Impact of natural organic matter on bromate removal in the sulfite/UV-L advanced reduction process

Bahngmi Jung, Aya Safan, Venkata Sai Vamsi Botlaguduru, Bill Batchelor and Ahmed Abdel-Wahab

ABSTRACT

Advanced reduction processes (ARPs) are treatment processes that involve combining reducing reagents and activating tools to produce highly reactive reducing free radicals. The process has proven effective for treating oxidized contaminants, and the effects of process variables on the degradation kinetics of various target contaminants have been investigated in our previous studies. In natural environments, natural organic matter (NOM) is found in surface or ground water. NOM absorbs UV light and can react with photochemically produced radicals, thus affecting target contaminant photochemical reactions and further influencing the efficiency of ARP. This study examines the impact of humic acid (HA) and Suwanee River NOM on bromate reduction rates with UV irradiation using a low-pressure mercury UV lamp. The effects of the sulfite dose, solution pH, and light intensity are studied and the pseudo-first-order rate constants in the presence of HA ($k_{obs,HA}$) are compared to those observed in the absence of HA ($k_{obs}$). At low HA concentrations of 1 mg L$^{-1}$, $k_{obs,HA}$ was larger than $k_{obs}$; however, $k_{obs,HA}$ was less than $k_{obs}$ at higher HA concentrations. Furthermore, $k_{obs,HA}$ did not increase with increasing sulfite doses in the presence of HA, which is unlike the behavior of $k_{obs}$.

Key words | advanced reduction process, bromate, disinfection-byproducts, humic acid, sulfite radical, ultraviolet light

INTRODUCTION

Bromate is a disinfection byproduct (DBP) that enters drinking water following the ozonation of bromide-containing water (Haag & Hoigné 1985; WHO 2005). Typical concentrations of bromide in surface waters in the United States range from 0.014 mg L$^{-1}$ to 0.2 mg L$^{-1}$ (USEPA). Seawater contains high concentration of bromide around 67 mg L$^{-1}$ which leads to elevated levels of bromide in desalinated seawater (Flury & Papritz 1993). Disinfection of desalinated water before its use as a source of drinking water results in oxidation of bromide to bromate that is suspected to be a human carcinogen (Aljundi 2011). In the United States and European Union, the maximum acceptable contaminant level of bromate is 10 μg L$^{-1}$ (Huang et al. 2008). Therefore, it is necessary to remove bromate ions by drinking water treatments.

Our previous study showed that bromate is effectively treated by sulfite activated by UV irradiation (Jung et al. 2014; Botlaguduru et al. 2015). Several advanced reduction process (ARP) studies have shown that sulfite combined with ultraviolet light emitted through a low-pressure mercury UV lamp (UV-L, monochromatic at 254 nm) effectively removes various contaminants, including perchlorate, 1,2-dichloroethane (1,2-DCA), and vinyl chloride (VC) (Liu et al. 2013a, 2013b; Vellanki & Batchelor 2013; Vellanki et al. 2013; Yoon et al. 2013; Liu et al. 2014). Most of our ARP studies have examined effects of process variables (solutions pH,

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initial target contaminant concentrations, and sulfite doses) on the reduction kinetics of target contaminants and on reaction mechanisms in the absence of natural organic matter (NOM). Few studies have examined effects of organic compounds on the efficiency of ARP (Bensalah et al. 2015; Duan & Batchelor 2014). Duan & Batchelor (2014) examined NOM effects on perchlorate removal by ARP and found that NOM competes for UV light with sulfite. Their experimental results showed that NOM strongly inhibits perchlorate removal by sulfite/UV-L ARP.

NOM serves as one of the precursors of DBPs for drinking water treatments (Leenheer & Croué 2003; Hua & Reckhow 2007). It is known that hydrophobic NOM is a more important source of DBP precursors (e.g., trihalomethanes and haloacetic acids) than hydrophilic NOM (Croué et al. 2000; Liang & Singer 2003). In addition, the presence of NOM affects demands for coagulants and disinfectants during water treatment processes (Hua & Reckhow 2007). NOM presence may also cause membrane fouling (Yoon et al. 1998; Cai & Benjamin 2011) and may stimulate bacterial growth in distribution systems (Volk & LeChevallier 2002). NOM also contributes an undesirable taste and color to drinking water (Liu et al. 2008). NOM significantly affects human health through production of DBP, so it impacts the design and operation of water treatment processes for its removal. The most common and cost-effective means of removing NOM involves coagulation and flocculation followed by sedimentation/floatation and sand filtration (Masion et al. 2000; Hua & Reckhow 2007). NOM increases in raw water will hinder the efficiency of water treatment processes and increase water purification demands. Hence, water treatment facilities that do not meet water quality requirements are in need of additional mechanisms of NOM removal. Advanced oxidation processes (AOPs) serve as an additional resource (Matilainen & Sillanpää 2010). In AOPs, NOM is oxidized through a complex series of reactions initiated by the hydroxyl radical (·OH). When water that contains humic substances (HS) is irradiated by UV light, photons are absorbed by HS macromolecules, and UV absorbance causes direct photochemical transformations of HS molecules (Hoigne et al. 1989). It has also been reported that activated molecules act as precursors for the production of reactive intermediates (photoreactants) such as singlet oxygen (1O2), peroxy radicals (ROO·), hydrogen peroxide (H2O2), hydrated electrons (eaq·), and superoxide anions (O2·−) (Hoigne et al. 1989; Schmitt-Kopplin et al. 1998). Several studies have shown that UV irradiation degrades soluble organic matter in water, decreasing absorbance values, and producing low molecular weight organic acids (Kotzias et al. 1987; Backlund 1992; Allard et al. 1994; Corin et al. 1996). It has been proposed that these chemical alterations of humic materials via UV-photolysis affect the photodegradation of pollutants (Frimmel 1998). Therefore, we suggest that the presence of humic acid (HA) affects the effectiveness of ARP for bromate removal.

This study (i) examines effects of HA on bromate destruction kinetics in systems where sulfite is irradiated by UV-L, (ii) characterizes effects of process variables (solution pH, sulfite dose, and light intensity) on bromate destruction kinetics in the presence of HA, (iii) estimates quantum yields of bromate removal in the presence of HA, and (iv) compares the extent of bromate removal using a broadband UV source (UV-B) with emissions ranging from 280 nm to 320 nm, with that previously observed using low and medium pressure UV sources.

MATERIALS AND METHODS

Experimental procedures

Bromate, bromide, sulfite, and HA stock solutions were prepared by dissolving potassium bromate (99.9%, J.T. Baker), sodium bromide (99.9%, EMD Chemicals), sodium sulfite anhydrous (98%, Mallinckrodt Chemicals), and HA sodium salt (technical grade, Aldrich) into deoxygenated deionized water (DDW). A stock solution of 1,000 mg/L HA was prepared and diluted to produce the desired concentration. An HA solution of 100 mg L−1 had approximately 35.4 mg L−1 total organic carbon (TOC). In some batch experiments, Suwanee river NOM (SRNOM) was used and its concentration ranged from 5 mg L−1 to 40 mg L−1 as C. All solutions were prepared in an anaerobic chamber (Coy Laboratory Products Inc., USA). DDW was prepared by purging deionized water with 99.99% nitrogen for two hours and then stored in an anaerobic chamber. Duplicate samples were used for at least two reaction
times. In case duplicate samples were not prepared, sampling times were increased with samples from multiple reactors based on the kinetics observed in preliminary experiments. All UV irradiation experiments were carried out in 17-mL quartz cells (Starna 32/Q/10, Spectrosil® Quartz) with a 10-mm path length fitted with a polytetrafluoroethylene (PTFE) stopper. During the UV irradiation experiments, quartz cells were placed in a UV irradiation chamber (14.5 (H) × 33 (D) × 26 (W) cm; BioLink, Vilber Lourmat) equipped with five UV-L lamps (8 W, T-8C lamp, Vilber-Lourmat) that were monochromatic at 254 nm. A T-8M UV lamp (BioLink, Vilber Lourmat, USA) was used as a source of broad band UVB light (UV-B) and this produces light between 280 and 320 nm, with a major peak at 312 nm. UV irradiance was measured using light meters placed at the same location and elevation as the reactors. Light meters, ST-512 (UVC, 220–275 nm, calibration point 254 nm) and ST-513 (UVAB, 280–400 nm, calibration point 365 nm) were used for the UV-L and UV-B, respectively. The lamps were warmed for 10 min to reach a constant output, and then irradiation experiments were conducted. The samples from reactors that include HA were filtered using a 0.45 μm filter (Supor®-450, Life Sciences) prior to analysis by ion chromatography.

Analytical procedures

The bromate and bromide analysis was performed using a Dionex ICS-2000 ion chromatograph. The chromatograph was equipped with an AS autosampler, IonPac AS19 guard column (4 × 50 mm), IonPac AS19 separation column (4 × 250 mm), ASRS 300-4 mm suppressor, DS6 conductivity cell, and eluent generator. The mobile phase was 20 mmol L⁻¹ potassium hydroxide (KOH) held at a constant flow rate of 1 mL min⁻¹. Methodological accuracy and precision levels were determined by measuring seven replicates, and method detection limits were determined to be 3.1 μg L⁻¹ and 8.7 μg L⁻¹ for bromate and bromide, respectively. UV-Visible absorbance was measured using a Perkin Elmer (Lambda 25) UV-Visible spectrophotometer and a quartz cell with a 1 cm optical path length. pH levels were measured using a VWR pH-meter (model SympHony). NOM absorbs UV light ranging from 220 nm and 280 nm, and this range has been recommended as being appropriate for NOM measurements (Matilainen et al. 2011). In this study, HA absorbance was measured at a wavelength of 254 nm using a Perkin Elmer (Lambda 25) UV-Visible spectrophotometer.

RESULTS AND DISCUSSION

Effect of HA concentrations

Table 1 shows the experimental conditions and pseudo-first-order rate constants (kobs,HA) calculated based on the experimental conditions. Rate constants (kobs,HA) were determined through a nonlinear least squares regression using the nilinfit function in Matlab.

The presence of HA slowed bromate degradation, as shown in Figure 1(a). In the presence of 1 mg L⁻¹ HA the observed rate constant (kobs, HA) was 0.071 (min⁻¹) and was 0.030 (min⁻¹), for 5 mg L⁻¹.

Figure 1(b) shows that the presence of SRNOM at concentrations up to 40 mg L⁻¹ as C reduced bromate removal rates. The different effect of SRNOM compared to that of HA shows the chemical differences between these two materials. Bromide was the only product of bromate destruction in the presence and absence of SRNOM (Figure 1(c)). Bromide recovery (the ratio of a final bromide molar concentration to the initial molar bromate concentration) was measured as 119%, 106%, and 109% when NOM concentrations were 0 mg L⁻¹, 5 mg L⁻¹ as C, and 10 mg L⁻¹ as C, respectively.

Siddiqui et al. studied NOM-free UV photolysis of bromate in the range of 15–50 μg L⁻¹ using a low-pressure mercury vapor lamp and medium-pressure mercury vapor lamp. They found that dissolved organic carbon due to NOM had adverse effect on the rate of bromate decay (Siddiqui et al. 1996). Duan & Batchelor (2014) also found that NOM strongly inhibits perchlorate removal rates observed for the sulfite/UV-L ARP and showed that NOM competes with sulfite for UV light, which reduces formation of reactive species. On the other hand, Minero et al. (1992) found that the presence of HA at low concentrations (10 ppm of organic carbon) increases the photolytic degradation of atrazine threefold under simulated solar light conditions. Prosen & Zupančič-Kralj (2005) examined HA...
effects on the degradation of atrazine with solar light. Their results showed that rate constants in sunlit solutions with $10^{-30}$ mg L$^{-1}$/C0 of HA were lower than those without HA, and at HA concentrations exceeding 70 mg L$^{-1}$/C0, rates were higher than those in the absence of HA.

These results show that NOM can enhance or inhibit degradation rates of target contaminants depending on its concentration and chemical characteristics. Inhibitory effects could be caused by the organic matter absorbing light and thereby reducing the amount of light available for direct or indirect photolytic reactions. It could also be caused by NOM acting as a scavenger for reactive species produced by other photochemical reactions that could degrade the target compound. The concentrations of HA used in these experiments would reduce the average light intensity in the system to 97% (1 mg L$^{-1}$/HA) or 86% (5 mg L$^{-1}$/HA) of the incident light intensity. Therefore, HA does not decrease light intensity greatly so HA would not cause major inhibitory effects on bromate degradation by this mechanism in our experimental system. Therefore, any inhibitory effect of HA is probably due to scavenging reactive species that otherwise would react with bromate.

A potential mechanism for the effect of HA in promoting bromate degradation is the production of reactive species by photolysis. Several studies have shown that it is possible to produce hydrated electrons through HA photolysis (Zepp et al. 1987; Aguer et al. 1999; Thomas-Smith & Blough 2000; Aguer et al. 2002). Additionally, HA is an effective radical scavenger, so it can inhibit bromate degradation in this way. Another possible explanation for HA promoting bromate removal is by scavenging reactive oxidants that convert bromate degradation products back to bromate. This dual role played by

<table>
<thead>
<tr>
<th>Exp. no.</th>
<th>Light intensity$^c$ (μWcm$^{-2}$)</th>
<th>Bromate conc. (mmol L$^{-1}$)</th>
<th>Sulfite conc. (mmol L$^{-1}$)</th>
<th>HA conc. (mgL$^{-1}$)</th>
<th>pH$^e$</th>
<th>$k_{obs,HA}$ (min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4,900</td>
<td>0.004</td>
<td>0</td>
<td>0</td>
<td>~6.8</td>
<td>0.017 (± 0.003)$^b$</td>
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<td>0.06</td>
<td>1</td>
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<td>0.071 (± 0.036)</td>
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<tr>
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<td>0.030 (± 0.005)</td>
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<tr>
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<td>0</td>
<td>0$^d$</td>
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<td>0.066 (± 0.010)</td>
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<tr>
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<td>0.24</td>
<td>5$^d$</td>
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<td>0.034 (± 0.005)</td>
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<td>0.027 (± 0.002)</td>
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<td>0.016 (± 0.002)</td>
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<tr>
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<td>0.007 (± 0.001)</td>
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<td>0.045 (± 0.003)</td>
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<td>0.043 (± 0.006)</td>
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<td>0.047 (± 0.011)</td>
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<td>0.046 (± 0.006)</td>
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<tr>
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<td>0.019 (± 0.005)</td>
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<td>0.06</td>
<td>1</td>
<td>~6.8</td>
<td>0.023 (± 0.005)</td>
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<tr>
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<td>0.004</td>
<td>0.06</td>
<td>1</td>
<td>~6.8</td>
<td>0.026 (± 0.004)</td>
</tr>
<tr>
<td>20</td>
<td>1,140</td>
<td>0.004</td>
<td>0.06</td>
<td>1</td>
<td>~6.8</td>
<td></td>
</tr>
</tbody>
</table>

$^a$k$_{obs}$ was determined via a nonlinear-regression using Matlab.
$^b$Uncertainties represent 95% confidence limits for $k_{obs}$.
$^c$This denotes the light intensity produced by a UV-L lamp in exp. no. 1–20.
$^d$This is total organic carbon measured in solutions with SRNOM which were used for exps. no. 4–8. Except exp. no. 4–8, the source of NOM was HA sodium salt purchased from Aldrich.
$^e$pH$_0$ was usually measured when the solution was prepared, before UV irradiation.
$^f$5 mmol L$^{-1}$/phosphate buffer solution was used and 1 N HCl or 1 N NaOH were added to adjust pH levels.
NOM in promoting and hindering bromate degradation explains the results in Figure 1, which show how HA increases the rate of bromate removal at low HA concentrations, but decreases it at higher HA concentrations.

The chemical alteration of HA via UV-photolysis was studied through measurements of UV absorbance. Absorbance measurements at 254 nm were made for different concentrations of HA and the following regression equation was obtained: 

\[
\text{Abs} = 0.026 \times [\text{HA}] + 0.005
\]

(see Figure S2, supporting information, available with the online version of this paper). The HA solution prepared at 5 mg L\(^{-1}\), which does not contain sulfite, was irradiated by UV-L, and the absorbance of the HA solution was monitored over the irradiation period (Figure 2(a)). The absorbance at wavelengths above about 230 nm decreased with increasing UV irradiation (Figure 2(a)). It has been reported that approximately 20% of the observed decline of color in lakes is attributed to natural UV irradiance (Gjessing & Gjerdahl 1970) and that HA absorbance at 254 nm declines by 23% over 40 h in the presence of UV irradiance (Corin et al. 1996). Figure 2(c) shows the absorbance at 254 nm during UV irradiation in solutions with four different compositions: HA alone, HA + sulfite, HA + bromate, and HA + sulfite + bromate. HA absorbance at 254 nm after 60 min of irradiation decreased by 34%, and 30% for HA alone and HA + bromate, respectively. However the solutions with HA + sulfite and HA + sulfite + bromate did not show significant change in absorbance.
Effects of sulfite doses in the presence of HA

Effects of sulfite doses on bromate removal rates in the presence of HA were examined (Figure 3). A light control (bromate + sulfite, no light) was conducted and the results are shown in Figure S3 (available with the online version of this paper). Bromate removal was about 5% of initial bromate concentration by sulfite alone, in the absence of UV light. Sulfite concentrations varied from 0.0388 mmol L\(^{-1}\) to 0.195 mmol L\(^{-1}\) under UV irradiation. The rate constant remained constant as sulfite concentrations varied. Absorption of UV light by sulfite increases rapidly with decreasing wavelengths below 260 nm (Fischer & Warneck 1996; Liu et al. 2013b; Yoon et al. 2013) (see Figure S1, available with the online version of this paper). It has been shown that the sulfite-UV ARP is effective in degrading contaminants such as bromate, perchlorate, VC and 1,2-DCA (Liu et al. 2013a; Vellanki & Batchelor 2013; Liu et al. 2014). Additionally, a linear relation was found between rate constants and sulfite concentrations for bromate, VC, and 1,2-DCA. This shows that higher levels of sulfite produce more reactive radicals with UV-L irradiation, thus increasing rate constants for degradation of target contaminants. However, increasing sulfite doses did not enhance bromate reduction rates in the presence of [HA] = 1 mg L\(^{-1}\). The behavior shown in Figure 3 can be explained by recognizing that bromate is removed by two processes – direct photolysis and reaction with aqueous electrons or other reactive species formed by photolysis of sulfite. In the absence of HA, the observed rate constant is approximately equal to the photolysis rate.
constant at low values of sulfate, so the observed rate constant does not change with sulfate concentration. However, at higher sulfate concentrations, $k_{\text{obs}}$ is approximately equal to the rate constant due to reaction with aqueous electrons, which are produced at a rate proportional to the sulfate concentration, so $k_{\text{obs}}$ is proportional to the sulfate concentration. The value of $k_{\text{obs,HA}}$ is larger than $k_{\text{obs}}$ when the sulfate concentrations are low enough that $k_{\text{obs}}$ is controlled by photolysis. This means that HA is promoting photolysis of bromate, possibly by reacting with the first degradation product that could otherwise recombine to form bromate. At higher sulfate concentration, $k_{\text{obs,HA}}$ remains constant while $k_{\text{obs}}$ increases. This indicates that the removal mechanism for bromate in the presence of HA remains direct photolysis. This could be caused by HA scavenging the reactive species formed by sulfate photolysis so that they are unable to react with bromate.

Effects of pH in the presence of HA

The influence of the solution pH on bromate reduction kinetics in the sulfate/UV-L ARP was studied at pH levels of 7, 9, and 11 (Figure 4). The distribution of species in a sulfate solution (H$_2$SO$_3$, HSO$_3^-$, SO$_4^{2-}$) depends on pH, and sulfate ions dominate when pH $>$ pK$_a$ ($\approx$7.2). In the presence of HA, $k_{\text{obs,HA}}$ (0.191 (min$^{-1}$)) at pH 11 was 4.2 times larger than $k_{\text{obs,HA}}$ (0.046 (min$^{-1}$)) at pH 9, whereas in the absence of HA, $k_{\text{obs}}$ at pH 11 increased only 1.9 times relative to that at pH 9 (Jung et al. 2014). At pH 9 there would be approximately twice the concentration of sulfate ion as would exist at pH 7, so there should be about twice the rate of production of reactive species. If the mechanism for bromate reduction were reaction with these reactive species, the rate of bromate degradation should increase by about a factor of two. The fact that it remained constant is evidence that the mechanism of degradation is direct photolysis, not reaction with products of sulfate photolysis. Whether the increased value of $k_{\text{obs,HA}}$ at pH 11 is due to a shift in reaction mechanism cannot be determined with the existing data; however, degradation of perchlorate by the sulfate/UV-L ARP was observed to be much faster at pH values around 11 than at moderate pH (Vellanki & Batchelor 2013).

Figure 5 shows the absorbance spectra of HA solutions at different pH and irradiation times. The absorbance of HA...
increased with increasing pH levels. HA solutions of all pH values studied showed declines of absorbance during UV irradiation (Figure 5(a)). Figure 5(b) shows the effect of irradiation time on HA absorbance for the UV irradiation period. Reductions in HA absorbance after 50 min irradiation were 13%, 22%, and 34%, for pH 7, 9, and 11, respectively.

Duan & Batchelor (2014) found that the UV irradiation of NOM solutions removed 20% of initial NOM absorbance within 12.5 h. However, when sulfite was added to the solution at pH 11, almost 100% of the initial NOM absorbance was removed within 12.5 h, and thus they concluded that sulfite significantly enhances NOM degradation during UV-L irradiation. At high pH levels, the reactive species produced through photolysis may react with HA and decrease HA absorbance while increasing bromate $k_{obs,HA}$.

**Effect of light intensity in the presence of HA**

Figure 6 shows effects of light intensity on bromate removal rates in the presence of HA. Similar bromate removal rate constants were observed under increasing levels of light intensity ranging from 2,000 $\mu$Wcm$^{-2}$ to 4,000 $\mu$Wcm$^{-2}$, but generally $k_{obs,HA}$ of bromate increased with increasing light intensity in the range of between 1,140 $\mu$Wcm$^{-2}$ and 5,610 $\mu$Wcm$^{-2}$ (Figure 6(b)). This pattern differed from the
linear relationship found in the absence HA (Jung et al. 2014).

Quantum yields in the presence of HA

Bromate destruction by ARP can occur through direct photolysis of bromate or by reaction of bromate with products of the photolysis of sulfite (indirect photolysis) as shown in Equations (1) and (2). Our previous studies have reported quantum yields for bromate degradation as a measurement of ARP efficiency (Jung et al. 2014). When HA is present, its light absorption (Equation (3)) should be considered as well as that of bromate and sulfite.

SO$_3^2$ + hv → SO$_5^-$ + e$_{aq}$

(1)

BrO$_3$ + e$_{aq}$ + 2H$^+$ → BrO$_2^-$ + H$_2$O

(2)

HA + hv → HA$^*$ + e$_{aq}$

(3)

When there are multiple compounds present that are absorbing light, the light absorption of all species and the quantum yield of the target compound are calculated as the sum of light absorption rates of each individual compound (bromate, sulfite, and HA). Since the photon flux varies with position, the rate of light absorption will be a function of distance along the light path ($x$)

\[ P = I_0 \left[ \sum_{i=1}^{n} \epsilon'_i C_i \right] \exp \left[ -x \sum_{i=1}^{n} \epsilon'_i C_i \right] = I_0 \alpha \exp \left[ -\alpha x \right] \]  

(4)

where $\epsilon'_i$ is the molar extinction coefficient (base e) for the absorbing compound $i'$ at a specified wavelength (254 nm in this study, M$^{-1}$ cm$^{-1}$), $C_i$ is the molar concentration of the absorbing compound $i'$ (mol L$^{-1}$), $n$ is number of compounds, $I_0$ is photon irradiance entering the reactor (Einstein cm$^{-2}$ s$^{-1}$), $x$ is the distance along the light path (cm), $P$ is the rate of light (photon) absorption by all $n$ compounds (Einstein cm$^{-3}$ s$^{-1}$), and $\alpha$ is the sum $\sum \epsilon'_i C_i$.

The rate of light absorption by compound $j$ at point $x$ can be expressed as:

\[ P_j = I_0 \epsilon'_j C_j \exp[-\alpha x] \]  

(5)

where $P_j$ is the rate of light absorption by compound $j$ (Einstein cm$^{-2}$ s$^{-1}$), $\epsilon'_j$ is the molar extinction coefficient (base e) for the absorbing compound $j'$ at a specific wavelength (254 nm in this study, M$^{-1}$ cm$^{-1}$), and $C_j$ is the molar concentration of the absorbing compound $j'$ (mol L$^{-1}$).

The quantum yield is defined as the rate of some specified reaction resulting from photolysis to the rate of UV light absorption. So, the photolysis rate of compound $j$ ($r_j$) in the presence of multiple absorbing compounds at a position $x$ is:

\[ r_j = -\phi_j P_j = -\phi_j I_0 \epsilon'_j C_j \exp[-\alpha x] \]  

(6)

Assuming all compounds of the reactor are completely mixed, the average removal rate by photolysis ($r_{avg}$) can be obtained with integrating Equation (7) over the total light path ($L$):

\[ r_{avg} = \frac{1}{L} \int_0^L r_j dx \]  

(7)

\[ r_{avg} = -\phi_{avg} \frac{\epsilon'_{avg} C_{avg}}{\alpha} \left( \frac{I_0}{L} \right) (1 - \exp(-\alpha L)) \]  

(8)

Finally, Equation (9) can be rearranged to calculate quantum yield of bromate ($\phi_{bromate}$) in the presence of sulfite and HA.

\[ \phi_{bromate} = -\frac{r_{avg, bromate}}{\epsilon'_{bromate}/\alpha \cdot (I_0/L)(1 - \exp(-\alpha L))} \]  

(9)

where $\phi_{bromate}$ (mol Ein$^{-1}$) is the quantum yield of bromate at wavelength 254 nm, $r_{avg, bromate}$ is the average rate of bromate removal in the reactor, which was calculated as $r_{avg, bromate} = k_{obs} C_0$, where $k_{obs}$ is the pseudo-first-order rate constant of bromate degradation (min$^{-1}$) and $C_0$ is the initial bromate concentration (mol L$^{-1}$). 'i' refers to the light-absorbing compound that initiates the removal
mechanism. For direct photolysis ($\text{BrO}_3^- + h\nu \rightarrow \text{BrO}_3^-$), the reaction initiating the removal mechanism would be the absorption of light by bromate. For indirect photolysis, it would be sulfite absorbing light. For experiments conducted with bromate, sulfite and HA, $\alpha$ would be calculated as $\alpha = \varepsilon_{\text{bromate}} C_{\text{bromate}} + \varepsilon_{\text{sulfite}} C_{\text{sulfite}} + \varepsilon_{\text{HA}} C_{\text{HA}}$. The quantum yield for bromate removal by ARP in the presence of HA was calculated as 0.20 (mol Ein$^{-1}$) and 0.09 (molEin$^{-1}$), with HA = 1 mg L$^{-1}$ and HA = 5 mg L$^{-1}$, respectively (Table S1). Table S2 shows the summary of parameters used in calculating these quantum yields. (Tables S1 and S2 are available with the online version of this paper.)

**CONCLUSION**

Previous research has shown that bromate is rapidly and effectively destroyed by the sulfite/UV ARP using low- and medium-pressure mercury UV lamps. This study extends that work by examining the effects of HA on bromate removal using various sulfite/UV-L ARPs. HA could promote or hinder bromate removal. It could hinder bromate removal by absorbing UV light that otherwise would result in bromate degradation by direct or indirect photolysis, by scavenging reactive species formed by sulfite photolysis that otherwise could degrade bromate. Also, HA could promote bromate degradation by absorbing light and producing reactive species that degrade bromate or by scavenging reactive oxidants that otherwise would oxidize degradation intermediates back into bromate. This study shows that HA at low concentrations increases bromate removal, but at concentrations above 5 mg L$^{-1}$ it decreases bromate removal. In the presence of HA, the degradation rate constant was not affected by sulfite doses, which indicates that it was being degraded primarily by direct photolysis under the experimental conditions, rather than by reaction with reactive species formed by sulfite photolysis.

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**REFERENCES**


