



Trihalomethane formation potential of organic fractions in secondary effluent

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Abstract

Organic matter is known to be the precursor of numerous chlorination by-products. Organic matter in the secondary effluent from the Wenchang Wastewater Treatment Plant (Harbin, China) was physically separated into the following fractions: particulate organic carbon (1.2–0.45 μm), colloidal organic carbon (0.45–0.1 μm), fine colloidal organic carbon (0.1–0.025 μm), and dissolved organic carbon (DOC) (< 0.025 μm). Moreover, < 0.45 μm fraction was chemically separated into hydrophobic acid (HPO-A), hydrophobic neutral (HPO-N), transphilic acid (TPI-A), transphilic neutral (TPI-N), and hydrophilic fraction (HPI). The chlorine reactivity of these organic fractions obtained from both size and XAD fractionations were evaluated. The structural and chemical compositions of the HPO-A, HPO-N, TPI-A, and TPI-N isolates were characterized using elemental analysis (C, H, O, and N), Fourier transform infrared spectroscopy (FT-IR), and proton nuclear magnetic resonance spectroscopy (¹H-NMR). Results showed that DOC was dominant in terms of total concentration and trihalomethane formation potential (THMFP), and there was no statistical difference in both specific THMFP (STHMFP) and specific ultraviolet light absorbance among the 0.45, 0.1, and 0.025 μm filtrates. HPO-A had the highest STHMFP compared to other chemical fractions. HPO-A, HPO-N, TPI-A, and TPI-N contained 3.02%–3.52% of nitrogen. The molar ratio of H/C increased in the order of HPO-A < HPO-N < TPI-A < TPI-N. The O/C ratio was relatively high for TPI-N as compared to those for the other fractions. ¹H-NMR analysis of the four fractions indicated that the relative content of aromatic protons in HPO-A was significantly higher than those in the others. The ratio of aliphatic to aromatic protons increased in the order of HPO-A < HPO-N < TPI-A < TPI-N. FT-IR analysis of the four fractions showed that HPO-A had greater aromatic C=C content whereas HPO-N, TPI-A, and TPI-N had greater aliphatic C–H content. TPI-N contained more oxygen-containing functional groups than the other fractions.

Key words: organic carbon; trihalomethane formation potential (THMFP); chlorination; FT-IR; ¹H-NMR

Introduction

Organic matter is known to be the precursor of potentially harmful disinfection by-products (DBPs) in the chlorination, such as trihalomethanes (THMs) (Panyapinyopol *et al.*, 2005; Marhaba *et al.*, 2006). Secondary effluents that contain large amounts of organic matter are likely to be major contributors to the genesis of organics in major rivers (Ma *et al.*, 2001). However, the chlorine reactivity and structural characteristics of organic matter in effluent from wastewater treatment plant have rarely been studied.

Conventional filtration commonly uses a 0.45- μm pore size filter as a cutoff point for defining dissolved organic carbon (DOC) (Chow *et al.*, 2005). Most research focuses on THM precursors in the <0.45 μm fraction whereas the reactivity from organic matter >0.45 μm in THM formation has seldom been studied (Owen *et al.*, 1993). Moreover, a pore size of 0.45 μm is relatively large and 0.45- μm filtrate may contain a significant portion of organic carbon that is not reactive during chlorination

(Chow *et al.*, 2005). There is therefore, a need to further divide organic matter into more homogeneous fractions for analysis of THM precursors.

To understand the role and behavior of organic matter in aquatic environments, it is necessary to understand the chemistry of organic matter. The differentiation between each organic species might not be practical. Therefore, several past researches focused on grouping organic matter into several common groups according to the physical/chemical properties of organic species, e.g., polarity, size, and molecular weight (Panyapinyopol *et al.*, 2005). XAD resin method has been reported in many applications for fractionation of organic matter and is generally considered as the state-of-art method at present for such fractionation (Kim and Yu, 2005). The fractionation allows a thorough investigation of the THM formation and spectral characterization of the relatively well-defined fractions obtained.

The objective of this study was to investigate the chlorine reactivity and structural characteristics of organic fractions in the secondary effluent, which was taken from the Wenchang Wastewater Treatment Plant (WWTP)

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(Harbin, China). Such knowledge might assist in our understanding of the compositions and chemical properties of organic matter in secondary effluents, and provide improved insight into the development of more effective control of THM formation before reuse or discharge of secondary effluents.

1 Materials and methods

1.1 Chemicals

All chemical solutions were prepared from reagent-grade chemicals or stock solutions. Milli-Q water (Direct-Q 3 UV™, Millipore, USA) was used for all dilutions, samples, chemical preparations, and final glassware cleaning in this work. Solutions were stored at 4°C and brought to room temperature before use. A chlorine solution was prepared in the form of concentrated sodium hypochlorite (3000 mg/L) and it was periodically standardized by the iodometric method (APHA, 1995).

1.2 Sample collection and preservation

Undisinfected secondary effluent samples were collected from the WWTP. Samples were carefully collected and transferred to the laboratory in an ice cooler, stored in a cold room with a temperature controlled at 4°C to minimize changes in the constituents.

1.3 Size and XAD fractionation

The secondary effluent was filtered through a series of MF-Millipore mixed cellulose ester membrane filters with four different pore sizes: 1.2, 0.45, 0.1, and 0.025 µm. Before use, each filter was rinsed with 1000 ml Milli-Q water to remove any residual organic contaminants (Karanfil *et al.*, 2003). During sample filtration, an initial 25 ml of the filtrate on a filter must be wasted before samples for analysis are collected to minimize the impact of organic matter loss to filters (Karanfil *et al.*, 2003). The size fractionation of the secondary effluent was run in duplicate. According to Chow *et al.* (2005), particulate organic carbon (POC) was organic carbon that passed through a 1.2-µm filter but was retained by a 0.45-µm filter. Colloidal organic carbon (COC) was organic carbon that passed through a 0.45-µm filter but was retained by a 0.1-µm filter. Fine colloidal organic carbon (FCOC) was organic carbon that passed through a 0.1-µm filter but was retained by a 0.025-µm filter. DOC was organic carbon that passed through a 0.025-µm filter. Organic carbon and THMFP of individual fractions were determined as the difference between filtrates.

In addition, 0.45 µm filtrates were further characterized by XAD-fractionation. The organic carbon that passed through a 0.45-µm filter was fractionated into five classes: hydrophobic acid (HPO-A), hydrophobic neutral (HPO-N), transphilic acid (TPI-A), transphilic neutral (TPI-N), and hydrophilic fraction (HPI), using XAD-8/XAD-4 resin chromatography following established methods (Aiken *et al.*, 1992; Chow *et al.*, 2006). Briefly, 0.45-µm filtrates were acidified to pH 2 and passed through two columns

in a series containing XAD-8 and XAD-4 resins. After all the samples were run through the columns, each column was separately back eluted with 0.1 mol/L NaOH. The eluate from XAD-8 is defined as HPO-A and the eluate from XAD-4 is defined as TPI-A. HPO-N and TPI-N are those compounds that adsorb onto XAD-8 and XAD-4 resins, respectively, but are not dissolved during back elution with NaOH. HPI is the carbon in the XAD-4 effluent. HPO-A and TPI-A were eluted from the XAD-8 and XAD-4 columns, respectively, using 0.1 mol/L NaOH; isolates were desalted using cation exchange resin and freeze-dried using a vacuum freeze dry system. HPO-N and TPI-N were desorbed from the XAD resins using a 75% acetonitrile/25% Milli-Q water solution. Acetonitrile was subsequently removed using rotary-evaporation and the resin isolates were lyophilized. HPI was not isolated because of the large volume of water to be evaporated, which was stored at 4°C.

1.4 Chlorination

Prior to chlorination, all samples were diluted with Milli-Q water to produce a DOC concentration of 1 mg/L before chlorination. Freeze-dried HPO-A, HPO-N, TPI-A, TPI-N were reconstructed in Milli-Q water. HPI, the pH of which remained at 2 after the XAD fractionation, was adjusted to about pH 7 with NaOH.

Chlorination was performed on samples buffered with 0.05 mol/L phosphate at pH 7.0±0.1. Chlorine was added as sodium hypochlorite at a dose of 5 mg Cl₂/mgC. Chlorinated samples were incubated at 20°C in the dark for 7 d in headspace-free 250-ml, glass-stoppered BOD bottles. At the end of the reaction period, residual chlorine was quenched with sodium sulfite (Na₂SO₃), and the concentration of THMs was analyzed.

1.5 Analytical methods

Organic carbon was analyzed using a combustion technique with a Shimadzu TOC-5000 (total organic carbon analyzer, Shimadzu, Japan). UV absorbance was measured with a Shimadzu UV-2550 ultraviolet-visible (UV/VIS) spectrophotometer (Shimadzu, Japan) at 254 nm using a quartz cell with a 1-cm path length. The instrument was zeroed using Milli-Q water as a blank. Specific ultraviolet light absorbance (SUVA) was calculated as (UV-254/DOC) × 100.

THMs were extracted with methyl *tert*-butyl ether from the chlorinated samples using a modified Environmental Protection Agency method 551.1 and were analyzed by gas chromatography with an electron capture detector (GC/ECD, Hewlett Packard 5890 II, Hewlett Packard, USA).

Infrared spectra were obtained using 2–5 mg of organic fractions isolates in potassium bromide pellets. The Perkin Elmer Spectrum One B Fourier-transform infrared (FT-IR) spectrometer (Perkin Elmer, USA) was set to scan from 4000 to 400 cm⁻¹. All spectra were baseline corrected and normalized after acquisition to a maximum absorbance of 1.0 for comparative purposes.

A nuclear magnetic resonance (NMR) analyzer (Avance

400, Bruker, Switzerland) was used to obtain the $^1\text{H-NMR}$ spectra of organic fraction isolates. Approximately 50 mg of powder lyophilized was added to 0.5 ml D_2O in a 10-mm NMR tube.

The elemental composition of organic fraction isolates was analyzed in duplicate with an element analyzer (Flash EA1112, Thermo Electron SPA, Italy). The samples' carbon, hydrogen, and nitrogen were obtained directly from this analysis. The oxygen content was calculated from the difference.

2 Results and discussion

2.1 Size fractionation

When organic matter was physically fractionated, a significant amount of POC existed in the secondary effluent. More than 23% of the organic carbon was POC, indicating that a significant proportion of organic carbon remained in the particulate phase. In the secondary effluent DOC was the major fraction with approximately 73% of the organic carbon (Fig.1a). Both COC and FCOC were minor, comprising about 2% of the organic carbon in the secondary effluent. The relative distribution of organic

carbon fractions in the secondary effluent was as follows: $\text{DOC} \gg \text{POC} \gg \text{FCOC} \approx \text{COC}$.

Among the organic fractions, DOC and POC were the major reactive fractions for THMFP, contributing 85% and 10%, respectively (Fig.1b). Organic fractions COC and FCOC produced insignificant amount of THMFP. The amount of THM precursors in each organic fraction was not proportional to its organic carbon content (Fig.1). The difference in organic carbon and THMFP distribution implied that the reactivity of these organic fractions in forming THM differed.

By normalizing THMFP by the amount of organic carbon in each fraction, the specific THMFP (STHMFP) was obtained. For example, the STHMFP of DOC was equal to the difference in THMFP divided by the difference in organic carbon between 0.1 and 0.025 μm filtrate.

In these fractions, FCOC and POC had the highest and lowest STHMFP, with an average of 5.2 and 1.6 mmol/mol, respectively (Fig.2a). The STHMFP of COC and DOC had an average of 3.0 and 4.6 mmol/mol, respectively. The reactivity of FCOC was significantly higher than all other fractions, indicating that this fraction contained more THM precursors.

The SUVA is often taken as a parameter that indicates

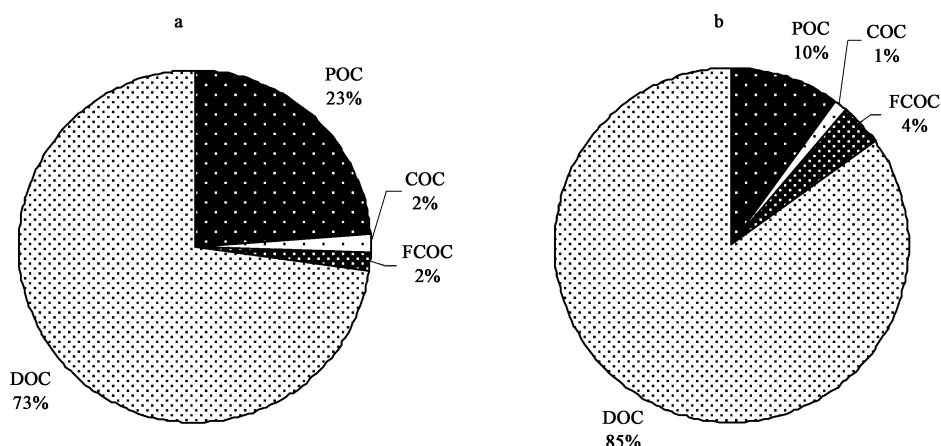


Fig. 1 Distribution of organic fractions from size fractionation in (a) organic carbon and (b) THMFP. THMFP: trihalomethane formation potential; POC: particulate organic carbon; COC: colloidal organic carbon; FCOC: fine colloidal organic carbon; DOC: dissolved organic carbon.

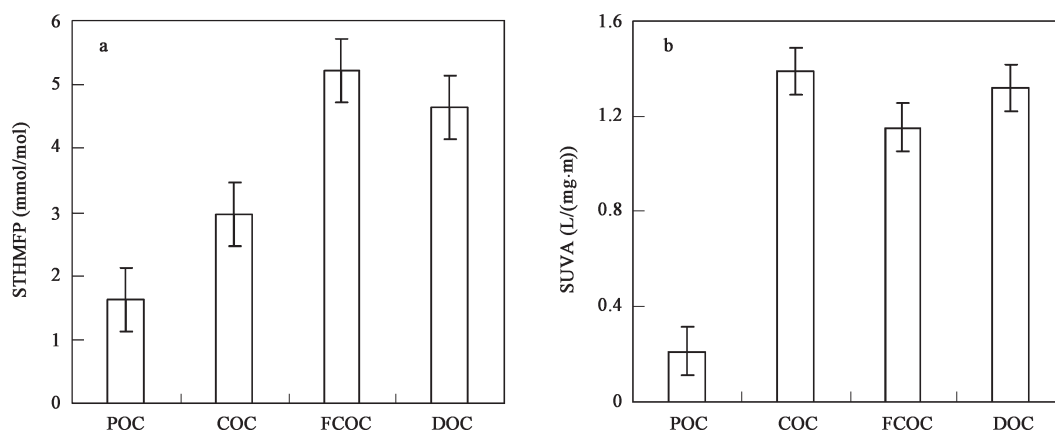


Fig. 2 STHMFP (a) and SUVA (b) of organic fractions from size fractionation. STHMFP: specific trihalomethane formation potential; SUVA: specific ultraviolet light absorbance at 254 nm.

the level of aromatic organics in the water. Hence, a higher SUVA should raise the level of THMFP (Marhaba *et al.*, 2006). The SUVA of POC, COC, FCOC, and DOC from the secondary effluent had an average of 0.21, 1.39, 1.15, and 1.32 L/(mg·m), respectively (Fig.2b). In addition SUVA and STHMFP were examined and a particularly high STHMFP but low SUVA of FCOC (Fig.2) was found. In contrast, higher SUVA but lower STHMFP of COC was recorded. The SUVA appeared not to be a good indicator for predicting the STHMFP of physical fractions in the secondary effluent.

Moreover, there was no statistical difference in both STHMFP and SUVA among the 0.45, 0.1, and 0.025 μm filtrates in this study (the STHMFP were 4.62, 4.65 and 4.63 mmol/mol and the SUVA were 1.32, 1.31 and 1.32 L/(mg·m) for the 0.45, 0.1 and 0.025 μm filtrates, respectively). The results implied that the 0.45- μm pore-size filter provided comparatively homogeneous organic carbon properties and enabled a good characterization of THM precursors for the secondary effluent. This finding is contrary to observations by Chow *et al.* (2005), who had examined the effects of filter pore size (1.2, 0.45, 0.1, and 0.025 μm) on characterizing organic carbon and THMFP of water extracts from soils. It was found that 0.025 μm filtrate contained more homogeneous organic fractions that have similar chemical characteristics whereas 0.45 μm filtrate potentially contained heterogeneous COC whose chemical behavior was source dependent.

The inconsistent results may be attributed to the significant difference between 0.45 μm filtrate turbidity in the two studies. Karanfil *et al.* (2005) reported that when filtrate turbidities were > 0.5 NTU (nephelometric turbidity unit) they increased the UV-254 values (and also SUVA). In the work conducted by Chow *et al.* (2005) with mineral soils extracts (with high proportion of COC), the 0.45 μm filtrates had high turbidity of 16 NTU, compared to less than 0.5 NTU for the 0.1 and 0.025 μm filtrates. They believed that turbidity blocks the light path when measuring UV absorbance of the 0.45 μm filtrates, resulting in erroneously high absorbance at UV-254. Furthermore, they pointed out that high proportion of COC caused water turbidity and some of the reactive functional groups

in COC were protected by colloids during chlorination. In this study, COC was only a minor fraction (2%) in the secondary effluent and its impact on turbidity was relatively small. This was confirmed by the turbidity of 0.39 NTU for the 0.45 μm filtrate. Thus, similar SUVA and STHMFP were recorded in the 0.45, 0.1, and 0.025 μm filtrates.

2.2 XAD fractionation

Organic carbon was chemically fractionated into five operational fractions: HPO-A, HPO-N, TPI-A, TPI-N, and HPI. The results from Fig.3a showed that HPO-A ranked first in the secondary effluent (37%), whereas HPI ranked second (34%). These two fractions alone constituted as much as 71%. HPO-N, TPI-A, and TPI-N were relatively minor, accounting for 9%, 12% and 8%, respectively.

Percentage distribution of THMFP of each organic fraction is shown in Fig.3b. HPO-A and HPI were the major fractions that contributed THM formation, corresponding to 51% and 24% of total THMFP in the secondary effluent. All other fractions were relatively minor, ranging from 6% to 12%.

To determine the reactivity of each chemical fraction, the STHMFP, which is equal to THMFP divided by the organic carbon concentration, was calculated. HPO-A was observed to give the highest STHMFP at 5.3 mmol/mol. The STHMFP of HPO-N, TPI-A, TPI-N, and HPI had an average of 2.5, 3.7, 3.2, and 2.7 mmol/mol, respectively (Fig.4). The reactivity of HPO-A was significantly higher than other fractions, indicating that this fraction contained more THM precursor. The results followed the trend of relative reactivity among fractions found in other studies: HPO-A $>$ TPI-A $>$ HPI (Owen *et al.*, 1993; Chow *et al.*, 2006).

We further examined SUVA and STHMFP of the chemical fractions. The SUVA sequence of the five fractions in the secondary effluent were HPO-N $>$ HPO-A $>$ TPI-A $>$ TPI-N $>$ HPI whereas the order of STHMFP was observed to be HPO-A $>$ TPI-A $>$ TPI-N $>$ HPI $>$ HPO-N (Fig.4). They were not in good agreement with each other. With respect to chemical fractions, SUVA was also found not to be a good surrogate parameter for monitoring

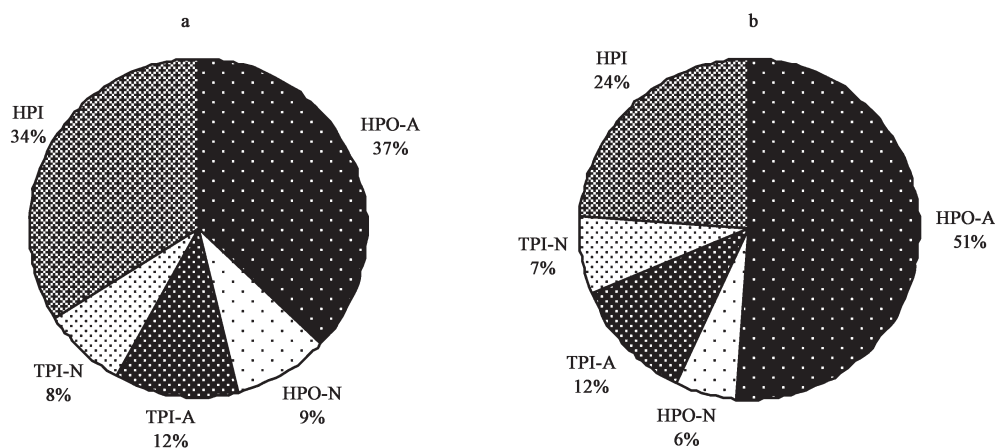


Fig. 3 Distribution of organic fractions from XAD fractionation in organic carbon (a) and THMFP (b). HPO-A: hydrophobic acid; HPO-N: hydrophobic neutral; TPI-A: transphilic acid; TPI-N: transphilic neutral; HPI: hydrophilic fraction.

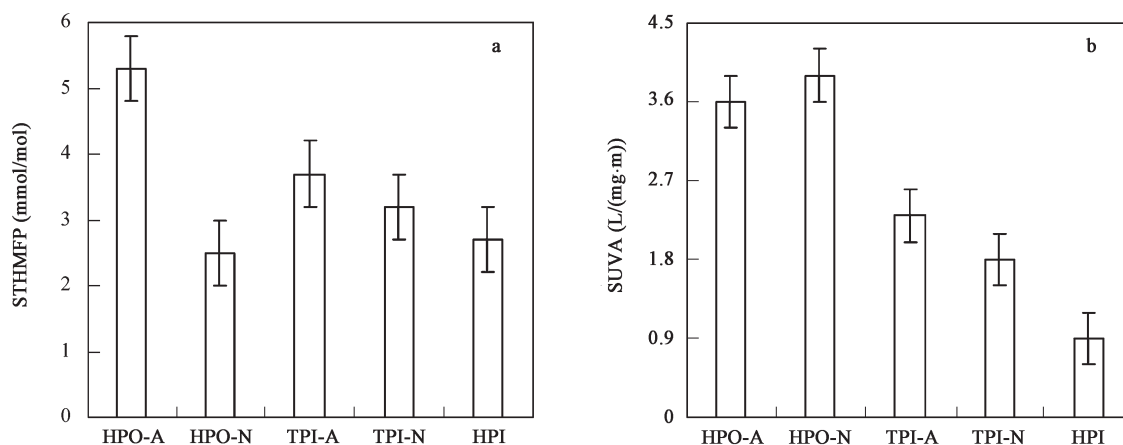


Fig. 4 STHMFP (a) and SUVA (b) of organic fractions from XAD fractionation.

THMFP in this study.

2.3 Structure of organic fractions

2.3.1 Elemental analysis

Elemental analysis is one of the most simple and important means of characterizing organic matter (Ma *et al.*, 2001). Along with some ratios such as H/C, O/C, and N/C, elemental analysis can provide valuable information of composition and possible structure of organic matter. The elemental compositions of these organic fractions and molar ratios calculated from elemental analyses are given in Table 1.

The H/C ratio shows the degree of aromatic condensation and maturity of humic substances (Chai *et al.*, 2007). The molar ratio of H/C increased in the order of HPO-A < HPO-N < TPI-A < TPI-N. The H/C ratio of HPO-A was relatively lower than those of the other fractions, reflecting the fact that HPO-A had more condensed or substituted aromatic ring structures. Steelink (1985) summarized that H/C ratios were clustered around 1.0 for most soil and aquatic humates and fulvates, and ratios above 1.3 might indicate that the material could be a nonhumic substance. The fractions HPO-N, TPI-A, and TPI-N isolated from the secondary effluent were non-humic materials based on this criterion.

The O/C ratio was relatively high for TPI-N as compared to those for the other fractions. This indicates a high content of carboxylic groups or carbohydrates in TPI-N.

Nitrogen content can help identify the source of carbon in organic matter. Aquatic organic matter derived from lignin (plant-derived) is relatively low in N, whereas microbial-derived organic matter is relatively high in N content (Quanrud *et al.*, 2004). The organic fractions isolated from the secondary effluent contained 3.02%–

3.52% of nitrogen. These values were higher than the 0.59%–2.07% reported in the literature for organic fractions isolated from natural waters (Ma *et al.*, 2001). The higher N content in these organic fractions may arise from microbial activity and decay during secondary wastewater treatment. The order of the N/C ratio was observed to be TPI-N > TPI-A > HPO-N > HPO-A. The N/C ratio of TPI-A was significantly higher than for HPO-A. Quanrud *et al.* (2004) reported similar trends for N/C ratios of TPI-A and HPO-A isolated from secondary effluent.

2.3.2 ¹H-NMR spectroscopic analysis

Figure 5 shows the ¹H-NMR spectra of HPO-A, HPO-N, TPI-A, and TPI-N. The spectrum of the method blank had only a large peak with the chemical shift at around 4.95 ppm (i.e. the chemical shift for D₂O). The spectra of the fractions were dominated by broad unresolved humps characteristic of complex mixtures.

In accordance with literature results of assignments for the chemical shift in ¹H-NMR spectra (Peuravuori and Pihlaja, 1998; Ma *et al.*, 2001), the resonance at 0.2–1.48 ppm (H_{A1}) corresponds primarily to methyl and methylene protons of carbons directly bonded to other carbons. The resonance at 1.48–2.92 ppm (H_{A2}) corresponds to methylene and methyne protons α to aromatic rings, or carboxyl and carbonyl groups. The full region, ca. 0.2–2.92 ppm, represents aliphatic protons. The region ca. 2.92–4.21 ppm (H_{R-O}) consists chiefly of protons attached to carbon atoms bound to oxygen. This region may be assigned to protons on carbon of methoxyl, carbohydrate, ether linkages, amino acids, and peptides. The resonance at 6.0–8.5 ppm (H_{Ar}) is generally attributed to aromatic protons including quinones, phenols, and oxygen containing heteroaromatics.

Integration of the peak areas for assessing relative contents (%) of different types of hydrogen atoms (H_{A1} , H_{A2} , H_{R-O} , H_{Ar}) in ¹H-NMR spectra was calculated electronically using Bruker software. Table 2 shows relative abundances of different types of hydrogen obtained for HPO-A, HPO-N, TPI-A, and TPI-N. The ratio of aliphatic to aromatic protons (P_{Ali}/P_{Aro} ratio) is equal to the sum of the percentages of H_{A1} and H_{A2} divided by the percentage of H_{Ar} .

In case of HPO-A, the percentages of H_{A2} and H_{Ar} were

Table 1 Elemental composition and molar ratios for HPO-A, TPI-A, HPO-N and TPI-N

Sample	Elemental composition (wt.%)				Molar ratio		
	C	H	O	N	H/C	O/C	N/C
HPO-A	60.61	6.13	30.13	3.13	1.21	0.37	0.044
HPO-N	46.15	5.01	45.82	3.02	1.30	0.74	0.056
TPI-A	47.09	5.31	44.08	3.52	1.35	0.70	0.064
TPI-N	37.21	4.78	54.67	3.34	1.54	1.10	0.077

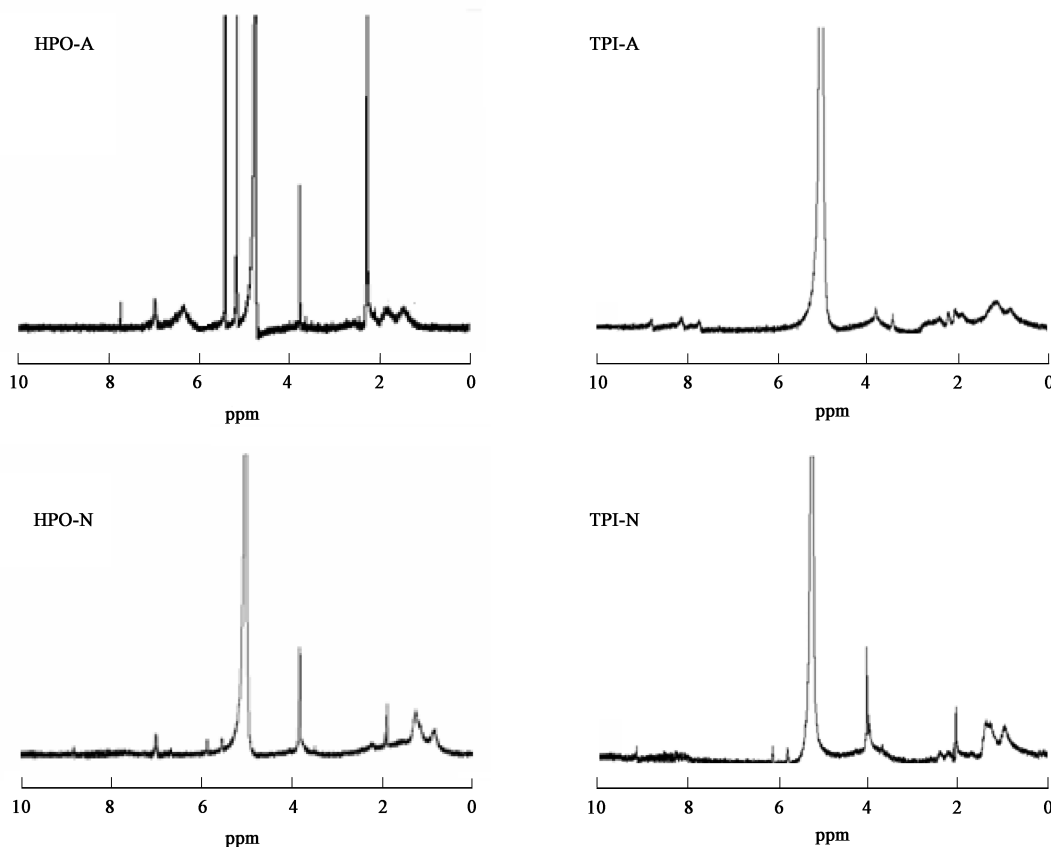


Fig. 5 $^1\text{H-NMR}$ spectra of HPO-A, HPO-N, TPI-A, and TPI-N.

Table 2 Relative abundances of different types of hydrogen

Hydrogen	Relative abundance (%)			
	HPO-A	HPO-N	TPI-A	TPI-N
H_{A1}	17.2	55.9	59.1	65.6
H_{A2}	47.7	20.7	27.6	3.3
H_{R-O}	3.0	16.2	10.8	30.2
H_{Ar}	32.1	7.2	2.5	0.9
P_{Ali}/P_{Aro} ratio	2.0	10.6	34.7	76.6

H_{A1} : methyl and methylene protons of carbons directly bonded to other carbons; H_{A2} : methylene and methyne protons α to aromatic rings, or carboxyl and carbonyl groups; H_{R-O} : protons attached to carbon atoms bound to oxygen; H_{Ar} : aromatic protons including quinones, phenols, oxygen containing heteroaromatics; P_{Ali}/P_{Aro} ratio: the ratio of aliphatic to aromatic protons.

the highest among the organic fractions analyzed (Table 2). Relatively low quantities of H_{A1} were observed in HPO-A and only trace quantities of H_{R-O} . Alternatively, HPO-N, TPI-A, and TPI-N showed relatively higher amounts of H_{A1} and H_{R-O} . In particular, TPI-N showed the highest amounts of H_{A1} and H_{R-O} , but showed the lowest amounts of H_{A2} and H_{Ar} .

Percentages of aliphatic protons ($H_{A1} + H_{A2}$), H_{R-O} , and H_{Ar} of the four fractions were in the range of 64.9%–86.7%, 3.0%–30.2% and 0.9%–32.1%, respectively. The P_{Ali}/P_{Aro} ratio increased in the order: HPO-A < HPO-N < TPI-A < TPI-N (Table 2), indicating the decreasing aromaticity of organic fractions in that order. These results were similar to the trend of H/C ratios obtained by elemental analyses, and therefore it was considered

that a correlation between aromaticity and the degree of humification of organic fractions was indicated.

2.3.3 FT-IR spectroscopic analysis

Infrared spectroscopy has also been widely used for gross characterization of organic matter and can provide valuable information on the structural and functional properties of organic matter molecules (Chen *et al.*, 2002). Interpretation of the absorption bands of organic matter was done as described in the literature (Davis *et al.*, 1999; Lin *et al.*, 2001; Barber *et al.*, 2001; Kim and Yu, 2005). The broad hump in the 3400 cm^{-1} region is due to the presence of OH groups (Fig.6). The bands at $2950\text{--}2850\text{ cm}^{-1}$ are attributed to aliphatic C–H, C–H₂, and C–H₃ stretching. The bands at $1725\text{--}1640\text{ cm}^{-1}$ are attributed to C=O stretching of carboxylic acids. The bands at $1640\text{--}1585\text{ cm}^{-1}$ are attributed to C=O stretching vibration of double bonds in cyclic and alicyclic compounds, ketones, and quinones. The band at 1600 cm^{-1} is attributed to aromatic C=C that are conjugated with C=O or COO⁻. The bands at $1470\text{--}1420$ and $1400\text{--}1390\text{ cm}^{-1}$ are attributed to aliphatic C–H deformation and C–H₂ deformation of C–H₃ groups, respectively. In addition, bands in the $1280\text{--}1137$ and $1090\text{--}1040\text{ cm}^{-1}$ region are attributed to C–O stretching of esters, ethers, and phenols, and C–O stretching of alcoholic compounds.

FT-IR spectra of the four organic fractions, HPO-A, HPO-N, TPI-A, and TPI-N (Fig.6), show rather similar absorption bands because many similar structural and

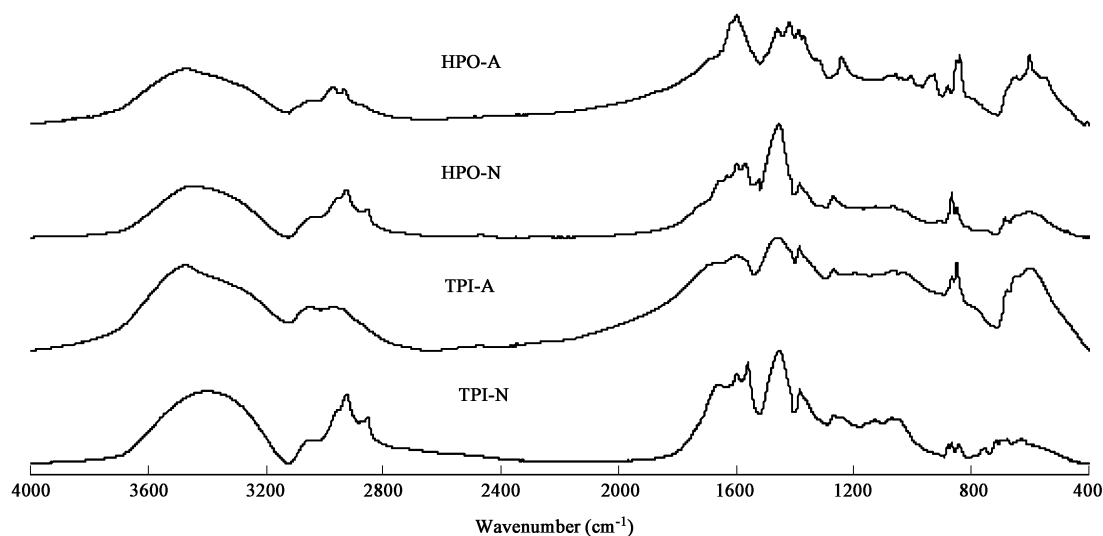


Fig. 6 FT-IR spectra of HPO-A, HPO-N, TPI-A, and TPI-N.

functional groups coexist in these organic matter macromolecules. However, differences in the relative intensity of some specific absorption bands were observed among these organic fractions. The organic fractions HPO-A, HPO-N, TPI-A, and TPI-N were characterized by aliphatic C–H ($2950\text{--}2850\text{ cm}^{-1}$, 1450 cm^{-1} and 1390 cm^{-1}), aromatic C=C (1600 cm^{-1}), C=O ($1640\text{--}1585\text{ cm}^{-1}$), and C–O ($1280\text{--}1137\text{ cm}^{-1}$ and $1090\text{--}1040\text{ cm}^{-1}$) peaks. The aliphatic C–H bands were more pronounced for HPO-N and TPI-N than HPO-A and TPI-A. The aromatic C=C peak was more prominent in HPO-A than in the others, which showed the highest adsorption intensity in the FT-IR spectra of HPO-A. For HPO-N, TPI-A, and TPI-N, the highest adsorption intensity in the FT-IR spectra was the peak at 1450 cm^{-1} . These observations suggest that HPO-A has greater aromatic C=C content whereas HPO-N, TPI-A, and TPI-N has greater aliphatic C–H content. Contrarily, the relative absorption intensity at $1640\text{--}1585\text{ cm}^{-1}$ for TPI-N (in comparison with other absorption bands within the same TPI-N spectrum) was stronger than that for the others. These results again confirm our previous observations that TPI-N was the most abundant in oxygen-containing functional groups as shown by both elemental and $^1\text{H-NMR}$ analyses.

3 Conclusions

Organic carbon in secondary effluent was fractionated by different pore size filters into POC, COC, FCOC, and DOC. Moreover, the $< 0.45\text{ }\mu\text{m}$ fraction was fractionated by XAD resins into HPO-A, HPO-N, TPI-A, TPI-N, and HPI. Results showed that DOC was dominant in terms of total concentration and THMFP, and there was no statistical difference in both STHMFP and SUVA between the 0.45 , 0.1 , and $0.025\text{ }\mu\text{m}$ filtrates. HPO-A had the highest reactivity in forming THM compared to other chemical fractions. The molar ratio of H/C increased in the order of HPO-A $<$ HPO-N $<$ TPI-A $<$ TPI-N. The $P_{\text{Ali}}/P_{\text{Aro}}$ ratio increased in the order of HPO-A $<$ HPO-

N $<$ TPI-A $<$ TPI-N. HPO-A had greater aromatic C=C content whereas HPO-N, TPI-A, and TPI-N had greater aliphatic C–H content. TPI-N was the most abundant in oxygen-containing functional groups.

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