Removal efficiency and economic cost comparison of hydrated electron-mediated reductive pathways for treatment of bromate

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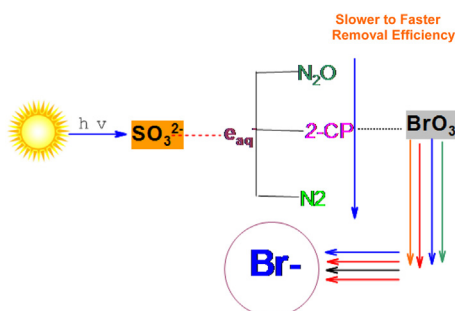[d] Urban Water Engineering, Department of Environmental Engineering, Technical University of Denmark, Denmark
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HIGHLIGHTS

- Efficiency of sulfite coupled with UV-254 in the removal of bromate was explored.
- The e_{aq}^- yield in UV-254/SO_3^{2-} process was verified using different e_{aq}^- scavengers.
- Impacts of different competitors on the reactivity of e_{aq}^- with bromate were explored.
- Second-order rate constant of bromate with e_{aq}^- was determined.
- Proposed pathways for conversion of bromate into bromide were developed.

GRAPHICAL ABSTRACT

ABSTRACT

Bromate, a potential carcinogen, is a well known highly persistent and environmentally recalcitrant contaminant. UV-254/sulfite-based advanced reductive pathways (ARPs) were proposed to eliminate bromate successfully from water. Experiments with N_2, N_2O, 2-chlorophenol, inorganic ions, and different pH (highly acidic to highly basic) proved that UV-254/sulfite successfully provides aqueous electron that effectively participate in bromate removal from water. Significant removal, 86%, of initially 39.0 μM bromate was achieved by UV-254/sulfite under conditions that dominate aqueous electron based pathways. The high second-order rate constant of 5.3×10^9 M^{-1} s^{-1} determined proved high reactivity of aqueous electron with bromate. The kinetic and removal efficiency of bromate showed linear relationship with the rate of aqueous electron formation. An increase in kinetic and removal efficiency of bromate was observed with increasing initial sulfite concentration and decreasing bromate concentration. The impacts of different initial concentrations of the typical ions commonly found in water were studied in detail to extend the UV-254/sulfite-based process for potential practical applications. The lower molar absorptivity of bromate at 254 nm determined proved insignificant removal of bromate under direct photolysis. The impacts of initial sulfite concentration on removal of bromate in UV-254/sulfite-based process also minimized role of direct photolysis. The cost evaluation and rapid decomposition of bromate into bromide proved UV-254/sulfite-based ARPs to be economical and highly rewarding in efficient decomposition of bromate and other inorganic oxyhalides.

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1. Introduction

Water is a finite and valuable resource of the universe and safe water is essential for all living organisms to sustain life on earth. However, water is continuously contaminated with emerging pollutants at varying concentrations with mostly exceeding the maximum acceptable concentrations (MAC) limits suggested by the international agencies [1,2]. Some of these pollutants are of greater concern due to their increased persistency, bioaccumulation, and toxicity [3–5]. Among these, one of the most common and environmentally malignant pollutants includes bromate (BrO_3^-), a disinfection by-product and possible human carcinogen, formed mostly from ozonation of bromide (Br^-) [6]. Also formation of BrO_3^- is reported to take place during desalination of seawater containing high concentration of Br^- [7]. The concentration of BrO_3^- formed has been found to be proportional to that of Br^- whose concentrations have been reported to vary widely depending upon geological conditions [7,8]. High level of BrO_3^- has been reported in water resources having high concentrations of Br^- [8]. BrO_3^- is reported to be genotoxic and classified as the group 2B carcinogen by the World Health Organization (WHO) [4,9]. Considering the potential health risks of BrO_3^-, a maximum acceptable level of 10 µg/L have been proposed by the international agencies, such as the WHO and United State Environmental Protection Agency (USEPA) [10]. Despite the maximum acceptable level suggested, no guidelines are proposed so far for the control of BrO_3^-. The present study focuses UV-254-mediated sulfite-based advanced reduction processes (ARPs) for the effective removal of BrO_3^- from contaminated water.
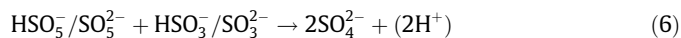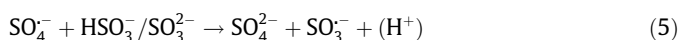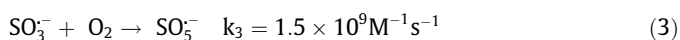
Based on the yield and use of hydrated electron (e_{aq}^-), the ARPs have been reported as the most effective and highly efficient in treating wide class of halogenated contaminants, such as halogenated organic compounds and BrO_3^-, in water [10–12]. The e_{aq}^- with their high redox potential (-2.9 V) readily attack halogenated contaminants through electron withdrawing reactions (as can be shown generally in reaction 1) and are reported to convert them into nontoxic products [6,13].

$$XO^- + e_{aq}^- \rightarrow X^- + O^{\cdot -} \tag{1}$$
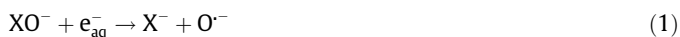
Among the ARPs, the most common processes include gamma radiation, UV-mediated ferrous ion (UV/Fe^{2+}), iodide ion (UV/I^-), and sulfite ion (UV/SO_3^{2-}) [7,13–16]. The gamma radiation processes is limited for treatment of halogenated compounds, it produces oxidizing species in equivalent concentration to reducing species [12,17]. Halogenated contaminants, due to the presence of electron withdrawing group (i.e., Cl, Br, and F etc.), show less reactivity towards oxidizing species [1]. Besides, the efficiency of e_{aq}^- in gamma radiation induced process is significantly affected by dissolved oxygen (O_2) [13,18]. Alternatively UV-mediated technology, such as UV/SO_3^{2-} that predominantly yield e_{aq}^- (as shown in reaction 2) in attractive quantum efficiencies is one of the most promising ARPs and has received significant attention recently [7,10].

$$SO_3^{2-} + h\nu \rightarrow SO_3^{\cdot -} + e_{aq}^- \tag{2}$$

The reaction of e_{aq}^- with O_2 in UV/SO_3^{2-} based ARPs is minimized by SO_3^- that undergo a chain of reactions with O_2 as shown in reactions (3)–(6) [19].

$$SO_3^{\cdot -} + O_2 \rightarrow SO_5^{\cdot -} \quad k_3 = 1.5 \times 10^9 M^{-1}s^{-1} \tag{3}$$

$$SO_5^{\cdot -} + HSO_3^- \rightarrow HSO_5^- + SO_3^{\cdot -} \tag{4a}$$

$$SO_5^{\cdot -} + SO_3^{2-} \rightarrow SO_4^{2-} + SO_4^{\cdot -} \tag{4b}$$

$$SO_4^{\cdot -} + HSO_3^-/SO_3^{2-} \rightarrow SO_4^{2-} + SO_3^{\cdot -} + (H^+) \tag{5}$$

$$HSO_5^-/SO_5^{2-} + HSO_3^-/SO_3^{2-} \rightarrow 2SO_4^{2-} + (2H^+) \tag{6}$$

The present study aims at using UV-254/SO_3^{2-}-based ARPs for effective removal of BrO_3^-. The kinetic and mechanistic pathways of the removal of BrO_3^- have been investigated employing different initial concentrations of BrO_3^- and SO_3^{2-}, second-order rate constant determination of BrO_3^- with e_{aq}^-, and elimination of Br^-. The effects of water quality parameters, such as pH and inorganic ions have been investigated on the performance of UV-254/SO_3^{2-} to extend the technique for potential practical applications. Besides, cost evaluation of the different UV-254-mediated processes has also been assessed under different conditions.

2. Materials and methods

2.1. Materials

The chemicals used in the present study were highly pure and used as received. Solid potassium bromate ($KBrO_3$), potassium bromide (KBr), and atrazine, purity 99.6% and used as a standard, were obtained from Supelco (PA, USA). Other chemicals, such as 2-chlorophenol (2-CP), sulfuric acid (H_2SO_4), sodium nitrite ($NaNO_2$), sodium nitrate ($NaNO_3$), sodium sulfate (Na_2SO_4), potassium chloride (KCl), sodium bicarbonate ($NaHCO_3$), potassium carbonate (K_2CO_3), ferric chloride ($FeCl_3 \cdot 6H_2O$), ferrous sulfate ($FeSO_4 \cdot 7H_2O$), and copper sulfate ($CuSO_4 \cdot 7H_2O$) were also of high purity and obtained from Scharlau. Sodium sulfite (Na_2SO_3) used as a source of aqueous electron under UV-254 illumination was purchased from Supelco (PA, USA). Nitrogen (N_2) and nitrous oxide (N_2O) gases with purity of 99.5% were used for sparging aqueous solutions of BrO_3^- in desired experiments. Phosphate and borate buffer (10 mM) were purchased from Fischer Scientific. Ultra pure water (having resistivity 18.2 MΩ·cm) and obtained from Milli-Q® system (Millipore) was used for preparation of experimental solutions.

2.2. Analysis

For analysis of bromate and bromide, ion chromatography (IC, Dionex) ICS-1500, fitted with IonPac AS-14 column (4×250 mm), pump (operating at 1900–2100 psi pressure), and Gilson 234 autosampler (used for direct injection of the samples), was used. The analysis of bromate and bromide was done following the method for anion determination using 8 mM Na_2CO_3/1 mM $NaHCO_3$ as an eluent at a flow rate of 1.10 mL·min^{-1}.

The atrazine, used in competition kinetic study was quantified using 1200 series high performance liquid chromatography (HPLC, Agilent, USA) fitted with quaternary pump and Eclipse XDB-C8 column (5 µm particle size, 4.6×150 mm). The HPLC was equipped with UV diode array detector (DAD) set at 222 nm. Acetonitrile and Milli-Q water (at 60:40 (v/v) ratio) was used as a mobile phase with a flow rate of 0.7 mL/min. The thermostat was set at 25 °C and sample volume injected was 20 µL.

2.3. Experimental procedure

The UV illumination of aqueous bromate solutions in the absence and presence of SO_3^{2-} was conducted using bench-scale photochemical reactor fitted with two low-pressure Hg lamps (15 W, Cole-Parmer) which emit light primarily at wavelength = 253.7 nm. The fluence rate of the source used in the present study was determined using KI/KIO_3 actinometry following the method reported by Rahn [20] and average fluence rate was determined to be 3.80 mW/cm^2. The initial pH of the solution (pH 9.8) was adjusted using borate buffer (10 mM). For studying the effects of pH in the pH range from 2.0 to 9.8, the pH was