



Total-organic-carbon-based quantitative estimation of microplastics in sewage

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ABSTRACT

Although many studies have been conducted to quantify microplastics in various aquatic environments, there is no easy and standardized analytical method or apparatus. Recently, a number of attempts have been made to standardize microplastic-measuring methods using micro-Fourier transform infrared spectroscopy (μ -FTIR), Raman spectroscopy, or pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS). However, they still require time-consuming and labor-intensive sample pretreatment, instrument configuration, and complex data processing. Especially, when sample matrix is as complex as sewage, the quantification of microplastics is even more difficult. Therefore, in this study, we have proposed an innovative method which quantifies total organic carbon (TOC) of plastic particles to estimate the mass of microplastics in sewage. Then, the method was applied to evaluate the fate of microplastics in sewage flowing into and out of a sewage treatment plant (STP). In the proposed method, sewage samples were collected and filtered using a sampling module equipped with stainless-steel filters to harvest particles between 45 μ m and 500 μ m. Then, the retentates of the filter were digested by Fenton's reagent to remove organic matters other than plastic particles before TOC determination. The method detection limit of the proposed method was 0.003 mg (0.15 μ g L⁻¹ for a 20 L sample), and the recovery efficiencies estimated with six different types of plastic particles were ranged from 76% to 98%. Using the proposed method, the performance of a STP in Seoul in excluding microplastics from sewage was evaluated; more than 99% of microplastics could be removed. In fact, the result was also confirmed by μ -FTIR.

1. Introduction

For the past years, dozens of studies have been reported on the occurrence and behavior of microplastics in water, soil, and air on land as well as in the ocean [1–4]. Controlling the contamination of the global water environment by microplastics will require significant efforts and budget, and be impossible to accomplish without changing industrial paradigms.

Microplastics in sewage have been a challenge to sewage treatment plants (STPs) which are designed to prevent various pollutants in sewage from entering the aquatic environment. Nonetheless, current STPs are evaluated using traditional water quality indicators (e.g., pH, biological or chemical oxygen demands (BOD or COD), total nitrogen or

phosphorus (TN or TP), and total organic carbon (TOC)) and recently emerging trace organic pollutants (e.g., pesticides, per- and poly-fluoroalkyl substances (PFAS), and pharmaceuticals and personal care products (PPCPs)) [5,6]. Although they are known present in sewage in a significant amount, microplastics are not routinely monitored in an STP simply due to the complexity associated with their measurement.

A few analytical techniques have been applied for characterizing or quantifying microplastics in water environment. They include micro-Fourier transform infrared spectroscopy (μ -FTIR), [7,8] Raman spectroscopy, [9,10] pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS), [11,12] and thermogravimetric analysis-thermal desorption-GC/MS (TGA-TD-GC/MS) [13]. In particular, spectroscopy methods, e.g., μ -FTIR and Raman techniques, are used to investigate the types,

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properties, and counts of microplastics. However, these methods are suffering from a large uncertainty associated with their results of particle numbers. Especially, when particles are many, varied, and overlapped, which is not uncommon in samples like sewage and sludge, the uncertainty can be larger. In addition, the usability of the methods is also limited by the size of microplastics that they can detect and count; they cannot count particles with a size of less than a few μm . Moreover, it takes 6–24 h to analyze each sample using these spectroscopic methods, excluding pretreatment steps to selectively separate microplastics. At any rate, these methods provide an intuitive way to understand the properties of microplastics and can be a synergistic technique in evaluating the performance of treatment processes when combined with other quantitative methods [14–16]. Thermo-analytical methods, such as TGA- and Py-GC/MS can selectively separate and detect plastic monomers. The methods can qualitatively and quantitatively determine microplastics traces at the μg level [17]. Potentially, these methods can be used for effectively tracking and controlling microplastics sources [18].

Before these analytical methods are applied for quantification, it is required a very extensive sample pretreatment steps for particle separation and concentration. A reagent- and labor-intensive, and time-consuming digestion step is applied to remove organic particles other than microplastics from a sample [19–21]. Especially, organic matters like biomass in natural water or sewage may inhibit accurate measurement of microplastics. So, H_2O_2 , Fenton's reagent, KOH, HCl, or HNO_3 has been tried to destroy the organic matters other than plastics sometimes with heat [21–23]. Among aforementioned reagents, Fenton's reagent ($\text{H}_2\text{O}_2 + \text{Fe(II)}$) especially with heat (greater than 50°C) has been selected by a few researchers since it reportedly digests organic matters in water well within a short digestion time (1 ~ 2 h) [24,25]. Nonetheless, these sample pretreatment and digestion steps along with delicate instrument manipulation often hinder a continuous or routine monitoring program for microplastics in the various water environment including sewage from being set up.

As stated above, the aforementioned methods have been applied for evaluating the fates of microplastics in STPs. The results from spectroscopic and thermo-analytical methods can be used as complementary data in evaluating the removal efficiency of a STP for microplastics and in improving treatment processes. Recently, Simon et al., [26] calculated the mass of 10–500 μm microplastics which were counted by a spectroscopic method. They emphasized the importance of evaluating microplastics by mass, not only by number. However, they roughly estimated microplastic mass. Nonetheless even a rough estimation of microplastic mass allowed them to evaluate the performance of STPs in removing microplastics from sewage.

In practice, plant operators may want to know how much plastics (e. g., in terms of particles or mass) flow into their plants and are removed. They may not be interested in determining the types or shapes of the plastic particles in their routine monitoring, since too many different types of plastic particles with different sizes and shapes are flowing into their plants. In addition, they lack a good knowledge in polymer science and analytical instruments, which are required to characterize these particles. It is like the case of BOD or COD which has been determined to quantify the biodegradable or relatively easily degradable organic contents of sewage in practice. Since there are a variety of different organic chemicals in sewage, it is impossible and impractical to analyze individual organic compounds [27].

Combustion-based TOC analyzers are widely used as a tool for evaluating the performance of an STP in removing organic pollutants from sewage [28]. By effectively combusting all the organic compounds some of which are even hardly oxidizable by a strong oxidant, namely, insoluble and macromolecular organic compounds such as humic substances and even plastic particles, a TOC analyzer can quantify carbon content of a water sample [29]. With a TOC analyzer, the carbon content of particulate substances can be analyzed even at a few μg level.

As aforementioned, organic particles other than microplastics in

sewage are removed selectively before spectroscopic or thermo-analytical methods are applied for quantifying microplastics correctly. By the same token, if organic materials other than microplastics on the stainless filter are dissolved out, the TOC measured with the filter by the TOC analyzer should represent the carbon content of the microplastics on the filter.

In this study, we propose an innovative a TOC-based method that can easily, accurately, and reliably estimate microplastics in sewage and that can be used as an alternative to the conventional spectroscopy-based or GC-based microplastic measurement methods. Firstly, sewage sample preparation and pretreatment are explained, and then the estimation procedure for quantifying TOC originating from microplastics (TOC_{MP}) in the sample is presented. Finally, this method is applied to evaluate the performance of an STP in eliminating microplastics in its influent. Then, the result was compared with the one obtained by $\mu\text{-FTIR}$.

We believe this is the first trial to estimate the microplastic content of sewage in terms of TOC. Due to its relative simplicity and easiness, the method can be used potentially as a tool for a routine monitoring of microplastics in sewage at an STP and for evaluating the performance of the STP in removing the microplastics.

2. Experimental

2.1. Chemicals and reagents

The abbreviations and properties of the polymers used in the experiment are shown in Table S1. D-(+)-glucose (CAS 50–99-7, Sigma-Aldrich, St. Louis, MO, USA) powder was used as a standard for the determination of microplastics. Humic acid sodium salt (CAS 68131–04-4) was purchased from Sigma-Aldrich (St. Louis, MO, USA) and used as a model hardly-degradable material for the digestion test. Polystyrene (PS, $(\text{C}_8\text{H}_8)_n$, C-content (wt. %): 92.3) standards by molecular weight were obtained as a standard for gel permeation chromatography (Polymer Standards Service, Mainz, Germany), and PS of 40–48 μm and polyethylene (PE, $(\text{CH}_2)_n$, C-content (wt. %): 85.7) of 125 μm were purchased from Sigma-Aldrich (St. Louis, MO, USA). Polypropylene (PP, $(\text{C}_3\text{H}_6)_n$, C-content (wt. %): 85.7), polyvinyl chloride (PVC, $(\text{C}_2\text{H}_3\text{Cl})_n$, C-content (wt. %): 37.8), polyethylene terephthalate (PET, $(\text{C}_{10}\text{H}_8\text{O}_4)_n$, C-content (wt. %): 62.5), and cellulose acetate (CA, $(\text{C}_{22}\text{H}_{33}\text{O}_{15})_n$, C-content (wt. %): 49.2), each of which has a film thickness of about 200 μm , were also purchased from Sigma-Aldrich (St. Louis, MO, USA) and cut to a size of about 200 μm . Hydrogen peroxide and iron (II) sulfate heptahydrate were purchased from Sigma-Aldrich and prepared as digestion reagents according to the laboratory method of National Oceanic and Atmospheric Administration (NOAA) [20]. Before measuring the TOC of raw and treated sewage, potassium hydrogen phthalate was dissolved in deionized water to prepare standard solutions ranging from 2 to 100 mg L^{-1} for calibrating the TOC analyzer.

2.2. Sampling and filtering

Collection of raw sewage and treated effluent was carried out using glass containers at 6:00–7:00 pm daily from February to March 2020 at J-STP located in Seoul, Korea. J-STP consists of four different treatment streams, each of which has a different main biological process along with primary and secondary settling tanks and disinfection. Four biological processes are the conventional activated sludge, bio-filters, the anaerobic/anoxic/oxic (A^2O ; flowrate: $275,000 \text{ m}^3 \text{ d}^{-1}$) process, and the Modified Ludzack Ettinger process. This study was performed with the samples collected from the treatment stream containing the A^2O process. Raw sewage was collected in the channel to a primary settling tank and the final effluent was collected from the discharging channel. The COD and SS of raw sewage were $220 \pm 56 \text{ mg L}^{-1}$, and $95 \pm 10.8 \text{ mg L}^{-1}$, respectively.

Influent and effluent samples of 0.2 L and 20 L, respectively, were filtered on site using house-made filtration devices (Fig. 1). Each sample

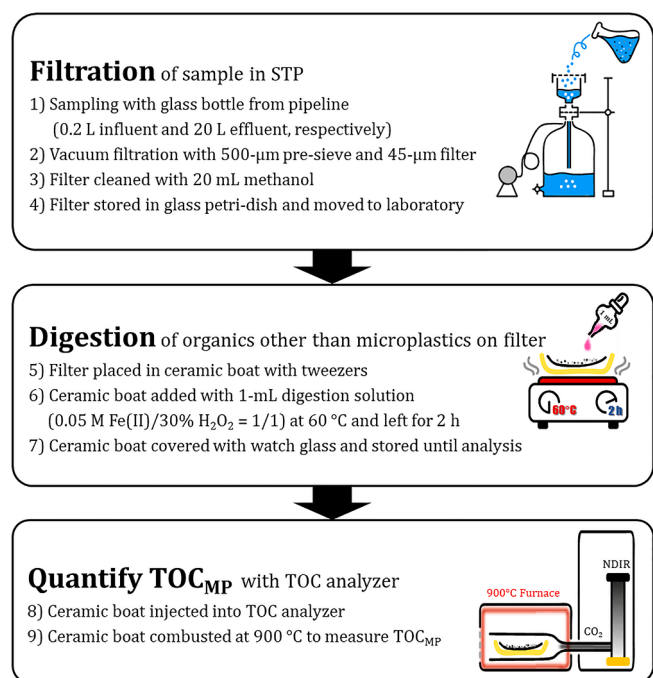


Fig. 1. Flowchart of the microplastic measurement process under the study.

was filtered through a 500- μm pre-sieve and a filter pack equipped with a 45- μm filter (diameter: 25 mm); the pre-sieve, filter and filter pack were all made of stainless steel. Before used, the filters were prepared by being washed sequentially with hexane, methanol, and water in the laboratory. Before and after filtering each sample, the filter was washed with 20 mL of methanol. After the filtration, the filter with retentate on it was placed in a glass Petri dish and moved to a laboratory.

Since most studies reported in the literature examined particles having a size of > tens μm [18] and found very few microplastics with a size of greater than 500 μm in the effluent of an STP, [30,31] the fraction of particles having a size of 45–500 μm was arbitrarily selected and studied. Previous studies showed that the mass of sewage microplastics having a size of 45–500 μm would range from sub- μg to sub- mg [32]. In fact, TOC of particles in this mass range can be easily quantified by a TOC analyzer.

2.3. Optimization of digestion condition

In this study, H_2O_2 and Fenton's reagent were considered as digestion reagents, with which sample digestion could be carried out to remove organic matters remaining on the surface of the stainless filter. Based on the literature, 0.05-M Fe(II) and 30% H_2O_2 were selected as digestion agents [20]. The Fe(II) solution was prepared by dissolving 7.5-g $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in 500-mL deionized water and subsequently adding 3-mL conc. sulfuric acid.

Before Fenton's reagent was applied, H_2O_2 was applied alone to degrade organics remaining on the filter for comparison. Then, Fenton's reagent ($\text{H}_2\text{O}_2 + \text{Fe(II)}$) was applied. For both cases, the optimal reaction temperature and time were determined by performing a series of experiments with reaction time and temperature varied; three reaction hours (i.e., 1, 2, and 4 h) and five temperatures (i.e., 20, 40, 60, 80, and 100 °C) were evaluated. Although it will be explained more in detail below, the optimal reaction time and temperature were determined to be 2 h and 60 °C, respectively. The volume of the Fenton's reagent was determined at 1 mL considering the size of the ceramic boat and filter used for TOC analysis.

2.4. Sample digestion

Once the filters were transported to the laboratory for the analysis, organic substances other than plastics were removed from them in the following way. Each filter was placed in a ceramic boat and the digestion was performed by adding 0.5 mL digestion reagent per hour for 2 h (0.05 M Fe(II) / 30% $\text{H}_2\text{O}_2 = 1/1$, v/v). This boat was then heated on a hotplate at 60 °C and digested for 2 h. The digested sample was not subjected to any additional pretreatment (e.g., filter elution, density separation, and re-filtration).

For the analysis of microplastics in sewage using $\mu\text{-FTIR}$, filter retentates were put into 20 mL of Fenton's reagent ($\text{H}_2\text{O}_2 + \text{Fe(II)}$; 10 mL of 30% H_2O_2 and 10 mL of 0.05 M Fe(II) solution) and digested at 60 °C for 2 h. Thereafter, the digested sample and 100 mL of 5 M NaCl were added to a 250 mL funnel flask and left for 24 h to allow density separation. The upper layer was filtered again with a 45 μm filter, and 10 mL of 30% H_2O_2 was passed through the filter and measured by $\mu\text{-FTIR}$.

2.5. TOC and $\mu\text{-FTIR}$ analysis

The ceramic boat containing the filter was then directly injected into a TOC analyzer (TOC-L, Shimadzu, Kyoto, Japan) with a solid-sample combustion unit (SSM-5000A, Shimadzu, Kyoto, Japan). The sample was combusted at 900 °C to measure its carbon content (Fig. 1). The TOC analysis of the filter retentate was completed within 8 min. The overall TOCs of water samples after filtered with a 500 μm sieve were also analyzed for comparison.

Microplastics in sewage samples were also analyzed by $\mu\text{-FTIR}$ (Nicolet iN10; ThermoFisher Scientific, Waltham, MA, USA) and the result was compared with that obtained by the proposed method. The background and sample spectrum were measured by 16 scans at a resolution of 4 cm^{-1} over a wavelength range of 4000–675 cm^{-1} . The spectra were compared to a commercial IR polymer database containing a spectral library and verified using the OMNIC Picta software (ThermoFisher Scientific, Waltham, MA, USA). For calculating standard errors and doing an ANOVA test both at a significant level of 0.05, we used MS-Excel (Version 2019; Microsoft, Seattle, WA, USA), and for data presentation, Origin (Version 2019b; OriginLab, Northampton, MA, USA) was used.

3. Results and discussion

3.1. Optimization of digestion method for sample-purification

A widely used method for selectively separating microplastics in environmental samples is digesting samples using 30% H_2O_2 . It is because H_2O_2 minimizes a damage to the microplastics in samples while effectively removing other organics that are potentially interfered with microplastic analysis [33–35]. However, the wet oxidation method using only H_2O_2 demands a long reaction time (less than 24 h) and a large amount of the reagent depending on the sample volume. Prata et al., [21] reported that the sample digestion using $\text{H}_2\text{O}_2 + \text{Fe(II)}$ and KOH showed the best decomposition efficiency for organic substances other than plastics: specifically, $\text{H}_2\text{O}_2 + \text{Fe(II)}$ for plant materials and KOH for animal tissues. An evaluation by Hurley et al., [19] also reported that Fenton's reagent would be the most suitable in degrading organics other than plastics while resulting in the smallest change in the amount and morphology of plastics. NOAA also recommends Fenton's reagent for oxidizing organics agglomerating with microplastics [20].

In this study, therefore, digestion reagents containing 30% H_2O_2 only and a mixture of 0.05 M Fe(II) and 30% H_2O_2 were tested to compare their efficiencies in digesting glucose and humic acid. These substances have been used as a standard material in evaluating the measurement methods for BOD, COD, or TOC, which are general water quality indicators for the organic pollutants in sewage. The digestion method was tested at different reaction temperatures ranging from room

temperature (about 20 °C) to 100 °C. The pH of the reagent was about 3 due to the concentrated sulfuric acid added when the reagent was prepared. Since the TOC analyzer was not affected by sample pH, the pH of the digestion solution was not carefully adjusted. As shown in Fig. 2, 60 °C was selected as the best temperature. As the temperature was raised from 20 °C to 60 °C, the digestion efficiency proportionally improved. Although a slight increase in digestion efficiency was noticed at temperatures higher than 60 °C, it was not significant. (Fig. 2).

The digestion reagent containing H₂O₂ only could degrade 13%–31% and 34%–63% of 10-mg glucose and 10-mg humic acid, respectively, while the one containing H₂O₂ + Fe(II) was able to remove 91%–98% and 63%–79%, respectively (Table 1). A similar result was obtained by Wu et al., [36] in their study; they could degrade 80% of humic acids in water at 30 °C using Fenton's reagent although the concentration reagent was much lower (0.5 ~ 5% for H₂O₂ and 40 mM for Fe(II)). In fact, further increase of Fenton's reagent did not result in any noticeable change in the oxidation efficiency. Similarly, Alvim et al., [22] could successfully isolate plastic particles microplastics in sludge via sample digestion using Fenton's reagent consisting of H₂O₂ (30%) and Fe(II) (20 mg mL⁻¹). Therefore, we believe the digestion protocol presented in this study be able to successfully remove organic matters in sewage other than microplastics. The required digestion times for both methods were similar, namely more than 2 h was required. In fact, when 1 mL of reagent was added and heated, it boiled and overflowed out of the vessel. Therefore, the digestion was performed by adding 0.5 mL every hour. As shown in Table 1, for longer reaction hours, more digestion reagent was added: 0.5 mL reagent for 1 h reaction vs. 2 mL for 4 h. For both reagents, i.e., H₂O₂ only and Fenton's reagent, the best digestion efficiencies could be obtained when digestion was carried out for 4 h. However, H₂O₂ + Fe(II) showed better digestion performance than H₂O₂. On the other hand, H₂O₂ + Fe(II) showed a negligible improvement in digestion at 4-h reaction comparing to at 2-h reaction. Therefore, we determined that 2-h sample digestion with 1.0-mL Fenton's reagent was the optimal condition for the sample pretreatment, since a more extended digestion showed only a slightly improved removal of the target organics. Therefore, the method digesting samples with the reagent of H₂O₂ + Fe(II) at 60 °C for 2 h was selected mainly because it

Table 1

Digestion efficiencies of H₂O₂ and Fenton's reagent for glucose and humic acid at varying digestion durations.

Oxidant Reaction time (h)	H ₂ O ₂			H ₂ O ₂ + Fe(II)		
	1 (0.5 mL in total)*	2 (1 mL in total)*	4 (2 mL in total)*	1 (0.5 mL in total)*	2 (1 mL in total)*	4 (2 mL in total)*
Glucose digestion (%), 10 mg, n = 5)	12.9 ± 0.3	14.5 ± 1.8	31.4 ± 7.0	91.4 ± 0.6	96.3 ± 0.5	97.5 ± 0.8
Humic acid digestion (%), 10 mg, n = 5)	34.0 ± 0.8	47.0 ± 1.1	63.0 ± 0.9	63.3 ± 1.6	74.8 ± 1.1	78.5 ± 1.3

*The amount of reagent added for the reaction time.

could decompose humic acids by more than 70%. Wu et al., [37] extracted humic substances (including humic acids and fulvic acids) from landfill leachate and performed Fenton oxidation experiments, and the removal efficiencies of about 60–70% (reacted for 2 h at pH 4.0) were observed, which were similar to our results.

In addition, in order to check the presence of non-plastic organic substances on a filter after digestion, additional experiments were carried out. First, raw sewage was filtered with a stainless filter and the remaining on the filter was sequentially extracted with methanol, hexane, and tetrahydrofuran before and after the digestion. Then, the methanol-extract, hexane-extract, and tetrahydrofuran-extract were separately analyzed by a GC/MS and the results are presented in Fig. S1. The GC/MS peaks of methanol- and hexane-extracts shown before the digestion disappeared after the digestion (Fig. S1(b)), indicating that non-plastic organic substances could be destroyed during the digestion using Fenton's reagent. The large peaks observed from the methanol-extract in Fig. S1(a) were mostly corresponding to fatty acids and steroids. On the other hand, the peaks of the tetrahydrofuran-extracts did not change much, indicating the presence of similar plastic-originating organics both before and after the digestion, which confirms that the proposed digestion method could selectively destroy non-plastic organics in sewage.

The potential impact of the digestion reagent consisting of H₂O₂ + Fe(II) on the particles was evaluated by measuring TOC originating from plastics before and after digestion; the digestion was performed by exposing only the plastics to the reagent at 60 °C for 2 h. A total of six plastic types were selected and exposed to the digestion. The selected plastics include PE, PP, PVC, PET, PS, and CA. Polypropylene (39.6%), PE (25.6%) and PET (21.3%), PS were the most frequently detected plastic particles in the influent samples collected at 30 STPs in Korea [31]. In other studies, PP, PE, and PET were also identified as the frequently detected plastic types [38–40]. According to Geyer et al., [41], PVC along with PE, PP, PS, and PET are among the top-marketed plastic types worldwide. Since CA is used as cigarette filter, it is often detected in sewage or urban run-off [42]. It is also found in sewage sludge [43]. Although the change in the mass content of microplastics before and after digestion was not measured, the TOC mass of microplastics (i.e., PE, PP, PVC, PET, PS, and CA) in water was measured by the proposed method before and after digestion. All the plastics, except CA (its weight of CA was reduced by 13.6%), showed a minimal change in weight (-3.7% to 0.2%) after digestion (Table 2). A similar result was also observed by others (median 12.6% ± 0.7% for CA) [21]. Hydroxyl radicals generated through the Fenton reaction were presumed to break down the glycosidic bond of the cellulose chains in CA, leading to a decrease in polymerization [44]. Hurley et al., [19] observed that PP, PE, PS, PET, polycarbonate and polymethylmethacrylate were not degraded by Fenton's reagent. However, they found that 5.5% of PA 66

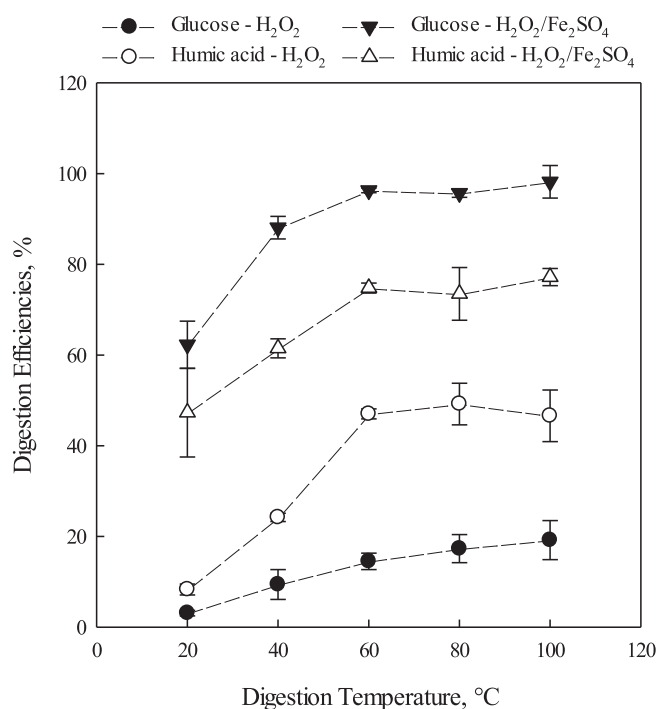


Fig. 2. Digestion efficiencies of H₂O₂ only and H₂O₂/FeSO₄ for glucose and humic acid at different digestion temperatures.

Table 2

Resistance of the polymers under optimal (at 60 °C for 2 h) digestion conditions with H₂O₂ + Fe(II).

Polymer	PS (40–48 µm)	PE (≈ 125 µm)	PP (≈ 200 µm)	PVC (≈ 200 µm)	PET (≈ 200 µm)	CA (≈ 200 µm)
Control (wt. %, n = 5)	91.4 ± 0.6	84.9 ± 0.1	84.8 ± 0.5	38.8 ± 0.4	56.9 ± 0.3	48.5 ± 0.6
Digested (wt. %, n = 5)	88.3 ± 0.6	84.6 ± 1.0	85.0 ± 0.1	38.8 ± 0.3	54.1 ± 0.8	41.9 ± 1.1
Difference (%)	−3.7	−0.4	0.2	−0.2	−5.0	−13.6

was lost after PA 66 was exposed to the digesting agent. In their Fenton's reagent-based digestion study with PE, PET, PP, and PS, Prata et al., [21] also observed the similar result with ours. In their study, the weight of CA was also slightly lost after the digestion. Nonetheless, they found that the physical properties of the polymer had not changed [21].

Based on the results of the current study and others', it could be assumed that the selected digestion method would have a little effect on the overall microplastics mass fraction of sewage.

3.2. Evaluation of proposed analytical methods

The linearity of the calibration curve, recovery efficiency, and method detection limit (MDL) of the proposed method quantifying microplastics in water were evaluated to validate the suitability of the proposed method. Liquid or solid glucose was used as standard materials for developing calibration curves for the determination of carbon in sewage microplastics (Fig. S2). The calibration curves developed by glucose were compared with those developed by arbitrarily selected standard materials, i.e., PS with different average molecular weights; however, there was no significant difference. The slopes of the calibration curves developed using PS and glucose (carbon content of 92% and 40%, respectively) were quite similar; the difference was only less than 1% (Table 3). Therefore, glucose, which can be easily weighed using a balance, was selected as the standard material. The calibration curve resulted in the coefficient of determination (R^2) of greater than 0.999 in the range of 0.2–30 mg-C. In addition, since it is difficult to directly measure the weight of carbon less than 0.2 mg (equivalent to 0.5 mg as glucose), another calibration curve was developed using glucose solution (Fig. S2 (b)).

The MDL of the analytical method based on TOC analysis was calculated according to the EPA method [45]; it was determined to be 0.003 mg (Table S2, see the Supplementary material). Samples for evaluating the recovery efficiency were prepared by adding plastic (i.e., PS, PE, PP, PVC, PET, and CA) particles of less than 5 mg individually to 10 L of ultrapure water in the laboratory. In the same manner, the influent (0.1 L) and effluent samples (10 L) from the local STP were

Table 3

Linearities of calibration for all four kinds of polystyrene (PS) with different average molecular weights and glucose as an TOC_{MP} standard material.

Carbon Content #	Glucose 0.4 g C g ⁻¹			PS21125 (MW*: 2,250) 0.93 g C g ⁻¹			PS23091 (MW*: 133,000) 0.93 g C g ⁻¹			PS80323 (MW*: 810,000) 0.93 g C g ⁻¹			PS-f850 (MW*: 8,500,000) 0.93 g C g ⁻¹		
	Sample wt., mg	mg as C**	area	Sample wt., mg	mg as C	area	Sample wt., mg	mg as C	area	Sample wt., mg	mg as C	area	Sample wt., mg	mg as C	area
1	4.9	1.9	302	0.5	0.5	49	0.4	0.4	45	0.5	0.4	65	0.4	0.4	76
2	11.5	4.6	727	1.3	1.2	191	1.3	1.2	170	0.9	0.9	114	1.3	1.2	188
3	20.9	8.4	1,349	5.5	5.0	739	4.5	4.2	622	5.0	4.6	677	4.6	4.3	642
4	38.3	15.3	2,415	10.2	9.4	1,420	10.0	9.2	1,388	9.7	8.9	1,355	9.8	9.1	1,389
5	70.5	28.2	4,550	29.9	27.6	4,360	29.1	26.9	4,303	29.2	27.0	4,384	29.2	27.0	4,380
slope	161			159			161			164			163		
intercept	−16			−33			−39			−47			−30		
R ²	0.9998			0.9997			0.9996			0.9995			0.9995		

* MW: molecular weights were given by the supplier.

** mg as C: The carbon content of each material was calculated by considering the molecular formula.

collected in pre-washed glass bottles and each plastic was added to the samples to evaluate the recovery efficiency. The spiked samples (six replicates) were filtered on a stainless filter and their retentates were digested. Then, TOC_{MPs} of the retentates on the filter were measured to find the recovery efficiency of the proposed method. The recovery efficiencies for the proposed method performed with pure water, influent sewage, and treated effluent were 89% ± 2.1%, 91% ± 2.0%, and 85% ± 1.8%, respectively, for different plastics (Table 4). The recovery efficiency of the method for the influent seemed slightly higher than that for the pure water or treated effluent, possibly due to the difference in sample sizes. Nonetheless, these recovery efficiency results were not statistically significant ($\alpha = 0.05$), which was found through an ANOVA test which had been performed with the recovery efficiencies presented in Table 4; the ANOVA test result is provided in Table S3. In summary, the aforementioned result implies that the proposed method is accurate and reliable enough to be utilized in a routine monitoring program of an STP for microplastics in sewage. Table S4 presents the detailed operating conditions of the TOC analyzers for particulate and liquid samples.

In addition, microplastics in treated effluent were quantified using TOC and Py-GC/MS and the results were compared. Detailed experimental conditions and results are presented as supplementary material (Table S5). In the case of Py-GC/MS analysis, microplastics were quantified by applying the method of Dierkes et al., [46]. For the specific experiment, polyethylene, polypropylene, and polystyamide 66 (commercially, called Nylon 66) were used as model plastics. For each plastic material, eight samples were prepared by adding 0.4 mg of it to 20 mL sewage effluent which was pre-filtered using a membrane filter (a nominal pore size of 0.4 µm). For comparison, the TOC result was transformed to the mass of each polymer. As shown in the table, only less than 5% difference could be observed between the result from the proposed method and that from Py-GC/MS, indicating the usability of the former.

3.3. Quantification of microplastics in STP

The proposed method based on TOC measurement was applied for quantifying microplastics in the wastewater flowing into the local STP and evaluating the STP performance in removing microplastics. In order to evaluate the microplastic contents of the influent and effluent of the STP, the carbon contents of the liquid samples and filtered solid samples were measured by TOC analyzers; the results are summarized in Fig. 3 and Table S6. During the sampling campaign, TOC and TOC_{MP} of the influent samples were measured to be 43.1 ± 4.9 mg L⁻¹ ($p = 0.05$) and 4.8 ± 0.8 mg L⁻¹ ($p = 0.05$), respectively. Therefore, it was calculated that TOC_{MP} accounted for 11.4% ± 2.0% ($p = 0.05$) of the influent organic substances. On the other hand, TOC and TOC_{MP} in the effluents were 4.0 ± 0.1 mg L⁻¹ ($p = 0.05$) and 0.017 ± 0.004 mg L⁻¹ ($p = 0.05$), respectively. About 0.4% of the organic substances in the effluent was estimated to be TOC_{MP}.

Table 4
Recovery efficiencies of proposed method for water samples spiked with polymers.

	Ultrapure water (10 L, $n = 6$ *)			Influent (0.1 L, $n = 6$)			Effluent (10 L, $n = 6$)		
	Polymer spiked ^{††} (mg as C)	Polymer measured (mg as C)	Recovery (%)	Polymer spiked ^{††} (mg as C)	Polymer measured (mg as C)	Recovery (%)	Polymer spiked ^{††} (mg as C)	Polymer measured (mg as C)	Recovery (%)
MP in Travel blank (mg)	0.02 ± 0.01			0.25 ± 0.11			0.39 ± 0.06		
PS (40–48 μm)	2.1 ± 0.2	1.9 ± 0.1	90	2.1 ± 0.3	2.2 ± 0.2	93	2.1 ± 0.3	2.2 ± 0.1	86
PE (≈125 μm)	2.2 ± 0.3	2.1 ± 0.1	95	1.9 ± 0.2	2.1 ± 0.2	92	2.6 ± 0.3	2.7 ± 0.2	89
PP (≈ 200 μm)	2.2 ± 0.2	2.1 ± 0.2	95	2.3 ± 0.2	2.5 ± 0.2	98	2.1 ± 0.2	2.2 ± 0.1	86
PVC (≈ 200 μm)	0.8 ± 0.2	0.7 ± 0.1	85	0.9 ± 0.2	1.1 ± 0.2	94	0.8 ± 0.2	1.0 ± 0.1	76
PET (≈ 200 μm)	1.6 ± 0.4	1.4 ± 0.1	86	1.1 ± 0.3	1.2 ± 0.2	86	1.2 ± 0.3	1.4 ± 0.1	84
CA (≈ 200 μm)	1.3 ± 0.3	1.1 ± 0.1	83	1.0 ± 0.2	1.1 ± 0.1	85	1.4 ± 0.3	1.6 ± 0.1	86

* 6 replicates were prepared.

** The amount of each polymer spiked to the matrixes was converted to C-mass by multiplying the C content of the polymer.

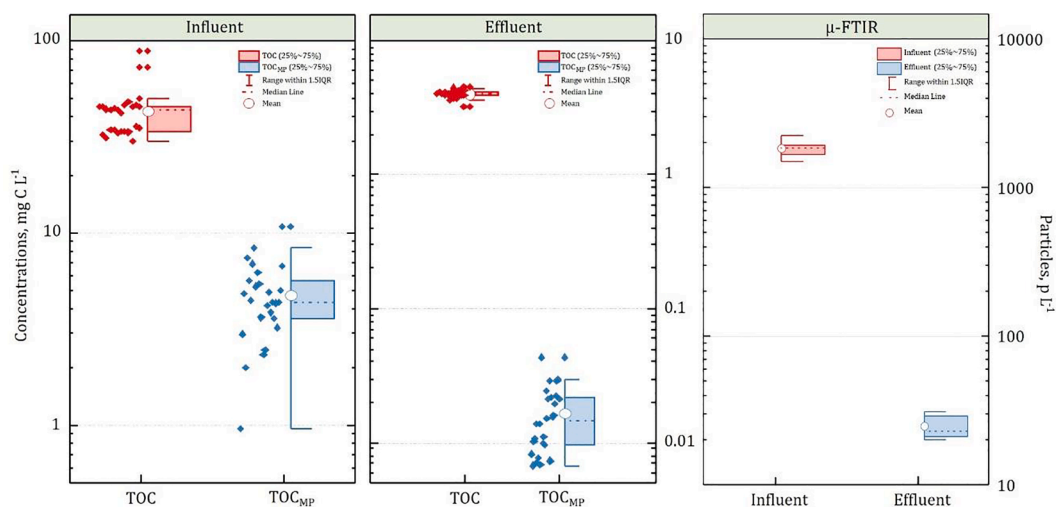


Fig. 3. Concentration profiles of a) influent and b) effluent for TOC and TOC_{MP} comparing with c) μ -FTIR in STP during the sampling campaign.

Based on our observation, it was concluded that the STP under this study could effectively remove both TOC and TOC_{MP}; removal efficiencies for TOC and TOC_{MP} were calculated to be $90.1\% \pm 0.8\%$ ($p = 0.05$) and $99.6\% \pm 0.1\%$ ($p = 0.05$), respectively. As discussed above, a fraction of organic matters in wastewater is non-biodegradable. Some of them is dissolved organic carbons; often more than 10% of influent organic content [27]. Therefore, it is logical to observe the removal efficiency of the STP for overall organic matters less than 90%, since the main organic treatment process of the STP is biological. The dissolved non-biodegradable organic matters might pass through the STP to the discharging point. On the other hand, microplastics with the size of 45–500 μm might be well removed by conventional particles-handling processes like coagulation and precipitation. With the aforementioned reason, the removal efficiency of TOC_{MP} was observed higher than that of overall TOC.

For comparison, in this study, the efficiency of the STP in removing microplastic was evaluated by the counting-based method using μ -FTIR. The processes of measuring the particles on a filter by μ -FTIR are shown in Fig S4, while 3-D signals from the μ -FTIR for the influent and effluent samples are shown in Fig. S5. Compared to particles in the influent, only smaller particles could be observed on the filter used for the effluent (Fig. S5). The number of particles in the influent and effluent samples were $1,837 \pm 262\text{p L}^{-1}$ ($n = 5$) and $25 \pm 15\text{p L}^{-1}$ ($n = 5$), respectively, showing the averaged removal efficiency of 98.7% (Table S6). In fact, our observation is consistent with the results from previous studies [24,31] in which the performances of STPs in removing microplastics were also evaluated using μ -FTIR. They also observed that about 99% of microplastics in the influent could be removed by STPs.

Lastly, we estimated the total mass of microplastics that were counted by an μ -FTIR using the approach taken by Primpke et al., [7], in which irregular shape of a plastic particle was transformed into a simpler one for mass calculation. The method is briefly illustrated in Fig. S6. The mass of the microplastics counted by the μ -FTIR was calculated 5.1 and 0.022 mg L^{-1} for the influent and effluent, respectively. The total masses of the μ -FTIR-counted microplastics were very comparable with those measured by TOC_{MP}. Since shapes of particles counted by an μ -FTIR were simplified (Fig. S6), the mass of the counted microplastics could be over- or under-estimated, possibly resulting in a larger uncertainty. Therefore, we believe that the performance of STP in removing microplastics in sewage can be easily estimated by a TOC analyzer. Other pyrolysis-GC-based analytical methods (e.g., Py-GC/MS) can quantify the mass of plastic particles in sewage, too. Even, they can identify types of plastic particles by analyzing monomers of plastics. However, the method may overestimate the amount of microplastics by quantifying monomers from hardly biodegradable polymeric compounds other than plastics in sewage. In addition, these methods require more expensive and sophisticated instruments and skilled operators. In the proposed method, however, the mass of microplastics in sewage can be easily estimated by a TOC analyzer which is routinely utilized in each STP.

To the best of our knowledge, this study is the first report that a TOC analyzer has been utilized to investigate the performance of an STP in removing microplastics from sewage. In a recent study, Mallow et al., [47] estimated the portion of microplastics in organic materials presented in the solid samples collected at a discharging canal of an industrial wastewater treatment plant using an elemental analyzer. Unlike

our study, they did not digest their solid samples but used a few mathematical equations to fractionate plastic-originating organic carbon. In short, they found that plastics accounted for 10%~29% of the organic materials in the samples.

4. Conclusion

In this study, a TOC-based method was proposed to estimate TOC originating from microplastics in sewage. The proposed method requires a relatively simpler digestion procedure comparing to other conventional methods using μ -FTIR or GC/MS. It uses only a small amount of digestion reagent and requires less time, while producing a good digestion efficiency. In addition, since the MDL of the proposed method can measure a sufficiently low level (0.003 mg) of microplastic-originating TOC, the method can be flexibly applied for the measurement of microplastics by adjusting the particle size (via applying filters with different pore sizes) and sample volume.

Using the proposed method, we evaluated the performance of a local STP in removing microplastics from sewage and found that more than 99% of microplastics could be removed from sewage by the STP. The result was also confirmed by μ -FTIR, which consequently demonstrated the usability of the proposed method for evaluating STP performance in terms of microplastic removal. At any rate, microplastics in sewage must have been removed along with sewage sludge since they are not degraded by conventional treatment technologies. It should be noted that the proposed method cannot characterize or quantify individual microplastics in sewage since it is based on the conventional TOC measurement technique. Characterization of microplastics flowing into as STP should be carried using a more sophisticated analytical method, e.g., μ -FTIR, and Py-GC/MS. Considering the characteristics of sewage generating from a city do not change much over the short period of time, detailed analysis of microplastics in sewage can be carried out intermittently. The information from the intermittently performed detailed microplastics analysis and the one from our proposed method will give plant operators a good idea of what kinds of microplastics are flowing into their plant and how they are removed.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Additional information can be downloaded as noted in the text. Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cej.2021.130182>.

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