



# Impacts of ferrate oxidation on natural organic matter and disinfection byproduct precursors



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## ABSTRACT

This study investigated the effectiveness of ferrate (Fe(VI)) oxidation in combination with ferric chloride coagulation on the removal of natural organic matter (NOM) and disinfection byproduct (DBP) precursors. Twelve natural waters were collected and four treatment scenarios were tested at bench-scale. Results showed that intermediate-ferrate treatment (i.e., coagulation and particle removal followed by ferrate oxidation) was most effective followed by pre-ferrate treatment (i.e., ferrate oxidation followed by coagulation and particle removal (conventional treatment)) or conventional treatment alone (i.e., no oxidation), and the least effective was ferrate oxidation alone (i.e., no coagulation). At typical doses, direct ferrate oxidation of raw water decreased DBP formation potentials (DBPPFs) by about 30% for trihalomethanes (THMs), 40% for trihaloacetic acids (THAAs), 10% for dihaloacetic acids (DHAAs), 30% for dihaloacetonitriles (DHANs), and 5% for halo ketones (HKs). The formation potential of chloropicrin (CP) consistently increased after direct ferrate oxidation. Pre-ferrate followed by conventional treatment was similar to conventional treatment alone for NOM and DBP precursor removal. Ferrate pre-oxidation had positive effects on subsequent coagulation/particle removal for THM and THAA precursor removal and may allow the use of lower coagulant doses due to the Fe(III) introduced by ferrate decomposition. On the other hand, intermediate-ferrate resulted in substantially improved removal of NOM and DBP precursors, which can be attributed to initial removal by coagulation and particle removal, leaving precursors that are particularly susceptible to oxidation by ferrate. The Fe(III) resulting from ferrate decay during intermediate-ferrate process was primarily present as particulate iron and could be effectively removed by filtration.

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## 1. Introduction

Although chlorine is the most commonly used disinfectant in drinking water treatment today, its use has for many years been a concern due to the formation of potentially carcinogenic disinfection byproducts (DBPs). In addition to the regulated DBPs, e.g., trihalomethanes (THMs) and five haloacetic acids (HAA5), other DBPs, which may have mutagenic and carcinogenic effects (e.g., haloacetonitriles (HANs), halo ketones (HKs), and chloropicrin (CP); Daniel et al., 1986; Robinson et al., 1989), have been detected in chlorinated waters. Natural organic matter (NOM) is a critically important source of DBP precursors; generally, 85–95% of NOM is dissolved. Therefore, a key approach for controlling DBPs in

finished drinking water is to maximize the removal of NOM prior to chlorination. Conventional treatment, encompassing coagulation, clarification, and particle filtration, is commonly used to convert dissolved NOM to particles and remove the particulate NOM as well as other particles from surface water supplies (Jacangelo et al., 1995). In addition, pre-oxidants such as ozone are often used to control taste and odor, partially oxidize NOM, including DBP precursors, provide primary disinfection credit, and aid subsequent coagulation (Camel and Bermond, 1998; Langlais et al., 1991). For this reason, the effectiveness of pre-oxidants for NOM and DBP precursor removal has been an active area of research.

Ferrate (Fe(VI)), has attracted increasing attention among drinking water treatment researchers because of its advantages over current technologies. In addition to being a potent disinfectant for a wide range of microorganisms (Cho et al., 2006; Hu et al., 2012; Jiang et al., 2007, 2006; Kazama, 1995, 1994; Schink and Waite, 1980), ferrate can selectively oxidize many aquatic

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contaminants with limited formation of hazardous byproducts (Sharma, 2013, 2010a). In addition, ferric iron resulting from ferrate decomposition might provide additional benefit by serving as an in-situ coagulant. Ferrate has been shown to be effective for the control of humic substances (Graham et al., 2010; Qu et al., 2003). Jiang and Wang (2003) found treatment with ferrate salts resulted in better removal of dissolved organic carbon (DOC), THM precursors, and UV<sub>254</sub> absorbing substances than treatment with low doses of ferric sulfate. The addition of ferrate pre-oxidation to a coagulation and clarification process was also found to improve removal of UV<sub>254</sub> absorbing substances in continuous flow experiments (Goodwill et al., 2016).

Strong pre-oxidants (e.g., ozone) may alter the structure and characteristics of NOM and thus impact NOM and DBP precursor removal by subsequent coagulation (Graham et al., 2010). The impacts of pre-ozonation on coagulation for NOM and DBP precursor removal are conflicting and site specific (Bose and Reckhow, 2007; Chiang et al., 2002; Graham et al., 2010; O'Melia et al., 1999; Wert and Rosario-Ortiz, 2011). The adverse impact of pre-oxidation on coagulation was attributed to oxidation-induced changes in NOM, rendering it more hydrophilic and fragmented (i.e., as indicated by lowered molecular weight distribution), making it more recalcitrant to removal by coagulation (Becker and O'Melia, 2001; Singer et al., 2003). Under acidic conditions, ferrate has a high oxidation-reduction potential and it is considered a strong oxidant (Sharma, 2002; Wood, 1958). Therefore, ferrate may be expected to substantially alter the properties of NOM and impact NOM and DBP precursor removal by subsequent coagulation.

Despite extensive research on the oxidation of specific trace pollutants by ferrate, little is known about the effectiveness of ferrate in combination with conventional treatment to remove NOM and DBP precursors in a conventional treatment train. Gan et al. (2015) studied the effect of ferrate pre-oxidation followed by chlorination on THM, HAN, CP, and chloral hydrate formation. The waters being oxidized were prepared using stock solutions of Suwannee river natural organic matter and model compounds. The effectiveness of ferrate oxidation for the treatment of natural drinking water sources or its impact on coagulation for DBP precursor removal were not studied. Yang et al. (2013) found ferrate oxidation decreased the formation potentials of THMs, HANs, and CP, and Lee et al. (2008) observed that a high dose of ferrate decreased the formation potential of *N*-nitrosodimethylamine (NDMA) by 46–84%, but the impact of ferrate pre-oxidation on coagulation was not investigated. The principal objectives of this research were to characterize the effectiveness of direct ferrate oxidation alone, pre-ferrate treatment (ferrate added prior to conventional treatment (coagulation followed by particle removal)), and intermediate-ferrate (ferrate added after conventional treatment) for NOM and DBP precursor removal in order to establish the most effective scheme for integrating ferrate into full-scale water treatment systems from the perspective of controlling DBPs. The impacts of varied ferrate oxidation conditions (e.g., ferrate dose and pH) on DBP formation potentials (DBPFPs), and the role of in-situ formed Fe(III) (resulting from ferrate reduction) on subsequent coagulation were also studied. The DBPs investigated in this study included THMs, HAAs, HANs, HKs, and CP.

## 2. Material and methods

### 2.1. Chemicals and reagents

Potassium ferrate (K<sub>2</sub>FeO<sub>4</sub>, 92%), reagent-grade 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonate) (ABTS), sodium borate decahydrate, boric acid, and other reagents were purchased from Sigma-Aldrich (St. Louis, MO, US) or Fisher-Scientific (Fair Lawn, NJ, US).

All aqueous solutions were prepared with ultrapure water produced by a Milli-Q system (Advantage A10, Millipore, Billerica, MA). The chlorine was sourced as a laboratory grade ~5.5% solution of sodium hypochlorite (Fisher-Scientific). The stock solution of boric acid buffer (1 M) was prepared by adding a weighed amount of boric acid to DI water and the pH was adjusted to 6.2 with sodium hydroxide solution. Similarly, the stock solution of borate buffer was prepared with sodium borate decahydrate and the pH was adjusted to pH 7.5 with sulfuric acid solution.

### 2.2. Raw waters

Twelve raw water samples were collected from drinking water utilities at locations in Massachusetts (MA), Vermont (VT), Kansas (KS), Texas (TX), and Connecticut (CT). In each case, large volume samples were collected in high density polyethylene containers and either transported directly to University of Massachusetts, Amherst, by the research team or shipped by overnight carrier. The three Norwalk samples were collected directly from the raw water reservoir at three levels (epilimnion, mesolimnion, and hypolimnion) during summer stratification. The Bolton sample was collected immediately downstream of the system intake. All eight of the remaining samples were collected from the plant intakes. These 12 samples represent a wide range in total organic carbon (TOC, 2.1–6.6 mg/L; see Table 1) and specific UV absorbance (SUVA) values (1.8–5.9 L/mg/m).

Chlorination of these waters shows a wide range in the resulting concentration of the regulated and non-regulated DBPs (Fig. SI-1), but the carbon-normalized concentrations are typical of most surface waters (e.g., Reckhow and Singer, 2011). Fig. SI-2 shows the specific DBP formation (normalized to TOC concentration) of the raw waters. All waters had relatively low levels of bromide as indicated by the low bromine substitution factor (BSF, i.e., the ratio of the molar concentration of bromine incorporated into a given class of DBP to the total molar concentration of chlorine and bromine in that class; Hua et al., 2006) for the THMs, trihaloacetic acids (THAAs), dihaloacetic acids (DHAAs), and dihaloacetonitriles (DHANs) (see Fig. SI-3).

### 2.3. Experimental methods

The raw waters were treated under four scenarios: I) Direct ferrate oxidation only followed by chlorination; II) Ferric chloride coagulation followed by settling/filtration/chlorination; III) Pre-ferrate treatment: ferrate addition followed by coagulation/settling/filtration/chlorination; and IV) Intermediate-ferrate treatment: ferrate addition after coagulation/settling/primary filtration and before final filtration and chlorination. The effectiveness of

**Table 1**  
Raw water characteristics.

Sample location	TOC (mg/L)	DOC (mg/L)	UV <sub>254</sub> (cm <sup>-1</sup> )	SUVA (L/mg/m)	pH	C <sub>opt, FeCl3</sub> (mg/L as Fe)
Amherst, MA	3.3	3.1	0.090	2.9	7.1	6.0
Bolton, VT	5.9	5.2	0.215	4.2	6.6	12
Gloucester, MA	5.8	5.7	0.294	5.2	5.5	10
Holton, KS	6.4	5.8	0.107	1.8	7.0	10
Houston, TX	6.6	6.5	0.221	3.4	7.3	10
Norwalk, CT (epi)	3.3	3.2	0.138	4.4	7.2	10
Norwalk, CT (meso)	4.4	4.3	0.161	3.7	7.2	11
Norwalk, CT (hypo)	2.8	2.8	0.106	3.8	6.5	11
Palmer, MA	2.0	2.0	0.041	2.0	6.5	4.0
Readsboro, VT	2.0	2.0	0.119	5.9	6.0	4.0
South Deerfield, MA	2.1	2.1	0.075	3.6	7.0	6.0
Stockbridge, MA	2.9	2.7	0.078	2.9	6.6	4.0

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