

EBEAM IRRADIATION FOR WATER REUSE: REMOVAL OF BROMATE

A Thesis

by

LI WANG

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Chair of Committee,	Bill Batchelor
Committee Members,	Kung-Hui Chu
	Yongheng Huang
Head of Department,	Robin Autenrieth

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ABSTRACT

Bromate (BrO_3^-) is a disinfection by-product that primarily results from ozonation of bromide-containing waters. Many studies have been launched to suppress BrO_3^- formation and to decontaminate BrO_3^- after its formation. Electron beam (eBeam) irradiation has been investigated in areas including both bacterial/viral disinfection and chemical contaminant removal. However, eBeam research on BrO_3^- removal is limited. Particularly, the application of eBeam to water reuse has not been investigated. Therefore, the goal of this research was to determine the feasibility of eBeam irradiation on BrO_3^- removal and to test the factors affecting the removal in a matrix simulating reclaimed water.

Experiments were conducted in Milli-Q water and the synthetic reclaimed water. The influences of nitrate, organic matter, dissolved oxygen, pH and alkalinity were studied. A model was developed to describe the relationship between BrO_3^- concentrations and absorbed eBeam doses. The dose constant was introduced and compared at different conditions to evaluate the effects.

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1. INTRODUCTION

Bromate (BrO_3^-) contamination of drinking water is primarily the result of disinfection with ozone. Exposure to bromate could cause tissue injuries, especially to the kidney and the central nervous system. Furthermore, BrO_3^- has been classified as a potent carcinogen by the International Agency for the Research on Cancer (IARC). Efforts have been made to investigate methods for BrO_3^- formation, suppression of formation and removal. In order to suppress BrO_3^- formation, pH adjustment and ammonia addition are commonly applied. Removal technologies including granular activated carbon adsorption, coagulation, UV irradiation, have been intensively studied to decontaminate BrO_3^- after its formation.

Over the past decade, electron beam irradiation has been studied for many applications. In the regime of environmental engineering, electron beam is primarily used to disinfect bacteria/virus and to remove chemical pollutants. However, there is little research on reductive degradation of bromate in aqueous solutions.

The purpose of this study is to evaluate the performance of electron beam irradiation in removing bromate from reclaimed wastewater. The objectives to achieve this purpose are as follows:

- 1) Test the efficacy of degrading BrO_3^- in Milli-Q water with electron beam irradiation;
- 2) Investigate the influence on BrO_3^- degradation of water quality in synthetic reclaimed wastewater, such as pH and alkalinity;

3) Study the scavenging effects on BrO_3^- degradation of compounds commonly found in reclaimed wastewater, such as nitrate, natural organic matters and dissolved oxygen.

2. BACKGROUND

2.1 Water Reuse

Water shortage is a challenge for municipalities located in arid and semi-arid areas. Reuse of wastewater presents a promising alternative, which requires a series of treatment processes with exceptional effectiveness and reliability to remove chemical and biological contaminants. It usually employs a combination of membrane processes, reverse osmosis (RO) and advanced oxidation process (e.g. UV). The effluent of RO contains very low dissolved organic matter (DOC). A state-of-art RO membrane was able to provide permeate with DOC less than 0.03 mg/L.¹ The alkalinity levels of RO effluent were mostly found to be in the range 25 to 70 mg/L as CaCO₃.^{2, 3} The pH levels are decreased through RO membrane, and adjustments are usually made back to neutral in order to prevent corrosion.^{3, 4}

2.2 Bromate Formation

Bromate (BrO₃⁻) contamination of drinking water is primarily the result of disinfection with ozone. Exposure to bromate could cause tissue injuries, especially to the kidney and the central nervous system. Furthermore, BrO₃⁻ has been classified as a potent carcinogen by the International Agency for the Research on Cancer (IARC). Efforts have been made to investigate methods for BrO₃⁻ formation, suppression of formation and removal. In order to suppress BrO₃⁻ formation, pH adjustment and ammonia addition are commonly applied. Removal technologies including granular activated carbon adsorption, coagulation, UV irradiation, have been intensively studied to decontaminate BrO₃⁻ after its formation.

Bromate is a disinfection by-product (DBP) that is primarily formed when bromide-containing waters are treated with ozone. Bromide can enter water as a result of geological dissolution, brackish water intrusion and human activities.⁵ Typical concentration ranges for bromide in groundwaters and surface waters are reported to be 0-2 mg/L,⁶ and 0-0.8 mg/L,^{7,8} respectively. There are two mechanisms being proposed to describe bromate formation during water ozonation.⁹ One involves reaction with molecular ozone and the other involves reaction with the hydroxide radical. In the molecular ozone mechanism, ozone oxidizes bromide to form hypobromous acid (HOBr) and its ionized form, hypobromite ion (OBr^-). These compounds further react with ozone to produce not only bromate but bromide.⁷ Based on the rate constants, it is calculated that 77% of hypobromite is reduced to bromide and 23% is transformed to bromate.⁵ The hydroxide radical mechanism begins when the hydroxyl radical is formed by ozone decomposition at $\text{pH} > 8$. The hydroxyl radical reacts with hypobromite, so there is no bromate formed if only bromide and the hydroxide radical are present initially.⁵ Figure 1 shows the mechanisms for bromate formation through direct reaction with molecular ozone and indirect reactions with secondary radicals ($\text{OH} \cdot$ and $\text{CO}_3^- \cdot$). The relative importance of the two bromate-forming mechanisms is influenced by type and concentration of natural organic matters in ozonized waters.

Bromate has been shown to be carcinogenic in the rat kidney.¹⁰ Orally administered bromate is rapidly absorbed from the gastrointestinal tract and causes gastrointestinal symptoms.¹¹ The International Agency for Research on Cancer (IARC) has classified it as a substance possibly carcinogenic to humans (Group 2B), and the

U.S. EPA has stipulated the maximum contaminant level (MCL) of 10 µg/L (annual average).¹²

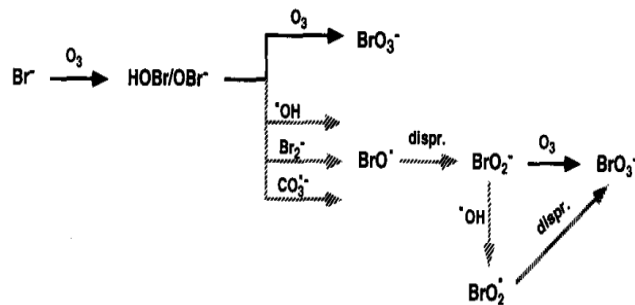


Fig 1. Reaction scheme for bromate formation⁵

2.3 Bromate Suppression and Removal Strategies

A number of strategies for suppression of bromate formation and removal after formation have been developed for water treatment during the past decades.

2.3.1 Formation Suppression Techniques

Suppression strategies are applied to minimize bromate formation during ozonation. pH adjustment and ammonia addition have been specified as best available technologies (BATs) by the US EPA and will be reviewed in this section.

pH Adjustment. The bromate formation mechanism is pH dependent, because HOBr is much less reactive towards ozone than OBr⁻ and the relative amounts of each is determined by pH. Therefore, reduction of pH can minimize bromate formation., Lower pH also leads to fewer hydroxide radicals, so there will be less bromate formed by the radical mechanism as well. A study conducted by Pinkernell et al. confirmed that 60%

bromate reduction was achieved by decreasing pH from 8 to 6 at an ozonation CT value of 10 mg/L-min.¹³ The major limitation for this adjustment is the cost of acid when treating high-alkalinity waters and the need for increasing pH after acid treatment.

Ammonia addition is another approach commonly applied in suppressing bromate formation. In waters without natural organic matter (NOM), ammonia addition results in a time lag for bromate formation, because hypobromite is quickly converted to monobromamine (NH₂Br), which is then slowly oxidized to nitrate and bromide. Thus, bromate would not be observed until ammonia is depleted.⁹ Ammonia addition could also reduce bromate formation by scavenging hydroxyl radicals. Bromate was reported to be reduced by addition of ammonia by 14%-84%, depending on the water quality and the levels of NOM.¹⁴ At the natural levels of NOM (e.g., 1.9-10.6 mg/L), bromate formation was found to fall by 14%-44% when 1.02 mg/L ammonia was added. Furthermore, Pinkernell et al. concluded that the efficiency of ammonia addition on depressing bromate formation decreases as ammonia concentration increases.¹³ As a consequence, ammonia addition is only applicable for those waters containing low levels of ammonia and NOM. NOM by itself can outcompete bromide to react with ozone and the hydroxyl radical, which leads to formation of less hypobromite and hypobromous acid.

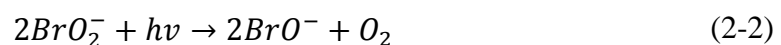
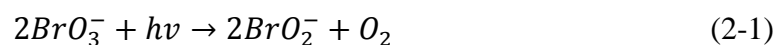
2.3.2 Removal Approaches

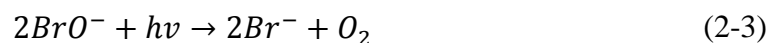
Many options to remove bromate after its formation have been studied for water treatment. In this section, the most common strategies will be evaluated.

Coagulants such as alum and ferric chloride were found to be ineffective in removing bromate from natural waters, with only 5% and 20% removals reported, respectively.¹⁵ Moreover, addition of coagulants requires further effort on sludge disposal.

Activated carbon in granular (GAC) or powdered (PAC) form is often applied as a post-ozonation approach to remove DBPs. It was proposed that bromate was incorporated with activated carbon surface and subsequent reduction of bromate to bromide occurs.¹⁶ Huang et al.'s rapid small-scale column test (RSSCT) indicated that GAC capacity for bromate removal was influenced by the GAC type, empty bed contact time (EBCT) and water quality.¹⁷ In their study of GAC that had been used for 12 months, 79-96% of bromate was removed. GAC has been classified as one BAT by US EPA. Likewise, PAC was found to achieve 63-99% bromate removal over 12-24 hour time frames.¹⁵ However, activated carbon capacity was highly inhibited by competition of dissolved organic matter and competing anions including nitrate, chloride and sulfate. Moreover, continuous use of GAC turns it into biological activated carbon (BAC), because of biological colonization. BAC has been shown to be incapable of removing bromate.¹⁸ As a result, only fresh GAC is capable of removing bromate.

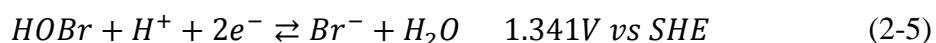
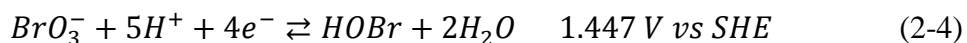
Ultraviolet (UV) irradiation is commonly used for water purification and it can convert bromate to bromide without producing secondary pollutants. The reactions of bromate under UV irradiation can be summarized as follows:¹⁹





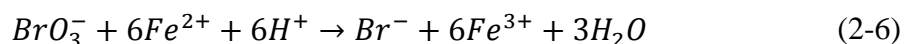
UV irradiation with medium-pressure lamps was investigated and demonstrated complete reduction of bromate to bromide with initial bromate concentration from 10-1000 $\mu\text{g/L}$ in Bensalah's research.²⁰ UV irradiation at a dose of 18 $\text{mW}\cdot\text{s}/\text{cm}^2$ removed about 50% of initial bromate of 1 mg/L , when irradiation time was 30 min.¹⁶ UV with semiconductor catalysts has recently emerged as innovative technologies for decomposing bromate. Huang et al. applied UV/ TiO_2 -graphene to reduce 99% of initial 0.08 mM bromate to bromide over 60 minutes.²¹ It was proposed that graphene acted as an electron acceptor and increased the electron transport from TiO_2 during UV irradiation. However, the removal efficiency is highly influenced by catalyst loadings as well as electron scavengers present in treated waters. A pilot-scale study showed that only 19% bromate was removed from secondary treated waters even at high levels of UV irradiation (300-696 $\text{mW}\cdot\text{s}/\text{cm}^2$),²² which indicated the negative influence of dissolved organic matter (DOC) and nitrate ions in source waters on bromate removal. The study confirmed that no removal was observed in the water with DOC concentration of 4.1 mg C/L and nitrate-nitrogen concentration of 4 mg N/L . The author also pointed out that at typical UV doses used in drinking water treatment ($<40 \text{ mW}\cdot\text{s}/\text{cm}^2$), the removal was thought to be negligible.

Electrochemical reduction has been applied in decontaminating bromate lately since it is relatively clean and environmentally friendly. Bromate and hypobromous acid both react as oxidants, so they can be reduced at cathodes in electrochemical cells. These reactions and their standard potentials are summarized as follows:²³



Zhao et al. demonstrated that the boron-doped diamond (BDD) electrode removed 90% bromate at the bias potential of -0.756 V (vs. Standard Hydrogen Electrode, SHE.) within 2 hours.²³ Many nanomaterials have been synthesized to modify the electrodes and highly enhance their performances. Li et al. modified the electrode with silver nanoparticles that had been deposited on multi-walled carbon nanotubes, and the electrode showed ability to reduce bromate.²⁴ However, the instability of electrodes and the inhibiting effect of coexistent ions, such as SO_4^{2-} and Cl^- , limit the wide application of electrochemical reduction.

Chemical reduction involving ferrous iron or zero-valent iron has also been found to degrade bromate in many studies. Gordon et al. found that ferrous iron was a good reducing agent for bromate at $\text{pH} > 7$.²⁵ The reaction can be expressed as:

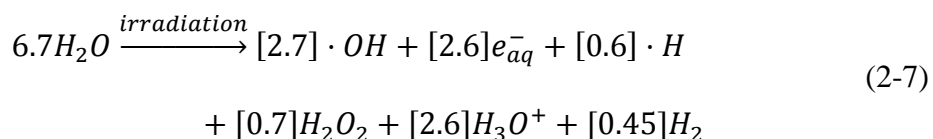


Zero-valent iron (ZVI) shows the ability to reduce bromate in many studies. Prior to chemical reduction, bromate adsorbs to ZVI and this adsorption step is influenced by the surface conditions of iron. Westerhoff reported that ZVI was able to reduce bromate to bromide under pH-neutral and aerobic conditions.²⁶ Li et al. calculated the activation energy to be 52.6 kJ/mol for the reduction.²⁷ Nano-ZVI (NZVI) was also evaluated for bromate reduction. Wang et al. applied three kinds of NZVI to degrade bromate that varied in average particle size and morphology, and they all were able to remove bromate from 1000 ppb to less than 10 ppb within 20 minutes.²⁸ These results show that

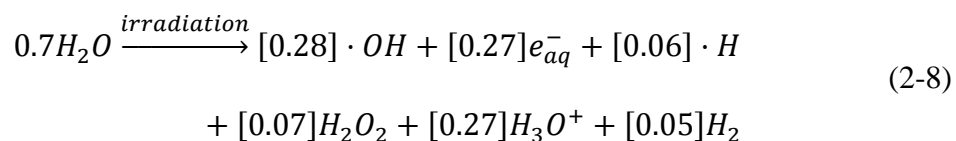
ZVI is feasible and promising for bromate reduction under different conditions and approximately all bromate ions are recovered as bromide. However, this technology faces notorious problems such as colorization and slurry deposition.

2.4 EBeam Technology and Its Applications

Electron beam (eBeam) technology involves irradiating a material by a stream of high energy electrons, which can be produced by electron accelerators. These high energy electrons interact with the irradiated materials to produce excited states of molecules, which can decay to form positive ions and electrons. For low dielectric materials, electrons do not escape the pull of the positive ions formed when they are produced and recombine. For high dielectric materials such as water, most electrons escape the pull of positive ions, which allows both the positive ions and electrons free to react with the water or dissolved components in it. These reactions result in the production of aqueous electrons (e_{aq}^-), hydroxyl radicals ($\cdot OH$), and hydrogen radicals ($\cdot H$), which can be described in the following equation:²⁹



The efficiency of conversion of water to radicals by high energy electron to products is described by the G value of the radical, which is defined as the number of radicals, excited states or other products formed by absorption of 100 eV of energy. The G values for the products in the above equation are the numbers in brackets expressed in molecules per 100 eV. The G values can be converted to yields expressed in units of $\mu\text{mol/J}$. Therefore, the above irradiation equation can be expressed as:



The numbers in the brackets represent the yields of each species in $\mu\text{mol/J}$.

The distribution of absorbed energy in water during eBeam irradiation is not uniform. As electrons penetrate through water, the transferred energy reaches a peak before declining, which is due to electron scattering and the ‘build-up’ effects. The penetration length and the build-up depth in water depends primarily on the electron energy. Fig 2 shows the percentage depth dose (PDD) of eBeam distribution in pure water for electron beams of varying energy.

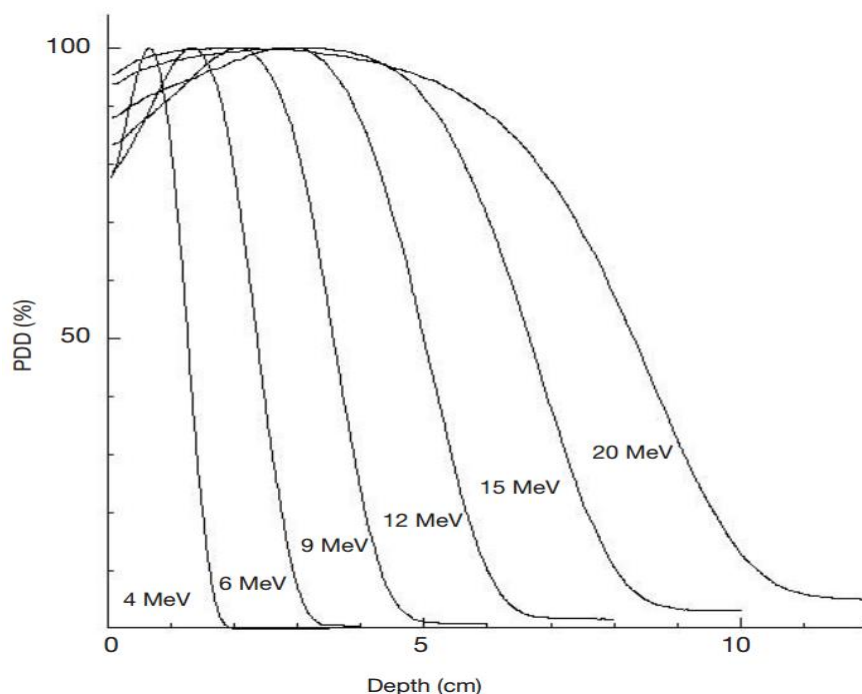
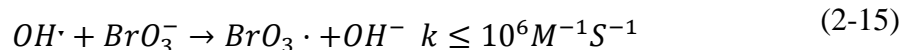
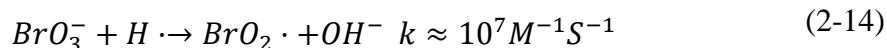
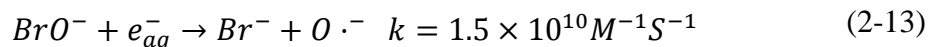
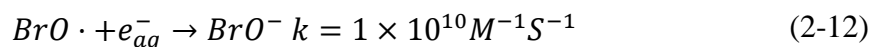
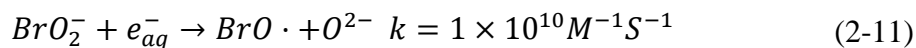
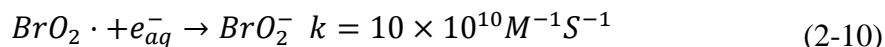
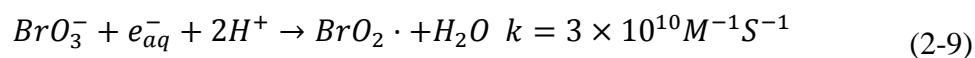


Fig 2. eBeam PDD distribution in pure water³⁰

EBeam irradiation has been applied to bacterial inactivation in the food industry. Jia Q. et al applied eBeam irradiation to disinfection of bacteria-inoculated tofu and found that the doses for 90% inactivation of *Staphylococcus aureus*, *Salmonella enteritidis* and *Listeria innocua* are 0.31, 0.35 and 0.27 kGy (a dose unit, equivalent to 1 kJ/kg), respectively.³¹ EBeam irradiation of water has also been used to disinfect bacteria/viruses and to remove chemical contaminants. Praveen C. et al demonstrated that both bacterial and viral pathogens in sewage sludge were reduced significantly with eBeam irradiation at dose of 10 kGy.³² Yoon Y. J. et al found that a dose of 10 kGy resulted in 99 % removal of acetone in a solution with initial concentration of 14 mg/L. The authors confirmed that e_{aq}^- is the reactive species that is the most responsible for degrading acetone.²⁹ Nickelsen M.G. et al applied eBeam in treating benzene and toluene with initial concentrations of 1.3 mg/L and 4.4 mg/L, and 99% removal doses were found to be 0.95 kGy and 1.65 kGy.³³ EBeam irradiation was shown to remove chlorinated benzenes (CBzs), and removal efficiencies of 41%, 87%, 84% and 84% were observed at 10 kGy for mono-CB, 1,3-diCB, 1,2-diCB and 1,4-diCB, respectively.³⁴ Half of an initial phenol concentration of 47 mg/L was decomposed by a dose of 2 kGy, and complete degradation was obtained when the dose was increased to 14 kGy.³⁵ Kim T.H. et al compared eBeam with traditional UV-C and ozone in removing antibiotics and found that 88.6% and 100% of 30 mg/L sulfamethoxazole (SMX) and chlortetracycline (CTCN) were removed with a dose of 1 kGy.³⁶ Their study concluded that eBeam was more efficient than two other techniques in terms of the electrical energy consumed in reducing concentrations of SMX and CTCN by a factor of 10. EBeam treatment for

pharmaceuticals and personal care products (PPCPs) was investigated by He S. J. et al.³⁷ Their results demonstrated that a dose of 0.5 kGy was capable of completely degrading diclofenac with initial concentrations below 40 mg/L.

Theoretically, BrO_3^- reacts with e_{aq}^- to form bromine-containing intermediates, which are further reduced to Br^- . The relevant reactions have been presented by Buxton et al. These reaction equations with rate constants (k) have been modified to be chemically balanced and are presented below:



The purpose of this study was to evaluate the efficacy and effectiveness of applying eBeam irradiation in removing trace amounts of BrO_3^- from reclaimed water. Currently, water reclamation is usually carried out by applying advanced oxidation processes (AOPs) after a series of membrane treatment steps. UV irradiation is commonly used in water treatment for disinfection purposes. As mentioned before, UV irradiation requires doses higher than are normally found in treatment processes to remove BrO_3^- effectively. Ebeam irradiation presents an alternative for removing BrO_3^- in water reuse processes. A study of eBeam treatment conducted by Siddiqui M. S. et al.

found that a dose of 1 kGy was sufficient to remove 70% of BrO_3^- from an initial concentration of 100 $\mu\text{g/L}$ in NOM-free water.³⁸ However, research on this subject is very limited, and the application of eBeam to water reuse has not been investigated.

3. EXPERIMENTAL SECTION

3.1 EBeam Facility

The eBeam irradiation facility is managed and operated by the National Center for Electron Beam Research (NCEBR), which is located on the campus of Texas A&M University, College Station. NCEBR is a leading academic and research organization in studying and commercializing of eBeam technology. NCEBR houses two vertically mounted opposing 10 MeV, 18 kW Electron Beam Linear Accelerators (LINAC). The travel length and build-up depth for a 10 MeV accelerator are about 5 cm and 3 cm in pure water³⁹. In this irradiation study, only one LINAC was applied, which was operated under average pulse current of 1500 μ A, pulse rate of 256 pps and scan frequency of 4.2 Hz.

The eBeam facility at NCEBR utilizes a single conveyance system to move the product through the scanning area of the LINAC chamber.

3.2 Sample Preparation

In order to simulate real conditions in water reclamation, typical concentrations of compounds found in the effluent of reverse osmosis (RO) were selected to be used to prepare the synthetic wastewater used in this research: pH 7.3, 10 mg/L NO_3^- , 50 mg- CaCO_3 /L alkalinity, 50 μ g-C/L DOC from fulvic acid (FA). Reverse osmosis rejects natural organic matter (NOM) with large molecular weight, so humic acid (HA) that has an average molecular weight between 2000 and 3000 Da would not be a good choice as a source of residual organic matter. However, fulvic acid (FA) has an average molecular weight that is less than 1000 Da⁴⁰, so it was chosen as the NOM surrogate in this study.

All samples, except the one on the effect of DO, were prepared in an anaerobic chamber (Coy Laboratory Products Inc., Grass Lake, MI, USA). The oxygen-free environment in the anaerobic chamber is maintained by filling it with a gas mixture (95% nitrogen and 5% hydrogen) and using palladium catalysts STAK-PAK (Coy Laboratory Products Inc., Grass Lake, MI, USA) to remove trace amounts of oxygen by reacting it with hydrogen. The chamber was equipped with an oxygen and hydrogen analyzer to monitor the gas components.

All reagents were ACS (American Chemistry Society) grade or higher and were used as received. Irradiated samples were prepared with ultrapure deionized water (18 M Ω). Standard bromate (1000 mg/L) and nitrate solutions (1000 mg/L) were purchased from Inorganic Ventures (Christiansburg, VA, USA). Stock solution of FA (500 mg/L) was prepared by dissolving Suwannee River Fulvic Acid Standard (International Humic Substances Society, St. Paul, MN, USA) in deionized water. A stock solution of alkalinity (500 mg-CaCO₃/L) was prepared by dissolving sodium bicarbonate into deionized water.

The irradiation experiments were conducted with a buffer of 0.1 mM total phosphate at desirable pH levels. The stock solution of buffer (100 mM) was made by dissolving 7.21 g potassium dihydrogen phosphate (KH₂PO₄) and 8.19 g potassium hydrogen phosphate (K₂HPO₄) in 1 liter of deionized water and adjusting to desired pH with 1 N NaOH and 1N H₂SO₄. The solution volumes were kept at 30 ml, and the depths were about 5 mm.

3.3 EBeam Irradiation

All irradiation experiments were conducted at the NCEBR. The samples were prepared in petri dishes and sealed with Parafilms (Bemis NA, Neenah, WI, USA) and resealable bags before being taken out of the anaerobic chamber. The samples were placed on the conveyance system to be irradiated. The desired doses were achieved by changing the conveyance speed. Attenuation of the eBeam was required to achieve doses smaller than 1 kGy and this was accomplished by placing tint boards between the LINAC and the irradiated samples. All irradiation experiments were done in triplicate. After eBeam irradiation, the samples were transferred to 50 ml vials and stored in a refrigerator which was set at 5 °C (by default) for about 12 hours until analysis.

3.4 Dose Measurement

The absorbed doses were measured by alanine dosimetry that had been validated to international standards. A Bruker E-scan spin spectrometer (Bruker BioSpin Corp., Billerica, MA) was used to read the dosimeters after they were irradiated and it provided the dose directly in units of kGy.

For doses larger than 1 kGy, the dosimeters (Farwest Technology Inc, Goleta, GA, USA) were placed on top of the petri dish to measure the energy delivered to the top of the glass. This was done to avoid open petri dishes and thus the dissolution of oxygen. To insure that these measurements represented the dose absorbed by the water, doses on top of the petri dish and the top of water within the petri dish were determined in the same systems. The results of these experiments are shown in Figure 3 and demonstrate that the measurements of the doses at the two locations were proportional to

each other. Therefore, the dose delivered to the water was obtained by multiplying dose measured at the top of the petri dish by 1.144. This experiment was not conducted in duplicate or triplicate.

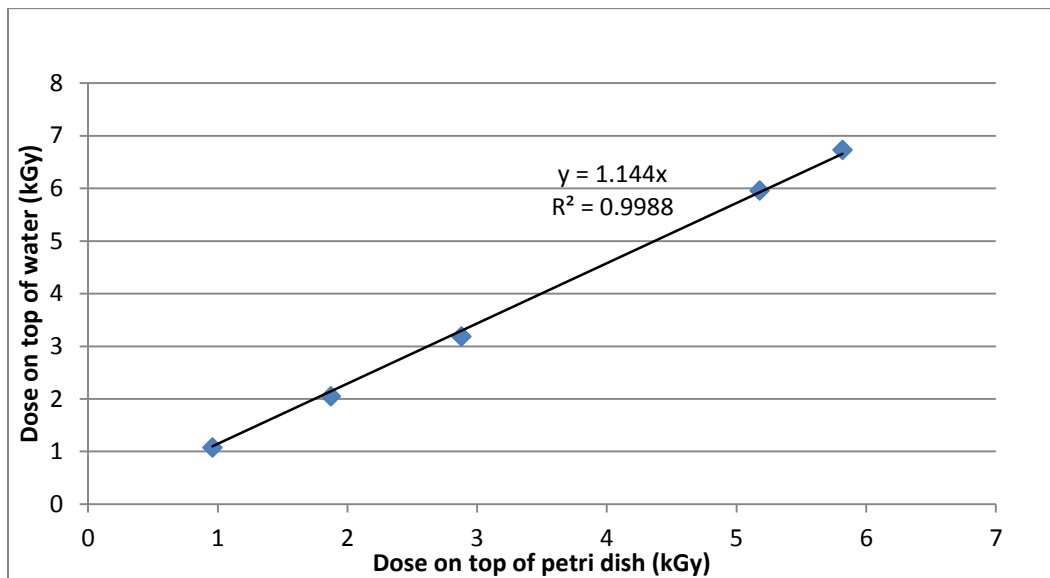


Fig 3. Relationship between dose on top of water and dose on top of petri dish

For doses smaller than 1 kGy, the dosimeters were placed in the reactors and floated on top of the solutions. Since the eBeam was attenuated in order to achieve doses less than 1 kGy, the dose on top of water and dose on top of petri dish might not follow the relationship shown in Fig.3.

3.5 Sample Analysis

The concentrations of BrO_3^- and Br^- were determined by ion chromatography (Dionex 500) with an IonPac AS19 analytical column (Thermofisher Scientific) and an

AG19 guard column (ThermoFisher Scientific). A 20 mM NaOH eluent was used and the AS 40 autosampler (Dionex) was assembled with a 1000- μ L injection loop so that it could detect very low concentrations of BrO_3^- and Br^- given the initial concentration of BrO_3^- was about only 100 $\mu\text{g/L}$. The method detection limits were identified as 0.40 $\mu\text{g/L}$ and 0.37 $\mu\text{g/L}$ for BrO_3^- and Br^- respectively. The results of triplicate experiments were expressed as the mean \pm standard deviation.

4. RESULTS AND DISCUSSION

4.1 Degradation of Bromate in Milli-Q water

Initially, degradation was investigated using a background solution of Milli-Q water adjusted to pH 7.3 to test the efficacy of eBeam irradiation in removing BrO_3^- and converting it to Br^- . The effect of absorbed dose on degradation of BrO_3^- and production of Br^- are shown in Fig. 4. The recovery of bromide (C/C_0) was calculated as the ratio of the measured concentration of Br^- to the initial concentration of bromine in bromate. The measured concentrations of BrO_3^- are shown in Appendix 2. This figure indicates that a dose of 1 kGy was able to remove $95.6 \pm 1.8 \mu\text{g/L}$ BrO_3^- completely and that about 97 % of it was recovered as Br^- . Compared with previous study by Siddiqui et al. in which only 70% of BrO_3^- was recovered as Br^- in Milli-Q water, a better recovery was demonstrated in this study. The discrepancy could be explained by BrO_3^- being reduced in Siddiqui's study to HOBr/OBr^- instead of Br^- . The reduction of BrO_3^- was thought to be induced by reducing radicals such as e_{aq}^- and/or $\text{H}\cdot$, which will be discussed later.

4.1.1 Removal Efficiency

Removal efficiency can be expressed in different forms. Percent removal is commonly used in degradation studies.

$$\eta = \frac{C_0 - C_t}{C_0} \times 100\% \quad (4-1)$$

While in irradiation treatment, G values are used to evaluate the amount of removed compounds per unit absorbed dose, which can be calculated for degradation in water through the following equation:²⁹

$$G = \frac{(\Delta R) \times N_A}{D \times (6.24 \times 10^{19})} \quad (4-2)$$

where ΔR (mol/L) is the amount of removed compounds at dose of D (kGy), N_A is Avogadro's number, $6.02 \times 10^{23} \text{ mol}^{-1}$, 6.24×10^{19} is the conversion constant from kGy to 100 eV/L for water, and G is the removal efficiency in molecules per 100 eV.

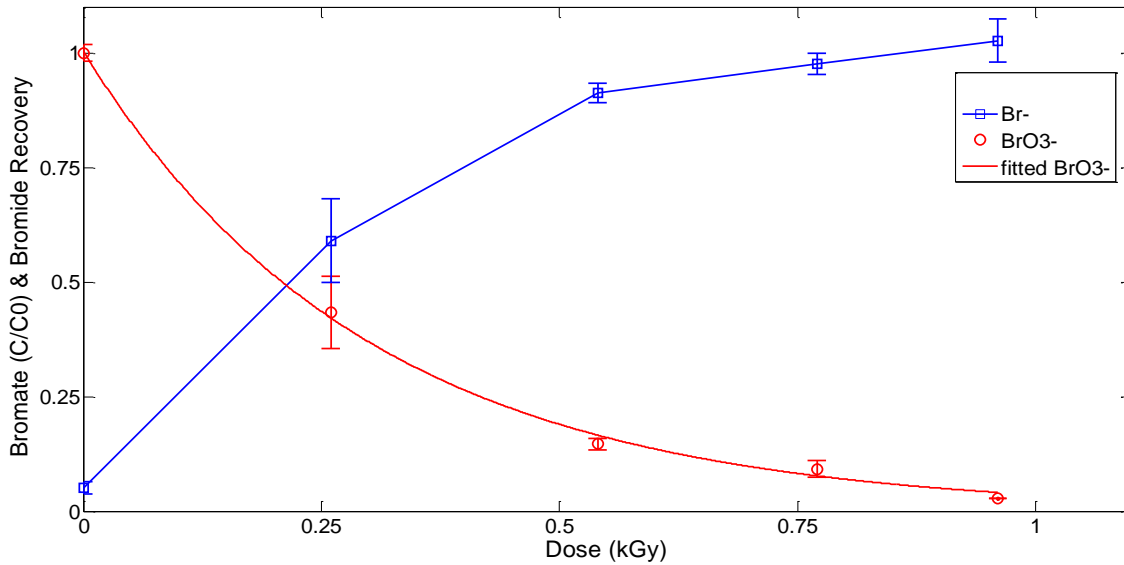


Fig 4. Effect of eBeam dose on degradation of BrO_3^- and recovery of Br^- in Milli-Q water. Error bars are the standard deviation of triplicate samples. The line for BrO_3^- is a model prediction.

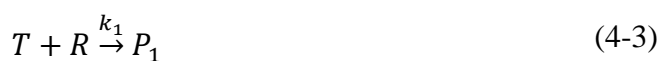
Table 1. BrO₃⁻ Removal Efficiency in Milli-Q Water

Dose (kGy)	η	G* 10 ³
0.26	56.7	15.7
0.54	85.5	11.4
0.77	90.9	8.5
0.96	100	7.5

Based on above equation, G values for each dose were calculated and shown in Table 1. The percentage removal of BrO₃⁻ increased with the dose. On the other hand, the G value decreased from 1.57×10⁻² to 7.5×10⁻² per 100 eV as the dose increased from 0.26 to 0.96 kGy. This feature follows the trend found in other studies.^{29, 41, 42} The reason behind the trend is that radical-radical recombination occurs more frequently at the higher doses because there is less of the target compound present to react with radicals. Therefore, the portion of radicals reacting with the target compound (BrO₃⁻) decreased for the higher doses, and thus the removal efficiency decreased.

4.1.2 Effect of Dose on Removal

A model can be developed to describe the relationship between contaminant removal and eBeam dose. Contaminant removal is accomplished by radicals in solution. Two pathways for radical reactions are important: radical reaction (e_{aq}⁻) with target (BrO₃⁻) and radical reaction with scavengers (NO₃⁻, H⁺, et al.).





where S, T and R represent scavengers toward active radicals, target compound (BrO_3^-), and active radicals (e_{aq}^-) respectively. P_1 and P_2 are corresponding products.

The reaction rates are:

$$r_1 = k_1 * [T] * [R] \quad (4-5)$$

$$r_2 = k_2 * [S] * [R] \quad (4-6)$$

where [T], [R] and [S] are corresponding species concentrations.

According to the water irradiation equation, the production rate (r_3) of e_{aq}^- is:

$$r_3 = r_{\text{dose}} * g_e * \rho \quad (4-7)$$

where r_{dose} is the dose rate defined as the dose absorbed per unit time (energy/mass-time), which is constant for eBeam irradiation, g_e is the yield for e_{aq}^- (number/energy), and ρ is the density of the irradiated solution (mass/volume).

The model assumes that the radical reactions are extremely fast, and therefore the derivatives of their concentration with time ($d[R]/dt$) would be very close to zero, compared to the rates of the other reactions. This is because the radicals react with targets and scavengers soon after they are produced, so the concentration of radicals remains very low, which means there can be little change in concentration with time. Based on this assumption, the material balance equation for the radical in a batch reactor becomes the following equation.

$$\frac{d[R]}{dt} = r_3 - (r_1 + r_2) = 0 \quad (4-8)$$

Plugging in r_1 and r_2 and rearranging,

$$r_3 = k_1 * [T] * [R] + k_2 * [S] * [R] \quad (4-9)$$

Therefore,

$$[R] = \frac{r_3}{k_1 * [T] + k_2 * [S]} \quad (4-10)$$

This can be used to modify the rate equation for the target compound,

$$r_1 = k_1 * [T] * [R] = \frac{k_1 * [T] * r_3}{k_1 * [T] + k_2 * [S]} \quad (4-11)$$

Since the scavenger concentration [S] is usually higher than the target concentration [T] (mg/L vs vs $\mu\text{g/L}$), and is often more reactive, so $k_2 * [S] \gg k_1 * [T]$.

This assumption allows the equation to be simplified as:

$$r_1 = \frac{k_1 * [T] * r_3}{k_2 * [S]} \quad (4-12)$$

For a batch system,

$$r_1 = - \frac{d[T]}{dt} \quad (4-13)$$

Equating the two formulas,

$$\frac{d[T]}{dt} = - \frac{k_1 * [T] * r_3}{k_2 * [S]} \quad (4-14)$$

Solving,

$$\int \frac{d[T]}{[T]} = - \frac{k_1}{k_2} \int \frac{r_3}{[S]} dt \quad (4-15)$$

Integrating both sides while assuming that the scavenger concentration is constant,

$$\int \frac{d[T]}{[T]} = \ln \frac{T}{T_0} \quad (4-16)$$

$$\frac{k_1}{k_2} \int \frac{r_3}{[S]} dt = \frac{k_1}{k_2 * [S]} \int r_{dose} * g_e * \rho dt \quad (4-17)$$

Given g_e and ρ do not change with time, and the absorbed dose can be expressed as:

$$D = \int r_{dose} * dt \quad (4-18)$$

$$\ln \frac{T}{T_0} = - \frac{k_1}{k_2 * [S]} * D \quad (4-19)$$

Substituting for the dose constant and rearranging gives:

$$T = T_0 e^{-kD} \quad (4-20)$$

where the dose constant is:

$$k = \frac{k_1}{k_2 * [S]} \quad (4-21)$$

As shown in equation (4-20), the concentration of residual BrO_3^- and eBeam dose can be described by an exponential model. In this study, k , the dose constant (kGy^{-1}), was evaluated in order to investigate the influence of water quality and a radical scavenger on BrO_3^- degradation.

The line fitted to BrO_3^- degradation in Fig 4 was acquired by applying the function ‘fit’ in Matlab. This Matlab function is commonly used to fit curves or surfaces to data. The ‘fit’ function requires the user to specify the type of model to be used and ‘exp1’ was chosen. This choice causes the ‘fit’ function to fit the data to an exponential model and details about this model are shown in Appendix 1. The ‘fit’ function output the values of the dose constant and the 95% confidence interval. The coefficient of determination (R^2) was obtained by using the function ‘cftool’ in Matlab with the fitting

model customized as 'a*exp(-b*x)'. By doing so, the dose constant of 3.34 kGy⁻¹ with 95% confidence interval (2.95, 3.73), and R² of 0.9985 were obtained for BrO₃⁻ degradation in Milli-Q water. Since the MCL for BrO₃⁻ stipulated by U.S. EPA is 10 µg/L (about 90% of initial concentration set in this research), D_{0.9}, the dose required for 90% BrO₃⁻ removal, was calculated from the following equation:

$$D_{0.9} = \ln 0.1 / (-k) \quad (4-22)$$

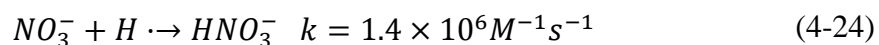
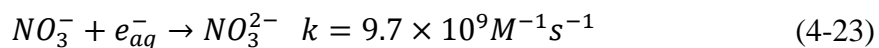
For the matrix of Milli-Q water, 0.7 kGy was sufficient to meet the EPA regulation on BrO₃⁻ when the initial concentration was 100 µg/L.

4.2 Effect of Nitrate

4.2.1 Effect of Dose on Removal

The presence of radical scavengers is thought to influence the performance of eBeam treatment. Therefore, experiments were conducted with a synthetic solution designed to represent effluent from RO treatment as might be applied to a wastewater intended for direct potable reuse. The base composition of this solution was 50 mg/L alkalinity as CaCO₃, 50 µg/L fulvic acid (FA) as C, adjusted to pH 7.3. Use of this solution allowed investigation of the efficacy and efficiency of eBeam treatment under more realistic scenarios.

Nitrate (NO₃⁻) is universally present in surface water and groundwater, so the effects of NO₃⁻ on BrO₃⁻ removal were of interest. It has been confirmed that NO₃⁻ reacts very rapidly with e_{aq}⁻ (k=9.7×10⁹ mol⁻¹s⁻¹) and H· (k=1.4×10⁶ mol⁻¹s⁻¹).⁴³ Many studies have concluded that the presence of NO₃⁻ significantly inhibits reduction processes induced by e_{aq}⁻ and H· radicals.^{29, 44} The related reactions include:



Four levels of NO₃⁻ (0, 5, 10, 20 mg/L) were investigated for their effect on BrO₃⁻ degradation with 10 MeV eBeam irradiation. The matrix included 50 mg/L alkalinity as CaCO₃, 50 µg/L FA as C, adjusted to pH 7.3. The initial concentration for BrO₃⁻ was measured as 99.8 ± 1.0 µg/L.

Dose constants were obtained by conducting a non-linear regression from each set of experimental data (Appendix 3) and were compared to evaluate the effects. The results are shown in Table 2.

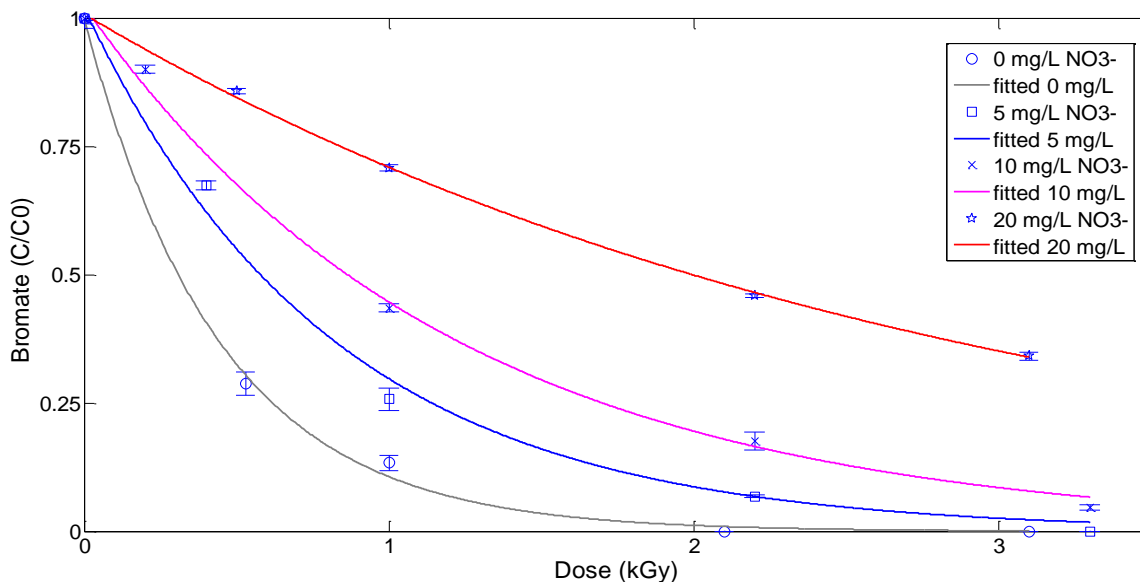


Fig 5. Effect of eBeam dose on BrO_3^- removal at various NO_3^- concentrations. Error bars indicate the standard deviation of triplicate samples. Lines are model predictions.

The addition of NO_3^- decreased the dose constant as expected. It is worth mentioning that NO_3^- concentrations were 50 to 200 times those of BrO_3^- when the irradiation treatment started. A dose constant of 0.35 kGy^{-1} was still obtained when 20 mg/L NO_3^- was used. This phenomenon could be explained by the high activities between BrO_3^- and its intermediates with e_{aq}^- and $\text{H}\cdot$. The kinetic constants for BrO_3^- and its degradation intermediates with e_{aq}^- have been reported to be on the order of 10^9 and $10^{10} \text{ mol}^{-1}\text{s}^{-1}$, which are about the same or one order of magnitude larger than those of

NO_3^- and its radicals.^{10, 23, 26} In addition, reactivity of $\text{H}\cdot$ towards BrO_3^- is one order higher than that towards NO_3^- . Therefore, the reduction of BrO_3^- was slowed by the presence of nitrate, but it could still be observed.

Comparing the dose constants obtained from 0 mg/L NO_3^- and Milli-Q water (2.33 vs 3.38 kGy^{-1}), the value from synthetic solution in absence of NO_3^- was 70% of that from Milli-Q water. Apparently, the matrix of FA, HCO_3^- exerted negative influence on BrO_3^- removal.

Accordingly, $D_{0.9}$ increased as NO_3^- was added. The presence of 20 mg/L NO_3^- requires 6.6 kGy to meet EPA regulation, while only 1 kGy is needed for NO_3^- -free waters.

Table 2. Dose Constants for Removal of BrO_3^- at Different NO_3^- Concentrations.

NO_3^- (mg/L)	k (kGy^{-1})	95% Confidence	R^2	$D_{0.9}$ (kGy)
		interval		
0	2.33	1.88-2.79	0.9973	1.0
5	1.24	0.88-1.59	0.9932	1.9
10	0.83	0.66-1.00	0.9962	2.8
20	0.35	0.33-0.36	0.9988	6.6

4.2.2 Model for Effect of Nitrate on Removal

From the data of BrO_3^- degradation with different NO_3^- concentrations, it appears that addition of NO_3^- exerts significant effect. The model developed to describe the effect of dose on removal expressed the dose constant as being inversely proportional to the concentration of scavengers (Equation (4-21)). One of the scavengers in this experimental system is NO_3^- , so the total concentration of scavengers can be expressed as the sum of nitrate and other scavengers. Referring to (3-21), the following equation could be obtained:

$$k = \frac{a}{[\text{NO}_3^-] + b} \quad (4-25)$$

where $a = k_1/k_2$ and $b =$ sum of concentrations of other scavengers, which is assumed to be constant.

To evaluate the feasibility of this simple model, the MATLAB tool “cftool” was used to fit Equation (4-20) to the data for dose constant obtained at different nitrate concentrations and the results are shown in Fig. 6. The Matlab ‘cftool’ gave values of ‘a’ and ‘b’ as $12.0 \text{ (kGy)}^{-1}(\text{mg/L})$ (95% confidence interval of 5.7 - 18.2) and 5.10 mg/L (95% confidence interval of 2.07 - 8.13). As shown in the figure, the confidence interval shrinks as nitrate level increases from 0 to 20 mg/L. This is because experimental errors were larger when BrO_3^- degraded too fast at zero and low nitrate levels. A value for R^2 of 0.9903 was obtained for this fit. It appears that the basic model explains the effect of NO_3^- very well, and could be used to predict this effect in waters with a similar matrix of other scavengers at an eBeam energy of 10 MeV.

The scavenging process of NO_3^- exerts negative effects on BrO_3^- removal, which is supported by both experimental results and kinetic modeling.

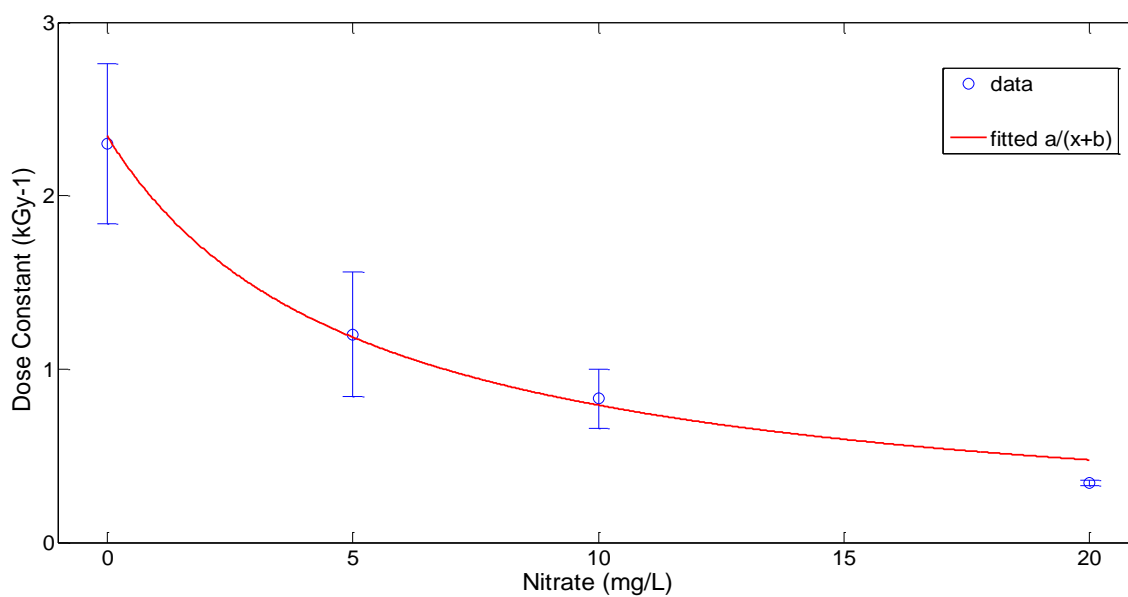


Fig 6. Dose constant (kGy^{-1}) as a function of NO_3^- concentration (mg/L). Error bars indicate 95% confidence intervals. Line represents model prediction.

4.3 Effect of Fulvic Acid

As a ubiquitous constituent in aquatic systems, the influence of NOM on degradation processes has been tested in many studies. Kim et al. found that degradation of methylmercury was accelerated in the presence of FA, while it fashioned oppositely in the presence of HA.⁴⁰ The efficiency of removing diclofenac was found to increase as HA increased from 0 to 60 mg/L, but decreased as the level of HA increased from 60 to 80 mg/L.⁴⁵ However, the effects of FA on BrO_3^- degradation through radical reactions have not been investigated. In this section, the effect of four levels of FA (0, 25, 50 and 100 $\mu\text{g-C/L}$) on BrO_3^- reduction was evaluated. The eBeam energy was 8.5 MeV for this set of experiments. The matrix included 10 mg/L NO_3^- and 50 mg/L alkalinity as CaCO_3 . The initial concentration for BrO_3^- was measured as $102 \pm 1.4 \mu\text{g/L}$.

The results of fitting dose constants to the data (Appendix 4) are shown in Table 3 and the effect of FA is shown in Figure 7. As FA concentration increased from 0 to 100 $\mu\text{g/L}$, the degradation of BrO_3^- does not appear to be influenced. FA is more likely to exist in a reduced form and is active in scavenging oxidants such as $\cdot\text{OH}$, instead of reacting with reducing radicals such as e_{aq}^- and $\text{H}\cdot$. Combined with the effect of NO_3^- , it is reasonable to conclude that the reduction of BrO_3^- is primarily carried out by e_{aq}^- and $\text{H}\cdot$ radicals.

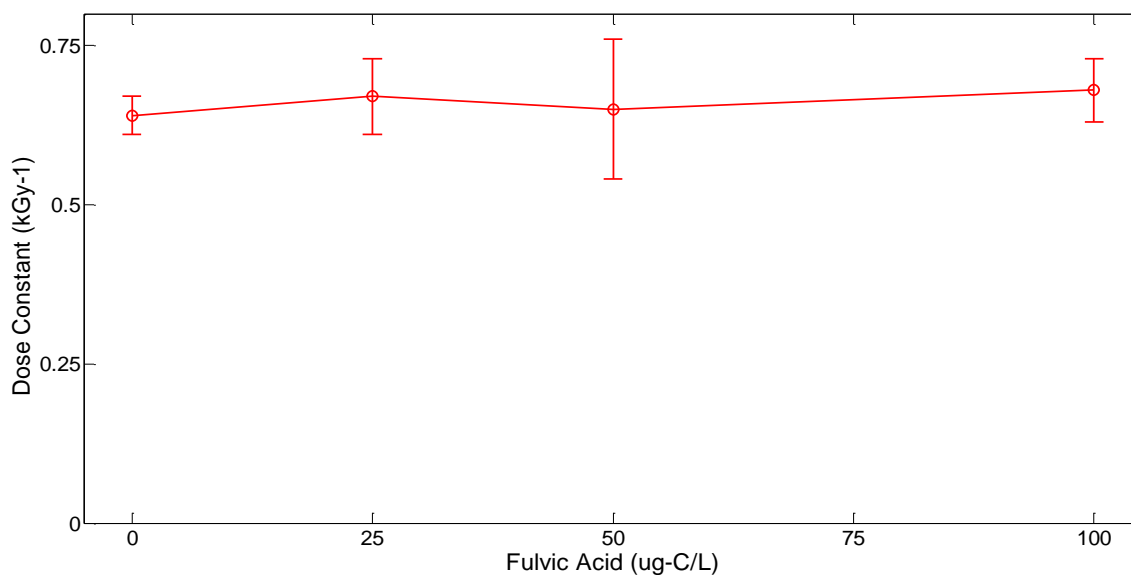


Fig 7. Dose constant (kGy^{-1}) as a function of FA concentration ($\mu\text{g-C/L}$). Error bars indicate 95% confidence intervals.

Table 3. Dose Constants for Removal of BrO_3^- at Different Fulvic Acid Concentrations.

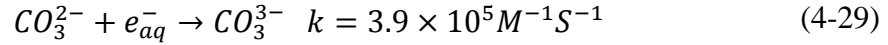
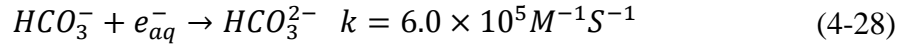
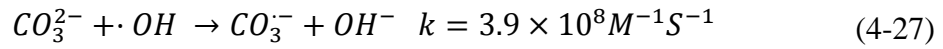
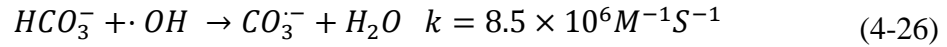
FA ($\mu\text{g/L}$)	95% Confidence			
	k (kGy^{-1})	interval	R^2	$D_{0.9}$ (kGy)
0	0.64	0.61~0.67	0.9992	3.6
25	0.67	0.60~0.73	0.9968	3.4
50	0.65	0.54~0.77	0.9962	3.5
100	0.68	0.64~0.73	0.9985	3.4

4.4 Effect of Alkalinity

Alkalinity is a major parameter of water quality. It measures bases in water that can accept hydrogen ions released by a strong acid. For natural waters, carbonate and bicarbonate ions account for most of the alkalinity, because of the widespread dissolution of carbonate rocks by reaction with carbon dioxide in ambient air. Alkalinity is usually expressed as equivalents of calcium carbonate (CaCO_3). Kim et al. found that alkalinity exerted negative effects on photo-decomposition of methylmercury. The kinetic constant decreased from 0.165 to 0.003 min^{-1} as alkalinity increased from 0 to $50,000 \text{ mg/L}$ as CaCO_3 .⁴⁰ Alkalinity also slowed down the photodegradation rate of 17β -estradiol under simulated solar irradiation because of the reaction with $\cdot\text{OH}$.⁴⁶

Four levels of alkalinity in the range from 0 to 100 mg/L as CaCO_3 were studied. The eBeam energy for this set of experiments was set at 10 MeV . The reactions occurred in a matrix including 10 mg/L NO_3^- , and $50 \mu\text{g-C/L FA}$. The initial concentration for BrO_3^- was measured as $101 \pm 1.1 \mu\text{g/L}$. The results of fitting dose constants to the data (Appendix 5) are shown in Table 4.

Since the pH was buffered around neutrality (pH 7.3), alkalinity was primarily in the form of bicarbonate (HCO_3^-). Visual Minteq showed that HCO_3^- accounted for 93% of total carbonate at pH 7.3. HCO_3^- is well known as a scavenger of $\cdot\text{OH}$ and e_{aq}^- .⁴³



The reactivity with e_{aq}^- is more than one order weaker than it is with $\cdot OH$, therefore carbonate alkalinity primarily worked as a $\cdot OH$ scavenger. As shown in Fig 8, the dose constant barely changes with carbonate alkalinity, which indicates that the hydroxyl radical is not important in degradation of BrO_3^- . Therefore, it is likely that reducing agents such as e_{aq}^- radicals are most responsible for removing BrO_3^- in this study.

Table 4. Dose Constants for Removal of BrO_3^- at Different Alkalinity Concentrations.

Alk (mg /L as -CaCO ₃)	k (kGy ⁻¹)	95% Confidence interval (kGy ⁻¹)	R ²	D _{0.9} (kGy)
0	0.72	0.84~0.60	0.9919	3.2
25	0.75	0.90~0.60	0.9885	3.1
50	0.83	0.66~1.00	0.9962	2.8
100	0.63	0.59~0.66	0.9991	3.7

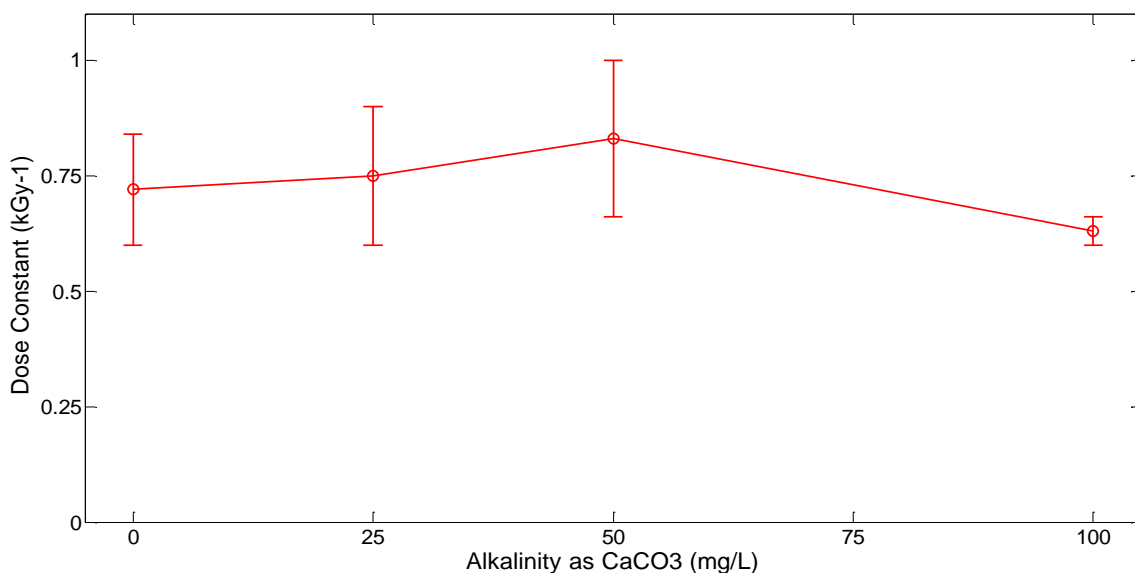
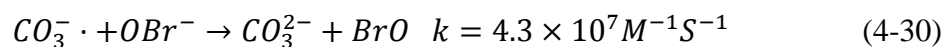


Fig 8. Dose constant (kGy⁻¹) as a function of alkalinity concentration as CaCO₃ (mg/L). Error bars indicate 95% confidence intervals.

The generation of carbonate radicals (CO₃^{-·}) from Equation (4-26) and (4-27) may slow down the reduction of BrO₃⁻ by e_{aq}⁻ radicals. Because CO₃^{-·} is a fairly strong oxidant and has been reported to be able to oxidize OBr⁻ (Equation (4-30)) as shown in Equation (4-30).⁴⁷

However, the rate constant is three orders less than that of the reaction between e_{aq}⁻ and OBr⁻. This competition was too moderate to affect the dose constant.



4.5 Effect of pH

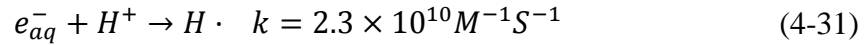
The dependence of pollutant degradation on pH has been confirmed in many studies. In this study, experiments with three levels of pH (5.0, 7.3 and 9.0) were conducted to probe its influence on BrO_3^- removal. This set of experiments was tested with eBeam energy of 8.5 MeV. The reactions occurred in a matrix including 10 mg/L NO_3^- , 50 $\mu\text{g/L}$ FA and 50 mg/L alkalinity as CaCO_3 . The initial concentration for BrO_3^- was measured as $98.5 \pm 4.3 \mu\text{g/L}$. The summary of experimental and fitting model results is shown in Table 5 and Fig 9. The detailed data are shown in Appendix 6.

Table 5. Dose Constants for Removal of BrO_3^- at Different pH.

pH	k (kGy^{-1})	95% Confidence interval (kGy^{-1})	R^2	$D_{0.9}$ (kGy)
5.0	0.45	0.41 - 0.48	0.9969	5.1
7.3	0.69	0.73 - 1.64	0.9993	3.3
9.0	0.66	0.60 - 0.72	0.9967	3.5

The adjustment of pH level not only changes the concentrations of H^+ and OH^- , but shifts the $\text{CO}_3^{2-}/\text{HCO}_3^-$ balance as well. However, the influence of alkalinity has been shown to be negligible in the previous section. The effect of pH could be simply ascribed to the reactions of H^+ and OH^- .

The dose constant increased from 0.45 to 0.69 kGy⁻¹ as pH changed from 5.0 to 7.3. At the lower pH, more hydrogen ions (H⁺) exist, which could scavenge e_{aq}⁻ according to Equation (4-31).



The rate constant is on the same order as the reduction of BrO₃⁻ by e_{aq}⁻ (Equation (2-9)). Given the concentrations of BrO₃⁻ and H⁺, the rates for both reactions (r₂₋₉ and r₄₋₃₁) can be calculated and compared. At neutral pH, r₄₋₃₁ was about one tenth of r₂₋₉, while at pH 5.0, the r₄₋₃₁ was about 10 times of r₂₋₉. So the removal of BrO₃⁻ was slowed down at pH 5.0 due to scavenging of aqueous electron by hydrogen ions. As pH increased to 9.0, r₂₋₉ was nearly three orders larger than r₄₋₃₁, the scavenging of e_{aq}⁻ causing by H⁺ was negligible at that pH. For the alkaline conditions, the dose constant barely changed when pH increased from 7.3 to 9.0. OH⁻ is not a strong scavenger for e_{aq}⁻. This behavior supports the hypothesis that removal of BrO₃⁻ was primarily induced by e_{aq}⁻.

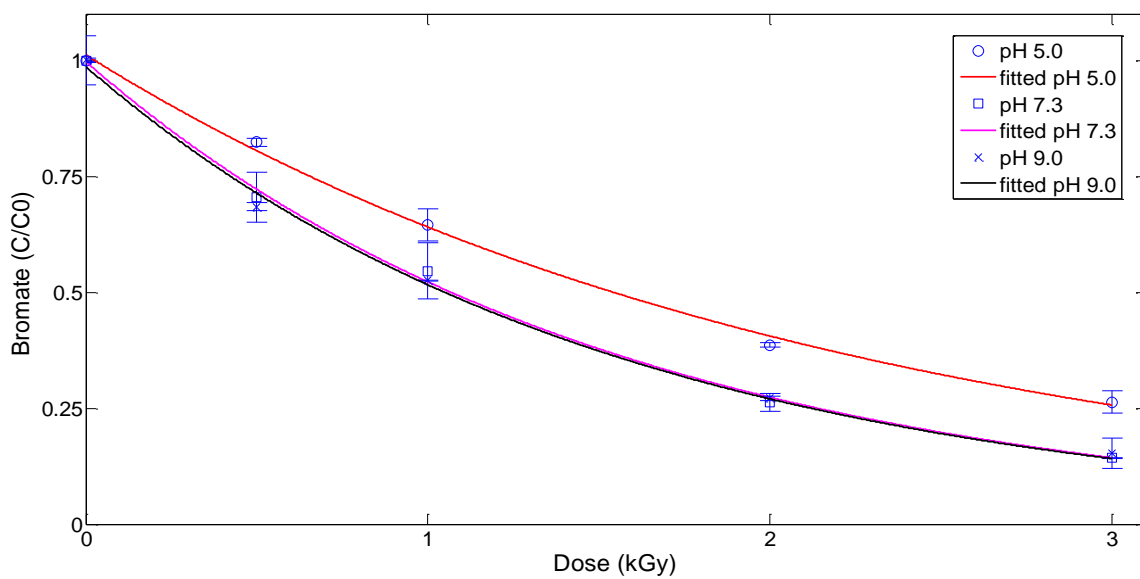


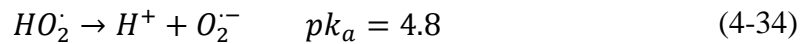
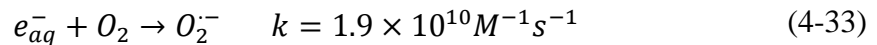
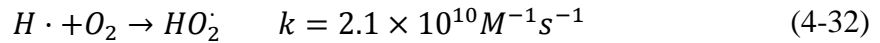
Fig 9. Effect of eBeam dose on BrO_3^- removal for different pH. Error bars indicate standard deviation.

4.6 Treatment in Presence of O₂

Since the reduction of BrO₃⁻ was believed to be primarily induced by e_{aq}⁻ and H·, the presence of dissolved oxygen (DO) could scavenge those reducing radicals and hinder the removal processes. On the other hand, consideration the effect of DO is of interest in applying the eBeam irradiation in practice, because treatment processes are usually in contact with ambient air so their effluents contain appreciable concentrations of dissolved oxygen. The effect was evaluated by conducting experiments with simulated water in equilibrium with air. The DO was measured as 8.4 mg/L.

As shown in the Fig 10, BrO₃⁻ behaved very differently when DO was present. BrO₃⁻ concentration in the presence of DO decreased with increasing dose at low doses (0-2 kGy), but increased at higher doses (3-4 kGy). At the doses of 3.0 and 4.1 kGy, the concentration of BrO₃⁻ is 78.3% and 86.1% of its initial value, respectively. When dose increased above 6.0 kGy, BrO₃⁻ concentration was observed to decrease again reaching 61.8% of its initial value at the highest dose (9.3 kGy).

The presence of DO would result in the formation of superoxide anion radical (O₂⁻). The reactions can be expressed as follow equations:^{48, 49}



The O₂⁻ that is formed may re-oxidize Br⁻ to BrO₃⁻. However, as dose increased and DO depleted, the removal of BrO₃⁻ increased at doses above 6 kGy. The dose

constant for the first 3 kGy was calculated as $0.21 (0.13 - 0.29) \text{ kGy}^{-1}$. The dose constant for doses above 3 kGy was $0.10 (0.09 - 0.11) \text{ kGy}^{-1}$.

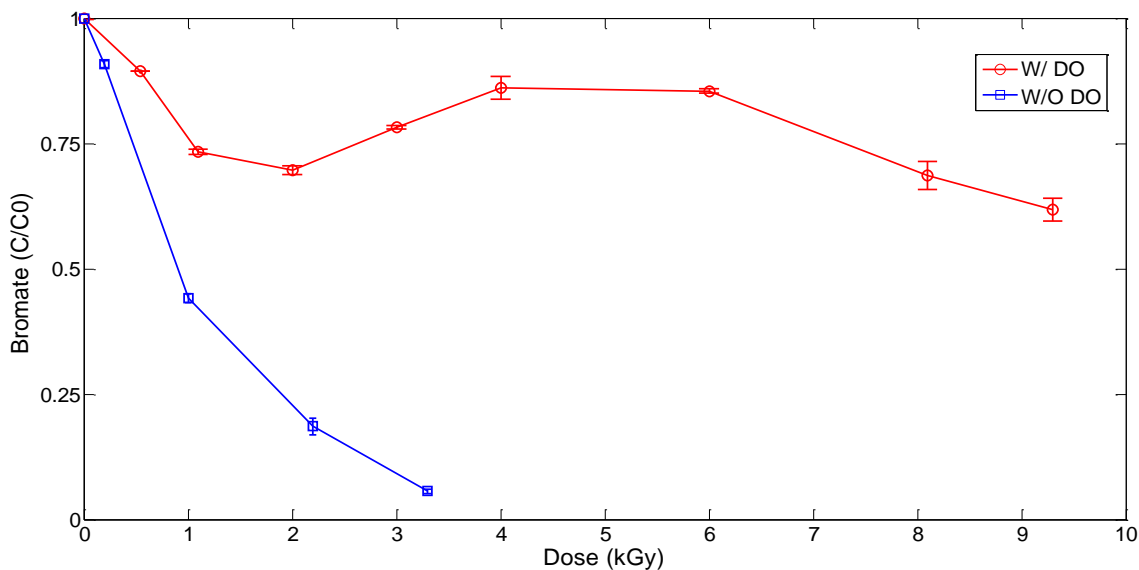


Fig 10. Effect of eBeam dose on concentration of BrO_3^- in absence and presence of DO (8.4 mg/L). Error bars are the standard deviation of triplicate samples.

Complete removal of BrO_3^- was expected at very high doses. According to the calculated dose constant of 0.10 kGy^{-1} , 90% removal would be achieved at a dose of 29 kGy. DO exert significant effect on BrO_3^- removal. To apply eBeam treatment to water that contains dissolved oxygen would require higher doses or deoxygenation in order to achieve desirable concentrations of BrO_3^- that would meet the regulations.

5. CONCLUSION

This study has shown that eBeam irradiation is effective in removing BrO_3^- in both Milli-Q water and synthesized reclaimed wastewater in the absence of oxygen. In the background of Milli-Q water, 97% of initial BrO_3^- was recovered as Br^- at a dose of 0.96 kGy. In the matrix of synthesized reclaimed wastewater, the effects of NO_3^- , fulvic acid, alkalinity, and aqueous pH were studied. The relationship of bromate concentration and absorbed doses followed an exponential decay model. The addition of NO_3^- decreased the removal efficiency and dose constant and this effect could be well explained by a basic degradation model. Aqueous pH exerted an influence on BrO_3^- removal. The dose constant decreased at the lowest pH (pH 5) tested, but was fairly constant at the neutral (pH 7.3) and the alkaline (pH 9) values. The effects of alkalinity and fulvic acid were negligible in the neutral pH, because CO_3^{2-} and fulvic acid are not strong scavengers for e_{aq}^- . In this study, degradation of BrO_3^- was only investigated in synthesized water. The reactions in real reclaimed water could be more completed, and further research regarding this aspect should be carried out in future.

Dissolved oxygen in water negatively influenced BrO_3^- reduction. A reoxidation of Br^- was observed after partial reduction of BrO_3^- . A substantially higher dose was required to completely remove BrO_3^- in the presence of oxygen. Therefore, prior deoxygenation is recommended to apply eBeam irradiation in reality.

In conclusion, eBeam irradiation would be a viable alternative to treat reclaimed wastewater if aqueous dissolved oxygen is well controlled. Moreover, eBeam treatment

does not require addition of reagents nor does it produce secondary wastes, which makes it a favorable substitution for those treatment processes do require huge amounts of reagents and/or produce unpleasant secondary wastes.

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APPENDIX 1

```
%%Calculate concentration & errorbar for bromate, PA1 is peak area for
bromate%%
X=[0 0.26 0.54 0.77 0.96];
PA1=[144553 60942 18024 8285 0
149011 50233 16042 7933 0
149868 73926 19918 13117 0];
C1=(PA1+4081.6)/1588.3;
E1=std(C1);
Y1=mean(C1);
errorbar(X,Y1,E1);
hold on
%% Calculate concentration & errobar for bromide, PA2 is peak area for
bromide%%
X=[0 0.26 0.54 0.77 0.96];
PA2=[5438 86164 134136 145517 154421
1584 98140 136975 145589 156262
2584 70669 130716 139461 143023];
C2=(PA2+4644.3)/2680.5;
E2=std(C2);
Y2=mean(C2);
errorbar(X,Y2,E2)
%% Fit curve for bromate degradation%%
xfit=X';
yfit=Y1';
f=fit(xfit,yfit,'exp1');
plot(f,xfit,yfit)
```

APPENDIX 2

Degradation of BrO_3^- in Milli-Q water

Table A-2. Summary of Experimental and Model Values for Concentration of BrO_3^- as Br^- in Milli-Q water for Various Doses

Dose (kGy)	Experimental ^a ($\mu\text{g/L}$)	Model ($\mu\text{g/L}$)
0	59.8	59.8
0.26	25.9	24.9
0.54	8.7	9.7
0.77	5.5	4.4
0.96	— ^b	2.3
^a Mean of triplicate experiments. ^b Below method detection limit.		

APPENDIX 3

Effect of NO_3^- on BrO_3^- Degradation

Table A-3. Summary of Experimental and Fitting Model Results for BrO_3^- at Different NO_3^- Concentrations

NO_3^- (mg/L)	Dose (kGy)	C/C ₀	
		Experimental ^a	Model
0	0	1	1
	0.5	0.29	0.31
	1	0.13	0.10
	2.1	^b -	0.01
	3.1	^b -	^b -
5	0	1	1
	0.4	0.67	0.61
	1	0.26	0.29
	2.	0.07	0.08
	3.3	^b -	0.02
10	0	1	1
	0.2	0.91	0.85
	1	0.44	0.44
	2.2	0.18	0.16
	3.3	0.05	0.07

Table A-3. Summary of Experimental and Fitting Model Results for BrO_3^- at Different NO_3^- Concentrations

NO_3^- (mg/L)	Dose (kGy)	C/C_0	
		Experimental ^a	Model
20	0	1	1
20	0.5	0.86	0.84
	1	0.71	0.71
	2.2	0.45	0.47
	3.1	0.34	0.34
^a Mean of triplicate experiments. ^b Below method detection limit			

APPENDIX 4

Effect of Fulvic Acid on BrO_3^- Degradation

Table A-4. Summary of Experimental and Fitting Model Results for BrO_3^- at Different Fulvic Acid Concentrations

FA ($\mu\text{g/L}$)	Dose (kGy)	C/C_0	
		Experimental ^a	Model
0	0	1.00	1.00
	0.5	0.74	0.73
	1	0.54	0.53
	2.3	0.24	0.23
	3	0.13	0.15
25	0	1.00	1.00
	0.5	0.74	0.72
	1	0.50	0.51
	2.1	0.24	0.25
	3.3	0.10	0.11
50	0	1.00	1.00
	0.6	0.75	0.68
	1	0.51	0.52
	2.1	0.21	0.25
	3.2	0.14	0.12

Table A-4. Summary of Experimental and Fitting Model Results for BrO_3^- at Different Fulvic Acid Concentrations

100	0	1.00	1.00
	0.5	0.72	0.71
	1	0.50	0.50
	2.2	0.21	0.22
	3.4	0.09	0.10
^a Mean of triplicate experiments.			

APPENDIX 5

Effect of alkalinity on BrO₃⁻ Degradation

Table A-5. Summary of Experimental and Fitting Model Results for BrO₃⁻ at Different Alkalinity Levels

Alk (mg-CaCO ₃ /L)	Dose (kGy)	C/C ₀	
		Experimental ^a	Model
0	0	1.00	1.00
	0.4	0.81	0.75
	1	0.49	0.49
	2.1	0.21	0.22
	3.1	0.07	0.11
25	0	1.00	1.00
	0.4	0.80	0.74
	1	0.48	0.47
	2	0.21	0.22
	2.9	0.06	0.11
50	0	1	1
	0.2	0.91	0.85
	1	0.44	0.44
	2.2	0.18	0.16
	3.3	0.05	0.07

Table A-5. Summary of Experimental and Fitting Model Results for BrO_3^- at Different Alkalinity Levels

Alk (mg- CaCO_3/L)	Dose (kGy)	C/C_0	
		Experimental ^a	Model
100	0	1.00	1.00
	0.5	0.73	0.76
	0.9	0.57	0.56
	2.2	0.25	0.25
	2.9	0.16	0.15
^a Mean of triplicate experiments.			

APPENDIX 6

Effect of pH on BrO₃⁻ Degradation

Table A-6. Summary of Experimental and Fitting Model Results for BrO₃⁻ at Different pH Levels

pH	Dose (kGy)	C/C ₀	
		Experimental ^a	Model
5.0	0	1	1
	0.5	0.82	0.80
	1	0.65	0.64
	2	0.39	0.41
	3	0.26	0.26
7.3	0	1	1
	0.5	0.70	0.71
	0.9	0.55	0.54
	2	0.26	0.25
	2.7	0.14	0.16
9.0	0	1	1
	0.5	0.68	0.72
	1	0.52	0.52
	2	0.27	0.27
	3	0.15	0.14
^a Mean of triplicate experiments.			

APPENDIX 7

BrO₃⁻ Degradation with/without DO

Table A-7. Comparison of BrO₃⁻ removal with/without DO

irradiation w DO		irradiation w/o DO	
Dose (kGy)	% removal ^a	Dose (kGy)	% removal ^a
0.5	10.7	0.2	56.7
1.1	26.7	1.0	85.5
2.0	30.3	2.2	90.9
3.0	21.7	3.3	100
4.1	13.9		
6.0	14.6		
8.1	31.4		
9.3	38.2		
^a Mean of triplicate experiments.			