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Fluorescence spectroscopy for monitoring reduction of natural organic matter and halogenated furanone precursors by biofiltration

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HIGHLIGHTS

- Unique removal performance of several fluorescence components by biofiltration.
- A humic-like component recalcitrant to biofiltration was identified.
- Granular activated carbon as a biofilter support media increased organic reduction.
- Halogenated furanone and genotoxicity was correlated to organic components.
- Results suggest polysaccharides as a possible halogenated furanone precursor.

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ABSTRACT

The application of fluorescence spectroscopy to monitor natural organic matter (NOM) reduction as a function of biofiltration performance was investigated. This study was conducted at pilot-scale where a conventional media filter was compared to six biofilters employing varying enhancement strategies. Overall reductions of NOM were identified by measuring dissolved organic carbon (DOC), and UV absorbance at 254 nm, as well as characterization of organic sub-fractions by liquid chromatography –organic carbon detection (LC-OCD) and parallel factors analysis (PARAFAC) of fluorescence excitation-emission matrices (FEEM). The biofilter using granular activated carbon media, with exhausted absorptive capacity, was found to provide the highest removal of all identified PARAFAC components. A microbial or processed humic-like component was found to be most amenable to biodegradation by biofilters and removal by conventional treatment. One refractory humic-like component, detectable only by FEEM-PARAFAC, was not well removed by biofiltration or conventional treatment. All biofilters removed protein-like material to a high degree relative to conventional treatment. The formation potential of two halogenated furanones, 3-chloro-4(dichloromethyl)-2(5H)-furanone (MX) and mucochloric acid (MCA), as well as overall treated water genotoxicity are also reported. Using the organic characterization results possible halogenated furanone and genotoxicity precursors are identified. Comparison of FEEM-PARAFAC and LC-OCD results revealed polysaccharides as potential MX/MCA precursors.

1. Introduction

Interest in biologically active media filtration (biofiltration) for the reduction of organic matter in drinking water has grown in recent years. Biofiltration represents an important water treatment option because of its low operational complexity coupled with the ability to reduce biodegradable organic matter (LeChevallier et al., 1992) and disinfection by-product (DBP) precursors, while achieving acceptable filtration performance with respect to particle removal (Emelko et al., 2006). Several biofilter enhancement strategies have been investigated, such as addition of nitrogen and phosphorous or coagulant, in an effort to augment performance (Lauderdale et al., 2012; Azzeh et al., 2015).

It has proven difficult to evaluate the impacts of biodegradation

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of natural organic matter (NOM) or benchmark the overall performance of biofilters. Organic matter in natural source waters is comprised of a wide range of compounds such as humic and fulvic acids, proteins, and carbohydrates, with varying molecular structures and chemical characteristics (Her et al., 2003). Traditional organic surrogates such as dissolved organic carbon (DOC) are not capable of quantifying these distinct sub-fractions, therefore provide a more broad representation of water quality. As such, methods capable of identifying the removal of specific organic sub-fractions would provide a more informative representation of biofiltration performance. For example, Peldszus et al. (2011) reported reduced protein-like material due to biofiltration, which in turn was thought to decrease ultrafiltration membrane fouling rates.

When combined with chlorine used for disinfection, NOM at drinking water treatment plants forms a wide range of DBPs. These by-products include commonly regulated compounds such as trihalomethanes (THMs) and haloacetic acids (HAAs), as well as less common and unregulated compounds of health concern such as the halogenated furanones: 3-chloro-4(dichloromethyl)-2(5H)-furanone (MX) and mucochloric acid (MCA) (Krasner et al., 2006). When formed in drinking water, these compounds can significantly contribute to a genotoxic response (Richardson et al., 2007) and as part of a review providing recommendations for the Fourth Drinking Water Contaminant Candidate List (CCL4), MX showed high risk relative to other DBPs (Roberson et al., 2015). Differing sub-fractions of organic matter are also known to have unique reactivity to disinfectants for formation of disinfection by-products (DBPs) (Barrett et al., 2000). As such, it is important to understand treatment performance specific to the removal of reactive organic sub-fractions in order to minimize DBP formation.

Fluorescence spectroscopy has been demonstrated to be a sensitive, accurate, and rapid NOM characterization technique (Peiris et al., 2010). The potential for implementation of online fluorescence monitoring for real time organic matter characterization offers great applicability to process control in water treatment. Several fluorescence excitation-emission matrix (FEEM) analysis techniques are reported in the literature, commonly tracking intensity changes of key wavelengths (Murphy et al., 2011). However, molecular structure has a noted effect on peak position which may have a degree of commonality among individual organic molecules causing convolution of organic fluorescence peaks (Persson and Wedborg, 2001). To account for this overlapping nature of organic classes, dimensionality reduction and deconvolution using multiway parallel factor (PARAFAC) analysis has been successful (Stedmon et al., 2003; Murphy et al., 2011).

This study focused on applying fluorescence spectroscopy as a monitoring method for biofilter performance. A comparison between conventional water treatment (coagulation, flocculation, settling, and dual media conventional filtration) to biofiltration at pilot-scale for the removal of NOM, DBP precursors of halogenated furanones, and genotoxicity was performed. Some biofilters were subject to continuous chemical enhancement strategies including the addition of nutrients, hydrogen peroxide, or in-line coagulant. The use of fluorescence-PARAFAC analysis is an increasingly popular method for characterization of NOM. This study presents novel data illustrating enhanced biofiltration performance in terms of fluorescence components as well as linking the components to formation potentials of emerging DBPs of concern.

2. Materials and methods

2.1. Source waters

Pilot-scale biofiltration studies were conducted with water from the Otonabee River, Peterborough, Ontario. Influent water quality parameters over the study period included temperature: 0–28 °C, pH: 7.3–8.6, turbidity: 0.3–2.4 NTU, DOC 4–6 mg/L.

2.2. Pilot plant configurations

The pilot system was comprised of six parallel biofiltration trains, as well as a conventional treatment configuration. Biofilters received raw water, while the conventional media filter was supplied with coagulated and settled water. To match full-scale operations, the conventional filter was operated with an empty bed contact time (EBCT) of 15 min and an aluminum sulphate (General Chemical, Parsipanny, NJ) dose of ~40 mg/L. The biofilters had an EBCT of 10 min. The conventional filter and five biofilters contained 50 cm of anthracite (effective size $d_{10} = 0.85$ mm, uniformity coefficient UC = 1.8) over 50 cm of sand ($d_{10} = 0.5$ mm, UC = 1.8). One biofilter was comprised of Filtrasorb 300 GAC (Calgon Carbon, Moon Township, PA) previously exhausted in adsorptive capacity following over 11 years of operation, over 50 cm of sand.

Several enhancement strategies were applied to investigate whether biofilter performance could be optimized, including the addition of phosphorous and nitrogen, hydrogen peroxide, and low coagulant dosing immediately prior to filtration. Based on previous work by Azzeh et al. (2015), phosphorus (as phosphoric acid), and nitrogen (as ammonium chloride) were each added at a concentration of 0.5 mg/L to examine the biological impact on DBP precursor biodegradation, even though these nutrients were not limited. Hydrogen peroxide was added at 0.2 mg/L to observe improvements on reduction of head loss (Lauderdale et al., 2012) and whether this treatment would impact DBP precursor removal. In-line aluminum sulphate was added at 0.2 mg/L as Al^{3+} to maximize organic removal (Azzeh et al., 2015), in particular the biopolymer sub-fraction.

All biofilters were backwashed with their own unchlorinated effluent three times per week, whereas the conventional filter was backwashed using chlorinated water from the full-scale plant to limit biological growth in the filter.

2.3. General organic measures and biofilter activity

Dissolved organic carbon (DOC) was measured using a persulfate wet oxidation method as described in Standard Method 5310 D (APHA, 2012) with O-I Corporation Model 1010 TOC Analyzer (College Station, Texas, USA). Ultraviolet absorbance (UVA) at 254 nm was determined using a CE 3055 model spectrophotometer (Cecil Instruments, Cambridge, England) with a quartz cuvette following Standard Method 5910 B (APHA, 2012).

Biological activity on the filter media was characterized by adenosine triphosphate (ATP) from a media sample taken from the top 5 cm of filter. ATP concentrations were assayed with a LuminUltra Deposit Surface Analysis kit (DSA-100C, Fredricton, NB) following the manufacturer's instructions.

2.4. Fluorescence

Fluorescence spectra of the treated water samples were collected with an Agilent Cary Eclipse fluorescence spectrophotometer. Optimal instrument settings were determined based on previous studies (Peiris et al., 2009, 2010) and in-house testing. Excitation and emission wavelength ranges were 230–380 nm (10 nm increments) and 250–600 nm (1 nm increments), respectively. All fluorescence spectra were collected post 0.45 μm membrane filtration to mirror the approach taken for LC-OCD and DOC analysis. A spectrum of Milli-Q water was collected on each sampling day as a reference for each set of samples and subtracted from