

Molecular transformation of dissolved organic matter in refinery wastewater

Yuguo Li, Chen He, Ze Li, Yuxi Zhang, Baichun Wu and Quan Shi

ABSTRACT

Dissolved organic matter (DOM) has an important impact on the water treatment and reuse of petroleum refinery wastewater. In order to improve the treatment efficiency, it is necessary to understand the chemical composition of the DOM in the treatment processes. In this paper, the molecular composition of DOM in wastewater samples from a representative refinery were characterized. The transformation of various compounds along the wastewater treatment processes was investigated. A total of 61 heteroatomic class species were detected from the DOM extracts, in which CHO (molecules composed of carbon, hydrogen, and oxygen atoms) and CHOS (CHO molecules that also contained sulfur) class species were the most abundant and account for 78.43% in relative mass peak abundance. The solid phase extraction DOM from the dichloromethane unextractable fraction exhibited a more complex molecular composition and contained more oxygen atoms than in the dichloromethane extract. During wastewater treatment processes, the chemical oxygen demand (COD) and ammonia-nitrogen were reduced by more than 90%. Volatile organic compounds (VOCs) accounted for about 30% of the total COD, in which benzene and toluene were dominant. After biochemical treatment, the VOCs were effectively removed but the molecular diversity of the DOM was increased and new compounds were generated. Sulfur-containing class species were more recalcitrant to biodegradation, so the origin and transformation of these compounds should be the subject of further research.

Key words | dissolved organic matter, Fourier transform ion cyclotron resonance mass spectrometry, purge and trap gas chromatography-mass spectrometry, refinery wastewater, solid phase extraction

HIGHLIGHTS

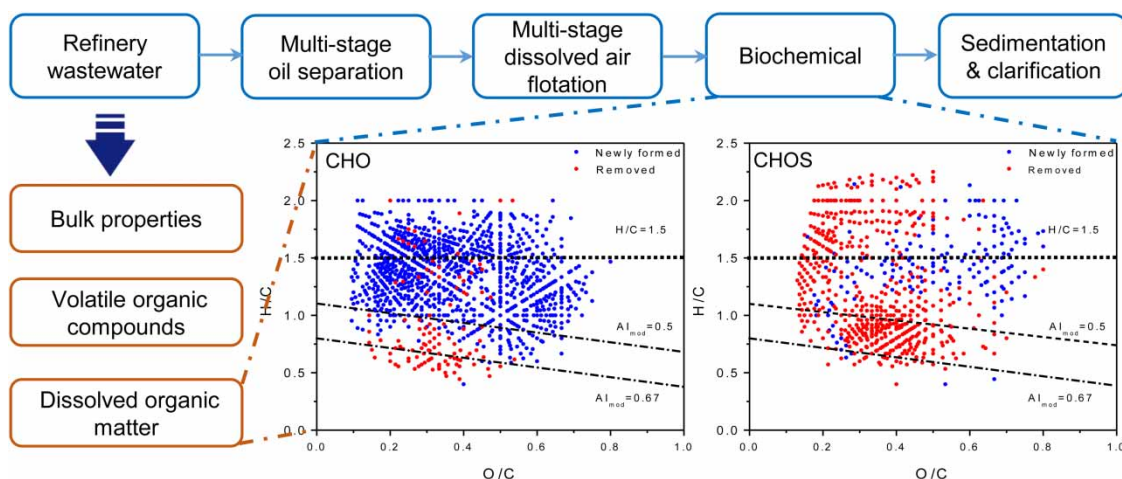
- Chemical composition of DOM in a petroleum refinery wastewater was comprehensively characterized by multiple techniques.
- Molecular composition was characterized by high-resolution mass spectrometry and GC-MS.
- Molecular transformation along the water processing stream was investigated.

Yuguo Li
Ze Li
Yuxi Zhang
Baichun Wu
State Key Laboratory of Petroleum Pollution Control,
CNPC Research Institute of Safety and Environmental Technology,
Beijing 102206,
China

Yuguo Li
Chen He
Quan Shi (corresponding author)
State Key Laboratory of Heavy Oil Processing,
China University of Petroleum,
Beijing 102249,
China
E-mail: sq@cup.edu.cn

Yuxi Zhang
Daqing Oilfield Water Company,
Daqing, Heilongjiang 163454,
China

GRAPHICAL ABSTRACT



INTRODUCTION

There is a growing interest in water reuse in industry because of the increasing water scarcity, droughts, and population numbers. Petroleum-refining operations generate a significant volume of treated wastewater. The wastewater produced by a petroleum refinery contains a complex composition of organic pollutants and is refractory in terms of degradation (Rahman & Al-Malack 2006; Abdelwahab *et al.* 2009; Yang *et al.* 2013; Yan *et al.* 2014). The dissolved organic matter (DOM) in the wastewater causes the coloration and odor of the water and leads to membrane fouling during reclamation treatment. It also affects the removing of metal ions by complexation. Furthermore, DOM can be a major precursor of carcinogenic disinfection by-products (Chon & Cho 2016; Wang & Chen 2018; Komatsu *et al.* 2020).

Refineries generally have many problems relevant to wastewater treatment, such as frequent fluctuations of the operation, low treatment efficiency, and difficulties in recycling water resources (Michael-Kordatou *et al.* 2015). The water quality can be characterized by using machine learning models (Alizadeh *et al.* 2018; Shamshirband *et al.* 2018; Asadi *et al.* 2019), but they cannot provide molecular composition information for pollutants in wastewater.

The removal of DOM depends on the type and amount of organic compounds present (Michael-Kordatou *et al.* 2015). DOM in refinery wastewater includes natural organic matter (NOM) and organic matter produced in petroleum processing (Nebbio & Piccolo 2013; Li *et al.* 2015b).

Some humic-like substances in the DOM are recalcitrant during the wastewater treatment processes (Wang & Chen 2018). Therefore, a better understanding of the chemical composition of DOM in treated wastewater effluents is needed. The analysis of the migration and transformation path of pollutants in the refinery wastewater provides a basis for improving the efficiency of wastewater treatment, optimizing the treatment process, and saving energy.

Bulk properties, such as elemental composition, chemical oxygen demand (COD), total organic carbon (TOC), and biological oxygen demand (BOD), can be used to describe the macroscopic properties of DOM (Diya'uddeen *et al.* 2011). Mass spectrometry techniques, such as gas chromatography-mass spectrometry (GC-MS) (Templier *et al.* 2005; Parsi *et al.* 2007) and liquid chromatography-mass spectrometry (LC-MS) (Reemtsma & These 2005; Mawhinney *et al.* 2009), have been used to analyze the molecular composition and structure of DOM (Janoš 2003; Matilainen *et al.* 2011). With ultra-high mass resolution and mass accuracy, Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) can accurately determine various combinations of the elements C, H, N, O, S and their main isotopes, making it possible to identify the molecular composition of complex compounds based on accurate molecular weight. FT-ICR MS has been used in the research of DOM in seawater (Hansen *et al.* 2019), river water, lake water (Liu *et al.* 2020), groundwater (Valle *et al.* 2020), glacial water (Smith *et al.* 2018; Chen *et al.* 2019a, 2019b) and

so on. FT-ICR MS has been widely used to reveal the molecular composition of DOM in natural aquatic systems (Koch *et al.* 2007; Sleighter & Hatcher 2007; Hertkorn *et al.* 2008), but has received little attention for the characterization of DOM in refinery wastewater treatment systems.

In our previous studies, (Li *et al.* 2015a, 2015b; Fang *et al.* 2017) electrospray ionization (ESI) coupled with FT-ICR MS has been successfully applied to the characterization of the DOM extracted from the refinery wastewater. The refinery was processing heavy crude oil, which produces wastewater containing large amounts of heteroatom oil components and leads to challenges for wastewater treatment.

In this study, a more representative refinery wastewater treatment plant was selected. In addition, a more comprehensive characterization of the molecular composition was conducted. By comparing the COD values of the samples, the proportion of volatile organic compounds (VOCs) in the pollutants can be judged macroscopically. The species and content of VOCs were directly characterized by purge and trap gas chromatography-mass spectrometry (P&T-GC-MS). In addition, the wastewater samples were separated into the organic phase and the aqueous phase and then characterized by negative-ion ESI FT-ICR MS. The purpose of this study was to investigate the molecular transformation of DOM in wastewater from a refinery to provide an overall assessment and guidance for the design and improvement of wastewater treatment process.

EXPERIMENTAL SECTION

Samples

Wastewater samples were obtained from a PetroChina refinery, which is one of the largest refineries in China.

In contrast to the refineries that we have previously studied (Li *et al.* 2015a, 2015b), this refinery processes light crude oil. Figure 1 shows the flow chart of the refinery wastewater treatment processes. The whole treatment consists of oil separation, dissolved air flotation, biochemical degradation and sedimentation, which represent the typical refinery wastewater treatment process. The oil separations include a DCI (Degremont® circular interceptor) separator and an API (America Petroleum Institute) separator. The two step flotations are both dissolved air flotation. The biodegradation is an anaerobic-anoxic-oxic (A2/O) system.

Samples #1–8 were sampled from the plant in April 2018 and filtered in laboratory with a 0.45 µm Pall Supor membrane, then kept in dark at 4 °C before analysis. Samples #1: raw wastewater; #2: effluent from oil separation; #3: effluent from the dissolved air flotation; #4: effluent after the secondary de-oiling; #5: effluent from the secondary flotation; #6: effluent after the biochemical degradation and sedimentation; #7: effluent from the secondary sedimentation; and #8: final discharge export.

Sample preparation

Figure 2 shows the scheme of sample preparation and characterization. The refinery wastewater (300 mL) was extracted with 50 mL of dichloromethane (DCM) which had been purified by distillation with a spinning-band distillation apparatus (B/R 9600, B/R Instrument Corp, USA). The DCM extracts were combined together and the organic phase DOM was obtained by removing DCM in a rotary evaporator. DOM in the aqueous phase was further extracted with an SPE cartridge (Li *et al.* 2015a). Briefly, the SPE cartridge (Agilent, Bond Elut PPL, 500 mg, 6 mL, USA) was rinsed with 20 mL methanol (purified by distillation before use) followed by 20 mL

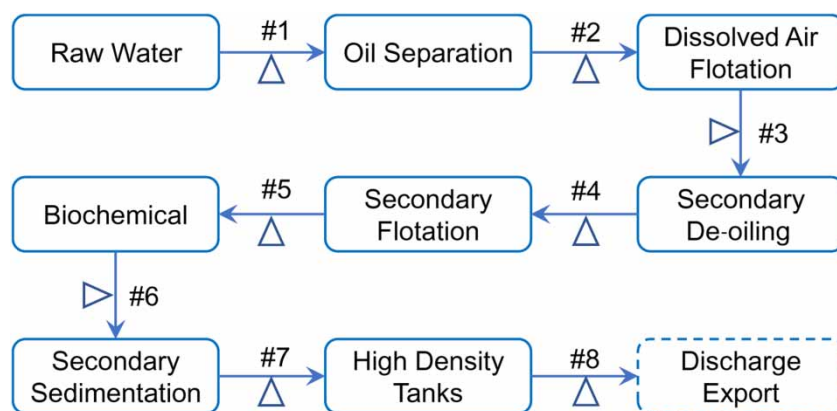


Figure 1 | Flowchart of the refinery wastewater treatment processes and sampling sites of this study.

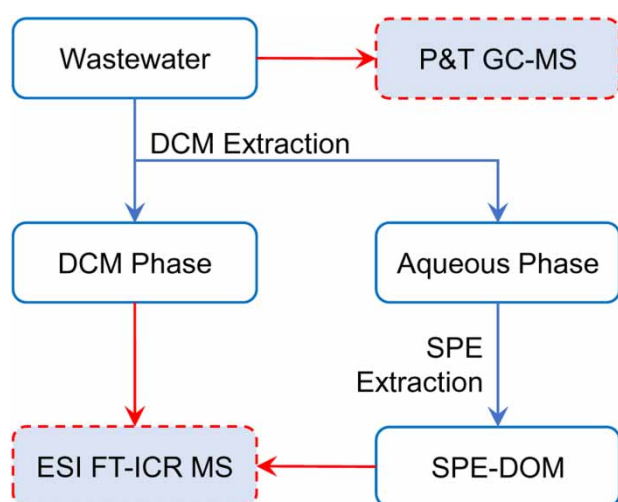


Figure 2 | Schematic diagram for DOM analyses of the refinery wastewater.

acidified ultrapure water (pH = 2, LC-MS grade). Then, the wastewater was acidified to pH = 2 with HCl (ACS, Merck, Germany) and then injected into the cartridge. Next, the cartridge was washed with 20 mL acidified ultrapure water to remove the salt and then dried with N₂ gas flow. Finally, the adsorbed DOM was eluted out of the cartridge with 10 mL methanol and stored at -18 °C in the dark.

COD and NH₃-N analysis

The COD and NH₃-N of all eight samples were analyzed with the U.S. Environmental Protection Agency digestion colorimetry of HACH[®] standard method. This method has the advantages of being quick and easy, giving accurate measurements, and having low reagent consumption.

After sufficient aeration, each sample was tested for three sets of parallel samples to obtain an average value. The average values of eight samples before and after aeration are shown in Table S1 (see Supplementary Information).

P&T GC-MS analysis

The P&T process was conducted using an Atomx 15-0000-200 automatic purge-capture sampling device (Teledyne Tekmar, USA). Operating conditions were as follows: valve oven temperature: 140 °C; transfer line temperature: 140 °C; sample mount temperature: 90 °C; water heater temperature: 90 °C; purge time: 11.0 min; purge flow 40 mL/min.

The VOCs in the refinery wastewater samples were analyzed with an Agilent 6890N gas chromatograph coupled with a 5975C mass spectrometer. A DB-5 MS UI column (60 m × 0.25 mm × 1.0 μm, Agilent, USA) was used. The

inlet temperature was 260 °C. The initial column temperature of the GC oven was programmed to rise from 40 °C to 260 °C at a rate of 5 °C/min, then held constant at 260 °C for 3 min. Helium (purity >99.999) was used as the carrier gas at a flow rate of 1 mL/min with a split ratio of 20:1. The 70 eV electron impact ion source was operated at a temperature of 235 °C; the quadrupole was running in full scan mode with a mass range of *m/z* 30–300 in a 1 second scan period.

Negative-ion ESI FT-ICR MS analysis

The DOM was analyzed using a Bruker Apex Ultra FT-ICR mass spectrometer equipped with a 9.4 T superconducting magnet. The Apollo II electrospray ion source was running in negative mode. The separated organic and aqueous phase SPE-DOM dissolved in methanol (50 mg/mL) were introduced by a syringe pump through the electrospray source at a rate of 250 μL/h. The typical operating conditions were: spray shield voltage, 3.8 kV; capillary column introduced voltage, 4.3 kV; capillary column end voltage, -300 V. The data size was set to 2 M words over a mass range of *m/z* 200–700. In order to enhance the signal-to-noise ratio and dynamic range, a data set of 128 FT-ICR scans were accumulated.

The mass calibration and data acquisition of FT-ICR MS have been described elsewhere (Shi *et al.* 2010; Pan *et al.* 2020). Data analysis was performed by using in-house software. Mass peaks with a signal-to-noise ratio ≥6 were considered for molecular formula assignment. The average mass error of all assigned molecular formulas was less than 1 ppm. To obtain semi-quantitative results, 5 × 10⁻⁶ mol/L equal deuterated stearic acid (C₁₈D₃₅H₁O₂) was added to each DOM sample as an internal standard. The peak intensity of each identified molecular formula was normalized to the internal standard in each sample. The ratio of intensity of each peak to the internal standard was defined as the relative abundance. The elemental combinations of molecular formulas were limited to those containing ¹²C₀₋₁₀₀, ¹H₂₋₂₀₀, ¹⁴N₀₋₃, ¹⁶O₀₋₃₀, and ³²S₀₋₄ atoms.

FT-ICR MS data related parameters integration were as follows: A modified aromaticity index (AI_{mod}) and double bond equivalents (DBE) were calculated for each assigned molecular formula according to Koch and Dittmar (Koch & Dittmar 2006). The intensity-weighted average of molecular formulas (CHO, CHON, CHOS, CHONS, i.e. molecules composed with carbon, hydrogen, and oxygen atoms, plus nitrogen, sulfur, or nitrogen and sulfur), and other parameters (hydrogen/carbon ratio (H/C), oxygen/carbon ratio (O/C), DBE, and AI_{mod}) were calculated for each SPE-DOM sample (Fang *et al.* 2019). Compound classification were

defined by aromaticity index (AI) and elemental ratios (O/C and H/C) (Dittmar & Koch 2006; Kellerman *et al.* 2014): Saturated compounds ($H/C > 2$), aliphatic compounds ($2.0 \geq H/C > 1.5$) (Li *et al.* 2018), highly unsaturated and phenolic compounds ($AI < 0.50$, $H/C < 1.5$), polyphenol-like compounds ($0.66 \geq AI \geq 0.50$), and polycyclic aromatic-like compounds ($AI \geq 0.66$) (Liu *et al.* 2010).

RESULTS AND DISCUSSION

Bulk properties

The COD and NH_3-N values of the samples are listed in Table 1. TOC is not listed because it was hard to obtain a credible value due to the high inorganic carbon present in the raw water and the loss of volatile compounds in the analysis. The COD values are lower than in refinery wastewater (Xia *et al.* 2000; Chao *et al.* 2019) and coal gasification wastewater (Fang *et al.* 2019; Wang *et al.* 2019), but are similar to chemical wastewater (Guan *et al.* 2019; Xia & Xia 2019; Zhang *et al.* 2019a, 2019b, 2019c) and domestic sewage (Lu *et al.* 2019).

The organic matter content in the wastewater is low compared to other refinery wastewater because the refinery processes light crude oil. The raw wastewater COD was controlled below 500 mg/L. In the whole process, the most effective way to remove COD was biochemical treatment. After a series of treatment processes, the COD and NH_3-N of effluent were about 30 mg/L and 0.01 mg/L. During the wastewater treatment processes, the COD and NH_3-N reduced by more than 90%. The effluent met the requirement of the Emission Standard of Pollutants for the Petroleum Chemistry Industry GB31571-2015 (China), in which the COD is less than 60 mg/L.

Characterization of VOCs by P&T GC-MS

Numerous VOCs have been confirmed as human carcinogens. Owing to the collection and treatment of wastewater, wastewater treatment plants have been identified as a primary VOC emission source (Cheng & Chou 2003). VOCs are defined as compounds having a boiling point of 50–250 °C

and a relatively low molecular weight. Table S1 (see Supplementary Information) shows the changes in COD before and after aeration. The COD value decreased by about 1/3 in the processing and VOCs in the refinery wastewater accounted for about 30% of the total COD contribution.

Figure 3 shows the total ion chromatograms of the VOCs of the wastewater. A total of 215 individual compounds, including alkanes, alkenes, alkynes, aromatic hydrocarbons, polycyclic aromatic hydrocarbons, organic phenols, alcohols, ketones, esters, thioethers, and thiophenes (see Supplementary Information Table S2) were tentatively identified. The most abundant compounds were benzene and toluene, followed by acetone and methyl ethyl ketone. Relative contents of benzene, toluene, 2-butanone, and acetone were 23.03%, 21.23%, 12.16%, and 9.55%, respectively. Alkanes were removed after air flotation. No VOCs were detected after biochemical treatment. It shows that most of the VOCs can be removed by sufficient aeration, biodegradation, and sludge interception (Malakar *et al.* 2017; Zhang *et al.* 2019a, 2019b, 2019c). The VOC concentration distribution was very similar to that assessed in the literature (Cheng & Chou 2003).

Molecular characterization of DCM-extracted DOM by FT-ICR MS

DCM-extracted DOM was characterized by negative-ion ESI, and a molecular weight distribution range of 200–600 was observed in the mass spectra (see Figure S1 in the Supplementary Information). Weakly polar and non-polar compounds are mainly present in the DCM phase. There are very few mass spectral peaks in the DCM phase compared to the aqueous phase. There were 349 molecular formulas in the raw wastewater, but 3,645 molecular formulas were detected after biochemical treatment. An increase was shown in the number of peaks after biochemical treatment, indicating the increase in molecular diversity after biochemical treatment (Chen *et al.* 2014a, 2014b, 2015).

Figure 4 shows the semi-quantitative relative abundance of class species identified in the DCM phase DOM, including O_2-O_9 , $N_1O_2-N_1O_8$, $N_2O_2-N_2O_7$, $O_3S_1-O_7S_1$ and $N_1O_3S_1-N_1O_7S_1$. The vertical coordinate represents the sum of the intensity of different DBEs of a compound. The O_2 and O_3S_1 class species were dominant in all wastewater samples. The O_2 compounds had the highest abundance in biochemical processes, presumably due to hydrocarbon oxidation in biochemical processes (Wang *et al.* 2014; Zhang *et al.* 2019a, 2019b, 2019c; Zhao *et al.* 2019). The O_3S_1 class species with four DBEs could be an alkylbenzene sulfonic

Table 1 | COD and NH_3-N of the wastewater (mg/L)

Samples	#1	#2	#3	#4	#5	#6	#7	#8
COD	442	482	413	376	361	51	44	30
NH_3-N	37.8	53.0	40.5	28.6	26.3	2.9	0.33	0.01

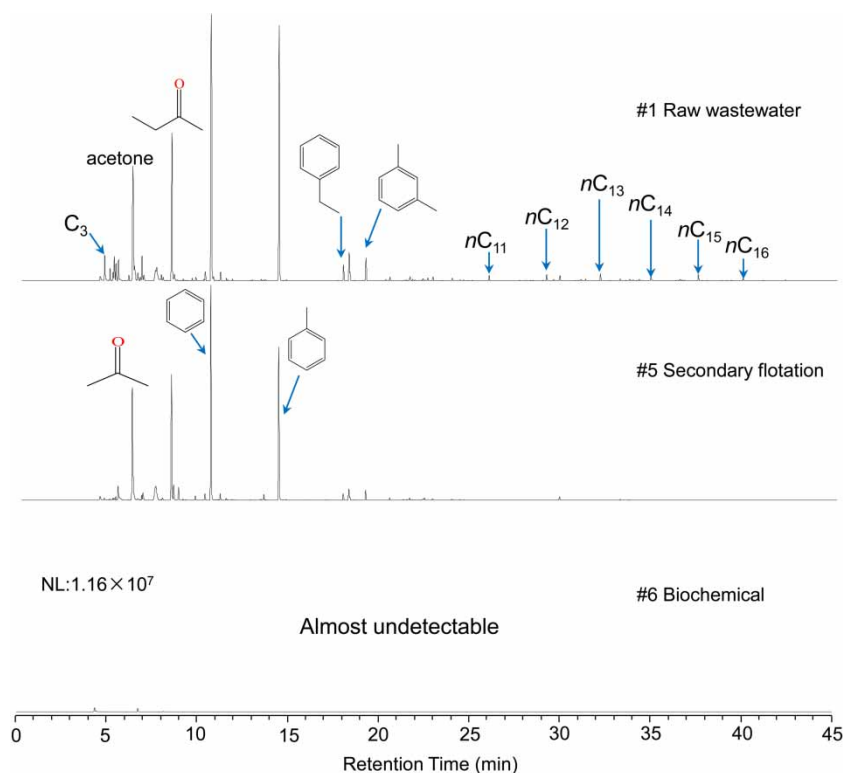


Figure 3 | Total ion GC-MS chromatograms of the VOCs in the wastewater.

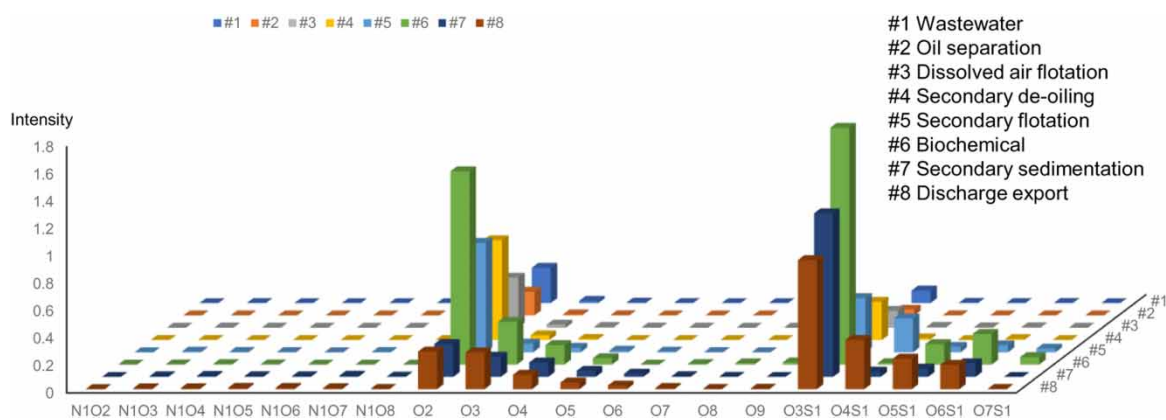


Figure 4 | Relative abundance of heteroatom class species of the DOM in the DCM phase for eight refinery wastewaters obtained by negative-ion ESI FT-ICR MS.

acid (Li *et al.* 2015a). It was likely to be derived from an alkylbenzene sulfonate plasma surfactant (Gonsior *et al.* 2011; Geng *et al.* 2018). The relative abundance of O₃S₁ class species increased significantly in oil separation, air flotation and biochemical treatment, but decreased after the second sedimentation plant. It is speculated that the flocculants partially adsorb the surfactants in the secondary sedimentation tank (Alizadeh *et al.* 2017; Duggan *et al.* 2019; Shende & Chau 2019). The reason for the increase is the easily ionized

selectivity of ESI for surfactants or microbial production during biodegradation (Mohamed *et al.* 2015; Phungsai *et al.* 2016; Song *et al.* 2018).

Molecular characterization of aqueous phase DOM by FT-ICR MS

DOM is rich in oxygen-containing polar compounds, which is suitable for characterization by negative-ion ESI (Pan *et al.*

2020). Figure S2 (see Supplementary Information) shows the broad-band ESI FT-ICR mass spectra of the aqueous phase DOM. The abundant peaks with m/z 297, 311, and 325 in the mass spectra of #1 to #5 were assigned as O_3S_1 classes with four DBEs, which is presumed to be an alkyl-benzene sulfonic acid surfactant (Bahri et al. 2018; Geng et al. 2018). In addition, the dominant peaks with m/z values greater than 440 in the mass spectrum of #6 were identified as polymers. The molecular weights of these polymer molecules differ by 44 Da, which corresponds to polyoxyethylene ether (Pei et al. 2016; Cadar et al. 2017; Fedela et al. 2018; Chen et al. 2019a, 2019b). They were flocculated by flocculants after the second sedimentation plant.

Figure 5 shows the relative abundance of compounds assigned in the mass spectra of the aqueous phase DOM. A total of 61 compound classes were detected in the negative-ion ESI FT-ICR mass spectra for each wastewater sample, including O_{2-15} , N_1O_{2-13} , N_2O_{3-12} , $O_{3-15}S_1$ and $N_1O_{3-12}S_1$ class species. The type of polar compounds was consistent with other refineries (Li et al. 2015a, 2015b; Fang et al. 2019). The relative abundance of all class species in petrochemical refinery wastewater decreases with the overall treatment processes. But traditional biological treatment of refractory wastewater has a low efficiency (Chen et al. 2014a). It can effectively remove small molecular hydrocarbons (Tran et al. 2015), whereas some organic contaminants with high molecular weight and complex molecular structure are found to be difficult to remove (Dai et al. 2016). The compounds with many oxygen atoms may include hydrophilic chemical groups such as carboxyl and phenol groups, which are commonly identified under

negative-ion ESI mode (Shon et al. 2006; Shi et al. 2010). For CHOS class species, the O_3S_1 class species was dominant and almost removed by the biochemical treatment.

The relative abundance of the CHON class and the CHONS class of all eight wastewater samples are shown in Figures S3 and S4 (see Supplementary Information). The relative abundance of OxS_1 , N_1OxS_1 class species decreased gradually with the treatment process, implying each step of the treatment was effective for sulfur-containing compounds (Geng et al. 2018; Fang et al. 2019). The relative abundance of Ox and N_1Ox class species decreased after de-oiling and flocculation but increased after biochemical treatment.

To compare the composition of DOM in the aqueous phase of all eight samples, the percentage contributions of individual compound classes normalized to the total ion signals were calculated and are presented in Table 2. In the raw wastewater, CHO and CHOS classes were the most abundant and accounted for 78.43% in terms of relative abundance. Molecular formulas totaling 3,501 to 5,012 were found in the eight refinery samples (Table 2). CHOS class species were found in all samples, which accounted for 21.94%–45.90% of all assigned molecular formulas and showed a decreasing trend during the water treatment processes. From #1 to #5, CHOS species accounted for a higher proportion than CHO species. After biochemical treatment, CHO species accounted for the highest proportion (29.67%–46.73%) but CHOS class species were reduced. These compounds may come from the oil feed itself and can be effectively removed (Fang et al. 2019). The AIs of CHOS and CHO species are 0.20–0.29 and 0.28–0.43, respectively.

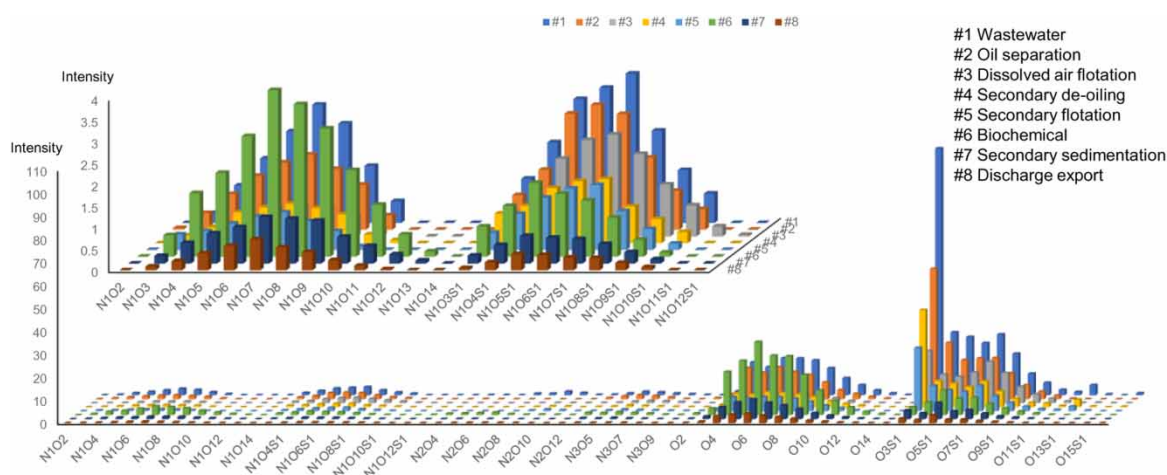


Figure 5 | Relative abundance of assigned classes of DOM in the aqueous phase from the refinery wastewater.

Table 2 | Molecular formulas assigned from ESI FT-ICR mass spectra of DOM in the aqueous phase and their average H/C, O/C, DBE, AI and percentage

Sample	Type	Number	H/C _{avg}	O/C _{avg}	DBE _{avg} ^a	AI _{avg} ^b	Percentage
#1	CHO	1,340	1.21	0.37	8.37	0.36	38.27
	CHON	341	1.13	0.38	9.24	0.44	9.74
	CHOS	1,406	1.46	0.29	5.71	0.22	40.16
	CHONS	414	1.19	0.38	8.27	0.36	11.83
	Total	3,501	1.37	0.32	6.65	0.27	100
#2	CHO	1,692	1.21	0.35	8.41	0.37	39.87
	CHON	477	1.13	0.36	9.54	0.44	11.24
	CHOS	1,504	1.52	0.30	5.31	0.20	35.44
	CHONS	571	1.22	0.36	8.34	0.35	13.45
	Total	4,244	1.39	0.32	6.56	0.27	100
#3	CHO	1,126	1.09	0.39	9.33	0.43	29.67
	CHON	268	1.02	0.39	10.21	0.51	7.06
	CHOS	1,742	1.32	0.35	7.00	0.29	45.90
	CHONS	659	1.11	0.40	9.22	0.41	17.36
	Total	3,795	1.25	0.36	7.69	0.33	100
#4	CHO	1,405	1.18	0.36	8.59	0.38	37.81
	CHON	374	1.11	0.37	9.53	0.45	10.06
	CHOS	1,453	1.43	0.29	5.96	0.24	39.10
	CHONS	484	1.22	0.37	8.15	0.35	13.02
	Total	3,716	1.35	0.32	6.89	0.29	100
#5	CHO	1,385	1.23	0.36	8.12	0.35	37.77
	CHON	346	1.16	0.36	8.90	0.43	9.44
	CHOS	1,469	1.41	0.32	6.15	0.24	40.06
	CHONS	467	1.21	0.38	8.12	0.35	12.74
	Total	3,667	1.34	0.33	6.92	0.29	100
#6	CHO	2,317	1.33	0.37	7.46	0.28	46.73
	CHON	1,137	1.24	0.41	8.47	0.35	22.93
	CHOS	1,088	1.33	0.38	6.46	0.25	21.94
	CHONS	416	1.31	0.38	6.89	0.28	8.39
	Total	4,958	1.32	0.38	7.36	0.28	100
#7	CHO	2,146	1.29	0.35	7.87	0.31	42.82
	CHON	1,047	1.24	0.40	8.62	0.35	20.89
	CHOS	1,293	1.33	0.34	6.82	0.26	25.80
	CHONS	526	1.23	0.38	7.94	0.33	10.49
	Total	5,012	1.30	0.35	7.61	0.30	100
#8	CHO	1,992	1.30	0.33	7.92	0.31	41.23
	CHON	1,036	1.18	0.39	9.07	0.41	21.44
	CHOS	1,253	1.30	0.32	7.29	0.29	25.94
	CHONS	550	1.23	0.40	8.03	0.33	11.38
	Total	4,831	1.29	0.34	7.85	0.31	100

^aDBE values were defined as: $DBE = C - 1/2H + 1/2N + 1$.

^bAI was the aromaticity index values and determined as: $AI = [1 + C - 1/2O - S - 1/2H] / [C - 1/2O - S - N - P]$ (Kim *et al.* 2003; Stenson *et al.* 2003; Koch & Dittmar 2016).

The van Krevelen (VK) diagram is usually used to illustrate the difference in molecular composition between wastewaters (Koch & Dittmar 2006; Sleighter & Hatcher 2007; Seidel *et al.* 2014; Yuan *et al.* 2017). Figure S5 (see Supplementary Information) shows the VK diagrams of CHO class species for the aqueous phase DOM of all eight samples. Colors represent different relative intensities. The darker the color, the greater the intensity. The peak intensity of each identified molecular formula was normalized to the peak intensity of the internal standard in each sample. The result can be drawn from the distribution of the different dots in the VK diagrams: (1) The range of O/C ratio of CHO compounds was 0.1–0.8 and the H/C ratio was 0.4–2.0. Distribution ranges of CHON, CHOS, and CHONS compounds were 0.1–0.8 O/C with 0.4–1.8 H/C, 0.1–0.8 O/C with 0.5–2.3 H/C, and 0.15–0.75 O/C with 0.5–2.1 H/C, respectively (Figures S6, S7, S8). CHOS compounds were widely distributed in the VK diagram (Figure S7). (2) The O/C ratio of CHO after biochemical treatment (#6) showed the widest distribution (0.1–0.8), implying that biochemical treatment increased the molecular composition diversity (Chen *et al.* 2014a, 2014b, 2015). (3) The H/C > 1.5 species, which correspond to lipids, proteins, and carbohydrates in natural DOM, decreased after biochemistry (Herzprung *et al.* 2012; Šantl-Temkiv *et al.* 2013; Antony *et al.* 2014; Feng *et al.* 2016).

The molecular transformation during specific water treatment processes was further assessed by comparing which molecular formulas were formed or removed. The molecular changes during oil separation, air flotation and biochemical treatment were plotted in VK diagrams, as shown in Figure 6. For CHO class species, the area of O/C lower than 0.5 were

removed but the area of H/C higher than about 1.5 were produced after biochemical treatment. The newly formed compounds included aliphatic compounds ($2.0 \geq \text{H/C} > 1.5$) and highly unsaturated and phenolic compounds ($\text{AI} < 0.50$, $\text{H/C} < 1.5$). In the meantime, polyphenol-like compounds ($0.66 \geq \text{AI} \geq 0.50$) and polycyclic-aromatic-like compounds ($\text{AI} \geq 0.66$) were removed. This shows that the biochemical process converts some CHO compounds with high AI values into phenols and aliphatic compounds (Dai *et al.* 2016). In contrast, for CHOS species, the biochemically removed molecules mainly had an O/C lower than 0.5 and the molecules produced were mainly in the range of O/C higher than about 0.5. The compounds removed after the biochemical process included aliphatic compounds ($2.0 \geq \text{H/C} > 1.5$), highly unsaturated and phenolic compounds ($\text{AI} < 0.50$, $\text{H/C} < 1.5$), polyphenol-like compounds ($0.66 \geq \text{AI} \geq 0.50$) with lower O/C. But aliphatic compounds ($2.0 \geq \text{H/C} > 1.5$), highly unsaturated and phenolic compounds ($\text{AI} < 0.50$, $\text{H/C} < 1.5$) with higher O/C were formed. This shows that the biochemical process removed some CHOS compounds with low oxygen numbers.

CONCLUSIONS

The DOM in refinery wastewater had a complex molecular composition, in which the small molecular VOCs accounted for about 30% of the total dissolved organic carbon. In the long processing stream, biochemical treatment was the most effective, removing more than 90% of COD and $\text{NH}_3\text{-N}$. A total of 61 heteroatomic class species were detected in the DOM extracts, in which

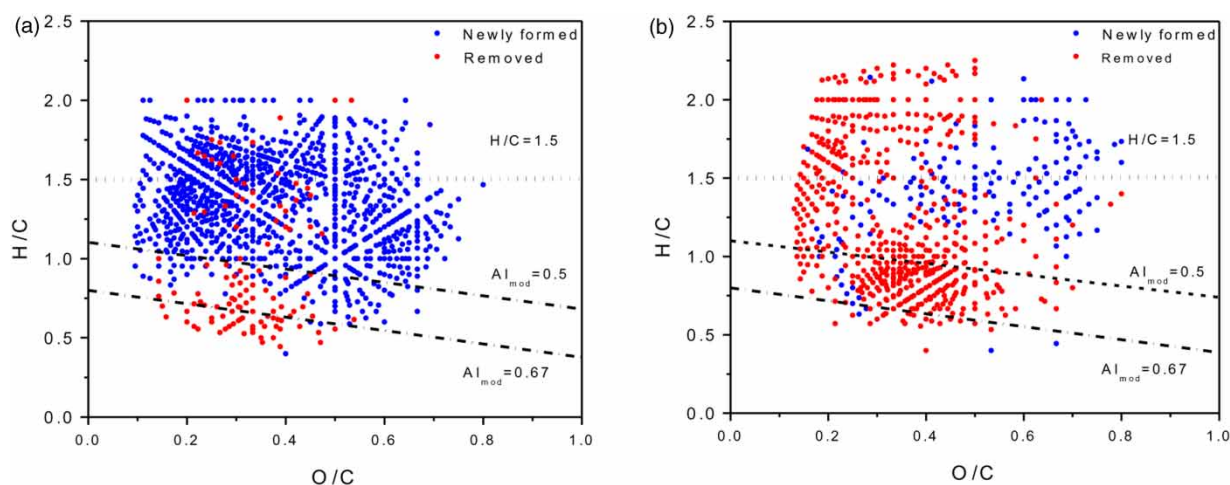


Figure 6 | VK diagrams of removed and newly formed CHO (a) and CHOS (b) molecular formulas in the aqueous phase of the biochemical treatment process.

CHO and CHOS class species were the most abundant and accounted for 78.43% in relative abundance. The SPE-DOM from the DCM unextractable fraction exhibited a more complex molecular composition and contained more oxygen atoms than that in the DCM extract. After biochemical treatment, the VOC was effectively removed but the molecular diversity of the DOM was increased and new compounds were generated. Sulfur-containing class species were more recalcitrant to biodegradation. To develop and optimize the technique for wastewater processing, molecular selectivity of various compounds for the process should be considered. Further quantitative analysis and structure characterization of the DOM molecules in refinery wastewater is needed.

ACKNOWLEDGEMENTS

This study was supported by the Open Project Program of the State Key Laboratory of Petroleum Pollution Control (Grant No. PPC2018012) and under the institute's basic science research and strategic reserve technology research fund (2017D-5008), CNPC Research Institute of Safety and Environmental Technology.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

REFERENCES

- Abdelwahab, O., Amin, N. K. & El-Ashtoukhy, E. S. 2009 [Electrochemical removal of phenol from oil refinery wastewater](#). *Journal of Hazardous materials* **163** (2–3), 711–716.
- Alizadeh, M. J., Jafari Nodoushan, E., Kalarestaghi, N. & Chau, K. W. 2017 [Toward multi-day-ahead forecasting of suspended sediment concentration using ensemble models](#). *Environmental Science and Pollution Research International* **24** (36), 28017–28025.
- Alizadeh, M. J., Kavianpour, M. R., Danesh, M., Adolf, J., Shamsirband, S. & Chau, K.-W. 2018 [Effect of river flow on the quality of estuarine and coastal waters using machine learning models](#). *Engineering Applications of Computational Fluid Mechanics* **12** (1), 810–823.
- Antony, R., Grannas, A. M., Willoughby, A. S., Sleighter, R. L., Thamban, M. & Hatcher, P. G. 2014 [Origin and sources of dissolved organic matter in snow on the East Antarctic ice sheet](#). *Environmental Science and Technology* **48** (11), 6151–6159.
- Asadi, E. I. M., Samadianfard, S., Ramli, M. F., Mosavi, A., Nabipour, N., Shamsirband, S., Hajnal, E. & Chau, K.-W. 2019 [Groundwater quality assessment for sustainable drinking and irrigation](#). *Sustainability* **12** (1), 177.
- Bahri, M., Mahdavi, A., Mirzaei, A., Mansouri, A. & Haghghat, F. 2018 [Integrated oxidation process and biological treatment for highly concentrated petrochemical effluents: a review](#). *Chemical Engineering and Processing – Process Intensification* **125**, 183–196.
- Cadar, D., Olteanu, N. L., Rogozea, E. A., Petcu, A. R., Meghea, A. & Mihaly, M. 2017 [Recovery of targeted hydrophilic compounds from simulated wastewaters using nonionic microemulsion systems](#). *Process Safety and Environmental Protection* **109**, 648–658.
- Chao, L., Meng, J., Wang, H. & Li, Y. 2019 [Comparative study of three filler modified A/O processes for refinery wastewater treatment](#). *Thchnology of Water Treatment* **45** (8), 103–107.
- Chen, C., Chen, H., Guo, X., Guo, S. & Yan, G. 2014a [Advanced ozone treatment of heavy oil refining wastewater by activated carbon supported iron oxide](#). *Journal of Industrial and Engineering Chemistry* **20** (5), 2782–2791.
- Chen, C., Wei, L., Guo, X., Guo, S. & Yan, G. 2014b [Investigation of heavy oil refinery wastewater treatment by integrated ozone and activated carbon-supported manganese oxides](#). *Fuel Processing Technology* **124**, 165–173.
- Chen, C., Yoza, B. A., Chen, H., Li, Q. & Guo, S. 2015 [Manganese sand ore is an economical and effective catalyst for ozonation of organic contaminants in petrochemical wastewater](#). *Water, Air, & Soil Pollution* **226** (6), 2–11.
- Chen, M., Li, C., Zeng, C., Zhang, F., Raymond, P. A. & Hur, J. 2019a [Immobilization of relic anthropogenic dissolved organic matter from alpine rivers in the Himalayan-Tibetan Plateau in winter](#). *Water Research* **160**, 97–106.
- Chen, Y., Wang, C., Dong, S., Jiang, L., Shi, Y., Li, X., Zou, W. & Tan, Z. 2019b [Microbial community assembly in detergent wastewater treatment bioreactors: influent rather than inoculum source plays a more important role](#). *Bioresource Technology* **287**, 121467.
- Cheng, W. H. & Chou, M. S. 2003 [VOC emission characteristics of petrochemical wastewater treatment facilities in southern Taiwan](#). *Journal of Environmental Science and Health, Part A: Toxic/Hazardous Substances & Environmental Engineering* **38** (11), 2521–2535.
- Chon, K. & Cho, J. 2016 [Fouling behavior of dissolved organic matter in nanofiltration membranes from a pilot-scale drinking water treatment plant: an autopsy study](#). *Chemical Engineering Journal* **295**, 268–277.
- Dai, X., Chen, C., Yan, G., Chen, Y. & Guo, S. 2016 [A comprehensive evaluation of re-circulated bio-filter as a pretreatment process for petroleum refinery wastewater](#). *Journal of Environmental Sciences (China)* **50**, 49–55.
- Dittmar, T. & Koch, B. P. 2006 [Thermogenic organic matter dissolved in the abyssal ocean](#). *Marine Chemistry* **102** (3–4), 208–217.

- Diya'uddeen, B. H., Wan Daud, W. M. A. & Abdul Aziz, A. R. 2011 Treatment technologies for petroleum refinery effluents: a review. *Process Safety and Environmental Protection* **89** (2), 95–105.
- Duggan, K. L., Morris, M., Bhatia, S. K., Khachan, M. M. & Lewis, K. E. 2019 Effects of cationic polyacrylamide and cationic starch on aquatic life. *Journal of Hazardous, Toxic, and Radioactive Waste* **23** (4), 04019022.
- Fang, Z., He, C., Li, Y. Y., Chung, K. H., Xu, C. M. & Shi, Q. 2017 Fractionation and characterization of dissolved organic matter (DOM) in refinery wastewater by revised phase retention and ion-exchange adsorption solid phase extraction followed by ESI FT-ICR MS. *Talanta* **162**, 466–473.
- Fang, Z., Li, L., Jiang, B., He, C., Li, Y., Xu, C. & Shi, Q. 2019 Molecular composition and transformation of dissolved organic matter (DOM) in coal gasification wastewater. *Energy & Fuels* **33** (4), 3003–3011.
- Fedeila, M., Hachaichi-Sadouk, Z., Bautista, L. F., Simarro, R. & Nateche, F. 2018 Biodegradation of anionic surfactants by *Alcaligenes faecalis*, *Enterobacter cloacae* and *Serratia marcescens* strains isolated from industrial wastewater. *Ecotoxicology and Environment Safety* **163**, 629–635.
- Feng, L., Xu, J., Kang, S., Li, X., Li, Y., Jiang, B. & Shi, Q. 2016 Chemical composition of microbe-derived dissolved organic matter in cryoconite in Tibetan plateau glaciers: insights from Fourier transform ion cyclotron resonance mass spectrometry analysis. *Environmental Science & Technology* **50** (24), 13215–13223.
- Geng, C., Cao, N., Xu, W., He, C., Yuan, Z., Liu, J., Shi, Q., Xu, C., Liu, S. & Zhao, H. 2018 Molecular characterization of organics removed by a covalently bound inorganic-organic hybrid coagulant for advanced treatment of municipal sewage. *Environmental Science & Technology* **52** (21), 12642–8.
- Gonsior, M., Zwartjes, M., Cooper, W. J., Song, W., Ishida, K. P., Tseng, L. Y., Jeung, M. K., Rosso, D., Hertkorn, N. & Schmitt-Kopplin, P. 2011 Molecular characterization of effluent organic matter identified by ultrahigh resolution mass spectrometry. *Water Research* **45** (9), 2943–2953.
- Guan, D., Feng, S., Zhang, L., Shi, Q., Zhao, S. & Xu, C. 2019 Mesoscale simulation for heavy petroleum system using structural unit and dissipative particle dynamics (SU-DPD) frameworks. *Energy & Fuels* **33** (2), 1049–1060.
- Hansen, C. T., Niggemann, J., Giebel, H. A., Simon, M., Bach, W. & Dittmar, T. 2019 Biodegradability of hydrothermally altered deep-sea dissolved organic matter. *Marine Chemistry* **217**, 103706.
- Hertkorn, N., Frommberger, M., Witt, M., Koch, B. P., Schmitt-Kopplin, P. & Perdue, E. M. 2008 Natural organic matter and the event horizon of mass spectrometry. *Analytical Chemistry* **80**, 8908–8919.
- Herzprung, P., von Tümpling, W., Hertkorn, N., Harir, M., Büttner, O., Bravidor, J., Friese, K. & Schmitt-Kopplin, P. 2012 Variations of DOM quality in inflows of a drinking water reservoir: linking of van Krevelen diagrams with EEMF spectra by rank correlation. *Environmental Science & Technology* **46** (10), 5511–5518.
- Janoš, P. 2003 Separation methods in the chemistry of humic substances. *Journal of Chromatography A* **983**, 1–18.
- Kellerman, A. M., Dittmar, T., Kothawala, D. N. & Tranvik, L. J. 2014 Chemodiversity of dissolved organic matter in lakes driven by climate and hydrology. *Nature Communications* **5**, 3804.
- Kim, S., Kramer, R. W. & Hatcher, P. G. 2003 Graphical method for analysis of ultrahigh-resolution broadband mass spectra of natural organic matter, the van Krevelen diagram. *Analytical Chemistry* **75**, 5336–5344.
- Koch, B. P. & Dittmar, T. 2006 From mass to structure: an aromaticity index for high-resolution mass data of natural organic matter. *Rapid Communications in Mass Spectrometry* **20** (5), 926–932.
- Koch, B. P. & Dittmar, T. 2016 From mass to structure: an aromaticity index for high-resolution mass data of natural organic matter. *Rapid Communications in Mass Spectrometry* **30** (1), 250.
- Koch, B. P., Dittmar, T., Witt, M. & Kattner, G. 2007 Fundamentals of molecular formula assignment to ultrahigh resolution mass data of natural organic matter. *Analytical Chemistry* **79**, 1758–1763.
- Komatsu, K., Onodera, T., Kohzu, A., Syutsubo, K. & Imai, A. 2020 Characterization of dissolved organic matter in wastewater during aerobic, anaerobic, and anoxic treatment processes by molecular size and fluorescence analyses. *Water Research* **171**, 115459.
- Li, Y., Fang, Z., He, C., Zhang, Y., Xu, C., Chung, K. H. & Shi, Q. 2015a Molecular characterization and transformation of dissolved organic matter in refinery wastewater from water treatment processes: characterization by Fourier transform ion cyclotron resonance mass spectrometry. *Energy & Fuels* **29** (11), 6956–6963.
- Li, Y., Xu, C., Chung, K. H. & Shi, Q. 2015b Molecular characterization of dissolved organic matter and its subfractions in refinery process water by Fourier transform ion cyclotron resonance mass spectrometry. *Energy & Fuels* **29** (5), 2923–2930.
- Li, X., Sun, G., Chen, S., Fang, Z., Yuan, H., Shi, Q. & Zhu, Y. 2018 Molecular chemodiversity of dissolved organic matter in paddy soils. *Environmental Science & Technology* **52** (3), 963–971.
- Liu, P., Shi, Q., Chung, K. H., Zhang, Y. H., Pan, N., Zhao, S. Q. & Xu, C. M. 2010 Molecular characterization of sulfur compounds in venezuela crude oil and Its SARA fractions by electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry. *Energy & Fuels* **24** (9), 5089–5096.
- Liu, Y., Ye, Q., Huang, W. L., Feng, L., Wang, Y. H., Xie, Z., Yong, S. S., Zhang, S., Jiang, B., Zheng, Y. & Wang, J. J. 2020 Spectroscopic and molecular-level characteristics of dissolved organic matter in the Pearl River Estuary, South China. *Science of the Total Environment* **710**, 136307.
- Lu, M., Zhang, W., Yu, Y. & Miu, Q. 2019 ABR and ornamental aquatic artificial combined treatment of domestic sewage. *Guangzhou Chemical Industry* **47** (14), 85–88.
- Malakar, S., Saha, P. D., Baskaran, D. & Rajamanickam, R. 2017 Comparative study of biofiltration process for treatment of

- VOCs emission from petroleum refinery wastewater – a review. *Environmental Technology & Innovation* **8**, 441–461.
- Matilainen, A., Gjessing, E. T., Lahtinen, T., Hed, L., Bhatnagar, A. & Sillanpää, M. 2011 An overview of the methods used in the characterisation of natural organic matter (NOM) in relation to drinking water treatment. *Chemosphere* **83** (11), 1431–1442.
- Mawhinney, D. B., Rosario-Ortiz, F. L., Baik, S., Vanderford, B. J. & Snyder, S. A. 2009 Characterization of fulvic acids by liquid chromatography-quadrupole time-of-flight mass spectrometry. *Journal of Chromatography A* **1216** (9), 1319–1324.
- Michael-Kordatou, I., Michael, C., Duan, X., He, X., Dionysiou, D. D., Mills, M. A. & Fatta-Kassinos, D. 2015 Dissolved effluent organic matter: characteristics and potential implications in wastewater treatment and reuse applications. *Water Research* **77**, 213–248.
- Mohamed, M. H., Wilson, L. D., Shah, J. R., Bailey, J., Peru, K. M. & Headley, J. V. 2015 A novel solid-state fractionation of naphthenic acid fraction components from oil sands process-affected water. *Chemosphere* **136**, 252–258.
- Nebbioso, A. & Piccolo, A. 2013 Molecular characterization of dissolved organic matter (DOM): a critical review. *Analytical and Bioanalytical Chemistry* **405** (1), 109–124.
- Pan, Q., Zhuo, X., He, C., Zhang, Y. & Shi, Q. 2020 Validation and evaluation of high-resolution orbitrap mass spectrometry on molecular characterization of dissolved organic matter. *ACS Omega* **5** (10), 5372–5379.
- Parsi, Z., Hartog, N., Górecki, T. & Poerschmann, J. 2007 Analytical pyrolysis as a tool for the characterization of natural organic matter – a comparison of different approaches. *Journal of Analytical and Applied Pyrolysis* **79** (1–2), 9–15.
- Pei, L., Wu, P., Liu, J. & Wang, J. 2016 Effect of nonionic surfactant on the micro-emulsifying water in silicone media. *Journal of Surfactants and Detergents* **20** (1), 247–254.
- Phungsai, P., Kurisu, F., Kasuga, I. & Furumai, H. 2016 Molecular characterization of low molecular weight dissolved organic matter in water reclamation processes using Orbitrap mass spectrometry. *Water Research* **100**, 526–536.
- Rahman, M. M. & Al-Malack, M. H. 2006 Performance of a crossflow membrane bioreactor (CF-MBR) when treating refinery wastewater. *Desalination* **191** (1–3), 16–26.
- Reemtsma, T. & These, A. 2005 Comparative investigation of low-molecular-weight fulvic acids of different origin by SEC-Q-TOF-MS: new insights into structure and formation. *Environmental Science & Technology* **39** (10), 3507–3512.
- Šantl-Temkiv, T., Finster, K., Dittmar, T., Hansen, B. M., Thyraug, R., Nielsen, N. W. & Karlson, U. G. 2013 Hailstones: a window into the microbial and chemical inventory of a storm cloud. *PLoS One* **8** (1), e53550.
- Seidel, M., Beck, M., Riedel, T., Waska, H., Suryaputra, I. G. N. A., Schnetger, B., Niggemann, J., Simon, M. & Dittmar, T. 2014 Biogeochemistry of dissolved organic matter in an anoxic intertidal creek bank. *Geochimica et Cosmochimica Acta* **140**, 418–434.
- Shamshirband, S., Jafari Nodoushan, E., Adolf, J. E., Abdul Manaf, A., Mosavi, A. & Chau, K. W. 2018 Ensemble models with uncertainty analysis for multi-day ahead forecasting of chlorophyll a concentration in coastal waters. *Engineering Applications of Computational Fluid Mechanics* **13** (1), 91–101.
- Shende, S. & Chau, K. W. 2019 Forecasting safe distance of a pumping well for effective riverbank filtration. *Journal of Hazardous Toxic and Radioactive Waste* **23** (2), 04018040.
- Shi, Q., Hou, D., Chung, K. H., Xu, C., Zhao, S. & Zhang, Y. 2010 Characterization of heteroatom compounds in a crude Oil and Its saturates, aromatics, resins, and asphaltenes (SARA) and non-basic nitrogen fractions analyzed by negative-ion electrospray ionization fourier transform ion cyclotron resonance mass spectrometry. *Energy & Fuels* **24** (4), 2545–2553.
- Shon, H. K., Vigneswaran, S. & Snyder, S. A. 2006 Effluent organic matter (EfOM) in wastewater: constituents, effects, and treatment. *Critical Reviews in Environmental Science and Technology* **36** (4), 327–374.
- Sleighter, R. L. & Hatcher, P. G. 2007 The application of electrospray ionization coupled to ultrahigh resolution mass spectrometry for the molecular characterization of natural organic matter. *Journal of Mass Spectrometry* **42** (5), 559–574.
- Smith, H. J., Tigges, M., D'Andrilli, J., Parker, A., Bothner, B. & Foreman, C. M. 2018 Dynamic processing of DOM: insight from exometabolomics, fluorescence spectroscopy, and mass spectrometry. *Limnology and Oceanography Letters* **3**, 225–235.
- Song, J., Li, M., Jiang, B., Wei, S., Fan, X. & Peng, P. 2018 Molecular characterization of water-soluble humic like substances in smoke particles emitted from combustion of biomass materials and coal using ultrahigh-resolution electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry. *Environmental Science & Technology* **52** (5), 2575–2585.
- Stenson, A. C., Marshall, A. G. & Cooper, W. T. 2003 Exact masses and chemical formulas of individual Suwannee River fulvic acids from ultrahigh resolution electrospray ionization Fourier transform ion cyclotron resonance mass spectra. *Analytical Chemistry* **75** (6), 1275–1284.
- Templier, J., Derenne, S., Croué, J. P. & Largeau, C. 2005 Comparative study of two fractions of riverine dissolved organic matter using various analytical pyrolytic methods and a ¹³C CP/MAS NMR approach. *Organic Geochemistry* **36** (10), 1418–1442.
- Tran, N. H., Ngo, H. H., Urase, T. & Gin, K. Y. 2015 A critical review on characterization strategies of organic matter for wastewater and water treatment processes. *Bioresour Technol* **193**, 523–533.
- Valle, J., Harir, M., Gonsior, M., Enrich-Prast, A., Schmitt-Kopplin, P., Bastviken, D. & Hertkorn, N. 2020 Molecular differences between water column and sediment pore water SPE-DOM in ten Swedish boreal lakes. *Water Research* **170**, 115320.
- Wang, M. & Chen, Y. 2018 Generation and characterization of DOM in wastewater treatment processes. *Chemosphere* **201**, 96–109.
- Wang, Q., Yan, G., Cai, B., Chen, C. & Guo, S. 2014 Characterization of dry-spun acrylic fiber wastewater by

- particle size distribution, biodegradability, and chemical composition. *CLEAN – Soil, Air, Water* **42** (10), 1393–1401.
- Wang, W., Gao, J. & Gao, J. 2019 Pretreatment_A_O_Ozone Oxidation_BAF advanced treatment of coal chemical wastewater. *Industrial Water Treatment* **39** (6), 103–106.
- Xia, J. & Xia, T. 2019 Commissioning and operation of petrochemical wastewater from seaport sewage treatment plant. *Water & Waste Water Engineering* **45**, 220–224.
- Xia, C., Huang, N. & He, X. 2000 Treatment of refinery wastewater with poly ferric aluminum silicate coagulant. *Environmental Protection of Chemical Industry* **20** (4), 29–32.
- Yan, L., Wang, Y., Li, J., Ma, H., Liu, H., Li, T. & Zhang, Y. 2014 Comparative study of different electrochemical methods for petroleum refinery wastewater treatment. *Desalination* **341**, 87–93.
- Yang, W., Li, X., Pan, B., Lv, L. & Zhang, W. 2013 Effective removal of effluent organic matter (EfOM) from bio-treated coking wastewater by a recyclable aminated hyper-cross-linked polymer. *Water Research* **47** (13), 4730–4738.
- Yuan, Z., He, C., Shi, Q., Xu, C., Li, Z., Wang, C., Zhao, H. & Ni, J. 2017 Molecular insights into the transformation of dissolved organic matter in landfill leachate concentrate during biodegradation and coagulation processes using ESI FT-ICR MS. *Environmental Science & Technology* **51** (14), 8110–8118.
- Zhang, M., Shi, Q., Song, X., Wang, H. & Bian, Z. 2019a Recent electrochemical methods in electrochemical degradation of halogenated organics: a review. *Environmental Science and Pollution Research International* **26** (11), 10457–10486.
- Zhang, M., Zhang, J. & Zhang, S. 2019b Pilot test_MBR_RO combined process advanced treatment of chemical wastewater. *Hebei Journal of Industrial Science and Technology* **36** (2), 135–141.
- Zhang, Y., Wei, C. & Yan, B. 2019c Emission characteristics and associated health risk assessment of volatile organic compounds from a typical coking wastewater treatment plant. *Science of the Total Environment* **693**, 133417.
- Zhao, L., Zhang, C., Li, H., Bao, M. & Sun, P. 2019 Regulation of different electron acceptors on petroleum hydrocarbon biotransformation to final products in activated sludge biosystems. *Bioprocess and Biosystems Engineering* **42** (4), 643–655.

First received 30 April 2020; accepted in revised form 7 July 2020. Available online 22 July 2020