

## Exploring the Reaction Mechanism for Ozone Oxidation of Petrochemical Reverse Osmosis Concentrate by Resin Adsorption Chromatography

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**Abstract**—Dissolved organic matter (DOM) in petrochemical reverse osmosis concentrate (ROC) is important for developing ROC advanced oxidation techniques. In this study, DOM before and after ozonation was fractionated using resin adsorbents into five classes: hydrophobic bases (HoB), hydrophobic acids (HoA), weakly hydrophobic acids (WHoA), hydrophobic neutrals (HoN) and hydrophilic matter (HiM). Hydrophobic organics dominate in DOM, in which HoN and HoA account for 29.2% and 19.5%, respectively. Ozone significantly decreases the percentage of HoN, while increases the concentration of WHoA and HiM. The UV-Vis analysis shows that ozonation decreases the molecular weight of DOM. In view of FTIR analysis, the unsaturated groups and aliphatic structures are destroyed greatly and converted to more C-O structures, which shows relatively high hydrophilicity and low molecular weight. Through the analysis of fluorescence spectroscopy, it is found that ozone decreases significantly the fluorescence intensity of humic-like and fulvic-like substances in DOM, while increases the fluorescence intensity of soluble microbial products.

**Keywords**-reverse osmosis concentrate (ROC); ozone oxidation; DOM fractions

### I. INTRODUCTION

Combined ultra-filtration (UF) and reverse osmosis (RO) membranes are widely used for direct reclamation of secondary sewage effluent from petrochemical enterprises. However, while RO membranes can remove efficiently most of organic and inorganic material, these rejected compounds are concentrated in the RO concentrate stream (ROC) [1]. ROC represents approximately 30~40% of the inflow, depending on the RO recovery ratio and contains salts, dissolved organic matter (DOM) that were not removed in biological wastewater treatment. The direct discharge of the large amount of ROC is a serious waste of water resource and may have a negative impact on the aquatic ecosystem. As a consequence, further treatment of the concentrate could be necessary.

Presently, there is an increasing concern over the treatment of ROC. In general, treatment methods can be divided into two groups: high-energy oxidative methods (sonolysis, advanced oxidation, electrochemical oxidation), and those that consume chemicals (coagulation and adsorption). Several studies have shown that ozone

treatment can be very efficient in the oxidation of a wide range of recalcitrant DOM [2-5]. In this study, ozonation is being investigated as a potential treatment option for ROC. However, studies about the reaction mechanism for ozonation of petrochemical ROC are still limited due to its complex composition of total DOM.

To understand the role of DOM in ozonation, it is often necessary to isolate DOM. Resin adsorption chromatography (RAC) is commonly used for isolating DOM from natural waters and has long been employed with a broad success [6]. Leenheer et al. [7] used resins to fractionate DOM of tertiary-treated municipal wastewater into hydrophobic acids, hydrophobic neutrals, hydrophilic acids, colloidal hydrophilic neutrals and dissolved hydrophilic neutrals. Imai et al. [8] modified the DOM fractionation method developed by Leenheer [9] and isolated DOM in effluents from sewage and human-wastes treatment plants into six classes: aquatic humic substances, hydrophobic neutrals and bases; hydrophilic acids, neutrals and bases. With the application of RAC, researchers have found out some characteristics of DOM from wastewater.

In this study, DOM in petrochemical ROC before and after ozonation was isolated into five classes using RAC technique. Combined with different analysis methods, the role of DOM characteristics was explored in ozonation of ROC. The results of this study will give us some fundamental ideas that which classes of DOM can be removed mostly in the ozonation of ROC.

### II. MATERIALS AND METHODS

#### A. Sample Collection and Preservation

ROC samples were collected from a wastewater treatment plant in a petrochemical enterprise. Water samples for this study were collected at RO site and filtered immediately through 0.45 μm glass filter and stored in the dark at 4°C until analysis.

#### B. Fractionation and Collection of DOM Fractions

The fractionation of DOM was performed following the procedure modified from Imai et al. [8], Leenheer [9] and Chefetz et al. [10]. ROC was firstly pumped through a glass column of Sigma-Aldrich XAD-8 resin (20–60 mesh). Hydrophobic bases (HoB) were then desorbed from the resin with 0.1 M HCl. The sample effluent was acidified to

pH 2 with 6 M HCl and cycled over two connected Sigma-Aldrich XAD-8 and Sigma-Aldrich XAD-4 resin (60–80 mesh), respectively. The effluent from the connected two columns was hydrophilic matter (HiM). Hydrophobic acids (HoA) and weakly hydrophobic acids (WHoA) were desorbed from XAD-8 and XAD-4 with 0.1 M NaOH, respectively. After HoA was desorbed, the XAD-8 resin was air-dried for about 12 h and was Soxhlet-extracted with methanol to obtain hydrophobic neutrals (HoN). The excess methanol was removed by vacuum-rotary evaporation at 40 °C.

### C. Organic Carbon Analysis

Dissolved organic carbon (DOC) was measured with a TOC analyzer (Multi N/C 3000) in accordance with Standard Method 5310D. The UV<sub>254</sub> to DOC ratio (SUVA) was reported to represent the aromatic characteristic of organic matters as they imparted the ability to absorb light in the UV range [11].

### D. Fourier Transform Infrared Spectroscopy (FTIR) Analysis

DOM powder obtained through freeze-drying the fractions was analyzed for the structural and chemical characteristics of DOM. KBr was mixed with the DOM

powder about the ratio of 100 to 1 and the FTIR spectra of the mixture were obtained by scanning it with FTIR spectrometer (Thermo Nicolet 5700, USA).

### E. Fluorescence Spectroscopy Analysis

Fluorescence spectra were recorded on a fluorescence spectrophotometer (model F-4500, Hitachi, Japan). Three-dimensional spectra were obtained by measuring the emission spectra in the range from 250 to 550 nm repeatedly, and at the excitation wavelengths from 230 to 420 nm, at 5 nm intervals in the excitation domain.

## III. RESULTS AND DISCUSSION

### A. Water Quality of ROC

Raw ROC samples were collected periodically at the RO site of petrochemical wastewater. As shown in table I, its SUVA is 1.65 L/(cm<sup>2</sup>·g) comparable with that of municipal wastewater [12]. Dissolved COD is about 95% of total COD, indicating that DOM is the main organics in ROC. The BOD/COD ratio is 0.24 below 0.30, showing that DOM is not so biodegradable which suggests that advanced oxidation such as ozonation may be a better pretreatment method.

TABLE I. WATER QUALITY OF ROC

pH	total alkalinity	Conductivity (ms/cm)	NH <sub>3</sub> -N (mg/L)	DOC (mg/L)	COD (mg/L)	Dissolved COD(mg/L)	BOD (mg/L)	SUVA L/(cm <sup>2</sup> ·g)
4.51±0.1	12.02±0.05	12.31±0.05	0.9	56.4±0.5	350±10	330±10	88.68±11	1.65±0.05

### B. Ozonation of ROC

Ozone was continuously introduced into 1 L raw ROC at a constant flow of 1.8 mg/min for 30 min. Ultraviolet spectrophotometry, FTIR and fluorescence spectroscopy were employed to characterize DOM before and after ozonation.

#### 1) UV-Vis analysis

The spectrophotometric scanning spectra (220–400 nm) of ROC before and after ozonation are shown in Fig.1 (a). Due to the existence of a variety of functional groups, there is no obvious characteristic peak among the scanning UV-visible region. It is observed that ROC after ozonation shows a significant decrease in absorbance among the range of 230–400 nm compared to ROC, indicating that O<sub>3</sub> sharply removed or varied the fractions with absorbance wavelength above 230 nm. Schnitzer et al. [13] suggested that aromatic C=C, ketone carbonyl C=O, and some auxochrome groups (such as C-OH and -NH<sub>2</sub>) showed obvious absorbance in 254-280 nm UV region.

UV<sub>254</sub> (absorbance of UV at 254 nm) to DOC ratio, i.e. SUVA<sub>254</sub>, is commonly reported to represent the aromatic character of organic matters as they imparted the ability to absorb light in the UV range [11]. UV<sub>250</sub>/UV<sub>365</sub> is also employed to represent the aromaticity and molecular weight of DOM. It is reported that lower UV<sub>250</sub>/UV<sub>365</sub> exhibits higher molecular weight [14]. Figure 1 (b) shows the

variation of specific UV absorbances during ROC ozonation for 30 min. It is observed that SUVA<sub>254</sub> decreases significantly during the initial 20 min, while varies gently in the final 10 min. On the contrary, UV<sub>250</sub>/UV<sub>365</sub> increases sharply during the initial 20 min and keep increasing slowly in the following 10 min. It can be concluded that some functional groups especially unsaturated bonds in ROC are subjected to O<sub>3</sub> attack in the initial 20 min, which results in the lower molecular weights and lower aromaticity.

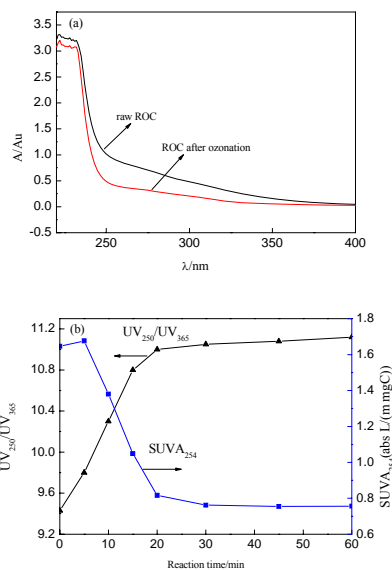


Figure 1. (a) Spectrophotometric scanning spectra of ROC before and after ozonation and (b) UV absorbance ratios at different wavelengths.

## 2) FTIR

The FTIR spectra of ROC before and after ozonation are shown in Figure 2. Interpretation of the absorption bands of DOM was done as described in the literature [7, 15-17].

ROC before and after ozonation are similar in spectra with three distinctive adsorption bands: 1600–1650 $\text{cm}^{-1}$  suggesting aromatic skeletal  $\nu\text{C}=\text{C}$  or aldehyde and ketone groups  $\nu\text{C}=\text{O}$ ; 1380–1400 $\text{cm}^{-1}$  attributed to aliphatic structures containing C—H functional groups; and 900–1200  $\text{cm}^{-1}$  largely due to carbohydrates  $\nu\text{C}-\text{C}$  or O-alkyl group  $\nu(\text{C}-\text{O})$ . It is observed that compared to raw ROC, the DOM after ozonation exhibited a relatively weak peak at 1631 $\text{cm}^{-1}$  which is defined as the aromatic structures, whereas the adsorption peak around 1380–1400 $\text{cm}^{-1}$  is obviously enhanced. The results indicate that the aromatic and long chain structures of ROC are destroyed under the attack of  $\text{O}_3$  leading to the decrease in aromaticity and molecular weights, which is consistent with the conclusion of UV-Vis analysis.

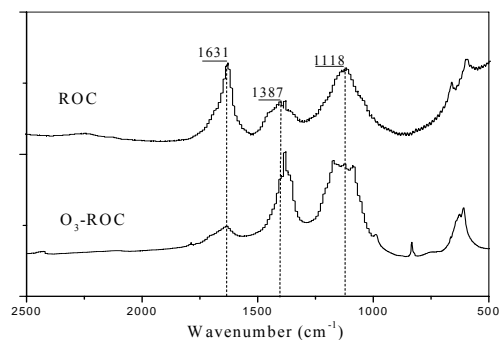


Figure 2. FTIR spectra of ROC before and after ozonation

## 3) 3D-EEM

Excitation emission matrix (EEM) was used to characterize ROC before and after ozonation. The contour maps of the results showed that ROC contains similar peaks with quite different fluorescence intensity (Figure 3). The substances and fluorescence intensity corresponding to the peaks are shown in Table II.

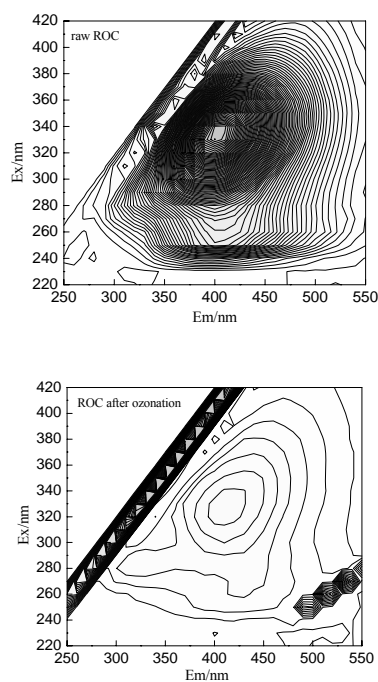


Figure 3. 3D-EEM spectra of ROC before and after ozonation

TABLE II. EEM PEAKS FOR THE DOM FRACTIONS.

	Ex/Em (nm/nm)	Fluorescence substances	Intensity (on a per carbon basis)
raw ROC	330/400	humic-acid like products	25.96
	250/400	fulvic-acid like products	7.75
ROC after ozonation	330/410	humic-acid like products	2.70
	260/418	fulvic-acid like products	1.45
	280/320	Soluble microbial products	1.69

Humic and fulvic acids are the main fluorescence substances in raw ROC, indicating a large amount of unsaturated aromatic structures. After ozonation, the intensity of humic and fulvic acids is greatly decreased and a new peak standing for soluble microbial products appears. The results are consistent with the above analysis. O<sub>3</sub> oxidizes and destroys the aromatic groups such as humic and fulvic acid-like products and accordingly results in the production of soluble microbial products to some extent, which are attributed to the increase of biodegradability.

### C. Fractionation of ROC before and after Ozonation

#### 1) DOC distribution and SUVA of DOM fractions

Ozone was continuously introduced into DOM for 30 min and resins were used to fractionate ROC before and after ozonation. The SUVA and DOC percentage of ROC fractions before and after ozonation are presented in Figure 4.

It is found that after ozonation, the DOC percentage of hydrophobic organics in raw ROC drops from 52.4% to 39.7%, in which a substantial decrease from 29.1% to 14.4% in the percentage of HoN is observed. Correspondingly, the DOC percentage of WHoA increases from 16.7% to 23.9% and HiM increases from 30.9% to 36.4%. On the other hand, 30 min ozonation results in a decrease of DOC by 18.3%, which suggests that ozonation results in a little mineralization, yet alters the structures of ROC to more hydrophilic.

The SUVA of raw ROC fractions is at 0.71–1.88 L/(mg·m), especially HoA showing the highest of 1.88 L/(mg·m). A significant decrease in SUVA of ROC fractions is observed after ozonation, suggesting the obvious change of aromatic structures. In particular, the SUVA of WhoA decreases from 1.78 L/(mg·m) to 0.60 L/(mg·m), while hydrophobic organics such as HoA and HoN still exhibit relatively high SUVA, 1.09 L/(mg·m) and 1.11 L/(mg·m), respectively.

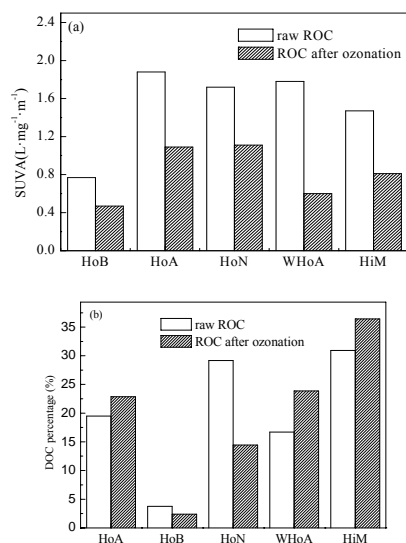


Figure 4. Distribution and SUVA of DOM fractions in ROC before and after ozonation. (a) SUVA and (b) DOC percentage.

### 2) FTIR Analysis of DOM Fractions

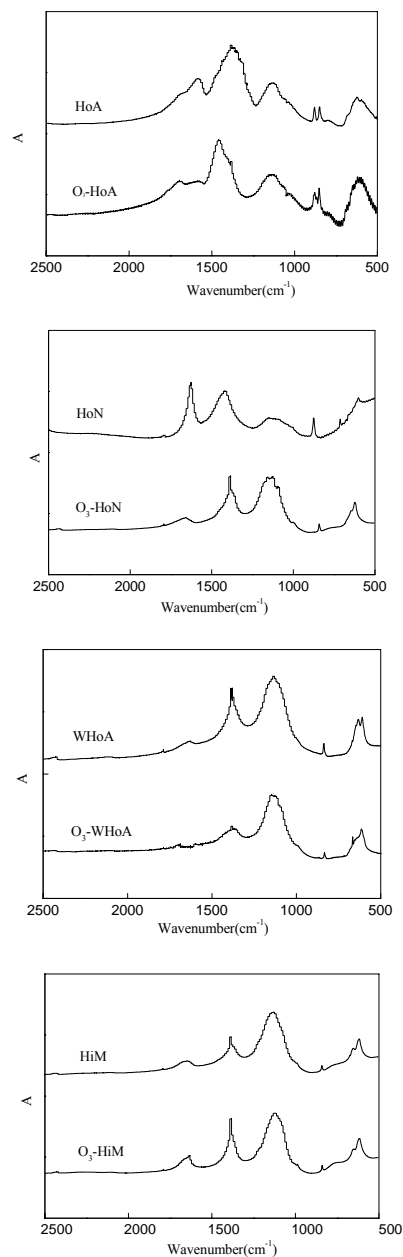


Figure 5. The FTIR spectra of DOM fractions before and after ozonation. DOM fractions of raw ROC are HoA, HoN, WhoA and HiM. DOM fractions of ROC after ozonation are O<sub>3</sub>-HoA, O<sub>3</sub>-HoN, O<sub>3</sub>-WhoA and O<sub>3</sub>-HiM.

Figure 5 shows the FTIR analysis of ROC fractions before and after ozonation. It is observed that there is a similar peak around 1600–1650 cm<sup>-1</sup> for the four main fractions of ROC which is defined as the aromatic structures containing C=C bonds. Compared to WHoA and HiM, the hydrophobic fractions exhibit a relatively strong peak around 1600–1650 cm<sup>-1</sup> suggesting relatively high aromaticity. After ozonation, the peaks around 1600–1650

cm<sup>-1</sup> of the hydrophobic fractions are significantly weakened, in particular HoN, whereas the peak around 900–1200 cm<sup>-1</sup> due to hydroxy acids or O-alky group  $\nu(\text{C—O})$  for HoN is greatly enhanced. It is believed that the decrease in aromatic structures and increase in  $\nu(\text{C—O})$  groups cause ROC to be more hydrophilic after ozonation.

### 3) 3D-EEM Analysis of DOM Fractions

Figure 6 shows the 3D-EEM spectra of ROC fractions before and after ozonation. The contour maps of the results show that different fractions exhibited different peaks and ozonation significantly decrease the fluorescence intensity. Table 3 exhibits the substances and fluorescence intensity corresponding to the peaks.

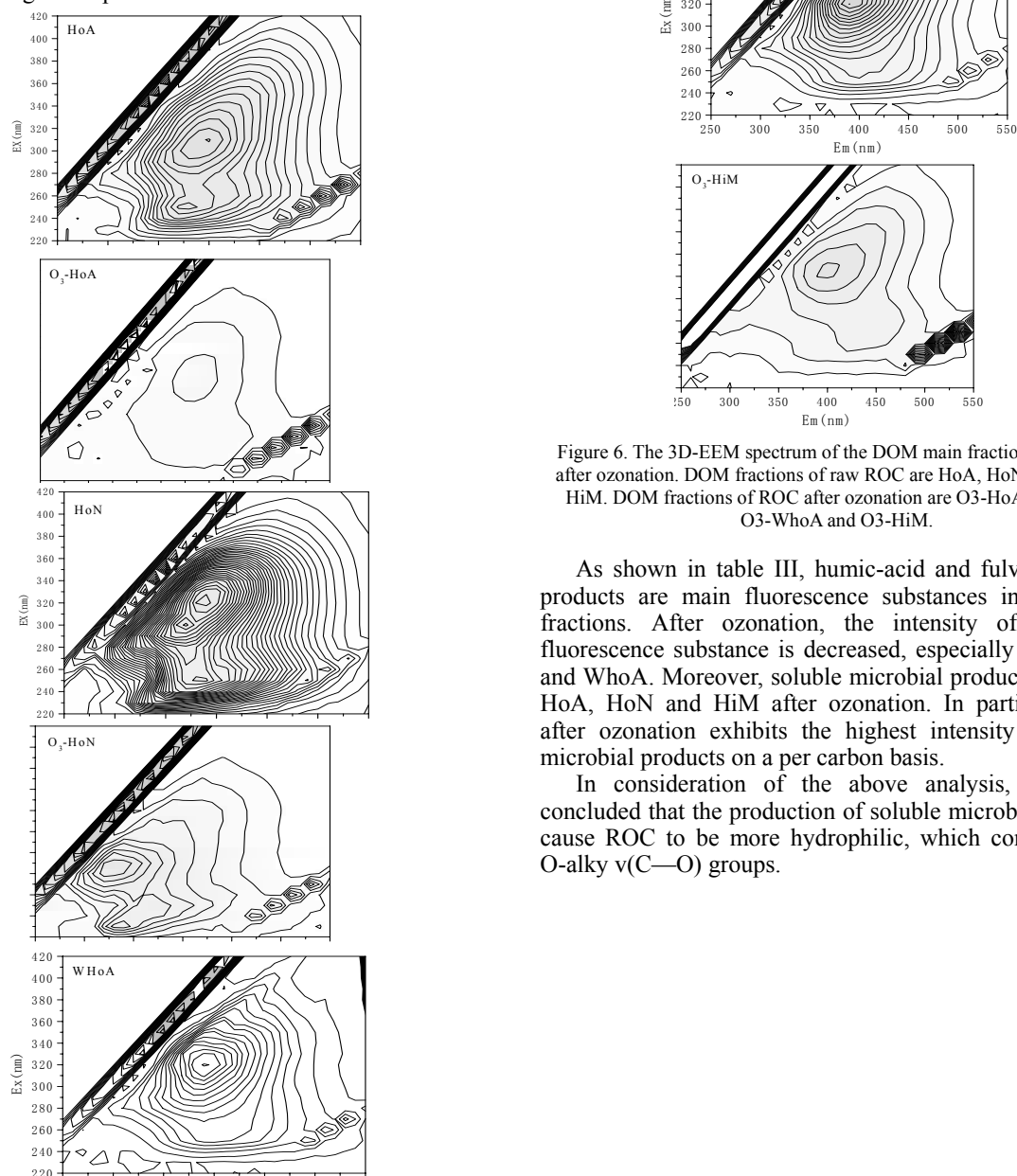


Figure 6. The 3D-EEM spectrum of the DOM main fraction before and after ozonation. DOM fractions of raw ROC are HoA, HoN, WhoA and HiM. DOM fractions of ROC after ozonation are O<sub>3</sub>-HoA, O<sub>3</sub>-HoN, O<sub>3</sub>-WhoA and O<sub>3</sub>-HiM.

As shown in table III, humic-acid and fulvic-acid like products are main fluorescence substances in raw ROC fractions. After ozonation, the intensity of the main fluorescence substance is decreased, especially HoA, HoN and WhoA. Moreover, soluble microbial products appear in HoA, HoN and HiM after ozonation. In particular, HiM after ozonation exhibits the highest intensity of soluble microbial products on a per carbon basis.

In consideration of the above analysis, it can be concluded that the production of soluble microbial products cause ROC to be more hydrophilic, which contains more O-alky  $\nu(\text{C—O})$  groups.

TABLE III. FLUORESCENCE PEAK AND INTENSITY OF DOM MAIN FRACTION BEFORE AND AFTER OZONATION

	raw ROC			ROC after ozonation		
	Ex/Em (nm/nm)	Fluorescence substances	Intensity (on a per carbon basis)	Ex/Em (nm/nm)	Fluorescence substances	Intensity (on a per carbon basis)
HoA	400/390	humic-acid like products	54	400/390	humic-acid like products	42
	250/380	fulvic-acid like products	24	295/295	Soluble microbial products	66
HoN	325/390	humic-acid like products	71	395/390	humic-acid like products	62
	250/390	fulvic-acid like products	38	285/300	fulvic-acid like products	37
				230/340	Soluble microbial products	56
WHoA	320/395	humic-acid like products	42	320/380	humic-acid like products	36
HiM	345/390	humic-acid like products	32	390/390	humic-acid like products	31
				298/280	Soluble microbial products	79

#### IV. CONCLUSIONS

Ozonation alters the structures of DOM in petrochemical ROC to be more hydrophilic. Using RAC technique, ROC before and after ozonation is isolated into five fractions: HoA, HoB, HoN, WHoA, and HiM. Hydrophobic organics dominate in raw ROC, in which HoN and HoA account for 29.2% and 19.5%, respectively. Ozone significantly decreases the percentage of HoN, while increases the concentration of WHoA and HiM, resulting in relatively high hydrophilicity of ROC.

Ozonation decreases the molecular weight of raw ROC. The unsaturated groups and aliphatic structures are destroyed greatly and converted to more C-O structures, which shows relatively high hydrophilicity and low molecular weight. Through the analysis of fluorescence spectroscopy, it is found that ozone decreases significantly the fluorescence intensity of humic-like and fulvic-like substances in DOM, whereas increases the fluorescence intensity of soluble microbial products. The production of soluble microbial products cause ROC to be more hydrophilic, which contains more O-alkyl v(C—O) groups.

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