Journal of Hazardous Materials 217–218 (2012) 164–170

Contents lists available at SciVerse ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Characterization and treatment of dissolved organic matter from oilfield produced waters

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ARTICLE INFO

Article history:
Received 22 December 2011
Received in revised form 29 February 2012
Accepted 3 March 2012
Available online 7 March 2012

Keywords:
Dissolved organic matter (DOM)
Oilfield produced water
Solid phase extraction
Volatile organic compounds (VOCs)

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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doi:10.1016/j.jhazmat.2012.03.006

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:

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

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