ACS ES&T Water

pubs.acs.org/estwater

Article

Mass Concentration and Removal Characteristics of Microplastics and Nanoplastics in a Drinking Water Treatment Plant

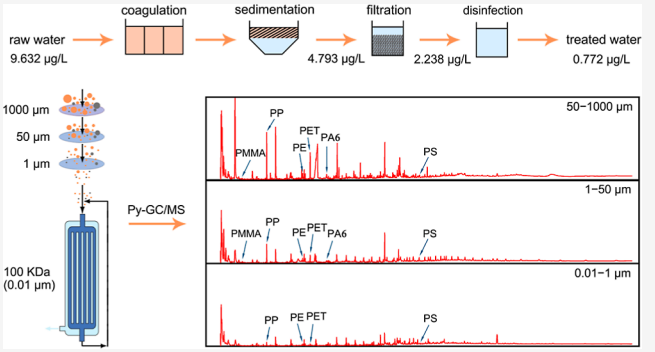
Yanghui Xu,[#] Qin Ou,[#] Xintu Wang, Jan Peter van der Hoek, and Gang Liu*

Cite This: https://doi.org/10.1021/acsestwater.4c00222

Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information

ABSTRACT: The occurrence and removal of microplastics (MPs) in drinking water treatment plants (DWTPs) have been evaluated based on particle number, while the mass concentration and removal characteristics based on the mass of MPs, and especially nanoplastics (NPs), remain unknown. This study employed pyrolysis gas chromatography−mass spectrometry (Py-GC/MS) to determine the mass concentration of MPs and NPs with different size ranges (0.01−1, 1−50, and 50−1000 μm) across the entire treatment process in a DWTP. The total polymers were measured at 9.63 ± 1.52 μg/L in raw water and 0.77 ± 0.05 μg/L in treated water, with the dominant polymers being polypropylene and polyethylene terephthalate. NPs (0.01−1 μm) accounted for only 3.2−5.3% of the total polymers, with an average concentration of 0.38 μg/L in raw water and 0.04 μg/L in treated water. Notably, NPs and sub-MPs (1−50 μm) demonstrated relatively low efficiency in the DWTP at 88.9 ± 3.2 and 88.0 ± 2.5%, respectively, compared with that of the large MPs (50−1000 μm) at 92.9 ± 0.3%. Overall, this study examined the occurrence of MPs and NPs, in a DWTP, emphasizing the significance of considering the mass concentration of MPs and NPs when assessing their pollution levels and removal characteristics.



KEYWORDS: *microplastics, nanoplastics, mass concentration, drinking water, drinking water treatment, Py-GC/MS*

INTRODUCTION

Currently, as emerging pollutants, microplastics (MPs) and nanoplastics (NPs) have received considerable attention, both from research communities and the public audience.[1−3] MPs are defined as plastic particles not exceeding a 1 mm size limit,[4−6] while the smallest size category of plastic particles (<1 μm) are known as NPs.[7−9] Global plastic production reached 400 million tons of plastic in 2020, and projections suggest a surge to 33 billion tons by 2050.[10] Improper disposal exacerbates the issue, leading to the widespread accumulation of MPs and NPs in a wide range of water bodies, including surface water, groundwater, and drinking water.[11−13] The exposure to MPs, especially NPs were reported to cause adverse effects on aquatic organisms,[14,15] and ecosystems.[16,17] Particularly, the occurrence of MPs and NPs in drinking water has also raised wide concern because of their potential impacts on human health.[2,18] Drinking water treatment plants (DWTPs) provide a necessary safeguard for drinking water supply, and information about the contamination level and removal characteristics of MPs and NPs in drinking water treatment processes is critical to assess their risks in drinking water.

The concentration and removal of MPs have been investigated by several studies using spectroscopic techniques, including Fourier transform infrared (FTIR) and focal plane array (FPA)-based FTIR,[19] laser direct infrared,[20] optical-photothermal infrared microspectroscopy,[21] and Raman microspectroscopy,[22] to measure particle number concentration. The reported levels of MPs (>1 μm) were 0−6614 ± 1132 items/L in raw water and 0−930 ± 72 items/L in treated water.[18,23,24] The conventional drinking water treatment including coagulation/sedimentation, sand filtration, and disinfection, and advanced treatment processes such as granular activated carbon (GAC) filtration and membrane filtration can remove most MPs (39.1−89.6%).[18,24,25] For instance, approximately 70−80% of MPs were found to be removed in three DWTPs of the Czech Republic and their average abundance ranged from 1473 ± 34 to 3605 ± 497 particles/L in raw water and from 338 ± 76 to 628 ± 28 particles/L in treated water.[18] The removal efficiency of MPs can be highly dependent on the size, shape, and composition of the particles as well as the specific treatment process used. Studies reported that coagulation combined with sedimenta-

Received: March 15, 2024
Revised: June 23, 2024
Accepted: June 24, 2024

tion had a removal efficiency of 40.5−54.5%, mainly for fibers' removal, and the presence of GAC filtration reduced the MP abundance by 56.8−60.9%, mainly for small-sized MPs (1−5 μm).[24] A simulated experiment conducted with polystyrene (PS) MPs suggested that combined coagulation/sedimentation and sand filtration could completely remove MPs larger than 20 μm, while approximately 16% of 10 μm MPs injected passed through the sand filter.[26] Notably, the pollution level and removal characteristics of MPs in DWTPs were mostly evaluated by the particle number instead of the mass.[18,23,24] As MPs exhibit a wide size distribution spanning 3 orders of magnitude, ranging from micrometers to millimeters, the variation in particle size greatly influences the overall pollution assessment when considering particle number as a metric.[27] During water treatment processes, such as coagulation/sedimentation and disinfection, MPs may undergo fragmentation into smaller particles.[23,26] This fragmentation leading to a higher particle count of smaller MPs might suggest a more significant pollution extent, but their overall mass might be relatively low compared to larger MPs.[27,28] In such cases, it is essential to consider the mass concentration of MPs and provide a reliable and comprehensive evaluation of the level and removal efficiency of MPs in water treatment processes.

Studies have explored the removal of model NPs in simulated drinking water treatments,[29] and pilot-scale DWTPs.[30] However, field investigation addressing the occurrence and removal of NPs in full-scale treatment plants is still lacking. Common spectral analysis methods, such as FTIR and Raman microspectroscopy, fail to detect NPs in actual samples due to the limited spatial resolution and matrix interference.[22,31,32] Thermal analytical methods, such as pyrolysis gas chromatography−mass spectrometry (Py-GC/MS), are another type of technique to identify and quantify MPs in environmental samples by determining the specific pyrolysis products of MPs.[33−36] By quantifying the mass concentration of MPs, Py-GC/MS is not limited by particle size and, thus, it can be feasible to detect NPs in actual environmental samples. However, a substantial quantity of NPs is necessary to achieve the limit of detection (LOD)/quantification (LOQ). Using a combination of ultrafiltration and hydrogen peroxide digestion, followed by Py-GC/MS analysis, the levels of NPs in surface water (0.283−0.793 μg/L) and groundwater (0.021−0.203 μg/L) were quantified,[37] but the cross-flow ultrafiltration led to the large loss of NPs from the sample.[38,39] Using Anopore filtration and Py-GC/MS, Li et al. found that NPs with sizes ranging from 58 to 255 nm had the highest abundance in tap water, with mass concentrations ranging from 1.67 to 2.08 μg/L.[40] These studies highlight the potential of using Py-GC/MS as a reliable method to quantitatively determine NPs in real waters. However, despite the growing concern about the potential risk of NPs in drinking water sources, information on their occurrence and removal in DWTPs remains limited. The small size of NPs may make them more difficult to remove through conventional water treatment processes, thereby posing a potential risk to human health. Therefore, further investigation is necessary to understand the extent of NP pollution in drinking water sources and their removal characteristics during the water treatment processes.

The main objective of this study is to assess the mass concentration and removal characteristics of MPs and NPs in a DWTP using Py-GC/MS. To achieve this objective, samples of raw water and treated water from various treatment processes, including coagulation/sedimentation, filtration, and disinfection, were collected from a DWTP in China. Microfiltration with pore sizes of 50 and 1000 μm and ultrafiltration with a molecular weight cutoff of 100 kDa (approximately 0.01 μm according to the manufacturer)[41,42] were used to collect NPs (0.01−1 μm), sub-MPs (1−50 μm) and large MPs (50−1000 μm). Hydrogen peroxide digestion was employed to eliminate the interference from the organic matrix. Py-GC/MS was used to detect the extracted MPs and NPs, including poly(methyl methacrylate) (PMMA), polypropylene (PP), PS, polyethylene (PE), polyethylene terephthalate (PET), and polyamide 6 (PA6), to evaluate their pollution levels and removal efficiency in the DWTP.

MATERIALS AND METHODS

Materials. PS NPs with a nominal size of 200 nm were purchased from Beijing Zhongkeleiming Technology Co. Ltd. (Beijing, China). PMMA (CAS 9011-14-7), PP (CAS 9003-07-0), PS (CAS 9003-53-6), PE (CAS 9002-88-4), PET (CAS 25038-59-9), and PA6 (CAS 63428-83-1) were obtained from Macklin Biochemical Co., Ltd. (Shanghai, China). The polymer granules were ground and separated using stainless steel sieves with mesh sizes of 50, 100, and 500 (approximately, 400, 100, and 30 μm pore size according to the manufacturer) to obtain fine polymer powders with sizes of 50−100 mesh and less than 500 mesh. Stainless steel membranes with pore sizes of 1000, 50, and 1 μm were purchased from Shuangte Filter Equipment Co. (Hebei, China). The polymer powders were cleaned with methanol, filtered using stainless steel membranes, and then dried in an oven at 65 °C. The purpose of cleaning with methanol is to remove any possible dissolved organic matter, and this cleaning process did not significantly affect the surface morphology or size of the powders, as described in Figure S1.[28] These polymer powders were used to generate calibration curves and determine the recovery. Sodium iodide (CAS 7681-82-5), dichloromethane (CAS 75-09-2), and methanol (CAS 67-56-1) were also obtained from Macklin Biochemical Co., Ltd. (Shanghai, China). To address the challenge of weighing small amounts of polymers when powders with low calibration concentrations were prepared, a dispersion of the polymer powder was prepared in a mixture of methylene chloride and methanol. This allowed for the accurate measurement of small amounts of polymers. A stock solution with a concentration of 10 g/L was prepared and continuously diluted to obtain plastic dispersions with concentrations ranging from 2 to 1000 mg/L. Detailed information about the preparation of standard calibration is described in Text S1.

Sampling. The DWTP selected for this study is located in Harbin, China, with a capacity of 25 million m^3/day. The facility sources raw water from the Songhua River and applies coagulation/sedimentation (coagulant: ferric aluminum polychloride), filtration (including rapid sand filtration, GAC filtration, and final sand filtration), and disinfection (disinfectant: sodium hypochlorite) to treat the water, as shown in Figure S2. Water samples were collected using a water pump (PE) from both the raw water and the effluent of each treatment unit and stored in plastic storage tanks (100 L; PE). To avoid any possible plastic contamination, the tanks were washed several times with ultrapure water (the resistivity of ultrapure water is approximately 18.25 MΩ·cm at 22 °C) before sampling. The tank port was covered with aluminum foil when water was extracted and then closed after sampling. A

https://doi.org/10.1021/acsestwater.4c00222
ACS EST Water XXXX, XXX, XXX−XXX

total of 200 L of raw water (2 tanks) and 600 L (6 tanks) of treated water after coagulation/sedimentation were sampled in the morning and afternoon of the same day, respectively, and transported to the laboratory for partial pretreatment (microfiltration and ultrafiltration, as shown in the next section). 600 L of treated water after sand filtration and 600 L of treated water after disinfection were collected and pretreated, respectively.

Sample Extraction and Pretreatment. The extraction of MPs and NPs from the water was achieved through the use of microfiltration, ultrafiltration, and hydrogen peroxide digestion, as described in our previous work.[28] Initially, the collected water (100 L of raw water and 300 L of treated water post-coagulation/sedimentation, sand filtration, and disinfection) was filtered by 1000, 50, and 1 μm stainless steel membranes to harvest MPs. MPs on membranes with sizes of 50−1000 and 1−50 μm were subjected to a 5 min sonication process in a clean 50 mL glass bottle filled with 10 mL ultrapure water. To prevent potential loss of MPs due to attachment on the membranes, the membranes were subsequently thoroughly rinsed with 10 mL of ultrapure water in the glass bottle using a wash bottle. This rinsing step was repeated at least three times to collect any remaining MPs. To collect NPs from water, the 1 μm filtered water was further concentrated by using a cross-flow ultrafiltration system with a 100 kDa membrane, which can separate particles of approximately 10 nm size. The detailed procedure for cross-flow ultrafiltration can be found in Text S2. Notably, the first step of membrane filtration may have filtered out some NPs that were aggregated or adsorbed on larger particles such as MPs in the water sample, and these NPs were excluded from the downstream analysis.

Next, the samples of MPs and concentrated filtered water containing NPs (0.01−1 μm) were dried at 90 °C in an oven. This step aimed to shorten the pretreatment time.[43,44] The method for extraction of MPs involved hydrogen peroxide digestion and density separation, and hydrogen peroxide digestion combined with centrifugal ultrafiltration was used for the extraction of NPs, as described in Text S3. The suspensions of MPs and NPs obtained were then dispersed in methanol and transferred into a 10 mL glass bottle. The suspension was evaporated at 65 °C until the final volume was adjusted to 1−2 mL. The resulting suspension was then transferred to an 80 μL pyrolysis cup using a pipet and dried at 60 °C in an oven. This step was repeated multiple times until all MPs and NPs were loaded, ensuring comprehensive detection by Py-GC/MS. For the pretreatment of each MP and NP sample, 100 L of raw water and 300 L of treated water after coagulation-sedimentation, sand filtration, and disinfection were employed. Two replicates were performed for subsequent detection.

Detection by Pyrolysis Gas Chromatography−Mass Spectrometry. Pyrolysis GC/MS measurements were conducted using a Multi-Shot Pyrolyzer EGA/PY-3030D (Frontier Laboratories, Saikon, Japan) attached to an Agilent 7890A Gas Chromatograph (Santa Clara, CA, USA) coupled with an HP-5MS column (30 m) and an Agilent 5975C mass-spectrometer detector. Pyrolysis was carried out under the parameters described in previous studies,[28,34] utilizing a pyrolysis temperature of 650 °C for 0.2 min and an interface temperature of 320 °C in single-shot mode. Helium was employed as the carrier gas, and an inlet liner was incorporated into the sample injection system. The pyrolysis product was injected with a split ratio of 50:1. Further information about the single-shot Py-GC/MS conditions is available in Table S3.

Six common plastic polymers, including PMMA, PP, PS, PE, PET, and PA6, were analyzed to determine their characteristic indicator ions based on previous studies.[19,34,45,46] Detailed information about the selection of indicators and quantification ions is available in Text S4. To test the selectivity of the indicator ions, the study also analyzed several organic substances such as wood, leaf, fish, humic acid, and black carbon (Table S4) based on previous studies.[33,45] The indicator ions selected for each polymer were methyl methacrylate (m/z 100), 2,4-dimethyl-1-heptene (m/z 126), 5-hexene1, 3, 5-triyltribenzene (m/z 312), ε-caprolactam (m/z 113), 1,12-tridecadiene (m/z 180), and vinyl benzoate (m/z 148) for PMMA,[33,34,47] PP,[48] PS,[33,47,49] PA6,[50,51] PE,[52,53] and PET,[45,52] respectively. Some natural organic materials, including wood, leaves, fish, humic acid, and black carbon, were selected to test the sensitivity of indicator ions. As shown in Table S4, these indicator ions for the six polymers were not affected by the tested natural materials.[33,45]

The calibration curves shown in Table S5 were established by analyzing varying amounts of the standard plastics, and the identification of a particular polymer in the sample was done by comparing the mass spectra of specific peaks with an analytical pyrolysis library (Figure S3).[36] The LOD is the lowest concentration that can be reliably detected, and the LOQ is the lowest concentration that can be reliably measured and quantified. LOD and LOQ (Table S6) were determined as 3 and 10 times the baseline noise, respectively (see Text S5 for details on the calculation of LOD/LOQ),[50] and then converted into method limits based on the volume of the original water samples that were tested (see Table S7 for the LOD/LOQ). The LODs of various polymers at different sampling sites ranged from 0.0003 to 0.0074 μg.

Quality Assurance and Quality Control. The precautions are important to minimize the risk of contamination that could potentially affect the results of the analysis.[54] Throughout the entire sampling and laboratory processes, cotton laboratory coats and polymer-free nitrile gloves were used to avoid contamination from synthetic fibers, and sample containers were covered with aluminum foil to prevent airborne contamination.[32,55,56] Before use, all stainless steel membranes, glass bottles, separation funnels, and the vacuum filtration device underwent three rounds of rinsing with ultrapure water to minimize possible contamination. During sampling and handling, several plastic materials, such as ultrafiltration membranes, centrifugal tubes, and pipet tips, were rinsed three times with ultrapure water, and the cross-flow ultrafiltration device was operated using ultrapure water for 10 min to minimize potential contamination. Table S7 shows possible plastic contamination during sample preparation. To ensure the absence of plastic contamination, three blank samples were prepared by treating 100 L of ultrapure water following the same steps as the sample treatment, including microfiltration, ultrafiltration, digestion, drying, and sample loading. The three blank samples were then analyzed using Py-GC/MS, and the results revealed significant peaks of benzene and styrene in the blank samples, as detailed in our previous work.[28] These peaks observed could potentially correspond to the pyrolysis products of oligomers or additives originating from the leaching of certain plastic materials.[57] However, no specific compounds of the selected six polymers were identified in the blank samples or the intensities were

https://doi.org/10.1021/acsestwater.4c00222
ACS EST Water XXXX, XXX, XXX−XXX

below detection limits, indicating that the treatment processes did not cause plastic contamination after careful cleaning. To evaluate the efficiency of the sample processing, a recovery experiment was conducted using PET, PS, and PP polymers with high, medium, and low density (Text S6). Three types of MPs with sizes ranging from 100−400 μm to 1−50 μm, as well as representative PS NPs with a size of 200 nm, were added to a river water sample and detected using the same procedure as the pretreatment.

RESULTS AND DISCUSSION

Method Validation. To evaluate the effectiveness of the analytical method, its linearity and accuracy were examined. The instrument's linearity and ranges were calculated using linear regressions, which yielded favorable results ($R^2 \geq 0.98$) (Table S5). The precision of Py-GC/MS detection was evaluated by repeating the analysis of each standard sample 5 times and calculating the relative standard deviations (RSDs) of the quantitative ion peak areas. The RSDs for the selected plastic polymers were found to be within acceptable limits, with values ranging from 6.9 to 19.0% for PMMA, PP, PS, PE, PET, and PA6 (Table S5). Vega-Herrera et al. employed ultrasonic-assisted extraction with toluene, reporting RSDs of 11 to 17% for selected MPs.[58] Ribeiro et al. utilized the accelerated solvent extraction method for MP calibration and RSDs ranged from 7.6 to 23.7%.[34] The relatively high RSDs observed for certain polymers can be attributed to uncertainties in weighing small quantities during the preparation of lower calibration levels, as well as the inherent limitations of indirect quantification using Py-GC/MS. The method was deemed valid as the RSDs were below 20%.[50] To evaluate the efficiency of the sample processing, a recovery experiment was conducted using PET, PS, and PP polymers (see Text S4 for details on the recovery of polymers). As shown in Table S9, the recovery percentages of the selected MPs were within the range of 60.7−79.1% for PP, PS, and PET, and 50.1−55.9% for PS NPs. Similar recovery percentages of MPs were also reported in previous studies (55−82%),[58,59] while Simon et al. achieved a recovery of 77.7 ± 11.6% for PS and 57.6 ± 25.1% for PE.[27] The average recovery of MPs did not exceed 90% due to sample loss resulting from physical adherence to container surfaces and potential errors in Py-GC/MS measurements. The recovery of NPs in this study was relatively low compared to other studies, ranging from 78 to 90.7%.[47,60] In addition to possible adherence to containers during the sampling and processing steps, the relatively large loss of NPs might further be attributed to the concentration step by cross-flow ultrafiltration.[61] However, given the low levels of NPs in drinking water, this step is a necessary and crucial pretreatment method for effectively treating large volumes of water and successfully detecting trace NPs within drinking water systems. It is important to note that the features of the MPs and NPs used for spiking did not encompass the full diversity of polymers present in the samples, considering variations in the concentration, size, type, and shape. To prevent introducing any unknown biases, the data were not corrected for recovery.

Polymer Abundance and Removal Efficiency in Water Treatment Processes. Figure 1a shows the chromatograms of representative MP and NP samples in raw water with sieving sizes of 50−1000, 1−50, and 0.01−1 μm, respectively. The identification of selected polymers in water samples was determined by analyzing the similarity of peaks at corresponding retention times to the standard characteristic peaks. The heatmap shows the average mass concentrations of six types of polymers with different size ranges during the whole treatment process in DWTP (Figure 1b). PP, PET, and PE were determined at all locations, while PS, PMMA, and PA6 were either not detected or below the limit of detection at certain locations. Large MPs (50−1000 μm) included all types of polymers, whereas for sub-MPs and NPs, the presence of several types of polymers, such as PS, PMMA, and PA6, was limited or undetectable at certain locations within the plant. The mass concentration of total polymers (0.01−1000 μm) ranged from 9.63 ± 1.52 μg/L in raw water to 0.77 ± 0.05 μg/L in treated water. Although several studies have quantified MPs in DWTP,[18,23,24] very few studies have analyzed the mass concentration of MPs as detected in the present study (see Table S10 summarizing studies on MP quantification in DWTPs). Using Py-GC/MS, the total amount of polymers (>1 μm) per site ranged from 0.006 to 0.093 μg/L and were detected in a drinking water supply system that collected water from two mountain lakes of Norway.[36] Similarly, In a Sweden DWTP, where the production of drinking water relies on artificial groundwater infiltration, the concentration of MPs

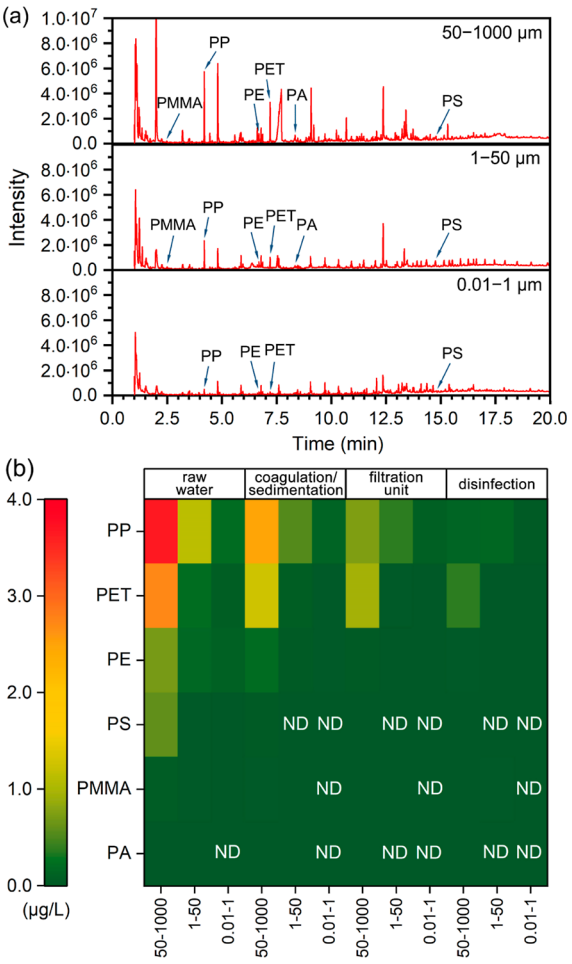


Figure 1. (a). Chromatograms from representative samples of MPs with the size ranges of 50−1000, 1−50, and 0.01−1 μm. (b). The average concentration and cumulative removal efficiency after different water treatments and heat map represent the average concentration of different types of polymers with different size ranges during the whole treatment process. The data correspond to original polymers in samples, not spiked ones.

https://doi.org/10.1021/acsestwater.4c00222
ACS EST Water XXXX, XXX, XXX−XXX

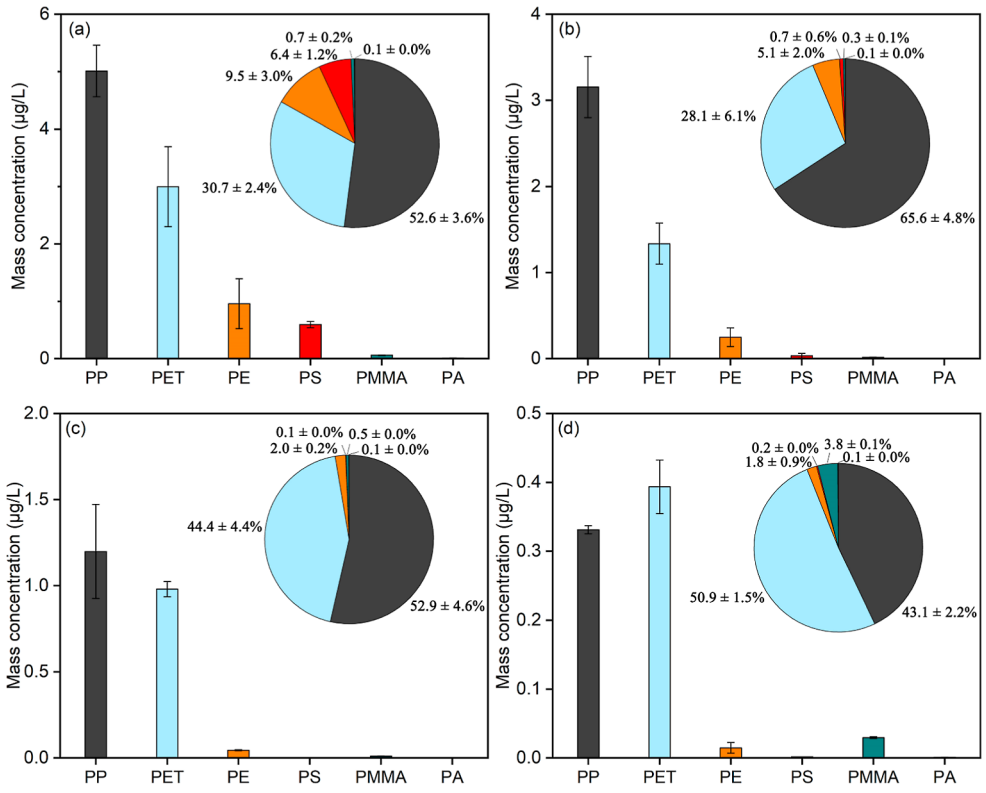


Figure 2. Polymer composition and proportion in raw water (a) and treated water after coagulation/sedimentation (b), filtration (c), and disinfection (d). Error bars indicate standard deviation (n = 2). The mean proportion was displayed in a pie chart.

(>6.6 μm) ranged from 0.0001 to 0.005 μg/L.[19] Comparatively, previous studies have reported significantly lower levels of MPs in DWTPs than the findings of this study, indicating that the source of drinking water may play an important role in the contamination levels of MPs in DWTPs. In tap water of the Barcelona Metropolitan Area, relatively high concentrations (0−9.654 μg/L) of MPs and NPs (0.7−20 μm) were identified, with median and mean values ranging from 0.514 to 1.583 μg/L.[58] Although various factors, including water sources and treatment processes, may contribute to the disparities observed in MP and NP contamination levels between tested DWTPs and tap water, it is important to note that tap water samples can be susceptible to potential contamination from various sources within the household plumbing system, such as fragments from taps, damaged faucet O-rings, or hoses connected to the tap.[58]

The overall removal efficiency of total polymers (0.01−1000 μm) was 91.9 ± 0.7% in the DWTP, which was relatively high compared to the reported MP removal efficiencies (39.1−89.6%) in previous studies (Table S10). Generally, DWTPs that use simple treatment processes like coagulation/flocculation and sand filtration have shown lower MP removal efficiencies, with 70% removal from a large reservoir in the Czech Republic,[18] and only 39.1% MP removal from Úhlava River at Milence, the Czech Republic.[23] More than 80% MP removal efficiencies were observed in some DWTPs with advanced treatment processes such as GAC filtration,[18,24] and pulse clarification.[25] The coagulation/sedimentation showed good performance (49.3 ± 6.0%) in the removal of total polymers, that was close to the removal efficiencies (40.5−62%) reported in previous studies.[18,24] There was an additional 27.4 ± 5.6% reduction of MP mass concentration after sand filtration (p > 0.05). The efficiency of sand filtration in removing MPs was previously studied to be 23.7−44.4%.[24,25] Notably, the disinfection with sodium hypochlorite further led to a 15.2 ± 0.4% reduction of polymers (p > 0.05), which might be due to the degradation of polymers. In another study, it was found that disinfection with chlorination had negligible influence on the removal of MPs.[24] Although it was not emphasized in the study, it appeared that UV and chlorination treatment had a slightly negative impact on MP removal (not statistically significant).[23] A simulated experiment indicated that UV-based oxidation treatment in drinking water resulted in the fragmentation of PS MPs (the total particle number concentration increased by 4.1 and 13.2% after UV and UV/H_2O_2 treatment) and chemical leaching.[26] Therefore, the differences in the removal efficiency of polymers after disinfection may be related to the quantification method used. Disinfection treatment may degrade polymers to some extent, leading to a decrease in mass concentration and a possible increase in particle number concentration. In previous studies, the concentration of MPs was mostly evaluated by particle number instead of particle mass, which might lead to a perception of disinfection negatively affecting MP removal efficiency.[23,26]

Polymer Composition and Proportion. Figure 2 shows the mass concentration and proportion of six types of polymers (0.01−1000 μm) after a series of treatment processes in the DWTP. PP and PET were dominant material types in the DWTP, accounting for 43.1−65.6 and 28.1−51.9%, with mass concentrations of 0.33−5.01 and 0.39−2.30 μg/L, respectively, followed by PE (0.02−0.96 μg/L, 1.8−9.5%), PS (0.002−0.59 μg/L, 0.1−6.4%), PMMA (0.01−0.06 μg/L, 0.3−3.8%), and PA6 (0.001−0.01 μg/L, 0.07−0.1%). In a separate study, PET (26−68%) and PP MPs (16−33%) were also the most common MPs in all drinking water samples,[18] whereas the

https://doi.org/10.1021/acsestwater.4c00222
ACS EST Water XXXX, XXX, XXX−XXX

results of Sarkar et al. showed that PET (43−56%) and PE (31−46%) were found to be the most prevalent MPs in DWTP.[25] Although the proportion of plastic polymers in this study was evaluated by mass concentration instead of particle number, PP, PE, and PET appeared to be very prevalent in DWTPs.[19,24,36] Notably, the proportion of plastic polymers changed after the polymers underwent a series of treatment processes. For instance, the proportion of PP initially increased from 52.6 ± 3.2 to 65.6 ± 4.8% ($p > 0.05$) after coagulation/sedimentation but decreased to 52.9 ± 4.6 and 43.1 ± 2.2% ($p > 0.05$) after final sand filtration and disinfection, respectively. On the contrary, the proportion of PET initially decreased ($p > 0.05$) after coagulation/sedimentation but increased ($p > 0.05$) after filtration and disinfection. It was related to their distinct removal efficiencies in different treatment processes. Thus, PP and PET emerged as the most prevalent materials in the DWTP, with PP being the most abundant material in raw water and PET being predominantly present in treated water.

The removal efficiencies of PET, PP, and PE in the DWTP were further evaluated and compared (Figure 3a). As calculated, PET showed a relatively low removal efficiency (86.4 ± 1.8%) compared to PP (93.3 ± 0.5%) and PE (98.5 ± 0.2%) ($p > 0.05$). Similarly, Gomiero et al. reported complete and 92% reductions for PP and PE, respectively, while PET showed an 80% reduction.[36] However, Wang et al. reported no significant differences in the removal efficiencies of PET, PP, and PE.[24] After the coagulation/sedimentation treatment, the removal efficiency of PP was relatively lower at 37.2 ± 1.5% compared to PET at 54.8 ± 2.5% ($p > 0.05$), which might be attributed to the difference in polymer density and shape. PP with a relatively low density (0.89−0.91 g/cm^3) tends to float rather than settle down, making it more difficult to remove by sedimentation.[62] In contrast, PET usually has a higher density (1.38 g/cm^3) and a fibrous shape,[63] which may make it more susceptible to entangling and aggregating with the coagulant, resulting in easier removal by sedimentation.[64] A jar test experiment indicated that greater removal of the PET fibers (97% removal) was achieved compared to the PE and PS microspheres (82 and 84%) during coagulation and flocculation.[64] However, the highest removal of PE (73.7 ± 0.6%) was observed here, and this might be due to the limited PE amounts present in the raw water samples before treatment.[36] During sand filtration, PP showed a higher removal efficiency at 62.5 ± 4.4% than PET at 24.9 ± 10.1% ($p > 0.05$), primarily for larger MPs (>50 μm), possibly attributed to differences in polymer density. PP with relatively low density might be more prone to surface layer retention while PET shows greater ability to penetrate the deeper layers.[65] Koutnik et al. reported that density becomes crucial when MPs surpass 50 μm in size, and PET with relatively high density demonstrated greater depth penetration into the sand layer than PP and PS.[65] Furthermore, the fibrous nature of PET that is commonly observed,[63] may also account for its higher penetration in sand filtration.[23] A study indicated that rapid sand filtration showed better performance in removing MP particulates (95.53%) than MP fibers (53.83%).[66] Negrete Velasco et al. also reported that average 89% of MP particulates and 81% of MP fibers (≥63 μm) were retained in filtration system in absence of coagulant.[67] Generally, while polymer density and shape are potentially influential factors in explaining the varying removal efficiency of different MPs in coagulation/sedimentation and sand filtration, the lack of real density and shape information makes it premature to conclusively determine whether density and shape truly play a significant role.

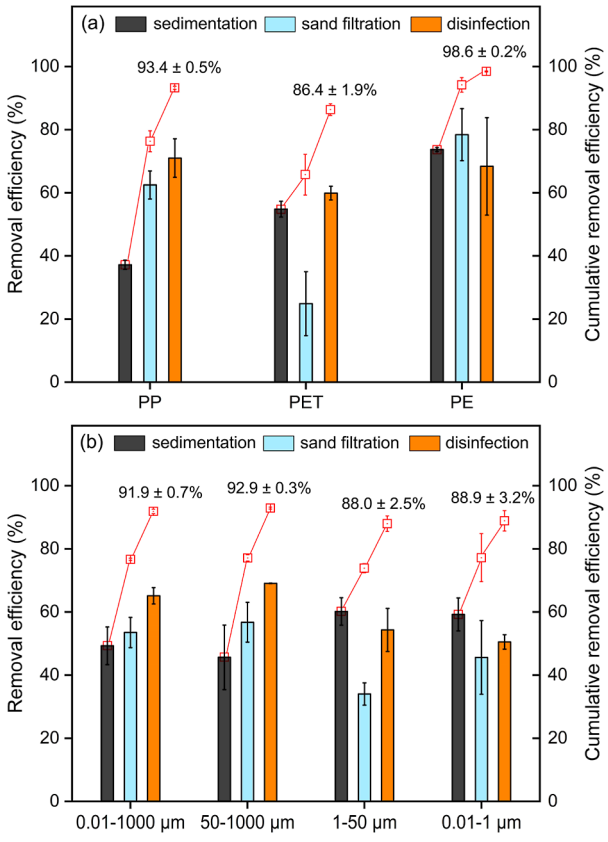


Figure 3. (a). Removal efficiency (bar) of main types of polymers (PP, PET, and PE) during coagulation/sedimentation, filtration, and disinfection and cumulative removal efficiency (point) of each polymer. (b). Removal efficiency (bar) of NPs and MPs with different size ranges during coagulation/sedimentation, filtration, and disinfection and cumulative removal efficiency (point) of NPs and MPs. Error bars indicate standard deviation ($n = 2$).

NPs in the DWTP. Figure 4 shows the mass concentration and proportion of NPs and MPs with different size ranges in DWTP. The levels of NPs (0.01−1 μm) in DWTP were found to range from 0.38 μg/L to 0.04 μg/L in raw and treated water, respectively. To date, there have been no studies examining NP contamination in DWTP (Table 1), making it difficult to compare the results of this study with others. The mass concentration of NPs in raw water was comparable to those reported in surface water, which ranged from 0.28 to 0.79 μg/L.[37] It is worth mentioning that a recent study reported much higher levels of NPs in tap water, with an abundance of NPs ranging in size from 58 to 255 nm found to be 1.67−2.08 μg/L.[40] Despite only focusing on a limited size range of NPs, the pollution levels reported were still higher than those found in the treated water of this study. Direct comparison between the two studies is difficult due to various factors such as differences in sampling methods and water sources. However, the high level of NPs reported by Li et al. in tap water[40] may be due to leaching from the drinking water distribution pipes.[36,68] Notably, only PP (54.3−87.6%), PET (7.6−19.3%), and PE (2.5−25.5%) NPs were detected in water samples of the tested DWTP in this study, with the exception of raw water where a few PS and PMMA NPs were identified (Figure 1b). In a separate study, PP, PET, and PE were also identified as the main types of NPs found in wastewater effluents.[28] Similarly,

https://doi.org/10.1021/acsestwater.4c00222
ACS EST Water XXXX, XXX, XXX−XXX

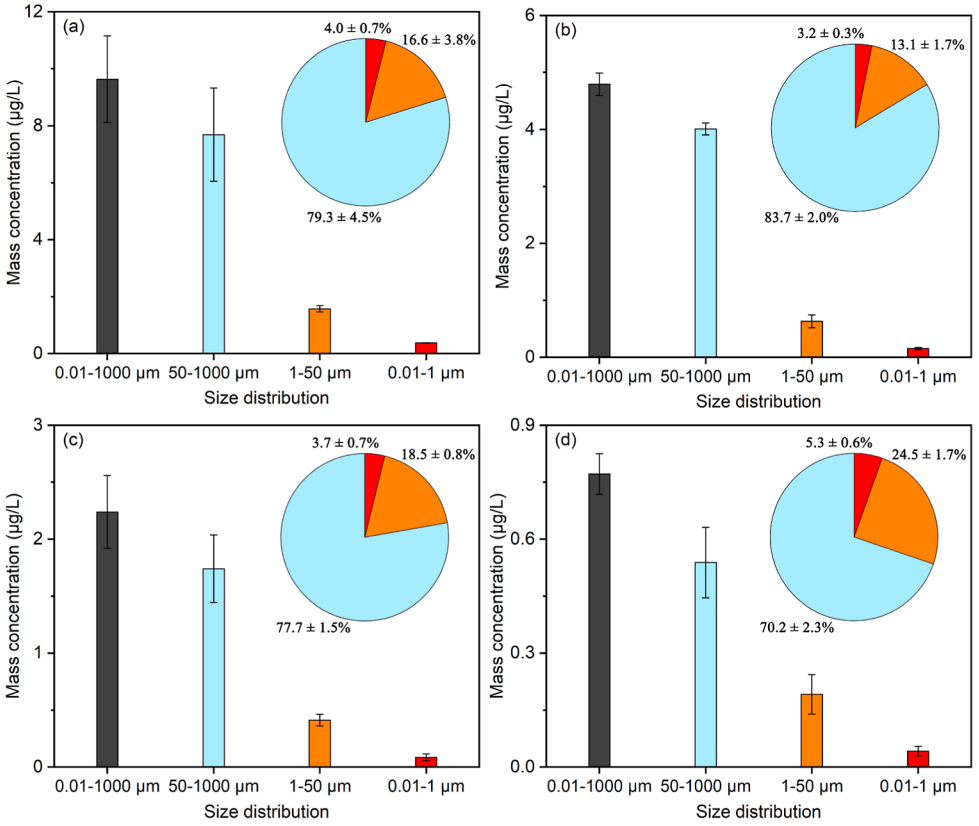


Figure 4. Mass concentration and proportion of NPs and MPs with different size range in raw water (a) and treated water after coagulation/sedimentation (b), filtration (c), and disinfection (d). Error bars indicate standard deviation (n = 2). The mean proportion was displayed in a pie chart.

Table 1. Comparison of the Concentrations and Types of NPs in Different Water Bodies

water sample	size (μm)	concentration (μg/L)	polymer type	references
wastewater treatment plant	0.01−1	0.71−26.23	PP, PE, PET, PMMA, PS, and PA	28
surface water	0.01−1	0.283−0.793	PP, PE, PET, PVC, PMMA, and PS	37
groundwater	0.01−1	0.021−0.203	PP, PE, PET, PVC, PMMA, and PS	37
tap water	0.70−20	0.001−9	IR, PB, PP, PE, PS, PA, and polydimethylsiloxanes	58
tap water	0.058−0.255	1.67−2.08	PO, PS, PVC, and PA	40
snow water	<0.22	5.4−27.4	PET	69
river water	0.3−1	0.24−0.73	PS	70
seawater	0.3−1	0−0.40	PS	70
river water	<1	1.92	PS	60
wastewater influent	<1	2.82	PS	60
DWTP	0.01−1	0.04−0.38	PP, PE, PET, PMMA, PS, and PA6	this study

PP and PE NPs were the most abundant components in both surface water and groundwater.[37] While limited studies have quantified NPs in DWTPs, Li et al. reported the presence of polyolefins (PO), PS, PVC, and PA6 NPs ranging in size from 20 to 450 nm in tap water.[40] In another study that quantified MPs and NPs (0.7−20 μm) in tap water, PE, PP, and PA6 were identified as frequently tested polymers, and the highest concentrations were observed for isoprene rubber (IR) and polybutadiene (PB) at 9.14 and 1.90 μg/L, respectively.[58] In general, NPs were found to have a similar composition and proportion to MPs,[28] suggesting that the presence and composition of NPs in polluted water may be related to global plastic demand.[2]

In DWTP sampled in this study, NPs only accounted for 3.2−5.3%, which was lower than that of sub-MPs (13.1−24.5%) and MPs (70.2−83.7%). Generally, the proportion of MPs and NPs decreased with decreasing particle size. Quantified by the particle number, Pivokonsky et al. found that the prevailing size category was 1−5 μm, comprising approximately 25−60% of the MPs, and MPs with the size of 5−10 μm were the second most abundant size group (30−50%).[18] Schymanski et al. also suggested MPs were the most abundant in the smallest detectable size class (5−10 μm), accounting for 39−56% of the total numbers.[32] In this study, the levels of MPs and NPs were quantified by mass rather than particle number, which is particularly important, as small-sized particles may exhibit high particle numbers but low mass concentrations. Therefore, it emphasizes the significance of evaluating the mass concentrations of MPs and NPs when assessing their level in drinking water.

The proportion of NPs initially decreased from 4.0 ± 0.7% in raw water to 3.2 ± 0.3% (p > 0.05) after coagulation/

https://doi.org/10.1021/acsestwater.4c00222
ACS EST Water XXXX, XXX, XXX−XXX

sedimentation and then increased to 5.3 ± 0.6% after sand filtration and disinfection ($p > 0.05$), which was related to different removal efficiencies of NPs and MPs in these treatment processes. The coagulation/sedimentation treatment was found to remove 59.2 ± 5.2% of NPs from raw water, which was close to the removal efficiency of sub-MPs (60.2 ± 4.3%) and higher than that of large MPs (45.7 ± 10.2%) ($p > 0.05$) (Figure 3b). There have been some debates about the influence of particle size on the removal of MPs through coagulation/sedimentation. Na et al. found that coagulation/sedimentation removed 77.4−95.3% of 20, 45, and 90 μm PS MPs, but relatively low removal efficiency was observed for 10 μm MPs (33.0−41.1%), which was explained by the increased attachment probability of larger MPs to flocs.[26] In contrast, other studies have shown that smaller MPs are more efficiently removed than larger MPs during coagulation/sedimentation.[64,71] The removal of large MPs is not solely determined by their affinity with the coagulant, but also by the incorporation of MPs into the floc; for a given floc size, larger particles are more easily rejected from the floc structure due to hydrodynamic forces that create a shear plane at the MP-floc interface during flocculation.[64,72] As reported, the coagulation and sedimentation process efficiently removed more than 90% of PS-COOH NPs in real surface water, likely due to the electrostatic and intermolecular interactions with the coagulant, despite the water being rich in inorganic ions and total organic carbon.[73] After sand filtration, NPs had a removal efficiency of 45.6 ± 11.7%, lower than that of large MPs (56.8 ± 6.3%) ($p > 0.05$) but higher than that of sub-MPs (34.0 ± 3.5%) ($p > 0.05$), which was somewhat different from previous findings that smaller MPs were more easily removed by sand filtration.[18,23,24,26] For instance, Wang et al. observed the sand filtration removed MPs in the size range of 1−5, 5−10 and 10−50 μm by 23.6−34.3, 33.7−67.1 and 60.0−90.6%, respectively.[24] However, the findings of Zhang et al. revealed an interesting trend where the lowest removal efficiency was observed for MPs in the middle size range (10−20 μm) at 86.9 ± 4.9% during granular filtration, followed by 1 μm MPs (94.9 ± 0.4%), 45−54 μm MPs (97.0 ± 3.0%), 180 nm NPs (98.9 ± 0.7%), and 106−125 μm MPs (99.9 ± 0.1%).[29] This observation was attributed to the combined effect of various filtration mechanisms: when the MP size was smaller than 1 μm, MPs tended to deposit or attach onto filtration grains, leading to higher removal efficiency; when the size of MPs exceeded 10−20 μm that may be beyond the space between filtration grains, making it more difficult for them to pass through.[29] Therefore, multiple mechanisms including physical straining, sedimentation, diffusion, and particle attachment, determines the removal of NPs and MPs during sand filtration, which can be influenced by factors such as particle size, shape, surface charge, and the characteristics of the filtration media.[26,74,75] In terms of the effect of disinfection, NPs showed a lowest removal efficiency (50.5 ± 2.3%), followed by sub-MPs (54.3 ± 6.8%) ($p > 0.05$) and large MPs (69.1 ± 0.1%) ($p > 0.05$). Despite being quantified by particle number, Wang et al. found that chlorination removed 1−5 and 5−10 μm MPs at efficiencies of −2.7−9.9 and −15.3−9.4%, respectively, both lower than the removal efficiency for 10−50 μm MPs (50−100%).[24] Notably, ozonation had a negative impact on the removal of MPs with the smallest size (1−5 μm), increasing the particle number concentration by 2.8−16%.[24] Na et al. also observed a decrease in the concentration of larger particles (9−10 μm) and a gradual increase in the number concentration of particles in the 1−2.5 μm size range over time during UV and UV/H_2O_2 treatment.[26] Therefore, the possible fragmentation from the disinfection of large MPs may contribute to the formation of NPs and MPs with smaller sizes, which in turn may result in lower removal efficiency of MPs with smaller sizes during disinfection. In summary, during coagulation/sedimentation, sand filtration, and disinfection processes, distinct mechanisms govern the removal efficiency of NPs in comparison to larger MPs and sub-MPs, leading to varying levels of effectiveness.

IMPLICATIONS AND LIMITATIONS

This study assessed the mass concentrations and removal properties of polymers of MPs and NPs in a DWTP, including coagulation/sedimentation, sand filtration, and disinfection. A total of six polymer types, including PP, PET, PE, PS, PMMA, and PA, were identified and quantified in the study, with PP and PET being the most prevalent. The levels of total polymers (ranging from 0.01 to 1000 μm) in the DWTP decreased from 9.63 μg/L in the raw water to 0.77 μg/L in the final treated water. The removal of polymers in coagulation/sedimentation, filtration, and disinfection treatments was related to the type and size of polymers, and different mechanisms were involved in the removal process. This study is the first to assess the pollution level and removal of NPs in DWTPs, contributing important data to the field of NP research. Additionally, the study underscores that exclusive reliance on particle number-based measurements may introduce bias, especially for smaller particles, and it emphasizes the critical importance of using mass-based measurements to achieve a comprehensive assessment of the levels and removal efficiency of MPs and NPs during water treatment processes. Furthermore, the findings of this study can help us to improve our understanding of the fate and removal mechanisms of MPs and NPs in DWTPs and support the development of effective strategies for their removal.

It is important to acknowledge that this study has certain limitations, concerning the analytical method. The investigation focused on a limited number of individual plastic polymers with a relatively high abundance of DWTPs. Detecting unusual plastic polymers or plastic composites by using Py-GC/MS may be challenging. This method's limitation may result in interference from plastic composites (e.g., PE−PP) and polymers with similar structures (e.g., different kinds of polyester). The observed relatively high RSDs for specific polymers may stem from uncertainties related to weighing small quantities during the preparation of lower calibration levels and the inherent challenges associated with the indirect quantification method using Py-GC/MS. Additionally, it is essential to note that relatively high RSDs, the small sample size, and uncertainties associated with the sampling process may introduce some bias in assessing the removal efficiency of polymers.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsestwater.4c00222.

Determination of standard curves of selected plastics (Text S1); Cross-flow Ultrafiltration (Text S2); The calculation of LOD/LOQ (Text S3); Selection of indicator ions of different plastic polymers (Text S4);

https://doi.org/10.1021/acsestwater.4c00222
ACS EST Water XXXX, XXX, XXX−XXX

Extraction of MPs and NPs (Text S5); Extraction and recovery percentage of MPs and NPs (Text S6). SEM images of raw plastics, methanol and 65 °C treated plastics and 90 °C treated plastics (Figure S1); The treatment steps of the DWTP (Figure S2); Results of similarity analysis and the characteristic peaks of a representative sample (Figure S3); The size distribution of PS NPs for recovery calculation (Figure S4); The size distribution of selected MPs (PET, PS and PP) for recovery calculation (Figure S5); Effect of 90 °C heating for 12 h on the mass of selected plastics (Table S1); Polymer density and ratio of methanol/dichloromethane (Table S2); Conditions for single shot Py-GC/MS measurements (Table S3). Potential interferences of selected natural polymers with polymer indicator ions (Table S4); Characteristic components and calibration functions of six plastics (Table S5); Method LOD and LOQ (Table S6); LOD and LOQ of different plastics at different sampling sites (Table S7); The composition of plastic materials used in sampling and sample preparation (Table S8); Recovery of selected MPs and NPs (Table S9); The concentration and composition of MPs in raw and treated water of different DWTPs (Table S10) (PDF)

AUTHOR INFORMATION

Corresponding Author

Gang Liu − *Key Laboratory of Drinking Water Science and Technology, Research Centre for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, P. R. China; University of Chinese Academy of Sciences, Beijing 100040, China;* orcid.org/0000-0002-4008-9017; Phone: 008617600879707; Email: gliu@rcees.ac.cn

Authors

Yanghui Xu − *Key Laboratory of Drinking Water Science and Technology, Research Centre for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, P. R. China; Section of Sanitary Engineering, Department of Water Management, Faculty of Civil Engineering and Geosciences, Delft University of Technology, Delft 2628 CN, The Netherlands*

Qin Ou − *Key Laboratory of Drinking Water Science and Technology, Research Centre for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, P. R. China; Section of Sanitary Engineering, Department of Water Management, Faculty of Civil Engineering and Geosciences, Delft University of Technology, Delft 2628 CN, The Netherlands*

Xintu Wang − *Key Laboratory of Drinking Water Science and Technology, Research Centre for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, P. R. China; College of Environmental Science and Engineering, Guilin University of Technology, Guangxi 541004, China*

Jan Peter van der Hoek − *Section of Sanitary Engineering, Department of Water Management, Faculty of Civil Engineering and Geosciences, Delft University of Technology, Delft 2628 CN, The Netherlands; Waternet, Department Research & Innovation, Amsterdam 1090 GJ, The Netherlands;* orcid.org/0000-0002-0674-388X

Complete contact information is available at: https://pubs.acs.org/10.1021/acsestwater.4c00222

Author Contributions

#Y.X. and Q.O. contributed equally to this manuscript.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The present work has been financially supported by the National Natural Science Foundation of China (52388101).

REFERENCES

(1) Hidalgo-Ruz, V.; Gutow, L.; Thompson, R. C.; Thiel, M. Microplastics in the marine environment: a review of the methods used for identification and quantification. *Environ. Sci. Technol.* **2012**, *46* (6), 3060−3075.

(2) Koelmans, A. A.; Mohamed Nor, N. H.; Hermsen, E.; Kooi, M.; Mintenig, S. M.; De France, J. Microplastics in freshwaters and drinking water: Critical review and assessment of data quality. *Water Res.* **2019**, *155*, 410−422.

(3) Osman, A. I.; Hosny, M.; Eltaweil, A. S.; Omar, S.; Elgarahy, A. M.; Farghali, M.; Yap, P. S.; Wu, Y. S.; Nagandran, S.; Batumalaie, K.; Gopinath, S. C. B.; John, O. D.; Sekar, M.; Saikia, T.; Karunanithi, P.; Hatta, M. H. M.; Akinyede, K. A. Microplastic sources, formation, toxicity and remediation: a review. *Environ. Chem. Lett.* **2023**, *21*, 2129−2169.

(4) Claessens, M.; De Meester, S.; Van Landuyt, L.; De Clerck, K.; Janssen, C. R. Occurrence and distribution of microplastics in marine sediments along the Belgian coast. *Mar. Pollut. Bull.* **2011**, *62* (10), 2199−2204.

(5) Song, Y. K.; Hong, S. H.; Jang, M.; Han, G. M.; Rani, M.; Lee, J.; Shim, W. J. A comparison of microscopic and spectroscopic identification methods for analysis of microplastics in environmental samples. *Mar. Pollut. Bull.* **2015**, *93* (1−2), 202−209.

(6) Van Cauwenberghe, L.; Vanreusel, A.; Mees, J.; Janssen, C. R. Microplastic pollution in deep-sea sediments. *Environ. Pollut.* **2013**, *182*, 495−499.

(7) Alimi, O. S.; Farner Budarz, J.; Hernandez, L. M.; Tufenkji, N. Microplastics and Nanoplastics in Aquatic Environments: Aggregation, Deposition, and Enhanced Contaminant Transport. *Environ. Sci. Technol.* **2018**, *52* (4), 1704−1724.

(8) Du, S.; Zhu, R.; Cai, Y.; Xu, N.; Yap, P. S.; Zhang, Y.; He, Y.; Zhang, Y. Environmental fate and impacts of microplastics in aquatic ecosystems: a review. *RSC Adv.* **2021**, *11* (26), 15762−15784.

(9) Wong, J. K. H.; Lee, K. K.; Tang, K. H. D.; Yap, P. S. Microplastics in the freshwater and terrestrial environments: Prevalence, fates, impacts and sustainable solutions. *Sci. Total Environ.* **2020**, *719*, 137512.

(10) Mithun, M. H.; Sunny, A. R.; Billah, M.; Sazzad, S. A.; Salehin, S.; Jahan, N.; Rahman, K.; Al Shiam, A.; Chowdhury, R.; Arafat, J. Assessing Impact of Microplastics on Aquatic Food System and Human Health. *Preprints* **2023**, DOI: 10.20944/preprints202311.1092.v1.

(11) Song, Y. K.; Hong, S. H.; Jang, M.; Kang, J. H.; Kwon, O. Y.; Han, G. M.; Shim, W. J. Large accumulation of micro-sized synthetic polymer particles in the sea surface microlayer. *Environ. Sci. Technol.* **2014**, *48* (16), 9014−9021.

(12) Auta, H. S.; Emenike, C. U.; Fauziah, S. H. Distribution and importance of microplastics in the marine environment: A review of the sources, fate, effects, and potential solutions. *Environ. Int.* **2017**, *102*, 165−176.

(13) Eerkes-Medrano, D.; Thompson, R. C.; Aldridge, D. C. Microplastics in freshwater systems: a review of the emerging threats, identification of knowledge gaps and prioritisation of research needs. *Water Res.* **2015**, *75*, 63−82.

(14) Jacob, H.; Besson, M.; Swarzenski, P. W.; Lecchini, D.; Metian, M. Effects of Virgin Micro- and Nanoplastics on Fish: Trends, Meta-Analysis, and Perspectives. *Environ. Sci. Technol.* **2020**, *54* (8), 4733−4745.

(15) Liu, G.; Jiang, R.; You, J.; Muir, D. C. G.; Zeng, E. Y. Microplastic Impacts on Microalgae Growth: Effects of Size and Humic Acid. *Environ. Sci. Technol.* **2020**, *54* (3), 1782−1789.
(16) Seeley, M. E.; Song, B.; Passie, R.; Hale, R. C. Microplastics affect sedimentary microbial communities and nitrogen cycling. *Nat. Commun.* **2020**, *11* (1), 2372.
(17) Yang, X.; He, Q.; Guo, F.; Sun, X.; Zhang, J.; Chen, M.; Vymazal, J.; Chen, Y. Nanoplastics Disturb Nitrogen Removal in Constructed Wetlands: Responses of Microbes and Macrophytes. *Environ. Sci. Technol.* **2020**, *54* (21), 14007−14016.
(18) Pivokonsky, M.; Cermakova, L.; Novotna, K.; Peer, P.; Cajthaml, T.; Janda, V. Occurrence of microplastics in raw and treated drinking water. *Sci. Total Environ.* **2018**, *643*, 1644−1651.
(19) Kirstein, I. V.; Hensel, F.; Gomiero, A.; Iordachescu, L.; Vianello, A.; Wittgren, H. B.; Vollertsen, J. Drinking plastics? - Quantification and qualification of microplastics in drinking water distribution systems by microFTIR and Py-GCMS. *Water Res.* **2021**, *188*, 116519.
(20) Liu, N.; Cheng, S.; Wang, X.; Li, Z.; Zheng, L.; Lyu, Y.; Ao, X.; Wu, H. Characterization of microplastics in the septic tank via laser direct infrared spectroscopy. *Water Res.* **2022**, *226*, 119293.
(21) Su, Y.; Hu, X.; Tang, H.; Lu, K.; Li, H.; Liu, S.; Xing, B.; Ji, R. Steam disinfection releases micro(nano)plastics from silicone-rubber baby teats as examined by optical photothermal infrared microspectroscopy. *Nat. Nanotechnol.* **2022**, *17* (1), 76−85.
(22) Kappler, A.; Windrich, F.; Loder, M. G.; Malanin, M.; Fischer, D.; Labrenz, M.; Eichhorn, K. J.; Voit, B. Identification of microplastics by FTIR and Raman microscopy: a novel silicon filter substrate opens the important spectral range below 1300 cm(−1) for FTIR transmission measurements. *Anal. Bioanal. Chem.* **2015**, *407* (22), 6791−6801.
(23) Pivokonsky, M.; Pivokonska, L.; Novotna, K.; Cermakova, L.; Klimtova, M. Occurrence and fate of microplastics at two different drinking water treatment plants within a river catchment. *Sci. Total Environ.* **2020**, *741*, 140236.
(24) Wang, Z.; Lin, T.; Chen, W. Occurrence and removal of microplastics in an advanced drinking water treatment plant (ADWTP). *Sci. Total Environ.* **2020**, *700*, 134520.
(25) Sarkar, D. J.; Das Sarkar, S.; Das, B. K.; Praharaj, J. K.; Mahajan, D. K.; Purokait, B.; Mohanty, T. R.; Mohanty, D.; Gogoi, P.; Kumar V, S.; Behera, B. K.; Manna, R. K.; Samanta, S. Microplastics removal efficiency of drinking water treatment plant with pulse clarifier. *J. Hazard. Mater.* **2021**, *413*, 125347.
(26) Na, S. H.; Kim, M. J.; Kim, J. T.; Jeong, S.; Lee, S.; Chung, J.; Kim, E. J. Microplastic removal in conventional drinking water treatment processes: Performance, mechanism, and potential risk. *Water Res.* **2021**, *202*, 117417.
(27) Simon, M.; van Alst, N.; Vollertsen, J. Quantification of microplastic mass and removal rates at wastewater treatment plants applying Focal Plane Array (FPA)-based Fourier Transform Infrared (FT-IR) imaging. *Water Res.* **2018**, *142*, 1−9.
(28) Xu, Y.; Ou, Q.; Wang, X.; Hou, F.; Li, P.; van der Hoek, J. P.; Liu, G. Assessing the Mass Concentration of Microplastics and Nanoplastics in Wastewater Treatment Plants by Pyrolysis Gas Chromatography-Mass Spectrometry. *Environ. Sci. Technol.* **2023**, *57* (8), 3114−3123.
(29) Zhang, Y.; Diehl, A.; Lewandowski, A.; Gopalakrishnan, K.; Baker, T. Removal efficiency of micro- and nanoplastics (180 nm−125 μm) during drinking water treatment. *Sci. Total Environ.* **2020**, *720*, 137383.
(30) Ramirez Arenas, L.; Ramseier Gentile, S.; Zimmermann, S.; Stoll, S. Fate and removal efficiency of polystyrene nanoplastics in a pilot drinking water treatment plant. *Sci. Total Environ.* **2022**, *813*, 152623.
(31) Löder, M. G. J.; Kuczera, M.; Mintenig, S.; Lorenz, C.; Gerdts, G. Focal plane array detector-based micro-Fourier-transform infrared imaging for the analysis of microplastics in environmental samples. *Environ. Chem.* **2015**, *12* (5), 563.
(32) Schymanski, D.; Goldbeck, C.; Humpf, H. U.; Furst, P. Analysis of microplastics in water by micro-Raman spectroscopy: Release of plastic particles from different packaging into mineral water. *Water Res.* **2018**, *129*, 154−162.
(33) Fischer, M.; Scholz-Bottcher, B. M. Simultaneous Trace Identification and Quantification of Common Types of Microplastics in Environmental Samples by Pyrolysis-Gas Chromatography-Mass Spectrometry. *Environ. Sci. Technol.* **2017**, *51* (9), 5052−5060.
(34) Ribeiro, F.; Okoffo, E. D.; O'Brien, J. W.; Fraissinet-Tachet, S.; O'Brien, S.; Gallen, M.; Samanipour, S.; Kaserzon, S.; Mueller, J. F.; Galloway, T.; Thomas, K. V. Quantitative Analysis of Selected Plastics in High-Commercial-Value Australian Seafood by Pyrolysis Gas Chromatography Mass Spectrometry. *Environ. Sci. Technol.* **2020**, *54* (15), 9408−9417.
(35) Zhang, X.; Zhang, H.; Yu, K.; Li, N.; Liu, Y.; Liu, X.; Zhang, H.; Yang, B.; Wu, W.; Gao, J.; Jiang, J. Rapid Monitoring Approach for Microplastics Using Portable Pyrolysis-Mass Spectrometry. *Anal. Chem.* **2020**, *92* (6), 4656−4662.
(36) Gomiero, A.; Øysæd, K. B.; Palmas, L.; Skogerbø, G. Application of GCMS-pyrolysis to estimate the levels of microplastics in a drinking water supply system. *J. Hazard. Mater.* **2021**, *416*, 125708.
(37) Xu, Y.; Ou, Q.; Jiao, M.; Liu, G.; van der Hoek, J. P. Identification and Quantification of Nanoplastics in Surface Water and Groundwater by Pyrolysis Gas Chromatography-Mass Spectrometry. *Environ. Sci. Technol.* **2022**, *56* (8), 4988−4997.
(38) Tang, Y.; Fan, K.; Herath, I.; Gustave, W.; Lin, C.; Qin, J.; Qiu, R. Contribution of free hydroxyl radical to the formation of micro(nano)plastics and release of additives during polyethylene degradation in water. *Environ. Pollut.* **2023**, *337*, 122590.
(39) Hurley, R. R.; Lusher, A. L.; Olsen, M.; Nizzetto, L. Validation of a Method for Extracting Microplastics from Complex, Organic-Rich, Environmental Matrices. *Environ. Sci. Technol.* **2018**, *52* (13), 7409−7417.
(40) Li, Y.; Wang, Z.; Guan, B. Separation and identification of nanoplastics in tap water. *Environ. Res.* **2022**, *204* (Pt B), 112134.
(41) Yu, H.; Huang, H.; Zhong, L.; Wu, S.; Yang, H.; Rong, H.; Liang, H.; Qu, F.; Ma, J. Evaluation of Front-Face Fluorescence for Assessing Cyanobacteria Fouling in Ultrafiltration. *Environ. Sci. Technol.* **2023**, *57* (45), 17649−17658.
(42) Imbrogno, A.; Lin, H. Y.; Minofar, B.; Schäfer, A. I. Nanofiber composite ultrafiltration membrane functionalized with cross-linked β-cyclodextrin for steroid hormone micropollutant removal. *J. Membr. Sci.* **2024**, *691*, 122212.
(43) Long, Z.; Pan, Z.; Wang, W.; Ren, J.; Yu, X.; Lin, L.; Lin, H.; Chen, H.; Jin, X. Microplastic abundance, characteristics, and removal in wastewater treatment plants in a coastal city of China. *Water Res.* **2019**, *155*, 255−265.
(44) Hendrickson, E.; Minor, E. C.; Schreiner, K. Microplastic Abundance and Composition in Western Lake Superior As Determined via Microscopy, Pyr-GC/MS, and FTIR. *Environ. Sci. Technol.* **2018**, *52* (4), 1787−1796.
(45) Okoffo, E. D.; Ribeiro, F.; O'Brien, J. W.; O'Brien, S.; Tscharke, B. J.; Gallen, M.; Samanipour, S.; Mueller, J. F.; Thomas, K. V. Identification and quantification of selected plastics in biosolids by pressurized liquid extraction combined with double-shot pyrolysis gas chromatography-mass spectrometry. *Sci. Total Environ.* **2020**, *715*, 136924.
(46) Zhou, X. X.; Hao, L. T.; Wang, H. Y.; Li, Y. J.; Liu, J. F. Cloud-Point Extraction Combined with Thermal Degradation for Nanoplastic Analysis Using Pyrolysis Gas Chromatography-Mass Spectrometry. *Anal. Chem.* **2019**, *91* (3), 1785−1790.
(47) Zhou, X. X.; He, S.; Gao, Y.; Chi, H. Y.; Wang, D. J.; Li, Z. C.; Yan, B. Quantitative Analysis of Polystyrene and Poly(methyl methacrylate) Nanoplastics in Tissues of Aquatic Animals. *Environ. Sci. Technol.* **2021**, *55* (5), 3032−3040.
(48) Blancho, F.; Davranche, M.; Hadri, H. E.; Grassl, B.; Gigault, J. Nanoplastics Identification in Complex Environmental Matrices:

https://doi.org/10.1021/acsestwater.4c00222
ACS EST Water XXXX, XXX, XXX−XXX

Strategies for Polystyrene and Polypropylene. *Environ. Sci. Technol.* **2021**, *55* (13), 8753−8759.
(49) Nuelle, M. T.; Dekiff, J. H.; Remy, D.; Fries, E. A new analytical approach for monitoring microplastics in marine sediments. *Environ. Pollut.* **2014**, *184*, 161−169.
(50) Hermabessiere, L.; Himber, C.; Boricaud, B.; Kazour, M.; Amara, R.; Cassone, A. L.; Laurentie, M.; Paul-Pont, I.; Soudant, P.; Dehaut, A.; Duflos, G. Optimization, performance, and application of a pyrolysis-GC/MS method for the identification of microplastics. *Anal. Bioanal. Chem.* **2018**, *410* (25), 6663−6676.
(51) Picó, Y.; Barceló, D. Pyrolysis gas chromatography-mass spectrometry in environmental analysis: Focus on organic matter and microplastics. *TrAC, Trends Anal. Chem.* **2020**, *130*, 115964.
(52) Dumichen, E.; Eisentraut, P.; Bannick, C. G.; Barthel, A. K.; Senz, R.; Braun, U. Fast identification of microplastics in complex environmental samples by a thermal degradation method. *Chemosphere* **2017**, *174*, 572−584.
(53) Dumichen, E.; Barthel, A. K.; Braun, U.; Bannick, C. G.; Brand, K.; Jekel, M.; Senz, R. Analysis of polyethylene microplastics in environmental samples, using a thermal decomposition method. *Water Res.* **2015**, *85*, 451−457.
(54) Cowger, W.; Booth, A. M.; Hamilton, B. M.; Thaysen, C.; Primpke, S.; Munno, K.; Lusher, A. L.; Dehaut, A.; Vaz, V. P.; Liboiron, M.; Devriese, L. I.; Hermabessiere, L.; Rochman, C.; Athey, S. N.; Lynch, J. M.; De Frond, H.; Gray, A.; Jones, O. A. H.; Brander, S.; Steele, C.; Moore, S.; Sanchez, A.; Nel, H. Reporting Guidelines to Increase the Reproducibility and Comparability of Research on Microplastics. *Appl. Spectrosc.* **2020**, *74* (9), 1066−1077.
(55) Johnson, A. C.; Ball, H.; Cross, R.; Horton, A. A.; Jurgens, M. D.; Read, D. S.; Vollertsen, J.; Svendsen, C. Identification and Quantification of Microplastics in Potable Water and Their Sources within Water Treatment Works in England and Wales. *Environ. Sci. Technol.* **2020**, *54* (19), 12326−12334.
(56) Shruti, V. C.; Perez-Guevara, F.; Kutralam-Muniasamy, G. Metro station free drinking water fountain- A potential "microplastics hotspot" for human consumption. *Environ. Pollut.* **2020**, *261*, 114227.
(57) Hoppe, M.; de Voogt, P.; Franz, R. Identification and quantification of oligomers as potential migrants in plastics food contact materials with a focus in polycondensates - A review. *Trends Food Sci. Technol.* **2016**, *50*, 118−130.
(58) Vega-Herrera, A.; Llorca, M.; Borrell-Diaz, X.; Redondo-Hasselerharm, P. E.; Abad, E.; Villanueva, C. M.; Farre, M. Polymers of micro(nano) plastic in household tap water of the Barcelona Metropolitan Area. *Water Res.* **2022**, *220*, 118645.
(59) Park, H. J.; Oh, M. J.; Kim, P. G.; Kim, G.; Jeong, D. H.; Ju, B. K.; Lee, W. S.; Chung, H. M.; Kang, H. J.; Kwon, J. H. National Reconnaissance Survey of Microplastics in Municipal Wastewater Treatment Plants in Korea. *Environ. Sci. Technol.* **2020**, *54* (3), 1503−1512.
(60) Zhou, X. X.; He, S.; Gao, Y.; Li, Z. C.; Chi, H. Y.; Li, C. J.; Wang, D. J.; Yan, B. Protein Corona-Mediated Extraction for Quantitative Analysis of Nanoplastics in Environmental Waters by Pyrolysis Gas Chromatography/Mass Spectrometry. *Anal. Chem.* **2021**, *93* (17), 6698−6705.
(61) Mintenig, S. M.; Bäuerlein, P. S.; Koelmans, A. A.; Dekker, S. C.; van Wezel, A. P. Closing the gap between small and smaller: towards a framework to analyse nano- and microplastics in aqueous environmental samples. *Environ. Sci.: Nano* **2018**, *5* (7), 1640−1649.
(62) Ma, B.; Xue, W.; Hu, C.; Liu, H.; Qu, J.; Li, L. Characteristics of microplastic removal via coagulation and ultrafiltration during drinking water treatment. *Chem. Eng. J.* **2019**, *359*, 159−167.
(63) Lares, M.; Ncibi, M. C.; Sillanpaa, M.; Sillanpaa, M. Occurrence, identification and removal of microplastic particles and fibers in conventional activated sludge process and advanced MBR technology. *Water Res.* **2018**, *133*, 236−246.
(64) Lapointe, M.; Farner, J. M.; Hernandez, L. M.; Tufenkji, N. Understanding and Improving Microplastic Removal during Water Treatment: Impact of Coagulation and Flocculation. *Environ. Sci. Technol.* **2020**, *54* (14), 8719−8727.
(65) Koutnik, V. S.; Leonard, J.; Brar, J.; Cao, S.; Glasman, J. B.; Cowger, W.; Ravi, S.; Mohanty, S. K. Transport of microplastics in stormwater treatment systems under freeze-thaw cycles: Critical role of plastic density. *Water Res.* **2022**, *222*, 118950.
(66) Bayo, J.; Lopez-Castellanos, J.; Olmos, S. Membrane bioreactor and rapid sand filtration for the removal of microplastics in an urban wastewater treatment plant. *Mar. Pollut. Bull.* **2020**, *156*, 111211.
(67) Negrete Velasco, A.; Ramseier Gentile, S.; Zimmermann, S.; Stoll, S. Contamination and Removal Efficiency of Microplastics and Synthetic Fibres in a Conventional Drinking Water Treatment Plant. *Front. Water* **2022**, *4*, 835451.
(68) Xu, Y.; He, Q.; Liu, C.; Huangfu, X. Are Micro- or Nanoplastics Leached from Drinking Water Distribution Systems? *Environ. Sci. Technol.* **2019**, *53* (16), 9339−9340.
(69) Materic, D.; Kasper-Giebl, A.; Kau, D.; Anten, M.; Greilinger, M.; Ludewig, E.; van Sebille, E.; Rockmann, T.; Holzinger, R. Micro- and Nanoplastics in Alpine Snow: A New Method for Chemical Identification and (Semi)Quantification in the Nanogram Range. *Environ. Sci. Technol.* **2020**, *54* (4), 2353−2359.
(70) Li, Q.; Lai, Y.; Li, P.; Liu, X.; Yao, Z.; Liu, J.; Yu, S. Evaluating the Occurrence of Polystyrene Nanoparticles in Environmental Waters by Agglomeration with Alkylated Ferroferric Oxide Followed by Micropore Membrane Filtration Collection and Py-GC/MS Analysis. *Environ. Sci. Technol.* **2022**, *56* (12), 8255−8265.
(71) Zhou, G.; Wang, Q.; Li, J.; Li, Q.; Xu, H.; Ye, Q.; Wang, Y.; Shu, S.; Zhang, J. Removal of polystyrene and polyethylene microplastics using PAC and FeCl(3) coagulation: Performance and mechanism. *Sci. Total Environ.* **2021**, *752*, 141837.
(72) Lapointe, M.; Barbeau, B. Characterization of ballasted flocs in water treatment using microscopy. *Water Res.* **2016**, *90*, 119−127.
(73) Gong, Y.; Bai, Y.; Zhao, D.; Wang, Q. Aggregation of carboxyl-modified polystyrene nanoplastics in water with aluminum chloride: Structural characterization and theoretical calculation. *Water Res.* **2022**, *208*, 117884.
(74) Lee, H.; Kim, S. C.; Chen, S.-C.; Segets, D.; Pui, D. Y. Predicting collision efficiencies of colloidal nanoparticles in single spherical and fibrous collectors using an individual particle tracking method. *Sep. Purif. Technol.* **2019**, *222*, 202−213.
(75) Bai, R.; Tien, C. Particle detachment in deep bed filtration. *J. Colloid Interface Sci.* **1997**, *186*, 307−317.

https://doi.org/10.1021/acsestwater.4c00222
ACS EST Water XXXX, XXX, XXX−XXX