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Characterization and treatment of dissolved organic matter from oilfield produced waters

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ABSTRACT

Dissolved organic matter (DOM) has been studied intensively in streams, lakes and oceans due to its role in the global carbon cycle and because it is a precursor of carcinogenic disinfection by-products in drinking water; however, relatively little research has been conducted on DOM in oilfield produced waters. In this study, recovery of DOM from two oilfield produced waters was relatively low (~34%), possibly due to the presence of high concentrations of volatile organic compounds (VOCs). A van Krevelen diagram of the extracted DOM suggested the presence of high concentrations of lipids, lignin, and proteins, but low concentrations of condensed hydrocarbons. Most of the compounds in the oilfield DOM contained sulfur in their structures. Fourier transform infrared (FTIR) spectra indicated the presence of methyl groups, amides, carboxylic acids, and aromatic compounds, which is in agreement with results of Fourier transform ion cyclotron resonance (FT-ICR) analysis. Qualitatively, DOM in oilfield produced waters is similar to that reported in oceans and freshwater, except that it contains much more sulfur and is less aromatic. Treatment studies conducted in a fluidized bed reactor suggested that volatilization of organics may be a more important mechanism of DOM removal than microbial degradation.

1. Introduction

Oilfield produced water is a by-product of petroleum exploration and development. It is characterized by high concentrations of both total dissolved solids (TDS) and dissolved organic matter (DOM), along with varying amounts of oil, grease, surfactants, and miscellaneous organic solvents [1]. Historically, oilfield produced water has been disposed of in large evaporation ponds. This practice is of present concern because of the emission to the atmosphere of volatile organic compounds (VOCs), which include many ozone precursor compounds. Together with additional VOC emissions from operations associated with petroleum production, ozone levels may readily exceed air quality standards in areas where oil development occurs [2,3]. High ozone levels are commonly associated with respiratory problems and incur a greater risk of mortality in humans [4].

In the literature, DOM is most often defined as that portion of organic matter in water that passes through a 0.45 μm filter [5]. The composition of DOM is complex and contains thousands of individual chemicals [1]. Much research has been done on DOM in marine waters as it is the largest reservoir of organic carbon in the ocean [6] and is an important component of the global carbon cycle [7]. Freshwater DOM has also been studied intensively as it is a precursor of carcinogenic by-products [8] such as trihalomethanes (THMs) and haloacetic acids (HAAs) formed during chlorination of drinking water [9]. Some fraction of DOM is reported to be easily degradable, while a substantial portion is refractory [10]; however, relatively little research has been performed on DOM from oilfield produced water, so its chemical characteristics and susceptibility to treatment remain less well understood.

Various technologies have been proposed for the treatment of oilfield produced waters with DOM removals ranging from 20% to 90% [1,11–13]; this large variation is likely due to the recalcitrance of some fraction of the DOM to microbial attack [14]. For example, humic and fulvic acids, which are known to comprise a significant fraction of DOM in freshwaters, are generally resistant to microbial degradation [15].

Compared to physical and chemical methods, biological treatment is more attractive for remediation of oilfield produced waters due to lower costs [16]. Various biological methods have been proposed and evaluated for the treatment of oilfield produced water. Fluidized bed reactors are particularly appealing due to their high efficiency, low cost, and small size [17]. Seybold et al. [18] used fluidized bed reactors (FBRs) packed with granular activated carbon (GAC) to remove 74% of the chemical oxygen demand (COD) of a produced water. A sequencing batch reactor (SBR) was designed by

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Baldoni-Andrey et al. [11] for total organic carbon (TOC) removal in a produced water from the Gulf of Guinea and achieved 80% removal. Another SBR was operated by Freire et al. [14] to treat an oilfield wastewater; they reported 50% COD removal. An activated sludge treatment unit operated by Tellez et al. [12] obtained 98–99% removal of total petroleum hydrocarbons (TPHs) from an oilfield produced water, while a batch study seeded with bacteria by Li et al. [13] was reported to achieve 70% COD removal. Lastly, Murray-Gulde et al. [19] employed a hybrid reverse osmosis constructed wetland treatment system that removed 80% of the TOC in a brackish oilfield produced water.

This study first focused on the extraction and characterization of DOM in produced waters. We then assessed DOM removal attributable to microbial degradation and volatilization in a laboratory-scale FBR.

2. Materials and methods

2.1. Chemicals

All chemicals used were of high quality and included the following: hydrochloric acid – HCl (36.5%, ACS grade, VWR International, West Chester, PA); methanol – CH_3OH (HPLC grade, EMD Chemicals Inc., Gibbstown, NJ); zero grade air (air with 1 ppm max. of CO, CO_2, or HC; Airgas, Cheyenne, WY); potassium hydrogen phthalate – $KHC_8H_4O_4$ or KHP (Nacalai Tesque Inc., Kyoto, Japan); sodium azide – NaN_3 (purified grade, Fisher Scientific, Fair Lawn, NJ); nanopure water (Barnstead Thermolyne Nanopure Water System, Dubuque, IA); Bushnell–Haas Broth (Difco) and glass beads (Jencons Scientific Ltd., Bedfordshire, England).

2.2. Oilfield produced waters

Two oilfield produced waters – Gibbs and Oxbow – were selected for analysis but were only available in limited quantities. Oxbow water was used when Gibbs water was depleted. Chemical characterization indicated that the two samples were nearly identical. The Gibbs water was obtained from the Gibbs Formation in Wyoming and was sampled by the Enhanced Oil Recovery Institute at the University of Wyoming. The Oxbow water was obtained from Prima Exploration (Oxbow Well 2-35 Thompson near Gillette, WY) courtesy of the Nalco Company. Both water samples were collected in several 20 L plastic containers, capped, and stored at room temperature.

For DOM extraction, five liters of Gibbs produced water were acidified to pH 2 with HCl immediately upon receipt, then stored in sealed glass containers and kept in a refrigerator at 4 °C. All oilfield produced water samples that were used to prepare DOM extracts were first filtered through hydrophilic cellulose ester membrane filters (GN-6 Metrical S-Pack Membrane Disc Filters, 0.45 μm pore size, 47 mm diameter, Pall Corporation, Ann Arbor, MI) to remove large particles. These larger particles contained particulate organic carbon, which was considered insoluble and would interfere with DOM characterization. Concentrations of particulate organic carbon in both of the produced waters were determined to be less than 30 mg/L.

2.3. Total organic carbon (TOC) and non-purgeable organic carbon (NPOC)

All TOC and non-purgeable organic carbon (NPOC) measurements were determined on a Total Organic Carbon analyzer (Shimadzu Corporation, Kyoto, Japan). Samples were automatically injected with a glass syringe into a platinum catalytic combustion tube (680 °C) in which organic carbon was combusted to carbon dioxide (CO_2). Carbon dioxide was then directed to a non-dispersive infrared detector (NDIR). For NPOC analysis, water samples were sparged with zero grade air for 90 s to removal purgeable carbon prior to injection. The airflow rate for sparging was 230 ml/min. All TOC and NPOC values were plotted as mean values of separate injections from replicate samples.

2.3.1. TOC and NPOC calibration curves

Since the TOC concentrations of the produced water samples used in this work varied between 50 and 700 mg/L, samples were diluted to fall within the range of the TOC calibration curve. TOC concentrations of 0, 0.5, 2, 5, and 8 mg/L were used for the NPOC calibration curve to accommodate NPOC concentrations in the oilfield waters of 10–200 mg/L; again, samples were diluted to fall within the range of the calibration curve. When plotted, the calibration curves resulted in linear regression coefficients of 0.99 and 1.00 for TOC and NPOC, respectively.

2.3.2. Total organic carbon (TOC) measurements

Several mechanical components of the TOC analyzer are very sensitive to salinity. Because oilfield produced waters usually contain high concentrations of various salts [e.g., concentration of TDS in Oxbow produced water was 26.6 g/L], it was necessary to dilute the samples (1:50 or 1:100) with nanopure water before analysis. Operating conditions for the TOC analyzer were as follows: carrier gas (zero grade air) at a flow rate of 150 ml/min; gas pressure at 200 kPa; injection volume 50 μl.

2.4. Solid phase extraction (SPE) of DOM

Immediately before extraction, aliquots of acidified oilfield produced water were filtered through 0.45 μm Whatman cellulose nitrate membrane filters according to the procedure described by Dittmar et al. [20]. Bond Elut PPL SPE cartridges (1 g PPL sorbent per cartridge, Varian, Palo Alto, CA) were rinsed with one cartridge volume of methanol immediately before use (see Fig. 1, Step 2). Six liters of oilfield produced water were then passed through the cartridges using a peristaltic variable flow mini pump (Control Company, Friendswood, TX) at a flow rate of 2 ml/min. Before elution, the cartridges were rinsed with 20 ml of 0.01 mol/L HCl to remove salts. The cartridges were then air dried, and the DOM was eluted with 6 ml of methanol at 2 ml/min into glass vials. The eluates were stored at −20 °C until analysis.

For calculation of the DOM recovery rate, the eluates were air dried and weighed. Assuming the DOM concentration was twice the TOC concentration [4], the DOM recovery rate was calculated as follows:

$$\mathrm{RR} = \frac{M_{\mathrm{DOM}}}{2C_{\mathrm{TOC,FW}}V_{\mathrm{FW}}} \quad (1)$$

where RR represents recovery rate, M_{DOM} is the mass of DOM in mg, $2C_{\mathrm{TOC,FW}}$ is the TOC concentration of the feed water in mg/L, and V_{FW} is the volume of feed water in L. Purgeable organic carbon (POC) was calculated as the difference between the TOC and the NPOC. The concentrations of TOC, NPOC and POC in the produced oilfield waters (on the order of hundreds of mg/L) were much higher than those commonly measured in seawater samples (e.g., <5 mg/L; [20]) and so would overload the SPE cartridge. For this reason, the produced water was diluted before extraction.

2.5. Fourier transform infrared (FTIR) spectroscopic characterization of DOM

The DOM eluates were stored in glass vials and air-dried for 5 h prior to analysis by Fourier transform infrared (FTIR) spectroscopy. A Perkin-Elmer Spectrum 1000 FTIR spectrophotometer was used to obtain spectra (16 scans from 4000 cm^{-1} to 400 cm^{-1}; resolution

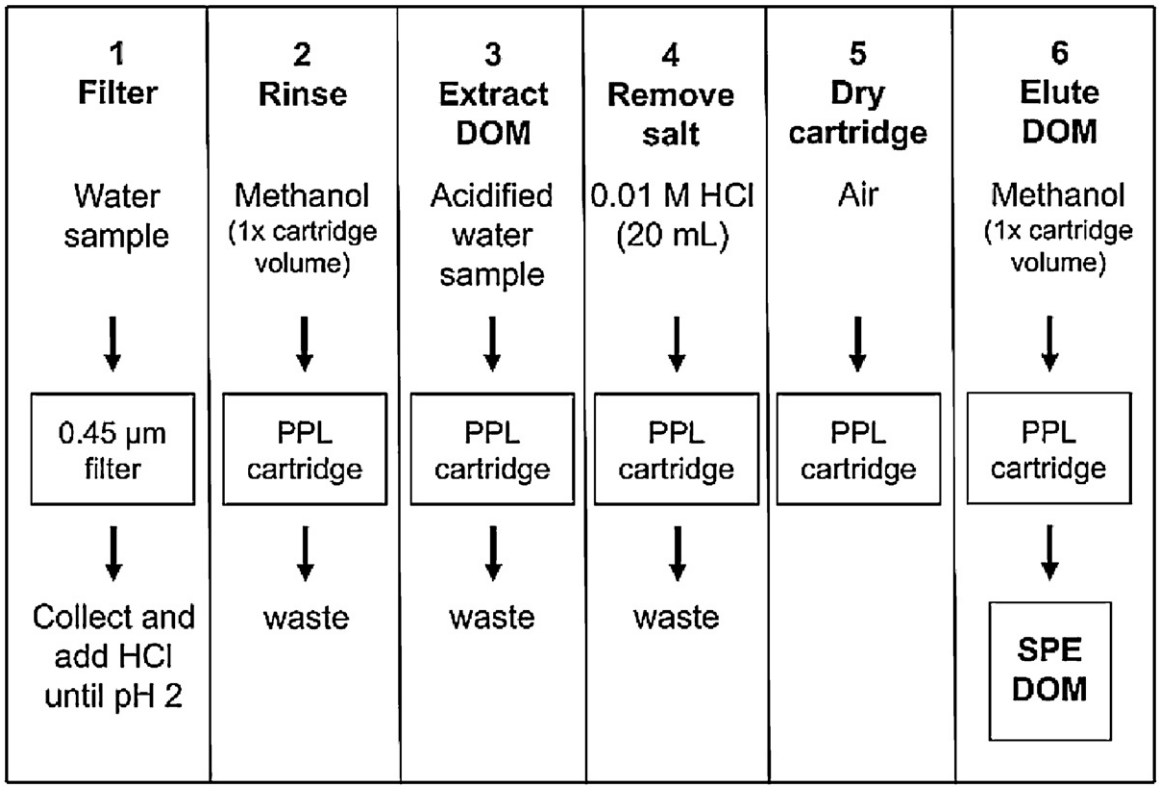

Fig. 1. Protocol for solid phase extraction (SPE) of DOM from oilfield produced water.

of 4 cm^{-1}; blank-corrected using a clean KBr pellet) in transmittance (%T) mode. Samples were mixed with KBr at a weight ratio of 1:100. Peak wave numbers were determined using the instrument software package (Perkin-Elmer Spectrum BX/1000 Software).

2.6. Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometric characterization of DOM

The solid phase extracts of the two oilfield produced waters were sent to the University of Oldenburg (Germany) for high resolution FT-ICR mass spectrometric analysis in electrospray ionization (ESI) negative mode. The criteria used for formulae calculations were as follows: (1) N, S and P (nitrogen, sulfur and phosphorus counts in a formula, respectively) should be $\leq$2; (2) O < C (oxygen and carbon counts); (3) O < (2 × P + S). Only peaks with signal-to-noise ratios $\geq$3 were considered legitimate peaks.

2.7. Assessment of DOM removal in a fluidized bed reactor (FBR)

Bacteria were routinely detected in the produced water samples used in this study; however, none of the batch-scale laboratory biodegradation assays (data not shown) confirmed any significant levels of biodegradation of organic substrates contained in the oilfield produced water. In an effort to quantitatively assess the potential for microbial degradation as well as volatilization of oilfield DOM, raw produced water was pumped through a FBR and changes in TOC and NPOC concentrations were monitored.

A vertical glass column reactor (volume: 154.6 cm^3) was packed with 2 mm diameter glass beads. Fluid and air were pumped through a single phase Vanton pump (1/4 HP; 1725 RPM; Baldor Electric Co., Ft. Smith, AR). Glass beads were used as the bed medium because of their minimal adsorption of organic compounds [21,22]. Conditions in the FBR were as follows: weight of glass beads 33.7 g; glass beads pack height 5 cm; fluidized height 31.5 cm. All tubing used was 1/2″ ID × 1/16″ wall PTFE Teflon Tubing (Saint-Gobain Performance Plastics Corp., Akron, OH). The hydraulic retention time (HRT) in the reactor was 0.12 ± 0.02 min. A volume of 0.5 L of oilfield produced water was kept in a reservoir beaker with a HRT of 0.48 ± 0.08 min. A tubing adapter was used to keep half of the tubing in the produced water. Air was pumped into the reactor with the produced water to keep the system aerobic. The system remained at room temperature during all experiments.

In addition to replicate runs in the FBR with raw produced water only, various amendments to the raw water were also made in replicate experiments, including the use of Bushnell–Haas Broth (Difco), which is commonly used in hydrocarbon biodegradation assays. Yeast extract was added in some experiments because it was expected to improve DOM removal. Measurements of TOC and NPOC were made at 0, 1, 3, 6, 9, 20, 30, and 40 h. Control tests were performed using sterile distilled water with an initial TOC concentration of 1.3 ± 0.2 mg/L. After 1 h, the TOC averaged 1.9 ± 0.7 mg/L, suggesting negligible TOC release from the system components of the FBR. For abiotic control experiments, 10 g/L of sodium azide (NaN_3) was added to the FBR to inhibit microbial growth.

3. Results and discussion

3.1. Solid phase extraction (SPE) of DOM

The extracted DOM was a viscous, yellowish-brown colored solid after air drying. For the Gibbs produced water, the concentration of DOM recovered initially by SPE was only 15 mg/L, which represents an estimated recovery of only 1.3%. Recycling wastewater or using a neutral pH did not increase recovery, while reducing the flow rate increased recovery only slightly. For Gibbs produced water that was diluted 1:150 with nanopure water, recovery was increased to 25%; for water diluted 1:1000, the recovery rate

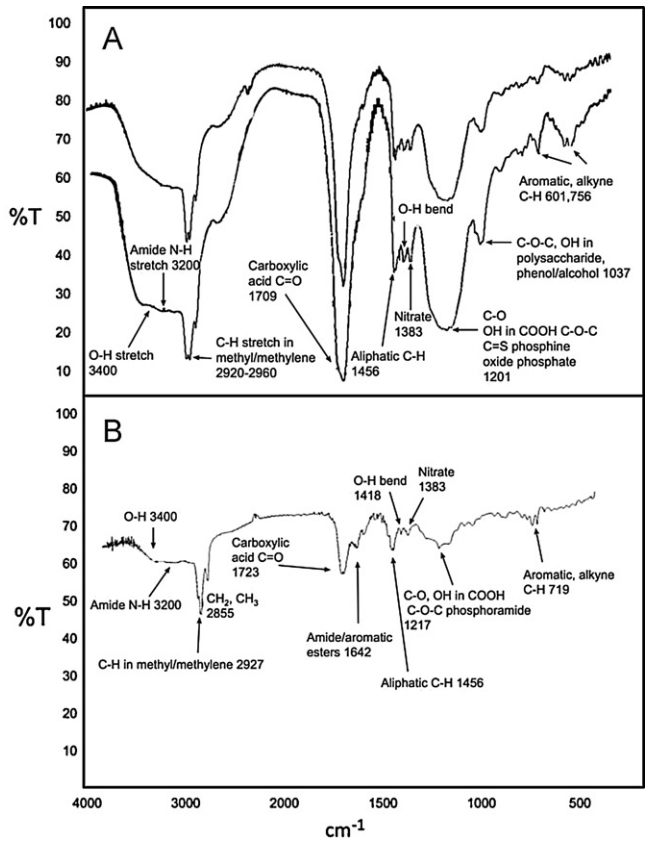

Fig. 2. FTIR spectrum of DOM extracted from Gibbs (panel A) and Oxbow (panel B) oilfield produced waters.

was 34%. For raw Oxbow produced water, the DOM recovery rate achieved was comparable.

There are two explanations for the low DOM recoveries. First, NPOC concentrations in the oilfield waters were significantly lower than the TOC concentrations, which suggests that large quantities of VOCs (e.g., benzene, toluene, volatile fatty acids) were likely present [1]. These compounds can effectively 'wash out' the DOM, just as methanol does [23] when used as an eluent in the DOM extraction procedure (see Fig. 1). A second possibility is that the SPE cartridge was simply overloaded; this is likely why dilution of the produced water prior to extraction resulted in increased rates of recovery.

3.2. FTIR characterization of DOM

The FTIR spectra of DOM extracted from the two oilfield produced waters are shown in Fig. 2 (Gibbs in panel A and Oxbow in panel B). Qualitatively speaking, the two waters exhibited very similar patterns; both contained structures with similar functional groups (e.g., methyl, amide, carboxyl) aliphatic and aromatic hydrocarbons. There were only two small differences. The peak at 1037 cm^{-1} in the Gibbs DOM contained peaks for C—O and OH groups that were not present in the Oxbow DOM. In addition, the peak at 1642 cm^{-1} in the Oxbow DOM contained weak peaks for amides or aromatic esters that were absent in the Gibbs DOM. Overall, however, FTIR analysis of the two oilfield produced waters used in this study suggests that they were qualitatively very similar in chemical composition.

3.3. FT-ICR characterization of DOM

A total of some 700 peaks were identified in the FT-ICR mass spectrum of DOM extracted from Gibbs produced water (see Fig. 3).

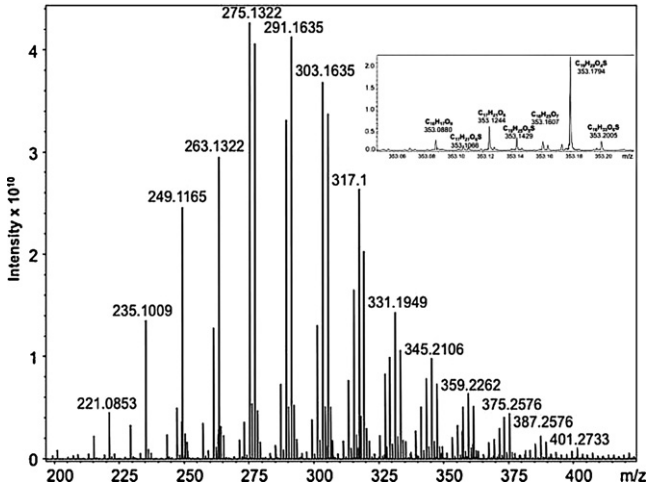

Fig. 3. High resolution mass spectrum of SPE DOM samples from Gibbs produced water. Insert of refined spectrum (353.05–353.22 *m*/*z*).

A common method for interpretation of such large spectral data sets is the van Krevelen diagram [24], which plots the elemental ratios of oxygen-to-carbon (O:C) on the *x*-axis and hydrogen-to-carbon (H:C) on the *y*-axis for each formula of DOM molecules. Major chemical classes are then assigned according to their characteristic O:C and H:C ratios [25].

Fig. 4 is the van Krevelen diagram constructed for the Gibbs DOM extracts where intensity (as represented by the intensity of the symbol) is synonymous with concentration. The results indicate the presence of high concentrations of lipids, proteins, and lignin with only minor concentrations of condensed hydrocarbons. The molecular weight of the Gibbs DOM is in the range of 200–400, lower than marine DOM [26]. Cellulose, highly condensed lignin, and tannins are notably absent. Marine DOM has been reported to consist of carbohydrates, amino acids, and lipids [27]. One important observation is that the oilfield DOM samples in this study contained far fewer condensed hydrocarbons than even ocean DOM [26]. Lignin, lipids, aliphatic amines and amides, amino sugars, carbohydrates, tannins, and condensed aromatics have all been identified in DOM extracted from a river to ocean transect area [28], while a peatland DOM was found to consist of humic acids, fulvic acids, esters, fatty acids, carbohydrates, and amino acids [29]. These results are remarkably similar to those obtained in this present study, except

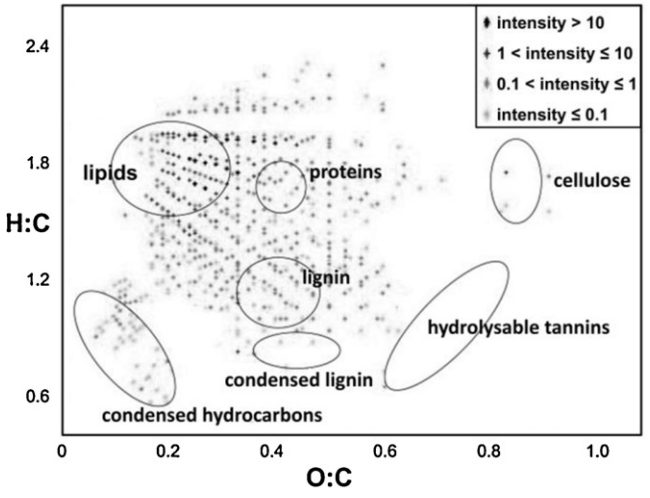

Fig. 4. van Krevelen diagram of DOM extracted from Gibbs oilfield produced water.

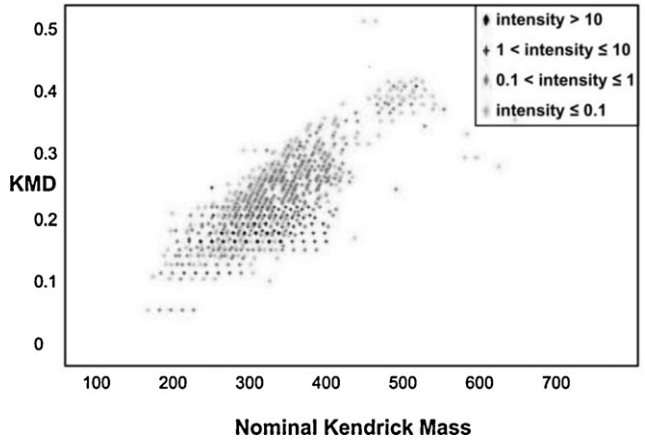

Fig. 5. Kendrick mass defect (KMD) diagram of DOM extracted from Gibbs oilfield produced water.

that the oilfield produced waters contain more sulfur and are generally much less aromatic.

A second spectral analysis method that can be applied to these data is Kendrick Mass Analysis [30,31] that calculates Kendrick exact mass (KEM) as follows:

$$\text{KEM} = \text{IUPAC Mass}\left(\frac{14}{14.01565}\right) \quad (2)$$

Members of a given alkylation (CH_2) series will have Kendrick masses differing by exactly 14 Daltons (Da), but will have the same Kendrick mass defect (KMD). KMD is the difference between the KEM and the Kendrick nominal mass, which is determined by rounding up the KEM to the nearest whole number. As shown in Fig. 5, the majority of compounds in the Gibbs DOM that are present in high concentrations have KMDs between 0.1 and 0.3. These values are much smaller than those typically found in petroleum-derived products [32]. Although largely qualitative, these results surprisingly suggest that the chemical classes present in oilfield produced waters are very different from those found in other by-products of petroleum origin [33].

A third method of analysis of FT-ICR spectra is double-bond equivalence (DBE), which is a measure of aromaticity [34] and is calculated as follows:

$$\text{DBE} = \text{C} - (0.5\text{H}) + (0.5\text{N}) + 1 \quad (3)$$

where C, H and N are carbon, hydrogen and nitrogen atoms in the DOM molecule, respectively.

Panel A of Fig. 6 plots the DBE value versus carbon number of all compounds detected in the Gibbs DOM. Panel B of Fig. 6 summarizes DBE data for all compounds that contain a single sulfur atom; the higher DBE values are suggestive of greater aromaticity. It is interesting to compare the DOM in oilfield produced water to heavy polar macromolecules like asphaltenes that are typical constituents of petroleum. The DBE data for asphaltenes [35] indicate that they have dramatically higher DBE values (20–35) than Gibbs DOM (0–16), clearly suggesting that DOM from our oilfield produced waters is much less aromatic than asphaltenes. Among all compounds identified in the DOM mass spectrum, it is estimated that some 65% of them possess sulfur moieties. Most of the sulfur-containing compounds fall into the same parental groups associated with the van Krevelen analysis (see Fig. 4) discussed previously.

3.4. DOM removal in a fluidized bed reactor (FBR)

Table 1 summarizes the TOC and NPOC changes in Oxbow oilfield produced water during treatment in the FBR, while Table 2

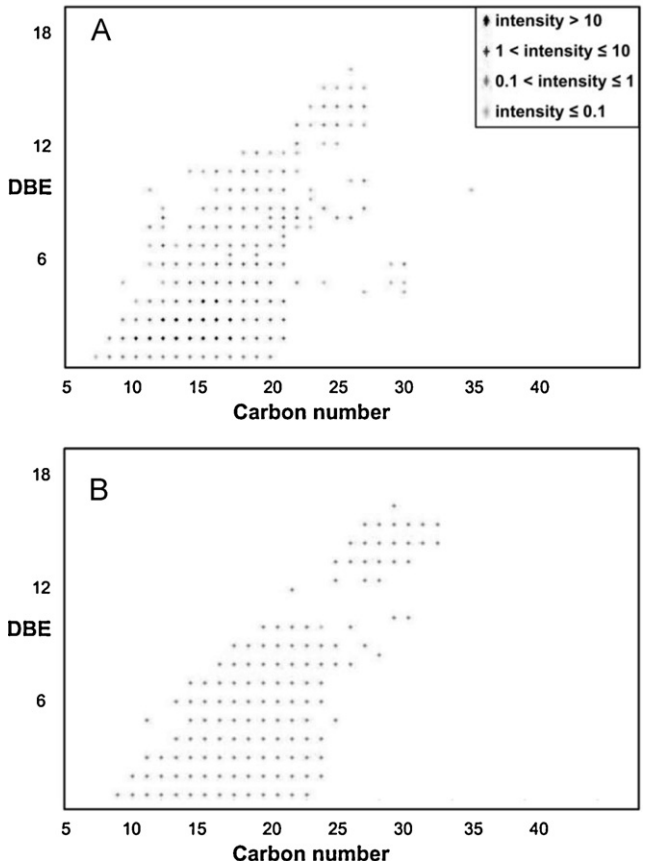

Fig. 6. Panel A: double-bond equivalence (DBE) diagram of DOM extracted from Gibbs oilfield produced water. Panel B: DBE diagram of single sulfur compounds in DOM extracted from Gibbs oilfield produced water.

estimates the contributions of various mechanisms to TOC removal in the reactor. Biodegradation, if it occurred at all, removed very little TOC, while TOC removal due to volatilization was estimated to range from 33.4% to 75.3% (221.7–499.8 mg/L). Addition of the biocide sodium azide (NaN_3) increased TOC removal, possibly due to the salt out effect; that is, when salt concentrations increased, water molecules became attracted to the salts and reduced the amount of water available to dissolve the DOM and so increased the Henry's law constant of the dissolved molecules [36]. As a consequence, volatilization of DOM was enhanced. The fact that NPOC remained unchanged during treatment in the reactor confirms that almost all of the TOC that was removed was comprised of volatile compounds.

Based on these results, it is reasonable to conclude that biodegradation contributed little to TOC removal in the reactor. In addition, there was no macroscopic evidence of biofilm development on the surface of the glass beads in the FBR. While it was possible to culture organisms directly from the water samples, our biodegradation assays clearly suggest that they were not able to degrade the more complex, nonvolatile organic constituents. Bacterial isolates were able to grow on simple substrates (e.g., glucose) or on mixtures of glucose and the oilfield-produced water, but were unable to grow on the oilfield-produced water when it was provided as the sole source of carbon and energy. Moreover, bacterial growth may have been inhibited due to the presence of surfactants in the produced water. Foam was apparent in all FBR runs as well as in the batch biodegradation tests. Surfactants are part of the DOM; their presence in oilfield produced waters might also serve as a barrier to oxygen diffusion, thereby reducing aerobic microbial activity [37].

Table 1
Mass balance on DOM removal from oilfield produced water (Oxbow) in fluidized bed reactor (all values in mg/L).

	TOC	NPOC	POC
Original concentrations in raw water	695.4 ± 14.5	94.4 ± 6.0	601.0 ± 12.8
Concentrations in treated water	175.9 ± 38.9	51.2 ± 5.5	124.7 ± 32.2
Total removal observed	519.4	43.2	476.3
Removal through biodegradation	0–43.1	NA	NA
Removal through flocculation[a]	0–136.7	NA	NA
Removal through volatilization	221.7–499.8	NA	NA

Since NPOC may be converted to POC, the cause of its removal was not clearly differentiated.
[a] Bushnell–Haas Broth contains 0.05 g/L $FeCl_3$.

Table 2
TOC removal from oilfield produced water in a fluidized bed reactor.

Experimental conditions	Possible mechanisms of removal	% TOC removal
Produced water (PW) only	Biodegradation (BIOD) + volatilization	54.7%
PW + Bushnell–Haas Broth + YE	BIOD + flocculation[a] + volatilization	75.3%
PW + Bushnell–Haas Broth + YE + NaN_3	Flocculation[a] + volatilization	68.8%
PW + NaN_3	Volatilization	71%

YE: yeast extract.
[a] Bushnell–Haas Broth contains 0.05 g/L $FeCl_3$.

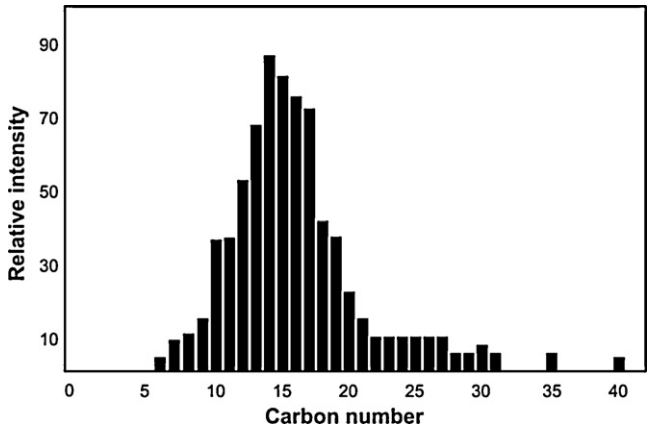

Fig. 7. Carbon number distribution in DOM extracted from Gibbs oilfield produced water.

Overall TOC removal achieved in this study is comparable to most other reports [11–14,18,19]. Despite impressive results from previous studies, none considered the effect of volatilization in their treatments; any removal they observed was attributed to microbial degradation. Our FBR study clearly suggests that volatilization is a more significant removal mechanism than biodegradation.

Nobrega [38] has suggested that compounds containing no more than 18 carbons be considered volatile. Fig. 7 illustrates the carbon number distribution in the DOM extracted from Gibbs produced water which was calculated by counting different molecules with the same carbon number. Of the 697 extracted compounds, a total of 533 may be classified as volatile, which accounts for approximately 68% of the DOM extracts by weight.

4. Conclusions

Recovery of DOM from two oilfield produced waters was relatively low (<35%), possibly due to the presence of a high proportion of volatile organic compounds. A van Krevelen diagram of the extracted DOM suggested the presence of high concentrations of lipids, proteins and lignin, but low concentrations of condensed hydrocarbons normally associated with petroleum production. FTIR spectra indicated the presence of various functional groups as well as some aliphatic and aromatic structures, which is in agreement with the FT-ICR analysis. DOM in the produced water is qualitatively very similar to DOM in freshwater and ocean samples, except that it contains much more sulfur and is significantly less aromatic. Results of fluidized bed reactor studies suggest that volatilization may be a more important removal mechanism than biodegradation in the treatment of oilfield produced waters, particularly when VOCs comprise a large fraction of the TOC or when bacteria are either absent or unable to degrade the organic constituents. If FBRs are used commercially to remove DOM from oilfield produced waters, then off-gas treatment will be required to reduce VOC emissions and prevent ozone formation.

Acknowledgments

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