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# Assessing the decontamination efficiency of a three-component flocculating system in the treatment of oilfield-produced water

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ABSTRACT

Produced water is a complex mixture of oil, water, dissolved solids, and suspended solids. It represents the largest volume of waste associated with the oil and gas industry, and its management is a costly aspect of oil recovery. Therefore, the development of effective treatment technologies for produced water is essential from both ecological and economic standpoints. We have developed a sensitive, fluorescence-based method to demonstrate the decontamination efficiency of a three-component polymeric flocculating system, the microencapsulating flocculating dispersion (MFD) technology. We have shown that the MFD technology can remove 90 ± 2% of the pyrene, a model wastewater contaminant, in a 0.4 ppm aqueous stock solution. The optimal flocculant concentrations used to remove pyrene was determined by fluorescence spectroscopy and zeta potential measurements. Under these conditions, flocculation and settling times were fast (i.e., <1 min). We have also demonstrated rapid removal of crude oil from an oilfield-produced water sample with a remarkable decontamination efficiency of ≥98 ± 1%. Using this fluorescence-based method, we will be better able to formulate the components of this technology and other polymeric flocculants in the treatment of oilfield-produced water, which will benefit wastewater treatment technologies.



## 1. Introduction

Increasing rates of human water consumption and a rapidly growing world population have resulted in water preservation jumping to the forefront of global issues (Gupta et al., 2012; Qu et al., 2012). Based on the necessity of water for human survival, as well as all living organisms, there is a need to appropriately manage the use of this valuable resource. An important aspect of responsible water management is the development of new methods for wastewater treatment. With extremely large volumes of wastewater generated daily by various industrial processes, the design and implementation of efficient treatment technologies would lead to immense ecological and economic benefits.

The largest volume waste stream associated with oil and gas exploration and production is produced water (Veil and Lee, 2011). Produced water is a complex mixture of oil, water, dissolved solids, and suspended solids. The management of produced water is a costly aspect of oil recovery. It is estimated

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that 21 billion barrels of produced water with varying oil content (220–2000 ppm (Multon and Viraraghavan, 2008)) are generated each year in the US alone (Veil and Lee, 2011). Currently, well site operators are required to meet specific environmental standards before disposing of oilfield-produced water. These standards have become increasingly more stringent, as current USEPA discharge limits for oil and grease content in water are 42 ppm per day or a 29 ppm monthly average (U.S. EPA, 2011). European standards now require all water to contain less than 10 ppm of total hydrocarbon content before disposal (Madaeni et al., 2013). As a result of these restrictions, many operators must contend with large amounts of contaminated water unacceptable for disposal. The development of effective treatment technologies will particularly benefit older oil well sites, which generate larger volumes of produced water than newer well sites (Igunnu and Chen, 2012; Szép and Kohlheb, 2010). In some cases, untreated produced water can be reused or recycled. However, these options may not be practical, cost-effective, or permitted by regulatory agencies (Veil and Lee, 2011). As a result, operators must treat produced water prior to reuse or disposal. Preferably, extensive treatment of produced water well below the required discharge limits could allow for its beneficial reuse in irrigation, rangeland restoration, animal consumption, and drinking water (Arthur et al., 2005).

The most common treatment method for produced water is physical separation, which is generally performed using separators, hydrocyclones, centrifuges, or membrane filtration (Veil and Lee, 2011). Although physical separation methods can generally recover free oil and some dispersed oil, they are not very effective in the recovery of finely dispersed oil (Fernandes et al., 2005). Further, physical separation methods for such emulsions often endure long cycle times and require multiple cycles until the produced water meets regulatory requirements (Veil and Lee, 2011). In order to improve the efficiency of the oil-water separation process, the particle size of the dispersed oil should be increased. This can be achieved through flocculation, where the addition of chemical additives or flocculants leads to the aggregation of dispersed oil in produced water. The resulting aggregates or flocs are then easily removed using physical separation methods. Although inorganic flocculants such as aluminum ($Al^{3+}$) and iron ($Fe^{3+}$) salts are still used today, they require high concentrations, which can lead to costly disposal of the resulting sludge. In addition, inorganic flocculants are strongly affected by the pH of the medium and do not form particularly strong flocs (Hocking et al., 1999; Brostow et al., 2009; Schramm, 2005). By contrast, polymeric flocculants are effective at low concentrations (i.e., ppm) and do not affect the pH of the medium. Further, the flocs formed from polymeric flocculants are generally larger, stronger, and settle more readily, (Brostow et al., 2009) allowing for efficient separation from the treated produced water.

The main objective of this paper is to develop a sensitive spectroscopic method to assess the decontamination efficiency of polymeric flocculants. Specifically, we will use a fluorescence-based method to demonstrate the decontamination efficiency of a three-component flocculating system, referred to as the microencapsulating flocculating dispersion (MFD) technology, in the treatment of oilfield-produced water. The MFD technology has been shown to remove contaminants from oil-in-water mixtures with high efficiency but the methods used to assess its efficiency relied primarily on turbidity or GC–MS measurements with reported detection limits of ca. 100 ppm (Sutherland, 2010). Initially, our method will use pyrene as a model contaminant. Pyrene is a well-known polyaromatic hydrocarbon (PAH) and an environmentally sensitive fluorescent molecule, which can be monitored spectroscopically. As well, PAHs are well-known constituents of crude oil and the primary organic contaminants found in oilfield-produced water (Steffens et al., 2011; Rivera-Figueroa et al., 2004). Therefore, the detection and removal of PAHs from produced water is important as they are harmful to human health, acting as both a mutagen and a carcinogen (Oanh et al., 2002). In addition, we will use zeta potential measurements to monitor the stability of the MFD system in order to identify conditions that will induce rapid floc formation. By examining the performance of the MFD system using our model system, we will establish an optimal formulation of flocculant concentrations and will demonstrate highly efficient decontamination of oilfield-produced water samples.

## 2. Experimental

### 2.1. Materials

Aqueous stock solutions of MFD (20% w/v), Activator (0.45% w/v), and Conditioner (0.01% w/v) were supplied by and used with the permission of ERIN Consulting Ltd. (Regina, SK, Canada). The chemical composition of these proprietary polymeric components was not disclosed to our laboratory. The crude oil and oilfield-produced water samples were generous gifts from Openfield Energy Ltd. (Weyburn, SK, Canada) and BP Exploration (Alaska) Inc. (Anchorage, AK, USA), respectively, and were collected at the wellhead. Sodium chloride (99.5+%, Sigma–Aldrich, Oakville, ON, Canada), methanol ($\geq$99.9%, Sigma–Aldrich) and Varsol were purchased and used as received. Pyrene (95+%, Sigma–Aldrich) was recrystallized from ethanol (95%) five times and sublimed once before use. Deionized water was obtained from a Milli-Q Gradient A10 water system (Millipore Corp., Mississauga, ON, Canada). Whatman filter paper (Grade 1, 42.5 mm d.; GE Canada, Mississauga, ON, Canada) and Chromspec syringe filters (0.2 μM, 25 mm d.; Chromatographic Specialties Inc., Brockville, ON, Canada) were purchased and used as received.

### 2.2. Instrumentation

Steady-state fluorescence spectra were collected with a PTI QuantaMaster spectrofluorometer (Birmingham, NJ, USA) at 21.0 ± 0.5 °C, and the excitation and emission slits were set such that the bandwidths were 2 nm. The data interval and integration time were 0.5 nm and 0.5 s, respectively. For the pyrene studies, excitation scans were recorded between 200 and 360 nm with the emission wavelength set to 380 nm. For the oilfield-produced water studies, emission scans were recorded between 370 and 650 nm with the excitation wavelength set to 360 nm. A baseline fluorescence spectrum of the respective solvent was subtracted from all fluorescence