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Potential organic matter management for industrial wastewater guidelines using advanced dissolved organic matter characterization tools

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ABSTRACT

Since 2021, national standards of South Korea for industrial wastewater discharge to surface water have changed from chemical oxygen demand to total organic carbon for the organic matter. Conventional organic matter parameters (e.g., biochemical oxygen demand, chemical oxygen demand and total organic carbon) are limited means of understanding the behavior of dissolved organic matter in industrial wastewater treatment processes. Thus, the current study used advanced dissolved organic matter characterization tools (e.g., fluorescence excitation emission matrix and size exclusion chromatography-organic carbon detection) to scrutinize industrial wastewater characteristics from three full-scale industrial wastewater treatment plants (IWTPs). The tools were conducive to tracking industrial wastewater sources of total organic carbon, influencing the overall performance of IWTPs, and proposing alternative processes to lower total organic carbon concentration in the effluent. The results of this study suggest that the diagnosis of IWTPs based on dissolved organic matter characteristics could be a useful tool for providing more insight into total organic carbon management.

1. Introduction

Industrial activities have diversified and expanded, resulting in a large increase of hazardous waste, including non-biodegradable and toxic compounds in industrial wastewater that are difficult to attenuate. Organic matter is the most relevant cause of water pollution. Particularly, dissolved organic matter (DOM) in wastewater systems either consumes dissolved oxygen (DO) or deteriorates water quality in aquatic environments. Therefore, wastewater needs to be adequately treated before discharge into water bodies. Over the years, biochemical oxygen demand (BOD) and chemical oxygen demand (COD) have been widely used and regarded as important environmental indicators of organic matter present in wastewater matrices.

Fig. 1 shows a chronological representation of the parameters of organic matter that have been used in South Korea for the management of organic matter in rivers and municipal and industrial wastewaters [23,36]. COD can be a relatively precise indicator that uses strong chemical oxidants, and it can be used to determine the oxidation state of organic substances [18]. However, some disadvantages of using COD include the presence of disruptive inorganic compounds that evoke measurement errors and thereby low reproducibility [2] and the production of hazardous wastes such as Hg(II) and Cr(VI) [17]. COD_{Mn} was included in wastewater discharge standards in South Korea. Because of its low empirical oxidation rate of approximately 30–60%, COD_{Mn} cannot determine the compounds that are difficult to degrade as accurately as COD_{Cr} [21]. Accordingly, there has been an ongoing discussion on the management of refractory organic matter in wastewater treatment; as a result, total organic carbon (TOC) has received much attention as a substitute for COD [17]. COD_{Mn}, which has been used in wastewater effluent standards in South Korea since 1981, was replaced with TOC in 2020 in the case of public industrial wastewater treatment plants (IWTPs) simultaneously receiving domestic wastewater and various types of industrial wastewater, and will be completely phased out by 2022 in the case of private IWTPs [36]. The fundamental motivation behind the introduction of the new policy arose from the need to minimize the amount of recalcitrant organic compounds in water bodies. Therefore, the Ministry of Environment in South Korea has been aiming to decrease the TOC concentration of industrial wastewater

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effluent entering into receiving water bodies.

TOC is an index that can quantify a wide range of organic matter by measuring the amount of carbon dioxide generated by directly oxidizing organic substances. Specifically, TOC is a method that directly measures the amount of carbon. Thus, it can not only accurately quantify the amount of organic substances in the water body, but can also possibly reduce any measurement errors that may occur in COD estimation. Therefore, organic matter that was not detected through COD may be reflected in TOC. Thus, TOC has been regarded as an alternative analytical method for the detection of non-degradable organic substances in water samples [34]. The specific advantages of TOC over COD analytical methods may include: (i) lower time-consumption required for analysis [6]; (ii) avoidance of the use of toxic chemical reagents and thereby lower production of residual by-products that need to be disposed of after analytical determinations [2]; and (iii) automatic measurement with a small number of samples [34]. In addition, TOC aids the detection of refractory organic matter containing more complex materials that is normally observed in industrial wastewater [11].

It is necessary to prepare TOC management plans for IWTPs that are facing difficulties in meeting the new industrial wastewater effluent guidelines, which are national regulatory standards for industrial wastewater discharge into surface water. Specifically, the suggested COD_{Mn}/TOC ratios for public IWTPs and private IWTPs are 1.3 and 1.8, respectively [36]. However, there are some public and private IWTPs where the ratios are lower than the specified ratios. This can occur because the determination of COD_{Mn} in the effluent can lead to a relatively lower amount of organic carbon; specifically, the organic matter is characterized by refractory compounds resulting in underestimation of COD_{Mn}. The organic matter loading in public IWTPs is directly affected by the effluent TOC discharged from industrial facilities located within the wastewater treatment area. Therefore, the effluent TOC of public IWTPs should be managed through appropriate reduction of the influent sources to meet the TOC standards. Thus, it is essential to investigate the source of non-biodegradable organic matter, which affects the overall performance of TOC removal in public IWTPs. The conventional organic matter parameters of BOD and COD, as well as TOC itself may provide limited information on aspects such as the biodegradability of industrial wastewater effluent through BOD/TOC or BOD/COD ratios. Further specific information on the components or characteristics of organic matter (i.e., composition and structure, hydrophilicity/hydrophobicity, aromaticity, and molecular weight distribution) in industrial wastewater may be useful for the enhancement of the performance of treatment plants.

DOM characterization was utilized to overcome the current limitations imposed by conventional global parameters. Specific ultraviolet absorbance (SUVA), which is determined by dividing the UV absorbance at 254 nm (UV_{254}) by the dissolved organic carbon (DOC) of a sample, can explain the aromaticity of wastewater samples [2]. The fluorescence excitation emission matrix (FEEM) explains the DOM characteristics by showing several well-known fluorescence peaks (T1, T2, A, B, and C) [27]. Liquid chromatography-organic carbon detection (LC-OCD) can provide apparent molecular weight distribution of DOC in wastewater samples [8]. Compared to conventional organic matter parameters, the bulk organic matter characterization parameters are characterized by relatively fast analysis with little preparation and fewer samples. In particular, the benefits of FEEM are that it is: (i) highly sensitive, non-destructive, and non-invasive; (ii) reagentless; and (iii) inexpensive. Thus, it can provide prompt feedback for the characterization of wastewater samples [9]. Based on this, advanced organic matter characterization tools can be used to track influent sources influencing the public IWTPs and to identify alternative processes to reduce TOC concentration in IWTP effluents. To date, an increasing number of researchers have focused on characterizing organic matter in industrial wastewater using advanced organic matter characterization tools. However, the application of analytical technology in industrial environments remains challenging in the context of the overall TOC management of IWTPs.

In this study, three IWTPs were investigated using advanced organic matter characterization tools and conventional organic matter parameters. The objectives of the study were twofold: (i) to investigate the various influent sources (i.e., either refractory or readily biodegradable) affecting a public IWTP and (ii) to suggest potential processes for IWTPs through lab-scale experiments based on organic matter compositions.

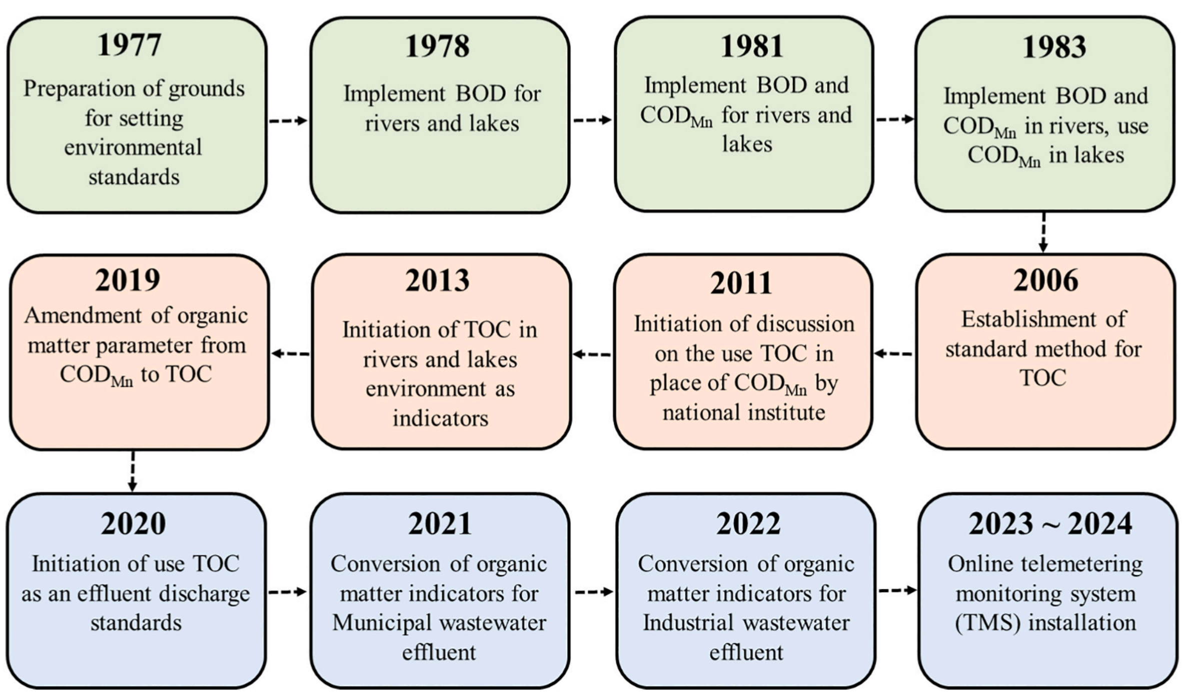

Fig. 1. Chronological history of organic matter guidelines in South Korea.

2. Materials and methods

2.1. Design of research

Three IWTPs that have exceeded the TOC standards for effluent discharge were selected one industrial park wastewater treatment plant (public IWTP) and two private IWTPs (a paper mill and a rubber/plastic producer). Sampling was carried out from July to October 2020 using the grab sampling method. The comprehensive approaches used in this study are presented in Fig. 2.

2.2. Characteristics of industrial wastewater treatment plant

General information regarding the selected IWTPs investigated in this study is tabulated in Table 1. Each treatment plant was characterized by its wastewater source. The public IWTP receives both domestic and industrial wastewaters. In particular, the public IWTP mainly accepts the following influent categories: (i) basic organic compounds (BOC) such as methyl chloride produced by the processing of coal tar and other mineral tar at high temperatures; (ii) basic inorganic compounds (BIC), including inorganic acids, metal and non-metal oxides (excluding metal oxides for inorganic dyes), alkalis; and (iii) byproducts of petroleum refining. One of the two private IWTPs treats wastewater from paper manufacturing only. The other IWTP is characterized by a small-scale facility that produces rubber and plastic (RP). Currently, biological wastewater treatment using an aerobic activated sludge process is being employed in the three IWTPs.

2.3. Analytical methods

The industrial wastewater samples collected from both the public and private IWTPs were subjected to various chemical analyses [BOD_5, COD_{Mn}, COD_{Cr}, TOC, and DOC (measured with the same sample used for TOC, but through 0.45 μm filtration)] using standard methods [24]. The concentration of mixed liquor suspended solids (MLSS) and mixed liquor volatile suspended solids (MLVSS) were determined using standard methods for the examination of water and wastewater [2]. Adenosine triphosphate (ATP) was employed to evaluate the activity of activated sludge according to the method described by Bäckman and Gytel [3]. The temperature and DO of each sample were measured using a DO probe (DO-31P, Japan). The pH was measured using a pH probe (HM-30P, Japan). The collected samples were immediately cooled in a cool box. The transport time for samples from the IWTPs to the laboratory where the chemical analyses and lab-scale experiments were conducted was approximately 3–5 h. Once the samples had arrived at the laboratory, they were either immediately analyzed or refrigerated prior to the analysis [24].

2.4. Bulk organic matter characterization

All samples used for analyses in bulk organic matter characterization experiments were filtered through a 0.45 μm polypropylene filter (Whatman, USA). The quantification of DOC in the wastewater investigated in this study was conducted using a TOC analyzer (TOC-V CPN, Shimadzu, Japan), and UV_{254} was measured using a spectrophotometer (DR5000, Hach, USA). The DOC was measured as non-purgeable organic carbon; DOC were determined in triplicate so the average DOC concentration was used for the determination of $SUVA_{254}$. UV_{254} measurements, deionized water was first placed in a quartz cell with a path length of 1 cm to set a reference (i.e., auto-zeroing); this was followed by sample measurements. Based on these two parameters, $SUVA_{254}$ can be calculated by dividing UV_{254} by DOC, indicating the aromaticity of the wastewater samples.

A spectrofluorometer (RF-5301, Shimadzu, Japan) with an arc lamp as a light source was used to investigate the fluorescent characteristics of DOC in each type of wastewater and consequently to produce three-dimensional FEEM spectra (i.e., contour plots of fluorescence intensities) using SigmaPlot 12.5 (SPSS Inc., USA). All samples were diluted under 2 mg/L of DOC to avoid fluorescence quenching [26]. FEEMs were measured within the temperature range of 20–25 °C [5]. The FEEM were scanned at excitation (ex)/emission (em) wavelengths of 220–400 nm in 10 nm excitation increments and 280–600 nm in 1 nm emission steps. The FEEM peaks monitored in this study can be classified into two categories: protein-like peaks (B, T1, and T2) and humic-like peaks (A and C). Specifically, the five peak regions observed in our study were as follows: protein-like peaks T1 (tryptophan-like, ex 220–240 nm, em 330–360 nm), T2 (tryptophan-like, ex 270–280 nm, em 330–360 nm), humic-like peaks A (ex 230–260 nm, em 400–450 nm) and C (ex 300–340 nm, em 400–450 nm) based on Park et al. [25], and B (tyrosine-like, ex 220–230 nm, em 309–321 nm) based on Henderson et al. [13].

To further determine the characteristics of DOC in terms of apparent

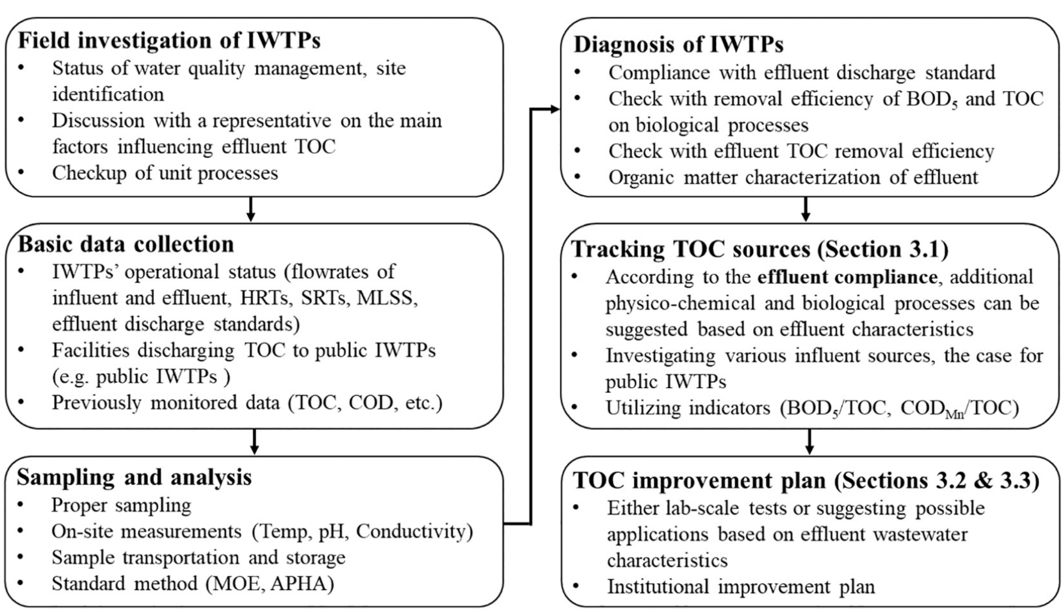

Fig. 2. Schematic diagram of TOC investigation for industrial wastewater treatment plants (IWTPs).

Table 1
Characteristics and total organic carbon (TOC) status of different types of industrial wastewater treatment plants (IWTPs).

IWTP type	Average influent flow (m^3/d)	Targeted wastewater	MLSS[b](mg/L)	SRT[c] (d)	HRT[d] (h)	Primary treatment	Secondary treatment	TOC Effluent (mg/L)	TOC[i] (mg/L)
PIWTP[a]	3400	Domestic + industrial wastewater	4000	40	17	Primary settling	DeNipho[f]	18.7	25
Paper	20,000	Paper wastewater	4500	–	–	Coagulation + DAF[e]	HPO-CAS[g]	44.6	40
Rubber & plastic	9	Rubber and plastic wastewater	3600	Infinite	–	Coagulation +dewatering	MBR[h]	156.5	180

[a] Public industrial wastewater treatment plant.
[b] Mixed liquor suspended solids.
[c] Solids retention time.
[d] Hydraulic retention time.
[e] Dissolved air flotation.
[f] De-nitrogen and Phosphorus.
[g] High purity oxygen-conventional activated sludge.
[h] Membrane bioreactor.
[i] TOC in discharge standards.

molecular weight distribution, size exclusion chromatography was performed using a LC-OCD (Model 8, DOC Labor, Germany). The LC-OCD allows the quantification of DOC into five sub-fractions: biopolymers (> 20 kDa), humic substances (1–20 kDa), building blocks (350–1000 Da), low molecular weight (LMW) acids (< 350 Da), and LMW neutrals (< 350 Da) [15]. It should be noted that the five types of DOC fractions mentioned above are classified based on natural organic matter (NOM). Therefore, all wastewater analyzed in this study was expressed in terms of the molecular weight represented by each type of organic carbon, except for the NOM-based paper mill wastewater.

2.5. Lab-scale of NF membrane experimental set up and procedures

The bench-scale cross-flow filtration unit consisted of an influent tank, a high-pressure pump, and a pressurized chamber where nanofiltration (NF) was performed. The bench-scale dead-end filtration unit was equipped with two analogue pressure gauges (WIKA, Germany). The cross-flow filtration experiment was performed at ambient temperature and 500 kPa, using effluent from industrial IWTPs that had been pre-treated with 1.2 μm filtration to avoid inclusion of large particles. The industrially treated effluent stream was introduced into the pressurized chamber through a 10 mm orifice using a high-pressure pump (HYDRA-CELL, model number: G03EKSGHFEHA, Wanner Engineering, Inc., USA). The composite NF permeate obtained over 24 h was collected in a plastic bottle placed on an electronic scale (A&D, model number: CB-12 K, Japan) connected to a data acquisition system for continuous monitoring of the flux as a function of time. The retentate that did not pass through the membrane was released back into the influent tank. The membrane used in this experiment was made of a polyamide (fully aromatic polyamide) thin film composite (NE2521, Toray Chemical Korea Inc., South Korea). A flat sheet membrane tailored from the spiral wound membrane element was placed inside the pressurized chamber, providing an effective filtration area of 42.5 cm^2. The molecular weight cutoff (MWCO) of this membrane was 200 Da; that is, organic carbon having a molecular weight smaller than 200 Da could pass through the nanomembrane, whereas organic carbon with a molecular weight greater than 200 Da was trapped. Prior to the experiments, the membrane was stored in deionized water for at least 24 h to avoid contamination.

3. Results and discussion

For TOC management of both public and private IWTPs, two main approaches were employed based on the effluent TOC concentration of each IWTP. To investigate the current risk of exceeding the secondary effluent standard of TOC, various influent sources entering the public IWTP were investigated to determine conventional organic matter parameters (i.e., BOD, COD, and TOC) as well as DOM characterization. In the case of individual IWTPs, a lab-scale test was conducted to improve the effluent TOC water quality standards. A potential alternative process was suggested based on the detailed characteristics of the effluent. In this case, the problem regarding the effluent TOC from each IWTP was first mentioned, followed by solutions that could be applied. Regarding the fractionation of LC-OCD, when organic matter in wastewater was a substance of natural origin, biopolymers, humic substances, building blocks, LMW acids, and LMW neutrals were used. However, when organic matter was a substance of synthetic or chemical origin, the molecular weight range corresponding to each sub-fraction of DOC was used rather than the conventional term used in LC-OCD for NOM.

3.1. Industrial park wastewater treatment plant (public IWTP)

For biological wastewater treatment, the public IWTP was operated as De Nitrogen and Phosphorus (DeNiPho) process. In the bioreactor, BOD_5 was reduced by 92%, COD_{Mn} by 90%, and TOC by 68.3%. The TOC concentration of the effluent was 17.6 mg/L, which met the discharge standard of 25 mg/L. The BOD_5/TOC of the effluent was 0.03, which indicated significantly low biodegradability [29]. In addition, the COD_{Mn}/TOC (which was only used in South Korea as a conversion rate from COD_{Mn} to TOC) was 0.34, which was lower than the value of 1.3 suggested by the MOE of South Korea for public IWTPs [36]; this indicated a large amount of refractory organic matter cannot be determined by COD in the effluent. The $SUVA_{254}$ of the influent was 0.93 L/mg-m, and it decreased moderately to a value of 0.62 L/mg-m in the effluent. Therefore, it can be derived that some fractions of aromatic organics were removed. Similar values have been reported by Jin et al. [16], who investigated dissolved effluent organic matter from a public IWTP treating mainly domestic wastewater.

Even though the public IWTP met the effluent criteria it indicated low value of COD_{Mn}/TOC; that is, nonbiodegradable organic matter remained in the effluent. In this case, tracking the causative substance seems to be more appropriate than the implementation of additional processes for the reduction of TOC in the effluent. To track the influent sources for optimum management of the public IWTP, it is essential to characterize the organic substances. As illustrated in Fig. 3(a), the public IWTP accepts three main influent sources. Influent source 1 mainly consists of wastewater from facilities producing BOC and BIC, based on the industry classification list of South Korea. More than 90% of the wastewater was generated from these two chemical facilities and flowed into the public IWTP. Influent sources 2 and 3 mainly consist of wastewater discharged from petroleum refining facilities and the chemical industry, respectively. Fig. 3(a) shows the DOC loading rate of

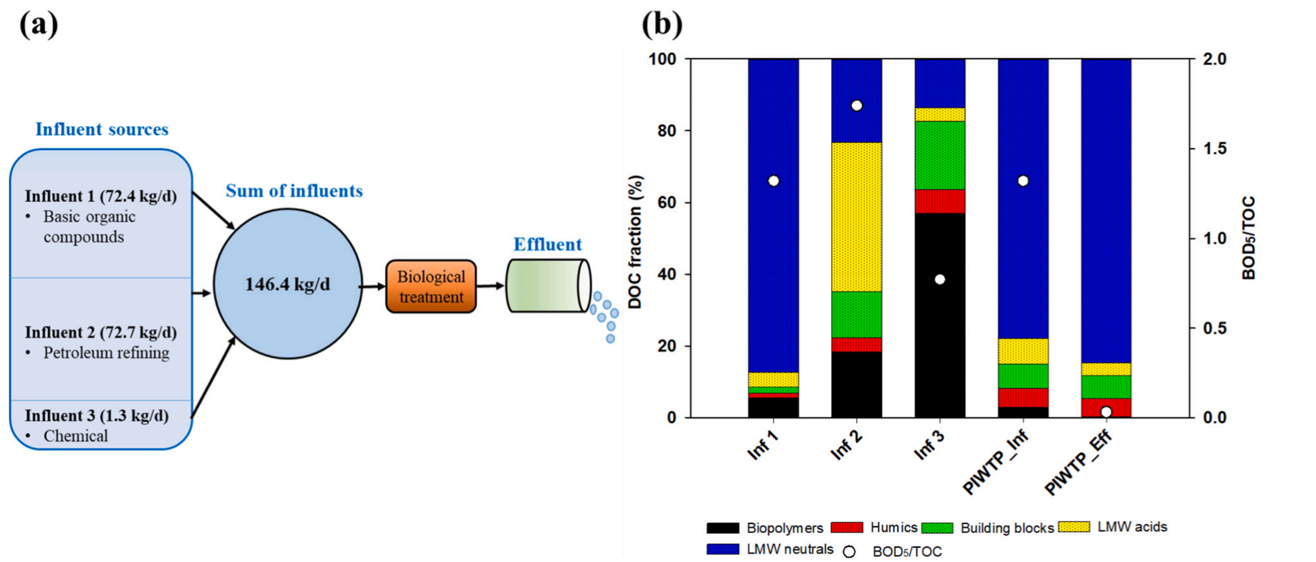

Fig. 3. (a) Loading rates of individual groups of hydrophilic dissolved organic carbon (DOC) entering into the public industrial wastewater treatment plant (IWTP), and (b) Fractions of individual groups of DOC including biopolymers, humic substances, building blocks, low molecular weight (LMW) acids and neutrals, and biochemical oxygen demand (BOD_5)/total organic carbon (TOC) ratios. "Inf" and "Eff" denote influent and effluent, respectively.

each influent source flowing into the public IWTP. The DOC loads of influent sources 1, 2, and 3 were 72.4 kg/d, 72.7 kg/d, and 1.3 kg/d, respectively; that is, influent sources 1 and 2 accounted for most of the DOC load of the public IWTP (> 99%). Domestic wastewater generated from a village located within the wastewater treatment area flows into the public IWTP, and it accounts for a relatively low proportion (8% on average) of the total flow rate generated. The loading rates of DOC was significantly lower than that of influent 1, 2, and 3. Therefore, it was not considered in the calculation of the DOC loading rate.

As previously described, the BOC facility (a member of influent source 1) considerably affected (> 95%) the DOC loading rate of influent source 1 in this study. Therefore, considering the DOC load alone, it can be observed that the BOC facility has a significant influence on the overall DOC of the public IWTP. However, compared to that of public IWTP influents as well as influent sources 2 and 3, the BOC facility reported a considerably low $SUVA_{254}$ of 0.05 L/mg-m, indicating that the wastewater of the BOC facility is relatively non-humic [33]. In addition, the BOD_5/TOC ratio of the BOC facility was 1.48, indicating relatively biodegradable organic substances. This result is in agreement with the results of a previous study [29] that reported that when the BOD_5/TOC ratio of raw wastewater is 1.2–2.0, it can be regarded as biodegradable organic matter. In this regard, influent source 1 (including the BOC facility) may not be the main contributor to the increased effluent TOC concentration of the public IWTP. Compared to influent source 1 (ultimately BOC facility wastewater), the $SUVA_{254}$ of influent 2 and 3 were 1.13 and 1.49, respectively; the BOD_5/TOC of influent 2 and 3 were 1.74 and 0.77, respectively.

Since BOD_5/TOC and TOC did not seem to be decisive indicators for determining organic matter characteristics, different carbon sources were tracked by LC-OCD analysis to investigate the characteristics of DOM, which helped in understanding the overall performance of the public IWTP. Fig. 3(b) shows the fraction of hydrophilic DOC compositions and the BOD_5/TOC ratio of each influent source and effluent. No precise calculation of mass balance was performed on the loading rates of TOC and DOC due to the limitations in the availability of data (Table S2). As shown in Fig. 3(b), five components of each wastewater type were identified by LC-OCD. The influent and effluent of the public IWTP were mainly composed of neutral organic carbon, smaller than 300 Da. The higher fraction of LMW carbon was attributed to the metabolism of microorganisms that converted large-molecular-size DOM in the influent into relatively LMW organics in the effluent [32]. Similarly, neutral organic carbon (< 300 Da) constituted the majority of influent source 1 (87.4%). In contrast, the major constituents of influent sources 2 and 3 were assigned to organic carbon acids (< 300 Da, 41.6%) and organic carbon (> 20 kDa, 57%), respectively. Considering the DOC loading rate towards the public IWTP, neutral organic carbon (< 300 Da) appears to be the key contributor to the DOC concentration and therefore accounts for the performance of the public IWTP. In the context of decreasing effluent DOC and thereby TOC concentration, the concentration of neutral organic carbon (< 300 Da) in the influent and effluent was 30.4 mg/L and 15.8 mg/L, respectively. This implies that 52% of neutral organic carbon (< 300 Da) was removed during the treatment process, most likely through biological treatment. In addition, the neutral organic carbon (< 300 Da) fraction contributed to 84.6% of the DOC in the effluent from public IWTP. The BOD removal rate in the process (including primary and secondary treatments) was 92%, and it was observed that most of the organic matter was biologically removed. Here, a discrepancy was observed in the neutral organic carbon (< 300 Da) in the context of biological wastewater treatment. Specifically, the neutral organic carbon (< 300 Da, i.e., LMW neutrals) is considered hydrophilic and bioavailable in the context of NOM [4]. In terms of industrial wastewater, the neutral organic carbon (< 300 Da) was not different. Thus, the results of this study show that most of the neutral organic carbon (< 300 Da) remaining in the effluent would be either biodegradable or slowly biodegradable, thereby requiring proper treatment and management.

As summarized in Table S2, the intensity of fluorescence of organic substances of influent source 1, including the BOC facility, was relatively much lower than that of influent sources 2 and 3, when normalized based on DOC concentration. That is, based on the normalized FEEM, influent sources 2 and 3 showed higher fluorescence intensity than influent source 1. Comparing influent sources 1 and 2 with similar DOC loading rates, the peaks T1, T2, B, A, and C of influent source 2 were 4.2, 4.4, 4.2, 2.9, and 2.4 times higher than those of influent source 1, respectively. (Table S2). This implies that the influent sources 2 and 3 have a greater influence on the sum of influent entering into the public IWTP and consequently to the overall performance of public IWTP in terms of TOC removal than influent source 1. In addition, as presented in Fig. S1, protein-like peaks T1 and T2 and tyrosine-like peak B were more prevalent than peaks A and C in all influent sources, indicating the presence of relatively biodegradable matter. This result is in agreement with the results reported by Yu et al. [35]. The SUVA values of influent sources 2 and 3 were 5.1 and 6.8 times higher than that of influent source 1, respectively, indicating the relatively low biodegradability of influent sources 2 and 3. Based on our investigations, the wastewater discharged from the BOC facility is possibly biologically removed, and the components of influent sources 2 and 3, characterized by relatively refractory organic matter, may remain in the effluent and thereby require additional management of TOC. Finally, although the biological treatment of TOC was satisfactory to some extent (77% removal rate), an improvement in the biological performance of TOC removal during the biological treatment process may be required through the alteration of some operating parameters, such as solids retention time and MLSS concentrations, to keep the effluent TOC concentration as low as possible.

3.2. Paper and pulp mill wastewater treatment plant

For biological wastewater treatment, the paper mill IWTP was operated as UNOX process utilizing high purity oxygen for aeration. The removal efficiencies of BOD_5, COD_{Mn}, and TOC were 94.7, 85.2 and 87.6%, respectively. Therefore, it can be seen that the bioreactor was being operating stably. The TOC concentration of the effluent for the paper mill IWTP was 49.5 mg/L, which did not meet the discharge standard of 40 mg/L. In addition, the COD_{Mn}/TOC ratio of the effluent was 1.6, which was lower than the value of 1.8 suggested by the MOE of South Korea, indicating that a moderate amount of non-biodegradable organic matter remained in the effluent. Similarly, the BOD_5/TOC value of the effluent from the paper industry was reported to be 0.50–0.75 [31]. The BOD_5/TOC of the effluent was 0.48 in this study and indicated that some biologically degradable organic matter remained in the effluent, which agrees with the fact that the BOD_5 concentration in the effluent was 23.6 mg/L; this is relatively high compared to the values reported by Eckenfelder [12]. The DOC/TOC of the effluent was 88.1% and the $SUVA_{254}$ value of the effluent was 2.44 L/mg-m. Coagulation aids reduction of the DOC when the $SUVA_{254}$ was higher than 2 L/mg-m, and the higher the $SUVA_{254}$, the higher the humic fractions in the DOC [33]. Because both adsorption and coagulation are favorable for the removal of humics in the DOC, these can be candidates for the overall reduction of DOC, and consequently, the TOC concentration in the effluent. However, an activated carbon adsorption process was already in operation for the final treatment of wastewater in this IWTP. In addition, the LC-OCD results showed that the organic carbon in the effluent was composed of a hydrophobic fraction (34.7%) and a hydrophilic fraction (65.3%); specifically, the each of hydrophilic DOC fraction was as follows: biopolymers (12%), humic substances (10.7%), building blocks (24.9%), LMW acids (13.1%), and LMW neutrals (39.4%). Moreover, a comparison was made on the results in terms of LC-OCD before and after the application of the activated carbon adsorption tank (for final discharge). The comparison revealed that a minor reduction was observed in building blocks, LMW acids, and LMW neutrals with activated carbon adsorption (not shown in this paper). Therefore, it was confirmed that LMW organic carbon is hardly removed by the adsorption mechanism, which agrees with the results of previous studies [4]. To achieve improved TOC concentrations, a lab-scale NF test was conducted. Land and capital cost restriction in the IWTP informed the selection of NF. In addition, the NF process would not be used to treat the entire quantity of wastewater for final discharge. That is, it may be suggested that a part of the effluent is treated with NF, and the rest is treated with the existing activated carbon adsorption process, so that the two treated effluents are blended, and subsequently discharged, rather than treating the entire wastewater with the NF process.

Fig. 4 shows the individual hydrophilic DOC concentrations in treated industrial wastewater and their concentrations after treatment with NF. The application of NF molecular weight distribution can provide detailed and useful information on organic matter characteristics. As shown in Fig. 4, the NF performance was successful, with a DOC removal of 93%. When considering the sub-fraction of DOC, the removal

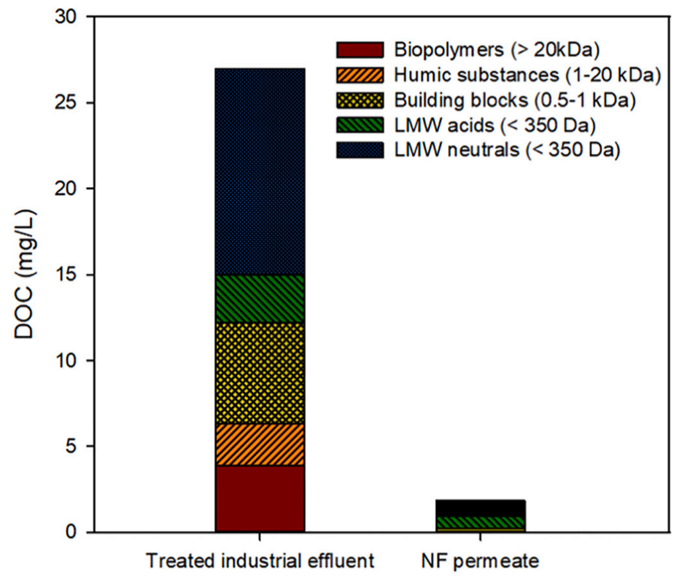

Fig. 4. Removal of individual groups of dissolved organic carbon (DOC) including biopolymers, humic substances, building blocks, low molecular weights (LMW) acids, and LMW neutrals of paper mill industrial wastewater treatment plant (IWTP). Samples were collected and measured in October 2020.

efficiencies of biopolymers, humic substances, building blocks, LMW acids, and LMW neutrals were > 99%, > 99%, 96%, 76%, and 93%, respectively. As expected, high molecular weight organic carbon entities, such as biopolymers, humic substances, and building blocks, were almost completely removed. However, contrary to previous observations that LMW neutrals are characterized by low electrostatic repulsion and thereby higher permeability through the NF membrane [22,30], the removal efficiency of LMW neutrals in this study was relatively high (93%). Since the MWCO of the NF membrane was 200 Da, it seems that the LMW neutrals were occupied with most of the organic carbon with a molecular weight greater than 200 Da. The NF membrane used in this study was made of polyamide, and the surface of the membrane had a positive charge at a low pH and a negative charge at a high pH. The pH of the treated industrial wastewater used in this study was 6.85, indicating a very weak acidity (i.e., almost neutral). Based on the Donnan effect [28], considering that the surface charge of LMW acids is negatively charged, some LMW acids could pass through the membrane (the membrane surface is partially positively charged), whereas others were excluded (the membrane surface is partially negatively charged). As a result, the removal rate of LMW acids was lower than that of LMW neutrals. LMW neutrals accounted for 50% of the remaining hydrophilic DOC in the permeate, followed by 38% of LMW acids, and 13% of building blocks. However, each showed a very low value (all below 1 mg/L). Additionally, the fluorescence characteristics of the paper mill wastewater are displayed in Fig. S2. Fig. S2(a) and S2(b) show the fluorescence properties of the paper mill wastewater before membrane filtration and the permeate after nano-membrane filtration, respectively. The industrially treated effluent [Fig. S2(a)] was characterized by the presence of three main FEEM peaks, T1, A, and C, and a less abundant peak T2. In particular, peak A was dominant, while peak T2 had the lowest intensity in the effluent. This result was in agreement with the results of a previous study [27]. However, Rodríguez-Vidal et al. [27] reported that peak C was dominant. This could be due to the different features of the pulp used for paper processing and thereby the different wastewater characteristics.

Five FEEM peaks were detected in the treated effluent; these were A, B, T1, C, and T2, in order of intensity. In particular, four FEEM peaks, A (fulvic-like), C (humic-like), B (tyrosine-like), and T1 (tryptophan-like) were dominant; this is in agreement with the findings of a previous study

[10]. In addition, the fact that the largest percentage of fulvic-like peak A remained in the effluent is in line with the findings of another recent study [27]. Although it has been reported that tyrosine-like peak B occupies a lower proportion than tryptophan-like peak T1 in wastewater [7], the converse was observed in this study (with a difference of approximately 10%). In addition, peaks T1 and B, which are protein-like peaks, can be biologically removed. The high intensity of these in the effluent may be related to the relatively high BOD concentration of 23.6 mg/L that remained in the effluent, requiring an improvement in the biological treatment of biodegradable compounds in the aerobic basin. In addition, the BOD removal rate was low (65%) in the biological treatment process. In the paper mill wastewater with such effluent characteristics, a significant reduction in fluorescence intensity (> 95%) was observed for all five peaks through the NF process, which is in agreement with the DOC removal of 93% in this study. Therefore, the NF membrane process was favorable for the removal of recalcitrant compounds and biodegradable compounds in this wastewater effluent.

3.3. Rubber and plastic wastewater treatment plant

A similar approach was used in the RP IWTP (due to footprint limitation in the existing IWTP as well as the treated effluent characteristics based on LC-OCD). For biological wastewater treatment, the RP IWTP was operated as membrane bioreactor (MBR) process. In the MBR, the removal efficiencies of BOD_5, COD_{Mn}, and TOC were 79, 76.1 and 72.2%, respectively. Since the RP IWTP has operated as MBR equipped with hollow fiber membrane with a nominal pore size of 0.2 μm. The NF process was applied to reduce the TOC concentration in the effluent. The TOC concentration of the effluent was 156.5 mg/L, which met the discharge standard of 180 mg/L for the RP IWTP. In addition, the COD_{Mn}/TOC ratio of the effluent was 1.7, which was slightly lower than that suggested by the MOE of South Korea (1.8), indicating that a moderate amount of non-biodegradable organic matter was present in the effluent of the RP wastewater. The DOC/TOC ratio in the effluent was 98%, which is in line with the MBR process. Interestingly, the $SUVA_{254}$ of the RP wastewater effluent was 0.09 L/mg-m; this is relatively low compared to those of other types of wastewater effluents investigated in this study, which ranged between 0.62 and 2.44 L/mg-m. Therefore, the characteristics of RP industrial wastewater are very different from those of wastewater originating from different industrial wastewater sources.

As displayed in Fig. S3(a), a relatively less abundant peak A and no peak C were detected in the treated effluent. In contrast, peaks T1, T2, and B, which are relatively readily biodegradable, were dominant (the order of intensity of these peaks was B, T1, and T2), and these peaks exhibited a ratio of 98% in the treated effluent. This indicated that biological wastewater treatment was not sufficient to reduce organic matter substances. The biological wastewater treatment corresponded to a BOD removal rate of 62% in the biological basin. The biodegradability of industrial wastewater effluent can be determined based on a BOD_5/COD_{Cr} ratio of 0.06 [12]. The BOD_5/COD_{Cr} value of the RP IWTP effluent was observed to be 0.07, which indicates that either biodegradable or non-degradable organic matter is discharged at a higher rate in the effluent than the rate of relatively readily biodegradable organic matter. However, since the absolute concentration of the BOD_5 and COD_{Cr} was 40.4 mg/L and 544.2 mg/L, respectively, it can be seen that insufficient biodegradation was achieved.

Although tracking a certain type of compound was beyond the scope of this study, in the context of improving the biological performance of MBR with regards to organic matter, the poor decomposition of protein-based organic components may be related to the surfactants used in the manufacturing process of the RP IWTP. Surfactants used in the process might negatively influence the metabolism of microorganisms in the MBR basin. However, the microbial activity in the bioreactor, expressed in terms of ATP, was 0.12 mg-ATP/g-MLVSS. Due to limited literature on the effect of ATP on activated sludge activity for industrial wastewater similar to RP IWTP, an exact comparison cannot be made. Nevertheless, according to Maeng et al. [20], who operated a lab-scale MBR that treated synthetic wastewater under different solids retention time (SRTs), the activity of activated sludge residing in the aerobic basin of RP IWTP was stable based on the ATP measured. This is in line with a moderate MLVSS/MLSS ratio of 0.76, similar to what has normally been observed in sludge from municipal wastewater [14]. Another reason for the low biodegradation of organic matter and consequently high intensity of fluorescence peaks T1, T2, and B could be that extremely long SRT resulted in a high concentration of extracellular polymeric substance (EPS) in the treated effluent. The analytical determination of EPSs was not carried out in this study; however, the presence of tyrosine-like fluorescence peak B in the treated effluent as well as in the NF permeate seems to be highly correlated with EPS [19]. As expected based on the previously described NF process on paper wastewater, the reduction of each of the fluorescence peaks through the NF process was highly variable; the removal rates of peaks T1, T2, B, and C were 90%, 86%, 87%, and 89%, respectively.

Fig. 5 shows the individual hydrophilic DOC concentrations in treated RP industrial wastewater and their concentrations after treatment with the NF process. As shown in Fig. 5, NF led to a 90% DOC removal. In particular, the organic carbon removal efficiencies of 1–20 kDa, 350–1000 Da, and LMW (acids and neutrals) were 98%, 94%, and 85%, respectively. As expected, the high molecular weight organic carbon was almost completely removed through the NF process. Similarly, as observed in the paper and pulp mill wastewater treatment plants, the removal of LMW carbon from RP wastewater was 85%, which suggests that the LMW carbon was not impacted by the electrostatic repulsion on the surface of the nano-membrane. In addition, most of the LMW carbon present in the treated effluent was characterized by a molecular weight greater than 200 Da. Considering the removal trends from the perspectives of fluorescence intensity and molecular weight, two-stage membrane processes (microfiltration followed by NF) could be applied to this type of wastewater.

Interestingly, NF membrane is characterized by the capacity of permeating mono-valent ions (e.g., sodium chloride), and rejection of divalent and multivalent ions (e.g., sodium sulfate). Such benefits offered by NF membrane facilitate a wide range of NF membrane application into industrial wastewater treatment [1]. In this context, the

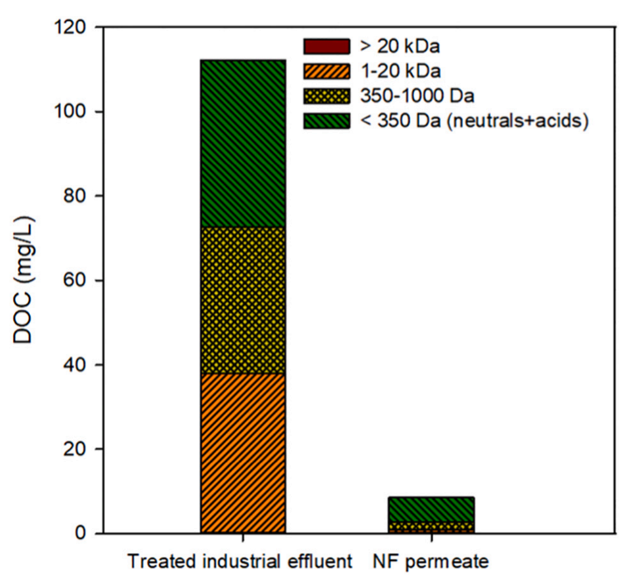

Fig. 5. Removal of individual groups of hydrophilic dissolved organic carbon (DOC) based on the molecular weight, including higher than 20 kDa, 1–20 kDa, 350–1000 Da, and lower than 350 Da (neutrals + acids) in the rubber and plastic (RP) industrial wastewater treatment plant (IWTP) through the NF process. Samples were collected and measured in October 2020.

present study was confirmed that the organic matter in the paper mill wastewater effluent was sufficiently removable by NF membrane. A promising strategy to improve the nonbiodegradable organic matter in the industrial wastewater effluent could be the application of the NF membrane process.

4. Conclusions

This research was conducted in the framework of lowering the TOC in the effluent of industrial wastewater matrices. The DOM characterization tools were useful in terms of tracking the various influent sources of TOC affecting the overall performance of the public IWTP (i.e., industrial park wastewater treatment plant) and understand the removal of TOC. Regarding the private IWTPs, the NF process completely eliminated hydrophilic DOC, as confirmed by LC-OCD. Despite the differences in wastewater characteristics of three selected IWTPs, bulk DOM characterization seems to be a suitable tool for tracking raw wastewater features for public IWTP process. Detailed organic matter characterization using a combination of $SUVA_{254}$ and LC-OCD could serve as an alternative tool for tracking the wastewater sources influencing the overall biological performance of public IWTPs, as well as for suggesting alternative processes. The lab-scale experiment (i.e., NF) was implemented in a batch-type reactor, thereby calling for large-scale experiments to support the potential installation of existing IWTPs. Additionally, our approach may serve as a guideline for countries that set TOC as the effluent standard in the future. Further research is needed to explore the organic matter characteristics of other industrial wastewaters, such as wastewater from petroleum refining facilities, reverse osmosis concentrate, beverage wastewater, and food processing wastewater, by using bulk organic matter characterization tools beyond the conventional organic matter parameters.

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

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jwpe.2022.102604.

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