WATER RESEARCH 45 (2011) 3263–3269

Available at www.sciencedirect.com

ScienceDirect

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

Comparison of advanced oxidation processes for the removal of natural organic matter

Rupa Lamsal, Margaret E. Walsh, Graham A. Gagnon[*]

Department of Civil & Resource Engineering, Dalhousie University, Halifax, NS B3J 1Z1, Canada

ARTICLE INFO

Article history:
Received 22 October 2010
Received in revised form
18 March 2011
Accepted 21 March 2011
Available online 29 March 2011

Keywords:
Advanced oxidation processes (AOPs)
Ozone (O_3)
Ultraviolet radiation (UV)
Natural organic matter (NOM)
Disinfection by-products (DBPs)
High performance size exclusion chromatography (HPSEC)

ABSTRACT

This study examined the impact of UV, ozone (O_3), advanced oxidation processes (AOPs) including O_3/UV, H_2O_2/UV H_2O_2/O_3 in the change of molecular weight distribution (MWD) and disinfection by-product formation potential (DBPFP). Bench-scale experiments were conducted with surface river water and changes in the UV absorbance at 254 nm (UV_{254}), total organic carbon (TOC), trihalomethane and haloacetic acid formation potential (THMFP, HAAFP) and MWD of the raw and oxidized water were analyzed to evaluate treatment performance. Combination of O_3 and UV with H_2O_2 was found to result in more TOC and UV_{254} reduction than the individual processes. The O_3/UV process was found to be the most effective AOP for NOM reduction, with TOC and UV_{254} reduced by 31 and 88%, respectively. Application of O_3/UV and H_2O_2/UV treatments to the source waters organics with 190–1500 Da molecular weight resulted in the near complete alteration of the molecular weight of NOM from >900 Da to <300 Da H_2O_2/UV was found to be the most effective treatment for the reduction of THM and HAA formation under uniform formation conditions. These results could hold particular significance for drinking water utilities with low alkalinity source waters that are investigating AOPs, as there are limited published studies that have evaluated the treatment efficacy of five different oxidation processes in parallel.

1. Introduction

Natural organic matter (NOM) is a complex heterogeneous mixture of different organic compounds with varying molecular size and properties. A common drinking water treatment goal is to remove NOM as it is a precursor for unwanted disinfection by-products (DBPs) during chemical disinfection processes, such as chlorine (Edzwald et al., 1985; Mosteo et al., 2009) and ozone (Gagnon et al., 1997; Schechter and Singer, 1995). NOM has also been shown to contribute to fouling on membrane surfaces (e.g., Hong and Elimelech, 1997; Her et al., 2008), the production of biologically unstable water (Rittmann and Snoeylink, 1984) and other unwanted water quality issues such as metal complexes (Ravichandran et al., 1998; Schmitt et al., 2002).

The application of advanced oxidation processes (AOPs) has gained significant interest in the drinking water industry as an additional tool for removing NOM and minimizing the formation of DBPs in drinking water (Zhou and Smith, 2001; Chin and Bérubé, 2005). Previous studies have focused on ozone (O_3) (e.g. Gagnon et al., 1997), ultraviolet radiation (UV) (e.g. Chin and Bérubé, 2005; Thomson et al., 2002) and AOPs including hydrogen peroxide (H_2O_2) in combination with UV (H_2O_2/UV) (e.g. Toor and Mohseni, 2007; Wang et al., 2006), O_3 in combination with UV (O_3/UV) (Amirsardari et al., 2001; Chin and Bérubé, 2005) and H_2O_2 in combination with O_3 (H_2O_2/O_3)

---

[*] *Corresponding author*. Tel.: +1 902 494 3268; fax: +1 902 494 3108.
E-mail address: graham.gagnon@dal.ca (G.A. Gagnon).

0043-1354/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.watres.2011.03.038

(e.g. Kleiser and Frimmel, 2000) to evaluate the potential for NOM reduction and the mitigation of DBP formation in finished water. Matilainenm and Sillanpää (2010) have provided a thorough review of published oxidation and AOPs studies that have been conducted on both natural and synthetic test waters. However, these studies have primarily focused on evaluating one or two oxidation or AOPs for NOM reduction. This study goes beyond the previously published studies by directly comparing the treatment efficacy of five different oxidation processes in parallel, in terms of changes to molecular weight distribution (MWD) of the source water, NOM reduction and subsequent minimization of disinfection by-product formation potential (DBPFP) from a low turbidity, highly colored surface water.

During advanced oxidation treatment, hydroxyl radicals (HO•) are formed which act as a strong oxidant and transform NOM. Westerhoff et al. (2007) directly measured the rate constants for reactions between HO• radicals and seven dissolved organic matter (DOM) isolates from different sources and observed rate constants in range from $1–5 \times 10^8$ $M^{-1}S^{-1}$, which is three to four orders of magnitude higher than for chlorine and ozone (Crittenden et al., 1999). Hydroxyl radicals produced during AOPs are capable of reducing total organic carbon (TOC) concentrations and DBPFP of raw water (Amirsardari et al., 2001; Chin and Bérubé, 2005; Kusakabe et al., 1990; Sierka and Amy, 1985; Glaze et al., 1982). Under strong advanced oxidation conditions (i.e. long irradiation time and/or higher H_2O_2 concentrations) NOM is mineralized, indicated by a decrease in TOC and DBPFP (Kleiser and Frimmel, 2000; Wang et al., 2006; Toor and Mohseni, 2007). However, such strong treatment conditions may not be economically feasible, and in commercial applications, low or moderate advanced oxidation conditions are applied. Under these conditions, NOM is partially oxidized and higher molecular weight compounds are transformed into smaller and more biodegradable compounds such as aldehydes and carboxylic acids (Backlund, 1992; Edwards and Benjamin, 1992; Gagnon et al., 1997; Sarathy and Mohseni, 2007). Such changes in the chemical characteristic of NOM also result in reducing TOC concentrations and/or alter the characteristics of the DBP precursor material potentially reducing its reactivity with chlorine.

The objective of this study was to compare O_3, UV and three AOPs including H_2O_2/O_3, H_2O_2/UV and O_3/UV for NOM removal and assess the impact on modifying the MWD of NOM following treatment. This study was conducted using laboratory-controlled conditions with a natural surface water source that has a low alkalinity (<5 mg/L as $CaCO_3$) and moderate level of total organic carbon (TOC of 3–4 mg/L). The effectiveness of each treatment process was evaluated by traditional metrics for NOM; namely, UV absorbance at 254 nm (UV_{254}), TOC concentration, specific UV absorbance (SUVA), trihalomethane formation potential (THMFP), and haloacetic acid formation potential (HAAFP). In addition, the MWD following each treatment was assessed using high performance size exclusion chromatography (HPSEC) analysis. HPSEC has been demonstrated to be an effective technique for determining the MWD of NOM (Pelakani et al., 1999). Determination of the MWD of NOM provides information on the specific fraction of NOM that plays important role in DBP formation (Amy et al., 1987; Chang and Young, 2000) and membrane fouling potential during water treatment (e.g. Her et al., 2008).

2. Materials and methods

2.1. Source water characterization

Surface water collected from the French River, which provides the drinking water in a northern shore community in Nova Scotia, Canada, was used for the bench-scale study. The French River water is characterized by its low alkalinity (<5 mg $CaCO_3$/L), low turbidity (<1.5 NTU), and high color level (>35 Pt–Co). The French River has general characteristics that are similar to other surface water sources in Nova Scotia and Atlantic Canada (Waller et al., 1996).

2.2. Experimental set-up

The laboratory scale batch set-up for the ozone experiments used in this study is shown in Fig. 1. It consists of a compressed air system, ozone generator, a contactor (reactor) and off-gas collection system. The reactor was a glass tank with a working volume of 10 L (0.305 cm diameter × 0.41 cm height). The inflow and outflow of the ozone gas line in the reactor was fitted with a laboratory stopper (Fisher scientific # 14141R) at the top of the reactor and sample was

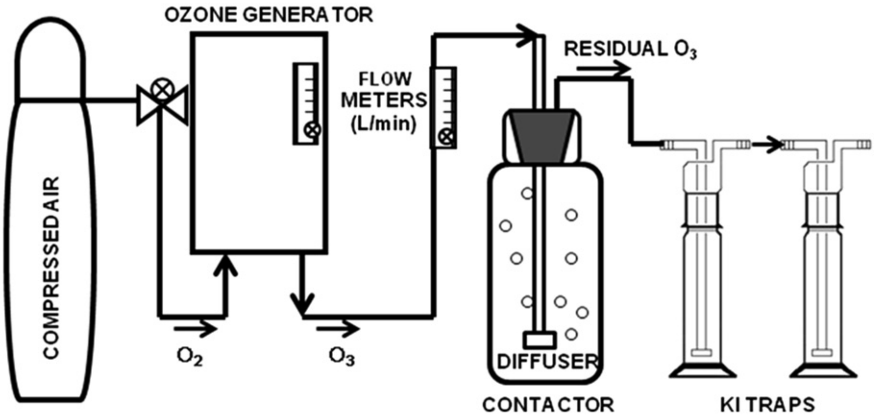

Fig. 1 – Schematic of laboratory set-up for ozone experiment.