) were a group of widely used plasticizers. Many PAEs were recognized as teratogenic compounds which could lead to disorders of the endocrine system, affect reproductive function, and induce some tumors (Gao et al., 2018). Six commonly used PAEs, such as bis(2-Ethylhexyl) phthalate (DEHP), diethyl phthalate (DEP), dibutyl phthalate (DBP), di-isobutyl phthalate (DIBP), butyl benzyl phthalate (BBP), and dimethyl phthalate (DMP) were added into plastics as additives were classified as priority pollutants (Clara et al., 2010; Gao et al., 2014). After being ingested by organisms, MPs are accumulated in organisms, and they can cause physical damage to organisms, such as internal esophagus injury and intestinal obstruction (Anbumani et al., 2018; Wright and Kelly, 2017). It can be seen that most of the literatures focus on the MWTP wastewater, and there is no systematic report on the occurrence of MPs and PAEs in sludge. Therefore, it is vital to study the occurrence and migration pathways of MPs and PAEs in the MWTP.

The effluent from a municipal wastewater treatment plant (MWTP) is considered as the main source of MPs and PAEs into the aquatic environment (Loraine and Pettigrove, 2006; Zhang et al., 2021a). Most traditional wastewater treatment processes are not designed to remove these persistent organic pollutants (Murphy et al., 2016). Residual MPs and PAEs are detected in the effluent and sludge. Jiang et al. (2020) reported that about 75.7% of MPs removed from the water phase were transferred to the sludge. Takdastan et al. (2021) found that after the primary and secondary treatments, the number of MPs in the effluent of an MWTP was reduced to 0.84 particles/L, and the concentration of DEHP in the effluent was as low as 8.13 μg/L. Most of the reported studies focused on the changes of MPs and PAEs in the influent and effluent of MWTP. Wang et al. (2020) investigated four MWTP effluents with MPs content of 276–1030 particles/L and PAEs concentration of 568.9–1847.5 ng/L, while their existence in the sludge is ignored. In addition, the ever-increasing production of sludge and the demand for the utilization of sludge led to the construction of more and more sludge thermal hydrolysis systems (Gao et al., 2014). However, information on the removal efficiency of MPs and PAEs during the thermal sludge hydrolysis is very limited. Although there are a few studies that investigated the removal of MPs and DEHP during wastewater treatment, no systematic research had been conducted on the occurrence levels of MPs and PAEs in MWTP. In addition, the behavior of MPs and PAEs during thermal hydrolysis of sludge had never been investigated.

In this study, the occurrence and removal of MPs and PAEs in wastewater and sludge were systematically investigated. The aims of this study are: 1) to investigate the occurrence level and distribution characteristics of MPs in different treatment units in the MWTP; 2) to explore the variations of PAEs during wastewater and sludge treatment processes.

2 Materials and methods

2.1 Sampling

Wastewater and sludge samples were collected from an MWTP in Beijing, China. The daily treatment capacity of the selected MWTP is 1×10^6 m^3. Domestic wastewater is the main source of this MWTP, and the effluent is discharged into the Qinghe River. The sampling sites are shown in Fig 1. The wastewater samples were taken from the grid, aeration grit chamber, biological reaction tank (A^2O process), secondary sedimentation tank, and UV disinfection tank, marked as W1, W2, W3, W4, W5. The sludge samples were taken from the sludge storage tank, dewatered sludge, hydrolyzed sludge, and digestion sludge marked as S1, S2, S3, and S4. About of 25 L

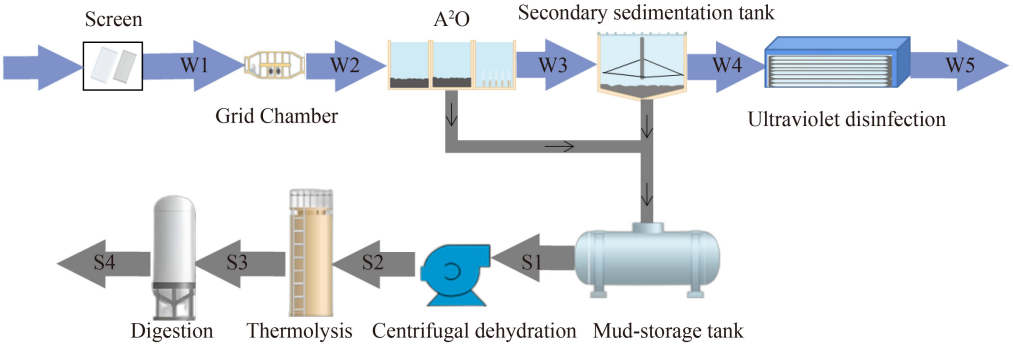

Fig. 1 Sampling points in the selected MWTP.

wastewater sample in each sampling point was collected by using a stainless-steel bucket, and about 1 kg sludge sample was collected through a glass bottle. All the samples were stored in a refrigerator at 4 °C.

2.2 Sample processing

The collected wastewater samples (20 L) were passed through combined mesh sieves with mesh sizes of 150, 100, 75, and 45 μm to separate solid MPs of different sizes. The collected MPs were flashed into a 250 mL conical flask using 200 mL ultrapure water. The beaker was heated in an oven at 60 °C for 48 h. To remove the adsorbed organic matter, 30 mL hydrogen peroxide (H_2O_2, 30%) was added to the sample and the temperature was maintained at 60 °C for 24 h in a water bath. As the color of the solution changed from deep brown to light yellow, the MP sample was rested in a fume hood for 3–5 d before being completely dried for density separation using a NaCl salt solution. Sodium chloride solution (1.2 g/cm^3, 100 mL) was added to the dried MP sample. The mixture was shaken thoroughly before being transferred into a 250 mL separation funnel. After standing for 6 h, the solid residual was collected. The process was repeated three times and all the supernatant was vacuum filtered through a 0.45 μm filter membrane (diameter 47 mm, Pall Co., Ltd., China). The collected MP sample was washed thoroughly to remove the residual salt. Finally, the sample was dried and stored for further observation and analysis.

Sludge samples were completely dried at 60 °C. 10 g dried sludge and 30 mL 30% H_2O_2 were mixed into the beaker. The mixture was heated at 60 °C for 12 h. After that, 100 mL zinc chloride solution (1.5 g/cm^3) was added to the mixed solution. The mixture was sonicated for 3–5 h before transferring into a separation funnel and allowed to stand for 3–5 h for density separation. The supernatant was collected by filtering onto a filter membrane, which was dried for further analysis.

2.3 Identification and characterization of MPs

The size of MPs was divided by sieves and measured by using ImageJ software. The detection range of ATR-FTIR is > 10 μm. MPs > 10 μm in size were picked with tweezers under the microscope and further identified with ATR-FTIR analysis. To study the size, color, shape of MPs, a fluorescent stereomicroscope (7.8x–160x, Leica M205FA, Germany) was used to record the images of MPs. The samples were stained with 5 μg/L Nile Red solution and dried at 50 °C for 10 min. Nile Red can stain microplastics in the range of 3 μm–5 mm (Shruti et al., 2022). After staining, the MPs emitted green fluorescence under blue light. The images were analyzed by ImageJ software.

As shown in Fig. 2(a), the color of MPs in the sample could be identified in the bright field microscopy image, and the Nile red staining had little effect on the observation of MPs (Fig. 2(b)). The automatic particle quantification from the fluorescence images was performed by ImageJ software (Fig. 2(c)). The process was set as follows: 1) the image was converted to 8-bit, 2) the image color was scaled, 3) 0 and 8 were used as the lowest and highest threshold values of pixel brightness, and 4) quantify particles based on the area (⩾ 400 μm^2). A total of 820 fluorescent particles were detected, and ATR FT-IR spectroscopy confirmed that 705 fluorescent particles were MPs particles. 86% of the fluorescent particles were MPs particles. So, all data deducted the "fake MPs".

ATR FT-IR (Vertex 70, Bruker, Germany) was used to analyze the 0.42–5.00 mm particles with a scanning range of 4000–400 cm^{-1}. The obtained infrared spectra were compared with Hummel's polymer and additive library to identify polymer types. The total number of MPs of different polymer types (N), was calculated from the number of the dyed particles on the filter membrane (n), and the proportion of the specific polymer type (ω). The formula is given in Eq. (1).

$$N = n \times \omega. \tag{1}$$

TGA-FTIR (STA449 F5 Jupiter/Nicolet iS10) was used in the experiments to detect the mass concentration of MPs in sludge. All the samples were used a 30%–35% H_2O_2 solution for a week-long treatment. The sludge samples were transferred to the crucible and heated from 30 °C to 650 °C at ramp rates of 30 °C/min (30 °C to 300 °C) and 15 °C/min (300 °C to 650 °C) The nitrogen purge rate was 30 mL/min. The mass loss of the sample was recorded as a function of temperature, and the pyrolysis products were continuously passed through a gas chamber located in FTIR (Nicolet iS10, Resolution: 4 cm^{-1}, Spectra: 4000–400 cm^{-1}).

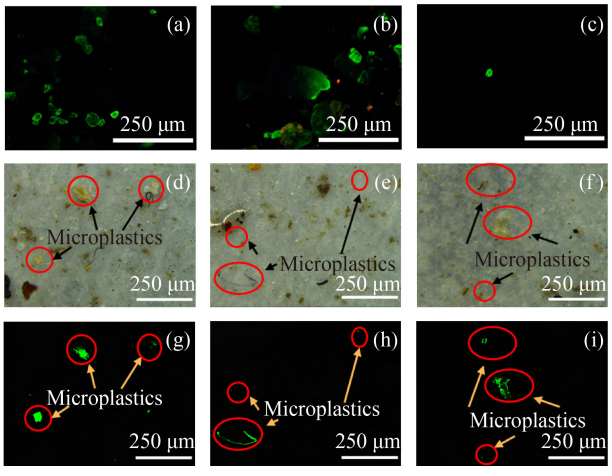

Fig. 2 The microscope images of MPs were stained with NR (a)–(c). The microscope images of MPs in the bright field after staining (d)–(f). The microscope images of the stained MPs in the dark field after processing with ImageJ software (g)–(i).

2.4 Quality control

To reduce the possibility of chemical contamination, the glassware was cleaned with ultrapure water before the MPs separation experiment. Strict quality control measures were implemented in the field sampling and laboratory testing. In the blank experiment, ultrapure water was filtered through organic filter paper and vacuum filter. The filter paper was exposed to the air for 24 h, and the surface of the filter paper was observed with a stereomicroscope to identify any potential microplastic contamination during the experiment. Since there was no MP on the surface of the filter paper, a background correction was not required.

To verify the experimental results, five different polymer particles, including polyethylene (PE), polypropylene (PP), polyethylene terephthalate (PET), nylon (PA), and polystyrene (PS) were used as spikes for testing the extraction efficiency. Particles with the sizes of 1–5 mm, 0.15–1 mm, and 0.1–0.15 mm respectively were added to the wastewater and sludge samples. The extraction test was carried out according to the same procedure as the sample treatment. The average recovery is between 90.83%–92.33% (Table S1), indicating that the test process is stable, reliable, and accurate.

2.5 GC-MS analysis

Solid-phase extraction was used to extract PAEs from wastewater. The wastewater sample was filtered through a 0.45 μm filter membrane. A C18 cartridge (Bond Elut, 500 mg, 6 mL) was activated in the sequence with n-hexane, methanol, and ultrapure water. 100 mL of the filtered wastewater sample was passed through the C18 cartridge. After the wastewater sample was filtered, 4 mL elution solvent was added into PAE elute. The eluent was blown to nearly dry with nitrogen, followed by dilution to 1 mL with n-hexane.

To extract PAEs from the sludge, the air-dried sludge was treated according to the QuEChERS method. 1 g of the air-dried sludge sample and 1 mL of ultrapure water were mixed in a 10 mL glass centrifuge tube. The mixture was shaken for 1 min. Then, 4 mL of acetonitrile with 1 g of anhydrous $MgSO_4$ and 0.25 g of NaCl were added into the centrifuge tube which was shaken immediately at 4000 r/min for 8 min. 3 mL of the supernatant was transferred from the centrifuge tube to another centrifuge tube containing 30 mg PSA (ethylenediamine-N-propyl) and 20 mg C18 packing. The mixture was centrifuged for 8 min, and 2 mL of the supernatant was taken out. The supernatant was blown to nearly dry with nitrogen before being diluted to 1 mL with n-hexane. Gas chromatography-mass spectroscopy (GC–MS, 7890/5975C-GC/MSD, Agilent) was used for PAEs analysis. The standard curves and detection limits of the six PAEs were summarized in Fig. S1 and Table S5.

3 Results and discussion

3.1 Categorization of MPs

Rapid identification of MPs by Nile red staining reduces the time to quantify the MPs under the microscope. ATR FT-IR detection was used to determine the polymer composition of the MPs. As shown in Fig. 3, the main functional groups of MPs were detected before and after Nile Red staining. The spectral regions related to Polyethylene (PE) included 2916, 2849, 1463, and 719 cm^{-1} bands, which proved that the polymer contained -CH_2 groups. The spectral regions related to polypropylene (PP) included -CH_2 and -CH_3 symmetric and antisymmetric vibrational modes corresponding to 2800–3100, 1460, and 1378 cm^{-1} bands, as well as the regions of 970 and 1155 cm^{-1} for $[CH_2CH(CH_3)]_n$ (Jung et al., 2018). Nylon (PA) related spectral regions included -C=O at 1640 and 1712 cm^{-1} bands and -C-N-H absorption peaks at 1250 and 1550 cm^{-1} bands (Asefnejad et al., 2011). The relevant spectral region of polyethylene terephthalate (PET) included the absorption peaks of -CH_2- at 1000–1500 cm^{-1} band, and the benzene ring substitution peaks at 499, 722, and 872 cm^{-1} (Chércoles Asensio et al., 2009). Compared with the unstained ATR FT-IR images, the ATR FT-IR spectra of the stained MPs had almost no significant shifts, so this method can be applied to the rapid detection of the composition of MPs in the MWTP.

3.2 Occurrence level and removal rate of MPs in MWTP

Figure 4 showed the removal rates of MPs in different wastewater and sludge treatment units in the selected MWTP. After being treated in the aerated grit tank, the MPs in the wastewater decreased by 57.0%, since most of

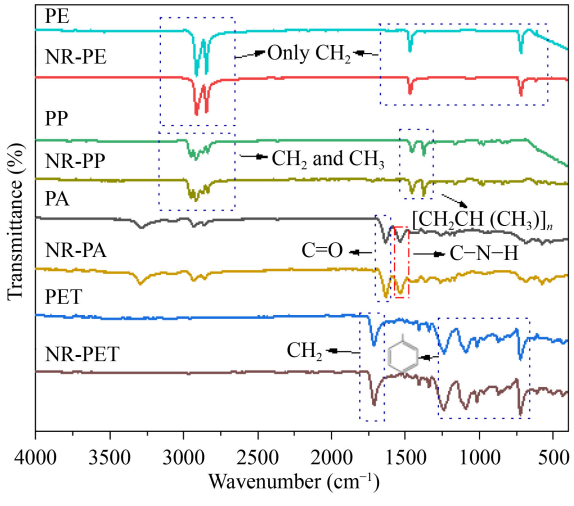

Fig. 3 ATR FT-IR spectra of PE, PP, PA, and PET before and after stained by Nile Red solution.

the MPs with a particle size greater than 3 mm were intercepted by the grit and settled in the grit chamber (Chércoles Asensio et al., 2009). The A^2O unit trapped about 34.6% of MPs from wastewater, attributed to the activated sludge adsorption. Compared with A^2O, 77.9% of MPs were removed in the secondary settling tank, which could be attributed to the addition of Fe^{2+} flocculant. The flocculation removal of MPs was caused by the adsorption of iron hydroxide aggregates (Ma et al., 2019). Fe^{2+} with a high positive charge was locally adsorbed on the surface of MPs, increasing the attractive force for the adsorption and aggregation of MPs. MPs could combine with particles in the wastewater to form flocs and settle into the sludge (Magni et al., 2019). The final effluent reduced the number of MPs from 0.96±0.08 to 0.30±0.14 particles/L.

Since the number of MPs in the influent was 15.46±0.37 particles/L (in Fig. 5(a)), the corresponding MPs removal rate was about 98.1%. These results were in agreement with the previous study (Murphy et al., 2016). The removal rates of MPs in different MWTPs were compared and shown in Table S2. In most studies, the removal rates of MPs in wastewater were in the range of 85.0%–99.9% (Lares et al., 2018). The difference in each study may be related to the different treatment processes (Long et al., 2019). Ma et al. (2019) pointed out that Al-based flocculants were more effective than Fe-based flocculants in removing MPs. Carr et al. (2016) displayed that after wastewater treatment, about 70%–98% of MPs were removed. The grid and grit chamber could remove about 50% of the MPs. The MPs number in wastewater can be reduced by about 80% after the secondary treatment, and the residual MPs can be further reduced up to 98% after tertiary treatment (Ziajahromi et al., 2017). By comparison with previous studies (Table S2), it was found that the removal rate of MPs was affected by the wastewater treatment process.

As shown in Fig. 5(b), the number of MPs in the mud-storage tank was 4.40±0.14 particles/g. About 73.8% of MPs in the wastewater were transferred into the sludge. The number of MPs after thermal hydrolysis decreased significantly to 0.29±0.04 particles/g (dry sludge). The main reason was that the fibers and large sizes fragments of MPs could be effectively converted into smaller particles, which were difficult to be collected and detected. Mason et al. (2016) and Li et al. (2018a) detected MPs in sludge and found that the occurrence levels of MPs were higher than that in this study.

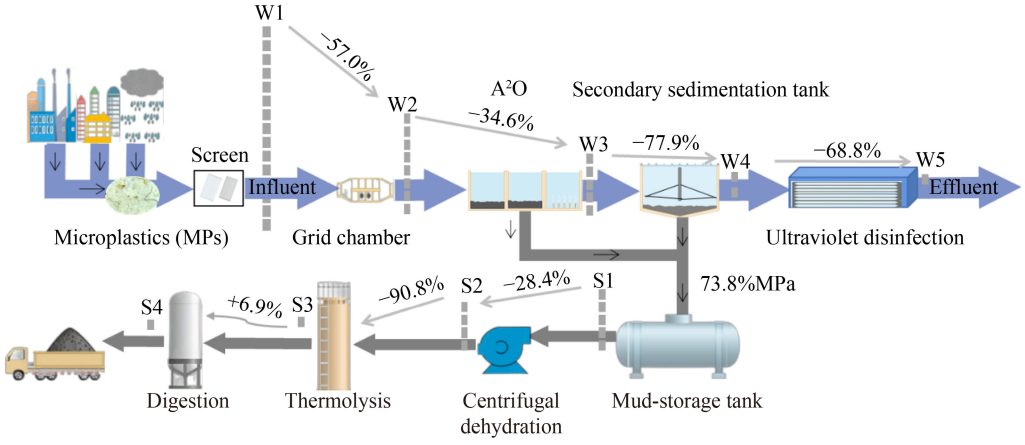

Fig. 4 Removal rates of MPs in the selected MWTP.

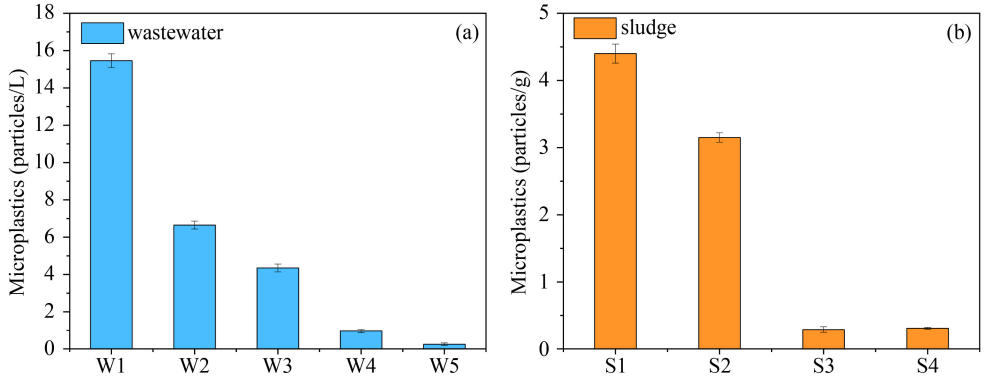

Fig. 5 Number of MPs in wastewater (a) and sludge (b) samples (Note: The error bars are standard deviation) (n = 3).

Compared with other studies, the removal rate of MPs in sludge in the selected MWTP was 93.0%, much higher than that in other MWTPs.

3.3 Characterization of MPs

The size distributions of MPs in wastewater from different sampling sites are shown in Fig. 6(a). MPs were separated into five different particle sizes. In all wastewater samples, the 0.15<MPs≤1 mm and 0.1< MPs≤0.15 mm MPs were the dominant MPs, accounting for 10.21%–31.44% and 13.89%–38.91% of the total number, respectively. The MPs with the size of 1<MPs≤ 5 mm was detected with the highest proportion of 46.73% in the W1 sample. However, this was decreased by 29.39% in the W2 sample. This is attributed to the fact that some large particles of MPs were captured by the grit tank. Different size MPs were also measured in the effluent of A^2O and the secondary sedimentation processes. Compared with the influent, the total number of MPs in the effluent was further reduced. For instance, the number of MPs in the W5 was as low as 0.2±0.07 particles/L. The removal rates of MPs with the size range of 1<MPs≤5 mm, 0.15<MPs≤1 mm, and 0.1<MPs≤ 0.15 mm was 99.9%, 98.5%, and 96.7%, respectively. However, the removal rates of MPs with the sizes of 0.075<MPs≤0.1 mm and 0.045<MPs≤0.075 mm decreased to 62.5% and 56.2%, much lower than those of larger particles. This confirmed that the grid and grit chamber had a poor interception on the small particle.

MPs with different sizes were also identified in sludge (Fig. 6(b)). The S1 sample was taken from the mud-storage tank (the sludge came from A^2O and secondary sedimentation tank). The dominant MPs in S1 had the size of 0.075<MPs≤0.1 mm with the highest concentration of 2.0±0.14 particles/g, accounting for 28.49% of the total number. The grid and grit chamber intercepted the majority of the large MPs (> 3 mm) (Jiang et al., 2020). During the thermal hydrolysis process, the sludge was heated to 165–170 °C by using steam to rupture the microbial cell wall. The mixture of water and organic matter was released. In this process, MPs could be easily broken down into smaller particle sizes, such as in the range of 1–100 nm nanoscale plastics, which could make MPs undetectable. Mason et al. (2016) reported that a large amount (57%) of MPs in the sludge are smaller than 0.355 mm.

Among all the samples, seven colors of MPs were detected (Fig. 7(a)) with the majority of them being clear or opaque MPs, accounting for 18.8%–40.5% and 16.7%–50.0%, respectively. In the W5, they were reduced to 0.07 ± 0.02 and 0.1 ± 0.04 particles/L, respectively (Table S3). Jiang et al. (2020) found that transparent, and white MPs accounted for 72.4% of the total number of MPs. With the decrease of the total number of MPs, the number of colored MPs increased slightly, but transparent and white MPs were the main types of MPs in all wastewater samples, which is consistent with some previous studies (Li et al., 2018b; Zhang et al., 2017). Compared with different sludge samples, orange-colored MPs in the S1 and S2 samples were more than those in the other samples. In sample S1, low numbers of black, red, green, and blue MPs were identified with the proportions of 6.8%, 10.0%, 2.2%, and 4.4%, respectively. Among seven wastewater treatment plants in Xiamen, China, the main type of MPs in the wastewater samples are white-colored, followed by transparent MPs (Long et al., 2019). The results were in agreement with the previous study (Li et al., 2018b), White and transparent MPs are more common than other colored MPs. Studies had shown that the colored MPs might carry more harmful chemicals (heavy metal ions and organic pollutants). Aquatic organisms could selectively ingest the colored MPs (Su et al., 2020). Therefore, attention has to be paid when using and discharging colored plastics.

The MPs could be in the form of fiber, fragment, film, and pellet. Fiber MPs were the most common type of MPs. Since the fiber MPs are extensively used and abundant, it is the main type of MPs in domestic wastewater. (Hartline et al., 2016). Therefore, it was easier to detect a large number of fiber MPs in the

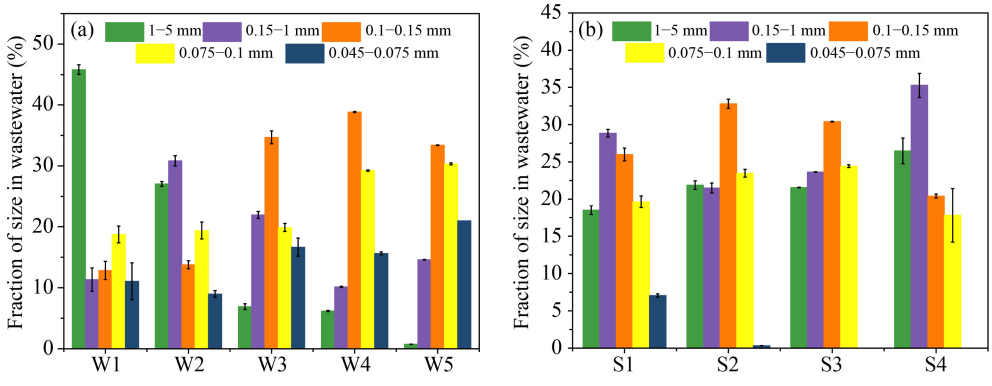

Fig. 6 Size distribution of MPs in wastewater (a) and sludge (b) samples (Note: The error bars are standard deviation) (n = 3).

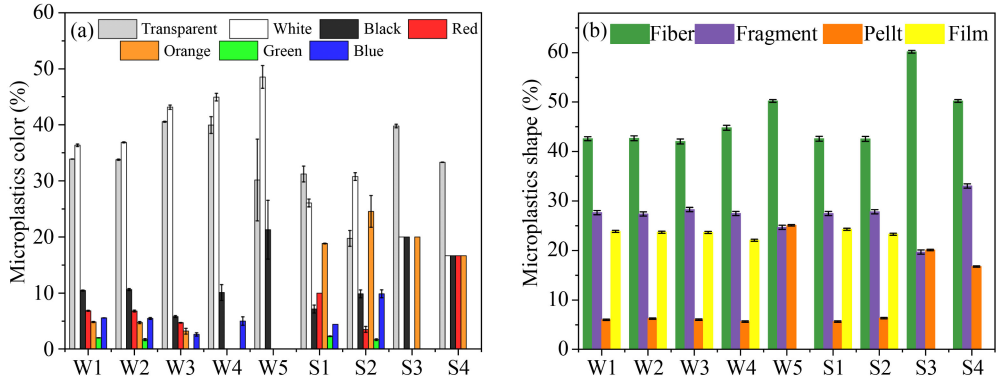

Fig. 7 Colors (A) and shapes (B) of MPs in wastewater and sludge samples (Note: The error bars are standard deviation) (n = 3).

effluent of wastewater treatment plants (Long et al., 2019). Among all sampling points, fiber MPs accounted for 42.1%–50.0% of the total MPs (Fig. 7(b)). Film and pellet MPs were also detected in the influent, although their proportions were very small with the abundances of 3.67 ± 0.09 and 0.91 ± 0.02 particles/L, respectively (Table S4). In the W2, W3, and W4 samples, film MPs were also accounted for a large proportion, ranging from 22.2%–24.1%. In the W1 samples, the proportions of fiber, fragment, and film were 42.11%, 27.96%, and 24.01%, respectively. The shape distribution of MPs in the influent was related to the source of waste. Fiber MPs came from domestic laundry wastewater. Because the debris and film MPs had a larger contact area than other shapes of MPs, they could be easily removed by grids and the A^2O process. However, single fiber and pellet MPs had small particle sizes and were not easy to be captured. The removal rates of fiber, fragment, and film MPs in the wastewater treatment process were 97.6%, 98.8%, and 100%, respectively. In the sludge, the contractions of the fragment MPs in sludge samples were higher (Fig. 7(b)). Previous research had also reached the same conclusion. Setälä et al. (2016) revealed that 50% of MPs in the effluent from Sweden wastewater treatment plants were fibers, which could be attributed to the release of synthetic fibers from laundry water.

3.4 Variations of PAEs concentrations in wastewater and sludge samples

The concentrations of typical PAEs (DMP, DEP, DIBP, DBP, BBP, DEHP) in wastewater and sludge were shown in Fig. 8. There were six kinds of PAEs detected in the influent. The removal rate of ΣPAEs in wastewater was 91.81% (from 76.66 μg/L to 6.28 μg/L, Table S6). The concentrations of various PAEs were in the order of DBP>BBP>DEP>DEHP>DIBP>DMP in wastewater. The physical and chemical properties of PAEs determined their final concentration in wastewater. Microbial degradation was considered to be the main way to remove PAEs in MWTPs (Zhang et al., 2021b). Four PAEs were detected in the W3 sample at the A^2O unit. The concentrations of four PAEs were in the order of DBP>BBP>DEHP>DMP, while DEP and DIBP were not detected. Hence, the removal rates of DEP and DIBP were almost 100%, while the removal rate of DMP was 80.53%. The reason could be attributed to the fact that biodegradation is more conducive for small molecules with a short alkyl chain and good water solubility (Gao et al., 2014). The biodegradation rate of PAEs could be negatively correlated to the alkyl chain length. The removal rates of DBP, BBP, and DEHP were 31.56%, 38.50%, and 32.8% in the A^2O process. As the molecular

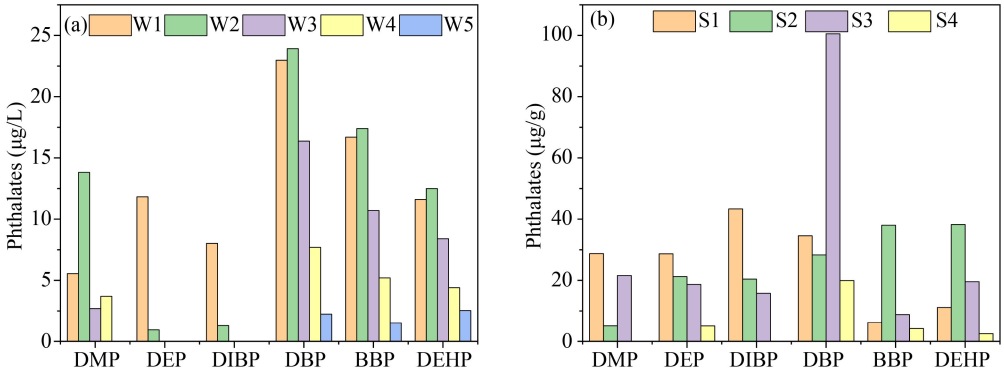

Fig. 8 Concentrations of PAEs in wastewater (a) and sludge (b) samples.

weight increased, the biodegradation rate decreased (Takdastan et al., 2021). Therefore, DBP, BBP, and DEHP were more difficult to be biodegraded. Wang et al. (2020) discovered that the total amount of MPs and PAEs has positively correlated in the MWTP effluent of each unit. As the total amount of MPs decreases, the total amount of PAEs also decreases. However, whether there is a direct relationship between the concentration of PAEs and the content of MPs, and whether there is an influence of the background value of PAEs, has not been directly proved. Therefore, the effect of MPs content in wastewater on the concentration of PAEs should be further studied.

As shown in Table S6, the average concentrations of ΣPAEs in S1, S2, S3, and S4 were 152.64, 151.32, 184.93, and 31.70 μg/g, respectively. Among the six detected PAEs, the concentration of DEHP in sludge was the highest, since it has a high molecular weight. It is difficult to be biodegraded and easy to be adsorbed and enriched in sludge. Among all the sludge samples, S2 has the highest DEHP content, followed by BBP. During the thermal hydrolysis of sludge, the concentration of ΣPAEs increased significantly. When the thermal hydrolysis temperature was increased to 80 °C, PAEs in MPs would be released into the sludge. However, in the anaerobic digestion stage, the concentration of ΣPAEs decreased from 184.93 to 31.70 μg/g with the corresponding removal rate of 82.86%. The MPs in the sludge was detected by TGA-FTIR (Fig. 9) (Yu et al., 2019). The gasification temperatures (at 300–550 °C) of different kinds of MPs were determined with increasing TGA temperature (Fig. S2). As shown in Fig. 9, the concentration of MPs in sludge was calculated by the appearance of a strong absorption band belonging to carbon dioxide (2400–2240 cm^{-1}) at 300–550 °C. The concentration of MPs was calculated from the mass loss of the sludge samples at 300–500 °C (Table S7). The detected MPs contents in sludge S1, S2, S3 and S4 were 80.00, 78.80, 53.33, and 46.00 μg/g, respectively. During the thermal hydrolysis of sludge, it was found that the total amount of MPs decreased from 78.80 to 53.33 μg/g, but the total amount of PAEs increased from 151.32 to 184.93 μg/g. This result indicated that PAEs can be released from MPs with increasing temperature, which have a synergistic effect and cause more serious harm to the environment and organisms (Takdastan et al., 2021).

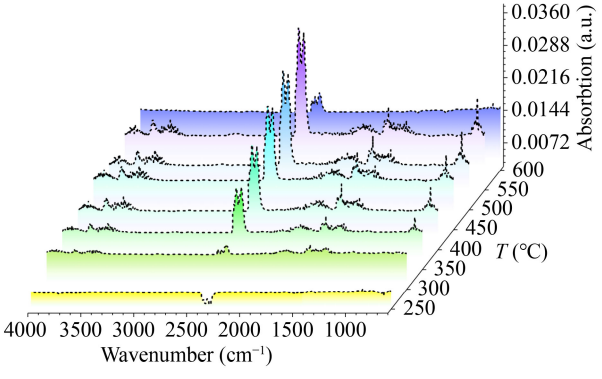

Fig. 9 Change of FTIR spectrum over temperature for the sludge sample.

4 Conclusions

In conclusion, the occurrence and migration of MPs in an MWTP and the concentrations of six PAEs in different units are measured. The MWTP significantly reduces the number of MPs (from 15.46 to 0.30 particles/L) and the concentration of ΣPAEs (from 76.66 to 6.28 μg/L) in wastewater, as well as in sludge (MPs: from 4.4 to 0.31 particles/g, PAEs: from 152.64 to 36.7μg/g). In the selected MWTP, the highest removal rates of MPs and PAEs are identified in the secondary treatment unit (A^2O and secondary sedimentation tank). About 85.6% of MPs are removed by secondary treatment, although about 73.8% of them are transferred to sludge. The size of the MPs (> 0.15 mm) and the shapes of MPs (fiber, fragment, and film) have a decisive effect on the removal rate of the MPs. After secondary treatment, the removal rate of 83.5% is achieved for total PAEs. A large number of MPs and PAEs in MWTP come from domestic wastewater. Wastewater discharge and sludge reuse will release the MPs and the PAEs back into the natural environment. To effectively reduce the risk of MPs and PAEs entering the natural environment through MWTPs, the discharge of MPs and PAEs standards should be formulated to provide technical support for the optimization of MWTP. In addition, compared with various traditional MWTP, some advanced techniques such as membrane treatment and bioactive filter processes should be developed.

In this study, there are some problems that need to be further studied. First, only one MWTP was studied, and the results may not be able to systematically account for the occurrence and migration of MPs and PAEs across the region. The occurrence and migration of MPs and PAEs in MWTP in different regions should be investigated in future studies. In addition, the different methods of sample collection and pretreatment could affect the MPs' estimated value ranges. Therefore, more research efforts are required to develop techniques for sampling and pretreatment of MPs to better compare concentrations of MPs in different MWTPs.

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