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Tracking oil and gas wastewater-derived organic matter in a hybrid biofilter membrane treatment system: A multi-analytical approach

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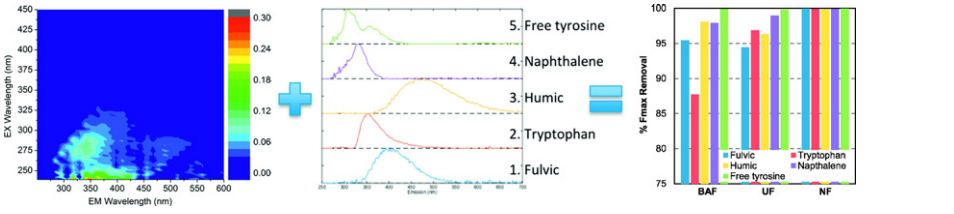
HIGHLIGHTS

- PARAFAC/3D fluorescence was used to quantify DOM in O&G produced water.
- PARAFAC/3D fluorescence was used to quantify removal of DOM throughout treatment.
- Five PARAFAC components were identified in O&G wastewaters throughout treatment.
- LC-OCD, LC-HRMS, and GC–MS results closely matched 3D fluorescence/PARAFAC results.
- Biologically active filters removed most of the DOM, with additional removal by NF.

GRAPHICAL ABSTRACT



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ABSTRACT

Dissolved organic matter (DOM) present in oil and gas (O&G) produced water and fracturing flowback was characterized and quantified by multiple analytical techniques throughout a hybrid biological-physical treatment process. Quantitative and qualitative analysis of DOM by liquid chromatography – organic carbon detection (LC-OCD), liquid chromatography–high-resolution mass spectrometry (LC-HRMS), gas chromatography–mass spectrometry (GC–MS), and 3D fluorescence spectroscopy, demonstrated increasing removal of all groups of DOM throughout the treatment train, with most removal occurring during biological pretreatment and some subsequent removal achieved during membrane treatment. Parallel factor analysis (PARAFAC) further validated these results and identified five fluorescent components, including DOM described as humic acids, fulvic acids, proteins, and aromatics. Tryptophan-like compounds bound by complexation to humics/fulvics were most difficult to remove biologically, while aromatics (particularly low molecular weight neutrals) were more challenging to remove with membranes. Strong correlation among PARAFAC, LC-OCD, LC-HRMS, and GC–MS suggests that PARAFAC can be a quick, affordable, and accurate tool for evaluating the presence or removal of specific DOM groups in O&G wastewater.

1. Introduction

1.1. O&G wastewater production and management

Large volumes of oil and gas (O&G) wastewater (i.e., fracturing flowback (FFB) and produced water (PW)) are constantly generated in the United States (US) and around the world. An astounding

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50 million cubic meters (13 billion gallons) from seven key shale plays are deep-well injected annually in the US, particularly in the West and Midwest regions where disposal wells are abundant and are the most affordable management option (Casey et al., 2014). However, increased seismicity in the US Midwest, associated with deep well disposal, has led to the closure of dozens of disposal wells (i.e., injection wells) (Murphy, 2016) and tighter regulations on those that remain operational (Keranen et al., 2014; Weingarten et al., 2015). This substantially limits new drilling activities and volumes of O&G that can be produced. Consequently, efforts to develop sustainable strategies for O&G wastewater treatment and reuse are intensifying.

Potential reuse applications include hydraulic fracturing, irrigation, livestock watering, and stream flow augmentation (Clark and Veil, 2009; Guerra et al., 2011). Many bench- and pilot-scale studies have been conducted to evaluate new technologies for PW treatment (Bell et al., 2017; Coday et al., 2015; Fakhru'l-Razi et al., 2009; Freedman et al., 2017; Stoll et al., 2015) and reuse (Burkhardt et al., 2015; Pica et al., 2017), and full-scale treatment facilities like the Chevron San Ardo facility in California and Pinedale Anticline disposal facility in Wyoming have been successfully treating PW for beneficial reuse for over a decade (Boschee, 2012; Myers, 2014). Yet, the economics is the primary factor influencing wastewater management strategies, especially for PW, which is highly challenging to treat (Shaffer et al., 2013).

1.2. Treatability of O&G wastewater

O&G wastewater contains high concentrations of total dissolved solids (TDS), often exceeding 30,000 mg/L, heavy metals, dissolved and free phase organic matter (up to 1700 mg/L total organic carbon (TOC)), and microorganisms (Benko and Drewes, 2008; Regnery et al., 2016a; Rosenblum et al., 2017). The treatability of different O&G wastewaters through biological and membrane processes was evaluated in recent studies and demonstrated the removal of up to 90% dissolved organic carbon (DOC) during biofilter pretreatment (Frank et al., 2017; Freedman et al., 2017; Riley et al., 2016), and >99% DOC and 93% TDS removal during subsequent low-pressure membrane desalination (Riley et al., 2016). While use of membrane and thermal desalination technologies often requires extensive pretreatment to prevent fouling and scaling, there is insufficient understanding of the composition of dissolved organic matter (DOM) in O&G wastewater and its fate during treatment with advanced processes (Bell et al., 2017; Regnery et al., 2016a). Several constituents make up the DOM of O&G wastewater, including fracking gels (e.g., guar gum), hydrocarbons (e.g., benzene, toluene, ethylbenzene, xylenes (BTEX), polycyclic aromatic hydrocarbons (PAHs), phenols), and natural organic matter (e.g., humic and fulvic acids).

1.3. Characterization of O&G wastewater

1.3.1. Analytical techniques to characterize DOM

Besides simple analysis of DOC, ultraviolet absorbance at 254 nm ($UV_{254\ nm}$), and chemical oxygen demand (COD) used to quantify bulk organic carbon concentrations, several advanced analytical techniques exist for characterizing and quantifying DOM in aqueous samples. These include liquid chromatography (LC) coupled with organic carbon detection (OCD) or high resolution mass spectrometry (HRMS), gas chromatography–mass spectrometry (GC–MS), and Fourier transform ion cyclotron resonance MS. However, these techniques are often costly, involve meticulous sample preparation, are time consuming to perform, and require trained personnel to process samples, interpret results, and perform system maintenance. Furthermore, quantitative analysis of organic constituents in aqueous solutions by established standardized methods is often challenging due to the complex and variable matrix of O&G wastewater (Regnery et al., 2016a).

1.3.2. 3D fluorescence spectroscopy

To facilitate widespread reuse of O&G wastewater, quick and effective characterization and quantification of DOM throughout treatment processes is required. One alternative approach to semi-quantitatively characterize DOM during O&G wastewater treatment is the use of three-dimensional (3D) fluorescence spectroscopy in combination with multivariate statistical analysis. 3D fluorescence spectroscopy produces excitation-emission matrices (EEMs) that describe the fluorescence intensity of dissolved organic water constituents via excitation and emission wavelengths (Fig. S-1 in the Supplementary Information document). Because fluorescence emission is a function of chemical structure and functional groups, the intensity or location of fluorescence can enable discrimination of various DOM types or sources (Baghoth et al., 2011; Henderson et al., 2009). Furthermore, 3D fluorescence measurements are quick and comparatively simple, requiring minimal sample preparation, sensitive (10–1000 times more sensitive than UV spectroscopy) (Tran et al., 2015), and affordable (particularly compared to MS methods)—permitting frequent, yet informative monitoring of DOM.

1.3.3. PARAFAC analysis

When comparison of intensity and locations of fluorescence among samples is done visually (i.e., peak picking), 3D fluorescence spectroscopy is a predominantly qualitative technique (Baghoth et al., 2011). While it is possible to observe changes in DOM concentrations or composition, visual inspection of EEMs may lead to misinterpretation, because various organic constituents possess overlaying chromophoric features or can fluoresce more strongly than others, independent of concentration. To overcome this limitation and provide a more quantitative assessment of EEMs, statistical tools such as parallel factor analysis (PARAFAC) are used to decompose the 3D EEMs into chemically independent groups of chromophores, termed components (Bro, 1997; Murphy et al., 2011). This enables the separation and assessment of overlapping chemical spectra that would not be visible otherwise. Typically, components are broadly described as humic-, fulvic, or protein-like (tyrosine- or tryptophan-like) organic substances (Leenheer and Croue, 2003; Murphy et al., 2011; Tran et al., 2015), but can also be related to specific anthropogenic chemicals by comparison with analytical standards (Dahm et al., 2012; Stahlschmidt et al., 2015). So far, PARAFAC analysis of 3D EEMs has successfully been applied for monitoring of organic components in several aquatic environments, including drinking water (Baghoth et al., 2011; Shutova et al., 2014), storm water (Murphy et al., 2011), aquifer recharge (Stahlschmidt et al., 2015), municipal wastewater (Cohen et al., 2014; Murphy et al., 2011), and offshore oil spills (Kim et al., 2010; Zhou et al., 2013). To our knowledge, PARAFAC has never been applied to O&G wastewaters throughout treatment. While various free-form ions (Fe^{3+}, Mg^{2+}, Ca^{2+}, Al^{3+}) can shift fluorescence of humic or fulvic standards (Elkins and Nelson, 2002; Sharpless and McGown, 1999), Henderson et al. (2009) suggested minimal effects of metal ions on fluorescence in recycled waste streams. Furthermore, sodium and chloride are not of particular concern for fluorescence quenching or enhancement (e.g., tryptophan) in EEMs (Tao and Hu, 1994). However, several studies have demonstrated the effects of pH on fluorescence intensity, revealing shifts in humic- and fulvic-like DOM at extreme pHs. Humics are most sensitive to increases in pH, exhibiting increased fluorescence intensity and a red shift; whereas, fulvics are stable within pH 4–10 and exhibit suppressed fluorescence at pH >10 (Patel-Sorrentino et al., 2002; Spencer et al., 2007).

In this study, a multi-analytical approach was chosen to further characterize DOM in three different O&G wastewaters and monitor its fate through a biophysical treatment train, including biologically active filtration (BAF), ultrafiltration (UF), and nanofiltration (NF). Corresponding water samples were analyzed by 3D fluorescence spectroscopy and PARAFAC (n = 109), LC-OCD (n = 8), LC-HRMS (n = 12), GC–MS (n = 10), DOC (n = 109), COD (n = 109), and $UV_{254\ nm}$ (n = 109) to