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Molecular investigation into the transformation of recalcitrant dissolved organic sulfur in refinery sour water during stripping process

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ABSTRACT

Refinery sour water primarily originates from the tops of towers in various units and coker condensate, and cannot be discharged directly to a wastewater treatment plant due to high levels of chemical oxygen demand (COD) and organic sulfur contents. Even after the recovery of H_2S from the sour water by the stripping process, the effluent still contains a high concentration of dissolved organic sulfur (DOS), which can have a huge bad influence. While chemical composition of dissolved organic matter (DOM) in refinery wastewater has been extensively studied, the investigation of recalcitrant DOS from sour waters remains unclear. In the present study, chemical composition of sour water DOMs (especially DOS) was investigated using fluorescence spectroscopy (excitation-emission matrix, EEM) and mass spectrometry, including gas chromatography-mass spectrometry (GC-MS) and high-resolution Orbitrap MS. The GC-MS and EEM results showed that volatile and low-aromaticity compounds were effectively removed during the stripping process, while compounds with high hydrophilicity and humification degree were found to be more recalcitrant. The Orbitrap MS results showed that weak-polar oxygenated sulfur compounds were easier to be removed than oxygenated compounds. However, the effluent still contained significant amounts of sulfur-containing compounds with multiple sulfur atoms, particularly in the form of highly unsaturated and aromatic compounds. The Orbitrap MS/MS results of CHOS-containing compounds from the effluent indicate that the sulfur atoms may exist as sulfonates, disulfide bonds, thioethers. Understanding the composition and structure of sour water DOS is crucial for the development of effective treatment processes that can target polysulfide compounds and minimize their impact on the environment.

1. Introduction

In petroleum refinery, sour water is a byproduct of various processes, mainly including crude distillation, catalytic cracking, continuous reforming unit, hydrofining and sulfur recovery unit (Zahid, 2019). For every barrel of crude oil processed, approximately one barrel of sour water is generated. Sour water contains high levels of sulfides and ammonia, as well as pollutants like phenol, cyanide, and oil. The concentration of dissolved organic carbon (DOC) in sulfur-containing sour water is high, with values reaching several hundred to tens of thousands ppm (de Farias Soares et al., 2021). It cannot be directly discharged to a wastewater treatment plant. The vapor stripping, which is part of the sulfur recovery unit, is primarily used to treat sour water from various sources throughout the refinery (Minier-Matar et al., 2017; Zahid, 2019). During the stripping process, H_2S and ammonia in the sour water are carried by steam to the top of the stripping tower, where they are condensed and sent to the sulfur recovery unit. Meanwhile, a large amount of dissolved organic sulfur (DOS) and recalcitrant organic matter gather at the bottom of the tower and are discharged to the wastewater treatment plant (Zhu et al., 2016; Kazemi et al., 2017).

Although stripping is an effective method for removing H_2S and ammonia from sour water, the resulting effluent still has a higher COD value and organic sulfur content than other wastewaters, such

as electric desalting wastewater (EDWs) and crude distillation wastewater (Li et al., 2021). The high concentration of organic sulfide in the stripping effluent can inhibit the activity of microorganisms in the biochemical treatment process of sewage treatment plants, greatly reducing the removal rate of COD, ammonia, total nitrogen and other pollutants in the biochemical system, resulting in reduced treatment efficiency. An efficient stripping treatment process can significantly reduce the treatment load of the biochemical treatment process. A molecular-level understanding of the chemical composition of DOS, particularly recalcitrant DOS, in sour water during the stripping process is crucial for determining the transformation mechanisms of DOM and developing new techniques to optimize removal performance. However, research on the molecular transformation of DOS during the stripping process is still limited.

Fluorescence spectroscopy, specifically the excitation-emission matrix (EEM) technique, is extensively employed for the characterization of the origins and constituents of fluorescent dissolved organic matter (FDOM) due to its high sensitivity, information content, low cost, and non-invasive nature (Zhang et al., 2021b). By detecting differences in light emission following excitation of fluorophores present in DOM, it is possible to discriminate among various types of DOM, including humic and fulvic acids, and proteinaceous material (Cohen et al., 2014). Gas chromatography mass spectrometry (GC-MS) offers accurate and objective insights into the chemical composition of non-polar and weak-polar compounds (Parsi et al., 2007; Ligon et al., 2008; Ye et al., 2020). High-resolution mass spectrometry (HRMS), such as FT-ICR-MS, Orbitrap MS, can provide detailed chemical information on DOM based on individual molecular formulas. In recent years, researchers have applied HRMS to determine the molecular composition and transformation of DOM in various wastewater treatment systems (Ciofi et al., 2014; Bataglion et al., 2015; Zark and Dittmar, 2018). Li et al. (2020) evaluated the DOM composition throughout a wastewater treatment plant, including oil separation, dissolved air flotation, and biochemical, using FT-ICR-MS. The results showed that sulfur-containing compounds were more recalcitrant to the bio-degradation, and the origin and transformation of these compounds should be paid attention to in further research. Additionally, high-resolution tandem multistage mass spectrometry (MS/MS) results have the potential to provide even more detailed information and insight into the chemical structure of DOM. Deng et al. (2022) studied the molecular structure of sulfonates in DOM from electric desalting wastewater and coal coking wastewater by Orbitrap MSMS. By identifying the specific molecular structures of DOM, MS/MS can provide insights into the origins and transformation mechanisms of DOM compounds, as well as their potential environmental impacts.

The aim of this study is to explore the molecular-level properties and transformations of recalcitrant DOS in sour water during the stripping process using EEM, GC-MS, and Orbitrap MS/MSMS. In particular, the molecular structural characteristics of organic multi-sulfur compounds present in sour water were firstly revealed. By improving our understanding of the behavior and fate of these compounds, it may be possible to develop more sustainable and effective wastewater management practices in the petroleum refining industry.

2. Materials and methods

2.1. Samples

Wastewater of stripping influent and effluent were collected from PetroChina Ningxia refinery. The sour water was treated using a low-pressure single stripper process. The sour influent,

containing H_2S and ammonia, enters from the upper part of the stripping tower. Then under the effect of flash evaporation, most of H_2S and ammonia enter the vapor phase and rise to the top of the stripping tower. The sour effluent is obtained at the bottom of the stripping tower. The influent primarily originated from various units such as atmospheric distillation unit, heavy oil catalytic cracking unit (RFCCU), gasoline and diesel hydrofinishing unit (HT), continuous reforming unit (CCR), and sulfur recovery unit (SRU) within the refinery. All samples were stored at 4 °C in the dark and filtered through the 0.45 μm membrane (Pall supor, USA) prior to analysis.

For the experiments, LC-MS grade pure water (H_2O) was procured from Fisher Scientific, USA, while analytical grade methanol (CH_3OH) and dichloromethane (CH_2Cl_2, DCM) were further distilled and used.

2.2. Sample preparation

To determine the content of volatile organic compounds (VOCs), the filtered sour waters were aerated. The DOC values of the sour waters were measured both before and after aeration. The 300 mL of aerated sour waters were subsequently subjected to solvent extraction, employing 150 mL of dichloromethane (DCM, CH_2Cl_2) for three times. And then, the organic phase DOM was obtained by removing CH_2Cl_2. The DOM in the liquid-liquid residual phase was further extracted using a solid-phase extraction (Agilent Bond Elut PPL, 500 mg, 6 mL) (Li et al., 2015). The detailed solid-phase extraction process is described in the Supporting Information. The process flow of sample preparation is shown in Fig. S1.

2.3. Analysis of sour water parameters

The TOC-5000 A analyzer (Shimadzu, Japan) were used to analyzed the total dissolved nitrogen (TDN) of the filtered samples, as well as the DOC of the samples before and after aeration, DCM extracts, and SPE extracts with the Chinese standard of HJ 501-2009. The chemical oxygen demand (COD) of all filtrated samples was analyzed with the HACH® standard method of HJT399-2007. The Multi EA3100 sulfur/nitrogen analyzer (Jena Analytical Instruments, Germany) was used to measure the organic sulfur content in the DCM and SPE extracts in accordance with ASTM D5453-2004 standard methods.

2.4. Excitation-emission matrix (EEM) analysis

The DOM in filtered samples were analyzed using an EEM fluorescence spectrometer (Horiba Scientific, Paris, France) with an excitation and emission wavelength of 220–450 and 250–600 nm, respectively. The EEM spectra of all samples were acquired by subtracting the pure water blank. Besides, the samples were diluted to a concentration where the UV-Vis absorbance was kept below 0.05 (arbitrary unit) to avoid the influence of inner filter effect, if necessary.

2.5. Purge and Trap (P&T) GC-MS analysis

The analysis of VOCs in the sour waters was performed using an OI Analytical Eclipse 4760&4100 automatic purge-capture sampling device (OI, USA) coupled with Waters GCT-MS analysis. The detail operating conditions of Purge and Trap (P&T) GC-MS is shown in Supporting Information.

2.6. Negative-ion ESI orbitrap MS/MSMS analysis

The Orbitrap Fusion MS (Thermo Scientific) mass spectrometer

were operated in negative mode with voltages of the negative ion spray, sheath gas (Arb) and aux gas (Arb) were, 2.6 kV, 5 and 2, respectively. The DCM and SPE extracts DOM dissolved in methanol (50 mg C/L) were injected at a rate of 4 μL/min and was acquired from 150 to 800 Da. The ion transfer tube temperature and the vaporizer temperature were set at 300 and 20 °C. The S-lens RF level was set at 60, and the injection time and the automated gain control (AGC) were set at 0.1 s and 5e5.

For tandem mass experiments, the targeted MS/MS data were acquired at the AGC of 5e4 and maximum injection time of 0.1 s, respectively. The precursor ions were filtered by the quadrupole, which operated at an isolation window of m/z 1. HCD was used as the frag-mentation technique. Collision energy was operated at 10%, 20% and 30%.

2.7. Data processing

Data analysis of the Orbitrap MS was performed by using in-house software (He et al., 2020a; Pan et al., 2020). The average mass error of all assigned molecular formulas was less than 1 ppm with the elemental combinations containing $^{12}C_{0−100}$, $^{1}H_{2−200}$, $^{14}N_{0−3}$, $^{16}O_{0−30}$, and $^{32}S_{0−5}$ atoms. Aromaticity index (AI_{mod}) and elemental ratios (O/C and H/C) were used to classify compounds as (Kellerman et al., 2014; Seidel et al., 2015): Aliphatic compounds (H/C>1.5); highly unsaturated and phenolic compounds (AI_{mod}<0.50, H/C<1.5); aromatic compounds (AI_{mod}≥0.50) with aliphatic side chains, such as polyphenols and polycyclic aromatics-like compounds (Liu et al., 2010; Camire et al., 2018). All the formulae assigned from the wastewater samples can be found in Table S2.

3. Results and discussion

3.1. Removal efficiency of organic matter from sour water in the stripping process

The bulk properties of the sour waters, including DOC, COD, TDN, and organic sulfur content are listed in Table 1. The contri-bution in TOC to the total DOC of VOC, DCM extract, and SPE extract fractions are determined separately. The values of DOC and COD decreased after the stripping process, with a removal efficiency of approximately 35% for DOC, 69% for COD, respectively. Meanwhile, DOC values of the DCM extracts and SPE extracts change signifi-cantly from 277 to 145 ppm and from 196 to 188 ppm, respectively. The DOM in DCM extracts is more easily removed during the stripping process, indicating that the DOM in treated sour water becomes more hydrophilic.

VOC in the sour waters contributes about 10%−20% of the total DOC. The relative ratios of VOC of the influent and the effluent were 16.8% and 10.5%, respectively. A total of 48 VOCs was detected in the influent, mainly including benzenes, phenols, amines, and so on. After stripping process, only a total of 18 compounds were detected, mainly including benzenes, phenols, amines, alkanes, and others (see Supporting Information Fig. S2 and Table S1). VOCs are

effectively removed during the stripping process. Particularly, the relative content of benzenes decreased from 82.55% in the influent to 6.21% in the effluent. The stripping process is more effective for removing benzenes than phenolic and amine compounds (Fig. S2). During the stripping process, the TDN value was reduced from 809 to 59 mg/L, with a removal efficiency of approximately 93%. The content of nitrogen compounds in sour water were substantially reduced.

However, the DOC, COD, TDN, and organic sulfur are still high in the effluent comparing with other refinery point wastewaters (Li et al., 2021). The sour waters also have relatively high organic sulfur contents, which are 113 mg/L in the influent and 77 mg/L in the effluent. About 31.9% of the organic sulfur was removed in the stripping process. It is also known that high concentrations of organic sulfur content can be corrosive to equipment and toxic to microorganisms in the wastewater treatment plant (Wang et al., 2018). However, the absence of small molecule sulfur-containing compounds in VOCs makes it more important to go deeper study-ing into DOS in sour water. Therefore, understanding the molecular composition and transformations of DOS is crucial for the effective treatment of organic sulfur compounds as well as minimize their impact on the equipment and environment.

3.2. Transformation of FDOM in the sour waters during stripping process

EEM fluorescence spectroscopy has been widely used to assess wastewaters by identifying aromatic hydrocarbons, polyaromatic hydrocarbons, humic acids, etc (Li et al., 2014). The sour waters exhibited two main fluorescence peaks with strong intensity in Ex/Em = 220−235/275−325 nm (region I) and Ex/Em = 250−300/275−325 nm (region II) (Fig. 1). The fluorescence peaks in the re-gion I may indicate simple aromatic compounds such as benzenes, phenols, or anilines (Chen et al., 2003; Li et al., 2013; Ye et al., 2021). The fluorescence peaks in region II represent two or three rings polycyclic aromatic compounds like naphthalene, polyphenolic compounds, or anthracenes linked with some acid functional groups (Li et al., 2014). After the stripping process, the UV ab-sorption intensity of FDOM in region I and II decreased.

The specific UV absorbance at 254 nm ($SUVA_{254}$) and humifi-cation index (HIX) have been proposed to distinguish the sources and composition of FDOM (Mohapatra et al., 2021; Zhang et al., 2021b). For example, $SUVA_{254}$ is an index for the aromaticity, mo-lecular weight, and hydrophilicity/hydrophobicity of DOM. The $SUVA_{254}$ value of sour water decreased from 3.48 to 0.58 (Table 1). The decrease of $SUVA_{254}$ for effluent suggests that the electron-rich and light-absorbing moieties with C=C and C=O double bond chromophores in DOM could be gradually destroyed, while hy-drophobic compounds are removed and/or hydrophilic compounds are produced during stripping process (Zhang et al., 2021a). The result indicates that the hydrophilic compounds are difficult to remove. The HIX is an index for the humification degree (Shi et al., 2021). The increase in HIX values for the effluent indicates that the humification degree of FDOM increases, the hydrogen to carbon (H/

Table 1
Basic water quality of the sour waters in the stripping process.

Samples	DOC				COD	TDN	Organic sulfur[c]			UV_{254}	$SUVA_{254}$	HIX
	Total	VOC	DCM[a]	SPE[b]			DCM	SPE	Total			
Influent	630	106 (16.8%[a])	277	196	4755	809	36	77	113	21.95	3.48	0.003
Effluent	410	43 (10.5%[a])	145	188	1495	59	11	66	77	2.37	0.58	0.008

[a] As a percentage of total organic carbon; a. Dichloromethane extract; b. Solid phase extraction product; c. Elemental content of sulfur. COD, DOC, TDN, and Organic sulfur (mg/L); Light absorbance at 254 nm (UV_{254}); specific UV_{254} (SUV_{254}).
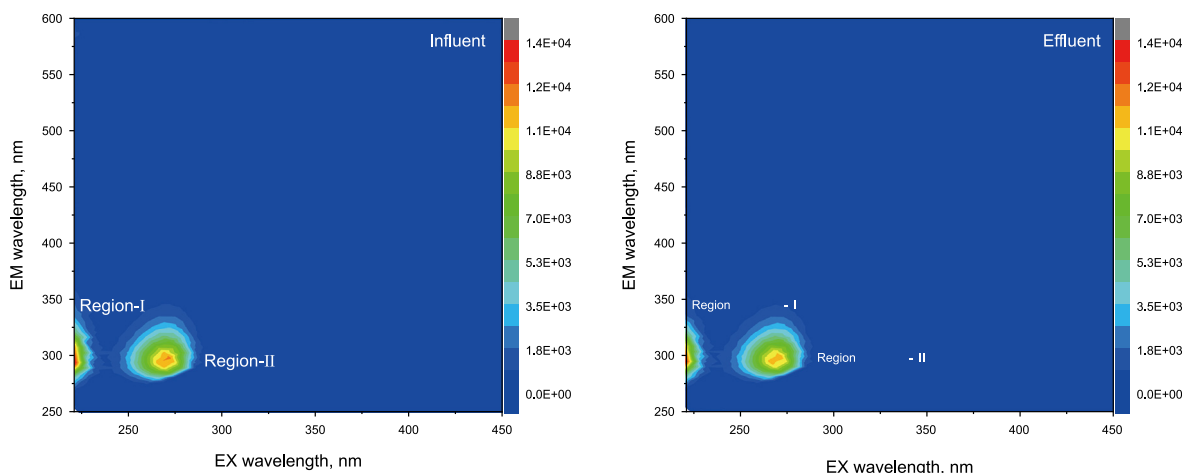
Fig. 1. EEM spectra of the influent and effluent from the stripping process.

C) ratio decreases, and the emission spectrum of fluorescent molecules experiences a red shift. This may reflect that some protein-like fluorophores are possibly combined with humic substances, resulting in the increase in humification degree. As a result, DOM in the effluent may be enriched in humic substances that are resistant to biodegradation and may have a more aromatic structure than the influent (Mohapatra et al., 2021) (Table 1).

3.3. Molecular composition and transformation of weak-polar DOS during stripping process

DCM is used to extract weak-polar and non-polar compounds from water, resulting in organic phase fractions (Li et al., 2015). The DCM extracts show a decrease in the content of organic sulfur from 36 to 11 ppm, respectively, indicating that the stripping process mainly removes weakly polar compounds. Negative-ion ESI MS analysis of the weak-polar compounds in the DCM extracts of sour waters detected a total of 5509 and 8748 molecular formulas in the influent and effluent, respectively, covering 141 heteroatom class species (Fig. S3). The dominant class of species in the DCM extracts is CHO compounds (containing C, H and O atoms), with relative abundances of 61.91% and 73.61% in the influent and effluent,

respectively. CHOS-containing compounds make up the second largest group in sour water DOM. The percentage of CHOS, CHNOS and CHS class compounds in the influent and effluent was 24.45%, 3.59%, 0.57% and 16.84%, 0.95%, 0.45%, respectively (Fig. 2). The relative abundance of CHOS class species in sour water was higher than that of other refinery wastewaters (Li et al., 2015; Fang et al., 2019). After the stripping process, the relative abundance of CHO class species increased, while the relative abundance of CHOS and CHNOS class species decreased, indicating that weakly polar oxygenated sulfur compounds are easier to remove than oxygenated compounds during the stripping process.

3.4. Molecular composition and transformation of polar DOS during stripping process

The DOC value in the sour water decreased from 630 to 410 ppm during the stripping process. However, the contents of DOC (from 196 to 188 ppm) and polar organic sulfur content (from 77 to 66 ppm) in the SPE extracts did not change much during the stripping process, indicating that the polar DOS in DOM was difficult to be removed by the stripping (Table 1). A total of 5124 and 7984 molecular formulas were detected in the influent and
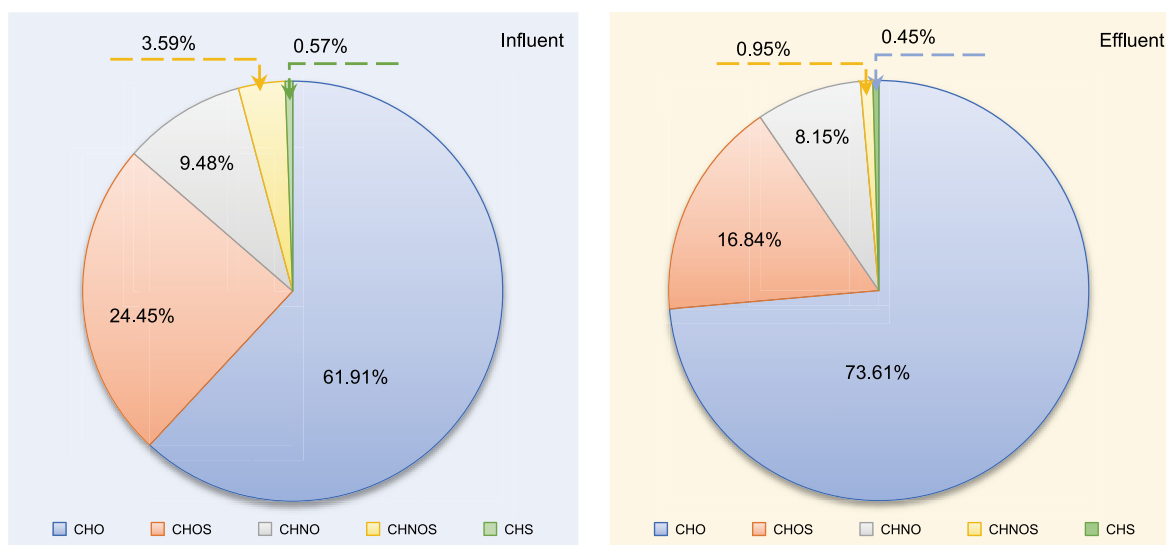

Fig. 2. Relative abundance of CHO, CHOS, CHNO, CHNOS, and CHS class species in the DCM extracts.

Table 2
Orbitrap MS intensity-weighted average (wa) molecular parameters of the DOM.

Samples	Influent			Effluent		
	All	CHOS	CHNOS	All	CHOS	CHNOS
m/z_{wa}	275	276	259	293	287	353
Formulae, #	5124	2888	1391	7984	3048	2835
RA%	100	91.01	6.56	100	83.85	8.07
C_{wa}	9.81	9.70	9.38	11.72	11.00	15.07
H_{wa}	13.15	13.03	12.56	12.65	11.63	17.84
O_{wa}	4.05	4.02	4.44	4.14	3.93	5.92
N_{wa}	0.08	0	1.05	0.15	0	1.21
S_{wa}	2.44	2.57	1.50	2.22	2.52	1.34
S/C_{wa}	0.31	0.33	0.17	0.24	0.27	0.10
H/C_{wa}	1.50	1.51	1.45	1.18	1.17	1.29
O/C_{wa}	0.45	0.46	0.49	0.39	0.39	0.42
DBE_{wa}^a	3.78	3.68	4.12	5.97	5.68	7.25
Aromatics compounds, %	4.03	3.23	0.1	8.97	5.77	0.72
Highly unsaturated, %	62.57	57.16	4.49	79.00	69.63	5.76
Aliphatics, %	33.40	30.62	1.97	12.03	8.45	1.58

DBE: double bond equivalents; O/C: oxygen to carbon ratio; H/C: hydrogen to carbon ratio; RA%: percent relative abundance; #: number of the assigned formulae.

effluent, respectively. The increase in the number of molecular formulas in the effluent may be attributed to the removal of certain high-content compounds during the stripping process, which allows for the detection of low-content compounds that were previously masked. A total of 155 heteroatom class species, including $N_{1-2}O_{1-16}S_{1-2}$, $N_{1-3}O_{1-15}$, O_{1-16}, and $O_{1-10}S_{1-5}$ classes, were detected in the sour water. The dominant formulas identified in the influent and effluent was CHOS classes, with the relative abundance of 91.01% and 83.85%, respectively (Table 2). Compared with wastewater collected from other refinery units such as EDWs and coking wastewater, the values of S_{wa} (2.44) and S/C_{wa} (0.31), as well as the relative abundance of CHOS classes in sour water are particularly high (Table 2) (He et al., 2020b, 2021; Li et al., 2021). The molecular formulas detected in the sour water included compounds with up to five sulfur atoms in their structure (Fig. 3). In addition, O_xS_{1-5} class compounds were also detected in the sour water of another refinery (Fig. S5) (Li et al., 2021), indicating that these compounds are not unique to the current study's wastewater sample.

To illustrate the transformation and degradation of DOM during the stripping process, van Krevelen diagrams for molecular compositions of CHOS class species were systematically analyzed (Fig. S4). The stripping process reduced the values of S_{wa} and S/C_{wa} from 2.44 to 0.31 to 2.22 and 0.24, respectively, indicating that some organic sulfides in sour water were recovered (Table 2). However, compared with EDWs, coking wastewater, and distillation wastewater, considerable amounts of sulfur-containing compounds are still present in the effluent (He et al., 2020b; Ye et al., 2020; Li et al., 2021). Highly unsaturated compounds (57.16%) and unsaturated aliphatic compounds (30.62%) dominate the CHOS class species in sour water (Table 2). Compared with the influent, the proportion of highly unsaturated compounds increased from 57.16% to 69.63%, while unsaturated aliphatic compounds decreased from 30.62% to 8.45% in the effluent. The aromatic compounds (4.03%) are mainly composed of O_xS_y class (3.23%) aromatic compounds, and their proportion increased from 3.23% to 5.77%. These results indicate that CHOS class compounds with highly unsaturated and aromatic compounds cannot be preferentially removed during the stripping process. Based on the heteroatom class distribution of CHOS class compounds, the $O_{1-10}S_{1-5}$ class compounds with the highest abundance in the highly
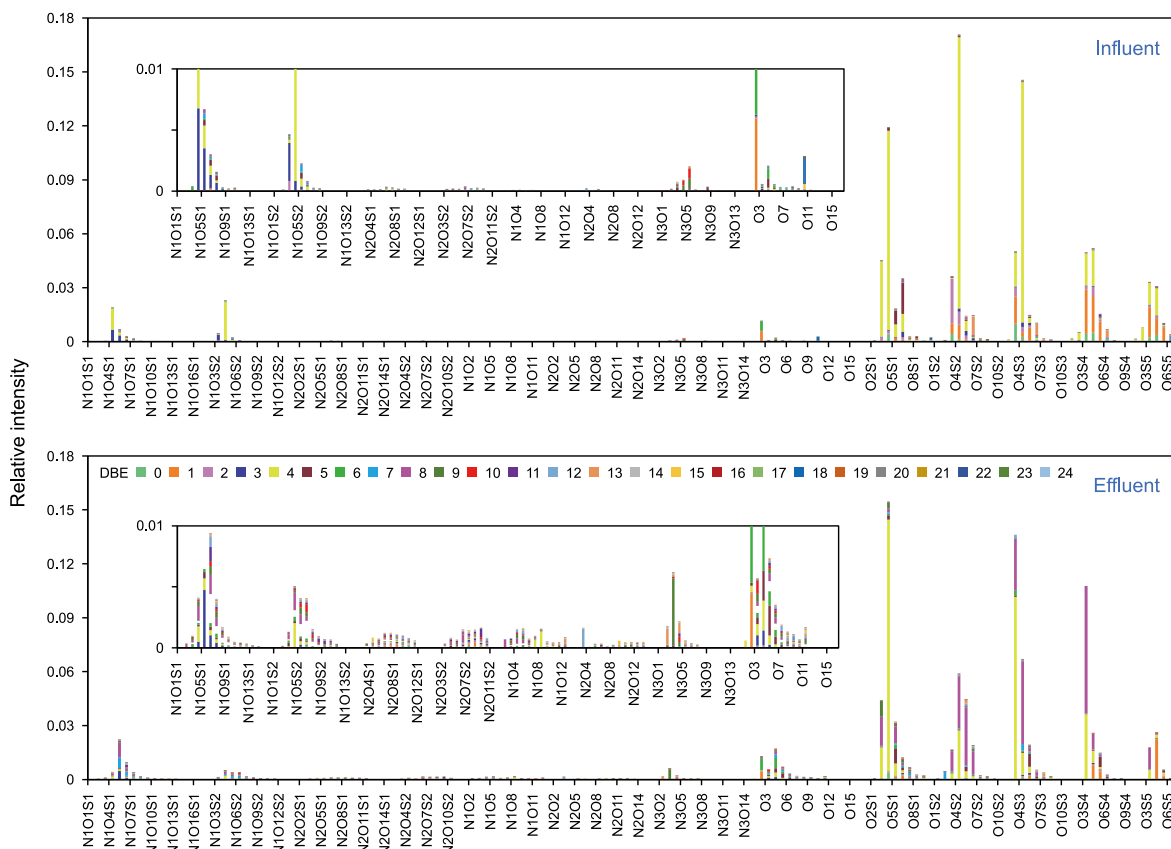

Fig. 3. Relative abundance of class species of DOM from the SPE extracts during the stripping process.
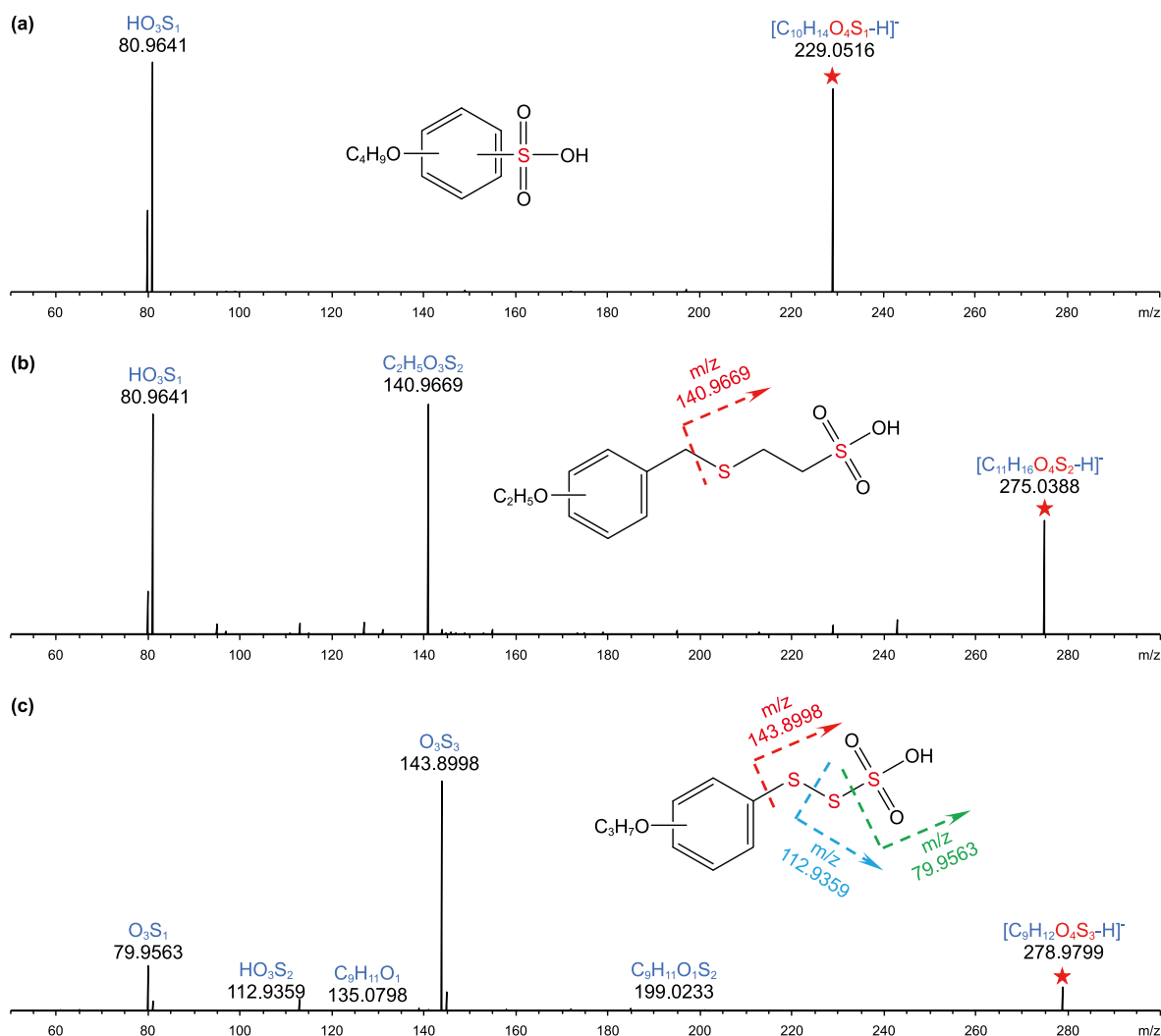
Fig. 4. MS/MS spectra of three representative compounds containing $C_{10}H_{14}O_4S_1$, $C_{11}H_{16}O_4S_2$, and $C_9H_{12}O_4S_3$ identified in the effluent.

unsaturated region were selected for structural analysis. This analysis of the structural characteristics of polar sulfides in sour water proves to be advantageous in the advancement and refinement of wastewater treatment technologies.

3.5. Molecular structure of the recalcitrant DOS in sour waters

Although the stripping process successfully removed large amounts of organics from the influent, some resistant and newly formed organics remained, especially the S-containing compounds (Fig. 3). Understanding the molecular structure of organic sulfur-containing compounds is crucial for the optimization of the stripping process. By identifying the specific functional groups and chemical bonds present in these compounds, it may be possible to develop more effective stripping methods that selectively target and remove the most problematic components of refinery wastewater. The relative abundance of O_xS_1 class compounds, which are characterized by the presence of a single sulfur atom, was generally high in the DOM of refinery wastewater. However, in the case of sour water, the relative abundance of O_xS_{1-5} class compounds, which contain sulfur atoms in the range of 1–5, was found to be the highest. This is a distinct characteristic that sets sour water apart from other types of refinery wastewater (Fig. 3) (Li et al., 2021; He et al., 2023). The excess of S atoms in the O_xS_{3-5} class compounds

would suggest the presence of additional S-containing functional groups beyond those found in the O_xS_{1-2} compounds.

To elucidate the molecular structures of the complex sulfur-containing compounds present in the sour water, non-targeted Orbitrap MS/MS analysis was performed. The representative compounds with the highest relative abundance within the O_xS_{3-5} class species were selected for further analysis. Specifically, compounds belonging to the $C_{10}H_{14}O_4S_1$, $C_{11}H_{16}O_4S_2$, and $C_9H_{12}O_4S_3$ class species were analyzed using a combination of mass spectrometry and other analytical techniques. These analyses allowed for the identification of specific functional groups and chemical bonds within the molecules, providing valuable information about the composition and complexity of the wastewater sample. By using this information to guide the development of more effective treatment methods, it may be possible to improve the overall efficiency and sustainability of refinery wastewater management (Fig. 4).

The DBE value of $C_{10}H_{14}O_4S_1$, $C_{11}H_{16}O_4S_2$, and $C_9H_{12}O_4S_3$ classes was 4. In the case of the $C_{10}H_{14}O_4S_1$ compound, the fragment ions observed during mass spectrometry analysis included HO_3S_1 (m/z 80.9641) and O_3S_1 (m/z 79.9571), which are consistent with the fragmentation pattern of 4-hydroxybenzenesulfonic acid, a standard compound used for comparison (Fig. S6). The analysis of the molecular structures of the sulfur-containing compounds identified in the sour water revealed that the O_4S_1 class compounds exist in

the form of sulfonate groups rather than sulfate groups. Furthermore, the remaining oxygen atom in these compounds was found to be either in the form of a hydroxyl group or an ether bond functional group (Fig. 4(a)) (Deng et al., 2022). The analysis of the $C_{11}H_{16}O_4S_2$ compound revealed that the fragment ions observed during mass spectrometry analysis primarily consisted of HO_3S_1 (m/z 80.9641) and $C_2H_5O_3S_2$ (m/z 140.9669), indicating the presence of a sulfonate group within the molecular structure. Notably, the absence of fragment ion peaks corresponding to the sulfoxide (O_1S_1) functional group suggests that this group is not present in the compound. Additionally, the absence of fragment ion peaks corresponding to the sulfhydryl (−SH) and thiophene functional groups suggests that the sulfur atom is present in the form of a thioether (Fig. 4(b)). The analysis of the $C_9H_{12}O_4S_3$ compound revealed that it contains a high abundance of the O_3S_3 fragment ion peak (m/z 143.8998). Meanwhile, Additionally, the simultaneous presence of the fragment ion peaks HO_3S_2 (m/z 112.9359) and O_3S_1 (m/z 79.9563) indicates that the sulfur atom may be attached to the sulfonate group in the form of a disulfide bond (Fig. 4(c)).

Based on the analysis of the molecular structures of the sulfur-containing compounds found in sour water, it is speculated that the O_xS_{1-5} class species may contain a range of functional groups, including sulfonate, disulfide bonds, and thioether groups. However, it's important to note that there are many possible isomers and other functional groups that may be present in these compounds. The complex nature of these compounds highlights the need for advanced analytical techniques like mass spectrometry, which can provide valuable insights into the specific functional groups present within the molecules. It may be possible to guide the development of more targeted treatment methods and to improve the overall efficiency and sustainability of refinery wastewater management by using this information.

4. Conclusions

In this study, EEM, P&T GC-MS and Orbitrap MS/MSMS was used to investigate the molecular composition and transformation of DOS in sour water during the stripping process. The DOC and organic sulfur content of the polar DOM obtained by SPE did not change much during the stripping process. The EEM results showed that the FDOM in the effluent, enriched in humic substances with more aromatic structure than the influent, is resistant to biodegradation. During stripping process, the VOCs of benzenes series, phenol and aniline in the sour water are preferentially removed. The Orbitrap MS results indicated that weak polar organic sulfur-containing compounds in the sour water can be partly recovered during the stripping process. However, the effluent still has a high organic sulfur content. Among them, the highly unsaturated and aromatics O_xS_{1-5} compounds are difficult to be recovered during the stripping process, which poses a challenge for DOS treatment in wastewater treatment plants. Negative-ion Orbitrap MS/MS analysis revealed that the O_xS_{1-5} compounds in sour water exist as sulfonic acid groups combined with thioethers, disulfides, ether bond, and hydroxyl functional groups, which were tentatively identified for the first time. These molecular-level insights into the composition and structure of organic sulfur compounds provide valuable information for understanding the transformation mechanisms and developing new techniques for their removal from wastewater.

CRediT authorship contribution statement

Yu-Guo Li: Writing − review & editing, Writing − original draft, Investigation, Formal analysis, Data curation. **Chen He:** Writing − review & editing, Writing − original draft, Investigation, Funding acquisition, Conceptualization. **Chun-Mao Chen:** Validation, Supervision. **Fan Liu:** Resources, Conceptualization. **Quan Shi:** Writing − review & editing, Project administration, Funding acquisition, Conceptualization.

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.petsci.2024.01.005.

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