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Effect of magnetic ion exchange and ozonation on disinfection by-product formation

Ryan S. Kingsbury [a,*], Philip C. Singer [b]

[a] CDM Smith, 5400 Glenwood Ave., Ste. 300, Raleigh, NC 27612, USA
[b] University of North Carolina, Chapel Hill, NC, USA

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ABSTRACT

The purpose of this research was to investigate the performance of treatment with magnetic ion exchange (MIEX) resin followed by ozonation in achieving disinfection goals while controlling bromate and chlorinated disinfection by-product (DBP) formation. Three water samples were collected from raw water supplies impacted by the San Francisco Bay Delta to represent the varying levels of bromide and total organic carbon (TOC) that occur throughout the year. A fourth water was prepared by spiking bromide into a portion of one of the samples. Samples of each water were pre-treated with alum or virgin MIEX resin, and the raw and treated waters were subsequently ozonated under semi-batch conditions to assess the impact of treatment on ozone demand, ozone exposure for disinfection ("CT"), and bromate formation. Finally, aliquots of raw, coagulated, resin-treated, and ozonated waters were chlorinated in order to measure trihalomethane formation potential (THMFP). In the waters studied, MIEX resin removed 41–68% of raw water TOC, compared to 12–44% for alum. MIEX resin also reduced the bromide concentration by 20–50%. The removal of TOC by alum and MIEX resin significantly reduced the ozone demand of all waters studied, resulting in higher dissolved ozone concentrations and CT values for a given amount of ozone transferred into solution. For a given level of disinfection (CT), the amount of bromate produced by ozonation of MIEX-treated waters was similar to or slightly less than that of raw water and significantly less than that of alum-treated water. MIEX resin removed 39–85% of THMFP compared to 16–56% removal by alum. Ozonation reduced THMFP by 35–45% in all cases. This work indicates that in bromide-rich waters in which ozone disinfection is used, MIEX resin is a more appropriate treatment than alum for the removal of organic carbon, as it achieves superior TOC and THM precursor removal and decreases the production of bromate from ozone.

1. Introduction

The San Francisco Bay Delta is a major source of drinking water to communities throughout central and southern California. Due to its connectivity to the Pacific Ocean and two major rivers, water quality in the Delta varies seasonally, exhibiting a wide range of salinity (16–133 mg/L chloride) and total organic carbon (TOC) concentrations (2.5–10.5 mg/L; CALFED, 2007). Runoff from areas of intensive agricultural activity in the watershed elevates TOC levels in the Delta during rainy periods, while the increased freshwater flow lowers salinity. During drier periods, seawater from the San

* Corresponding author.
E-mail address: ryanskingsbury@alumni.utexas.net (R.S. Kingsbury).
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Francisco Bay intrudes more readily into the Delta, increasing bromide and chloride levels while lowering TOC concentrations. This situation presents unique challenges for water treatment because both bromide and the natural organic material (NOM) comprising the TOC serve as disinfection by-product (DBP) precursors.

In response to these challenges, many utilities that draw water from the Delta employ ozone in order to control the formation of halogenated organic DBPs and because ozone is a more effective disinfectant against *Cryptosporidium* and other pathogens than free chlorine.

However, ozonation of bromide-containing waters can result in the formation of bromate, which is classified as a possible human carcinogen and is regulated in the US with a maximum contaminant level (MCL) of 10 μg/L (U.S. EPA, 2006b). Additionally, since ozone must often be used in combination with chlorine because it cannot provide a stable disinfectant residual in the distribution system, the presence of bromide in the water when chlorine is applied shifts the speciation of THMs and other halogenated by-products toward the more brominated forms which are thought to have a more detrimental public health impact than their chlorinated analogs (Richardson et al., 1999; Plewa et al., 2002).

In addition to serving as a DBP precursor, NOM can increase the ozone demand of a water, hampering the effectiveness of ozone for disinfection. Because higher amounts of ozone are needed to overcome the demand, the formation of oxidation by-products, such as aldehydes, is increased in waters with elevated NOM concentrations (Najm and Krasner, 1995; Johnson and Singer, 2004). These oxidation by-products, many of which are biodegradable, can cause biofilm problems in water distribution systems.

MIEX is a strong base anion exchange resin specifically designed to remove dissolved organic carbon (DOC) from water. It has been shown to remove DOC more effectively than enhanced coagulation (Singer and Bilyk, 2002; Fearing et al., 2004; Boyer and Singer, 2005; Humbert et al., 2005; Boyer and Singer, 2006) and to reduce the THM formation potential of water by up to 70% (Drikas et al., 2003; Mercer et al., 2004; Morran et al., 2004; Boyer and Singer, 2005). It is also able to remove bromide (Singer and Bilyk, 2002; Johnson and Singer, 2004; Humbert et al., 2005; Hsu and Singer, 2010). However, waters with high bromide concentrations also tend to have high concentrations of other dissolved salts, such as chloride, bicarbonate (alkalinity) and sulfate, which compete with bromide for exchange sites on the resin and therefore interfere with bromide removal (Singer and Bilyk, 2002; Johnson and Singer, 2004; Hsu and Singer, 2010). When used prior to ozonation, MIEX resin treatment has been shown to reduce the ozone demand and increase the level of *CT* (disinfection concentration, *C*, times contact time, *T*) achieved for a given amount of ozone transferred (Johnson and Singer, 2004; Wert et al., 2005).

Accordingly, this research was conducted to evaluate the combination of pre-treatment with MIEX resin followed by ozonation of Delta waters for achieving disinfection goals and controlling bromate and halogenated DBP formation. The research aims to confirm the above findings in an integrated set of experiments using several raw waters with different bromide and DOC concentrations, and to explore the implications of these findings for disinfection practice under challenging water quality conditions.

2. Experimental procedures

2.1. General approach

Water samples were collected from the North Bay Aqueduct (NBA), South Bay Aqueduct (SBA), and Lake Campbell (LC) in May, September, and December 2009, respectively, in order to capture some of the seasonal variability in TOC and salinity. A fourth water was prepared by spiking bromide into some of the Lake Campbell water. Upon receipt, the raw waters were analyzed for TOC, DOC, and ultraviolet (UV) absorbance at 254 nm. Portions of the raw water were used to conduct jar tests with MIEX resin and alum. Based on the effectiveness of the removal of organic material in these jar tests, a target dose of resin and alum were selected. Sixteen liters of the raw water were treated with the target MIEX resin or alum dose and subsequently ozonated in a semi-batch reactor to achieve a target dose of 1 mg O_3/mg TOC. The impact of each treatment on ozone demand, ozone exposure (CT), and bromate formation was evaluated. Finally, the raw, alum-treated, MIEX resin-treated, and ozonated waters were chlorinated under Uniform Formation Conditions (Summers et al., 1996) to determine their THM formation potential. The performance of MIEX resin in reducing ozone demand and DBP formation was compared to conventional alum coagulation and direct ozonation of the raw waters. Excitation–emission fluorescence spectroscopy was used to further characterize the NOM present in the raw, bulk-treated, and ozonated waters.

2.2. Sample collection and handling

All water samples were collected in a 208-L (55-gal) HDPE barrel by water treatment plant staff in California, shipped via freight carrier to the University of North Carolina, and placed in a refrigerator at 4 °C upon receipt. The waters were manually mixed for approximately 1 min before withdrawing aliquots for analysis or experimentation.

2.3. Magnetic ion exchange resin

Orica Watercare (Denver, CO) provided samples of virgin MIEX resin with both chloride and bicarbonate as the counterion. The resin was received in slurry form containing approximately 10% water by volume. Resin was stored in plastic containers at room temperature (20 °C), and deionized organic-free water (DOFW) was added, as needed, to each container to ensure that the resin remained in a wet slurry form during storage.

2.4. Preliminary jar testing

2.4.1. MIEX resin treatment

500 mL of raw water was measured into each of six glass beakers fitted with sampling ports approximately 2.5 cm from the bottom. MIEX resin doses of 0.5–2.0 mL/L were added to reflect operating conditions at full-scale MIEX plants