



Electron beam treatment for potable water reuse: Removal of bromate and perfluorooctanoic acid



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HIGHLIGHTS

- EBeam removes bromate and PFOA from synthetic water for potable reuse.
- Bromate degradation and PFOA defluorination are effectively explained by models.
- Nitrate, pH and dissolved oxygen negatively influenced bromate degradation.
- Nitrate and alkalinity exert positive influences on PFOA defluorination.
- PFOA defluorination is inhibited by humic acid and dissolved oxygen.

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ABSTRACT

Water reuse is an alternative strategy targeting water shortages. In this study, electron beam (eBeam) irradiation was investigated as a method for removing bromate and perfluorooctanoic acid (PFOA) from a synthetic water designed to simulate a treated wastewater intended for potable water reuse. In the absence of oxygen, an exponential model was able to relate bromate concentration to absorbed dose. However, a more complex model was needed to describe PFOA defluorination, so a model was developed that assumed formation of one partially defluorinated intermediate and this model was used to describe the relationship between free fluoride concentration and absorbed dose. Nitrate negatively affected the removal of bromate and the dose constant was inversely proportional to the nitrate concentration as predicted by a simple model that assumes the presence of radical scavengers. In contrast, the presence of nitrate improved the degradation of PFOA, possibly due to formation of oxidizing radicals or by other reactions of nitrate degradation products. Fulvic acid and alkalinity exerted negligible influences on bromate removal. Fulvic acid dampened the defluorination efficiency, probably due to the scavenging of oxidizing radicals such as the hydroxyl radical ($\cdot\text{OH}$). Alkalinity was found to accelerate PFOA defluorination, possibly because of the formation and reactivity of the carbonate radical ($\text{CO}_3^{\cdot-}$). As pH increased from 5.0 to 7.3, the dose constant for bromate removal increased from 0.45 kGy^{-1} to 0.69 kGy^{-1} , but it barely changed when pH was further increased to 9.0. In the presence of oxygen, both contaminants were degraded less efficiently and showed more complex patterns of degradation. Pretreatment to remove dissolved oxygen would probably be needed to apply eBeam in practice for degradation of bromate and PFOA.

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1. Introduction

As water shortages become increasingly serious problems confronting many areas, water reuse may represent an alternative solution to meeting growing water demands. Direct and indirect water reuse requires a series of physical, biological and chemical

processes with exceptional reliabilities. Technologies to address microbiological contaminants, disinfection by products, natural hormones and pharmaceuticals are imperative.

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 [1]. Typical concentration ranges for bromide in groundwaters and surface waters are reported to be 0–2 mg/L [2], and 0–0.8 mg/L [3,4], respectively.

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Nomenclature

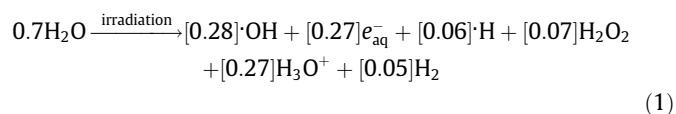
a	dose constant for first step of PFOA degradation (kGy^{-1})	k_1	second order rate constant between target and aqueous electron ($\text{mmol}^{-1} \text{L s}^{-1}$)
b	dose constant for second step of PFOA degradation (kGy^{-1})	k_2	second order rate constant between scavengers and aqueous electron ($\text{mmol}^{-1} \text{L s}^{-1}$)
D	absorbed dose (kGy)	n	number of fluorine atoms in partially defluorinated intermediate
f	fraction of PFOA degradation intermediate that is susceptible to complete defluorination	ρ	solution density (kg L^{-1})
g_e	yield of aqueous electron ($\mu\text{mol/J}$)	r_{dose}	dose rate defined as the dose absorbed per unit time (kGy s^{-1})
k	dose constant (kGy^{-1})		

There are two mechanisms being proposed to describe bromate formation during water ozonation [5]. 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 [3]. Bromate has been shown to be carcinogenic in the rat kidney [6]. Orally administered bromate is rapidly absorbed from the gastrointestinal tract and causes gastrointestinal symptoms [7]. 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 $10 \mu\text{g/L}$ (annual average) [8]. A number of strategies for suppression of bromate formation and removal after formation have been developed for water treatment. Formation suppression techniques include pH adjustment [9] and ammonia addition [10]. Removal approaches such as activated carbon [10–12], ultraviolet (UV) irradiation [13–15], electrochemical reduction [16] and chemical reduction [17–20] involving ferrous iron or zero-valent iron have been studied to remove bromate during past decades. A study of eBeam treatment found that a dose of 1kGy was sufficient to remove 70% of bromate from an initial concentration of $100 \mu\text{g/L}$ in NOM-free water [21].

Perfluorinated chemicals (PFCs) are used in manufacturing fluoropolymer and firefighting foams because of their hydrophobicity and oleophobicity. Perfluorooctanoic acid (PFOA) is one of the most abundant PFCs, and it is a stable intermediate during natural degradation of other PFCs. PFOA has been detected in various locations globally. A study in Osaka, Japan analyzed PFOA from 2006 to 2007, and it found the concentrations of PFOA ranged from 5.2 to 92 ng/L , and 2.3 to 84 ng/L in untreated and treated drinking water, respectively [22]. PFOA was also found in spring and groundwater samples collected in the Tokyo metropolitan area at concentrations in the range 0.47 – 60 ng/L [23]. Pan et al. confirmed that PFOA accounted for 19.7–94.4% of total PFCs measured in both influents and effluents from seven major wastewater treatment plants in Beijing [24]. The range of concentrations of PFOA measured in influents was 1.3 – 135 ng/L and 3.8 – 104 ng/L in effluents. In recycled water from four California wastewater treatment plants, PFOA was detected to be 10 – 190 ng/L [25]. PFOA has been tested to be positively related to increased tumor incidents in experimental rats, and to be associated with reduced birth weight when pregnant women were exposed to PFOA [26]. Because of the strong C–F bonds (116 kcal/mol), PFOA is very stable and there is no evidence showing it can be naturally degraded. Studies on advanced oxidation processes (AOPs) indicated that hydroxyl radicals ($\cdot\text{OH}$) could not successfully decompose PFOA due to the electronegativity of fluoride atoms [27,28]. Adsorption processes have been utilized to remove aqueous PFOA, with the adsorbents including polyaniline nanotubes [29], bamboo-derived activated carbon, and resins [30]. Direct UV photolysis [31] and UV irradiation

enhanced with carbonate (CO_3^{2-}) [32], sulfite (SO_3^{2-}) [33] and iodine (I^-) [34] have been studied to degrade PFOA. Sonochemical methods were demonstrated to remove PFOA in previous studies [35,36]. Most recently, a study on irradiation treatment by γ -ray with a ^{60}Co source achieved a complete mineralization of PFOA in a N_2 -saturated condition at pH 13 [37].

Yet there are no studies focused on removing bromate and PFOA from wastewater intended for water reuse. The technologies used for groundwater recharge in California usually include microfiltration, reverse osmosis (RO) and ultraviolet (UV) irradiation [38]. It has been reported that UV irradiation dose ($<40 \text{ mW}\cdot\text{s}/\text{cm}^2$) normally found in water treatment processes was not able to remove bromate effectively [15]. Direct UV photolysis is not efficient for PFOA degradation using typical sources of UV light and it produces intermediates whose toxicity needs to be carefully studied [31,32,39]. Electron beam (eBeam) irradiation presents as an alternative for removing bromate and PFOA particularly in water intended for reuse. EBeam technology involves irradiating a material by a stream of high energy electrons, which can be produced by electron accelerators. This results in water splitting to form a number of reactive species as shown in Eq. (1):



The numbers in the brackets represent the yields of each species expressed as the amount produced per amount of energy absorbed by the water. Eq. (1) indicates that eBeam irradiation is an advanced oxidation–reduction process, in that both oxidizing and reducing reactive species are produced. In addition to bromate reduction, eBeam irradiation of water has also been successfully used to disinfect bacterial and viral pathogens in sewage sludge [40], and to remove acetone [41], benzene [42], toluene [42], phenol [43], antibiotics [44], pharmaceuticals and personal care products [45] from water.

The objective of this study is to evaluate the effectiveness of applying eBeam irradiation in removing bromate and PFOA from water with similar characteristics as that intended for potable reuse.

2. Materials and methods

2.1. 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 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 water [46]. In this irradiation study, only one LINAC was applied, which was operated under average pulse current of 1500 μA , 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.

2.2. 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 [47], 50 mg- CaCO_3/L alkalinity [47,48], 50 $\mu\text{g-C/L}$ DOC [49] from fulvic acid (FA). In addition, 10 mg/L NO_3^- was selected to study the effects of nitrate on bromate and PFOA removal. 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 Da [50], 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 PFOA was prepared by dissolving perfluorooctanoic acid (95%, Alfa Aesar, MA, USA) in deionized water to make its concentration around 500 mg/L. A 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- CaCO_3/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 (KH_2PO_4) and 8.19 g potassium hydrogen phosphate (K_2HPO_4) in 1 L of deionized water and adjusting to desired pH with 1 N NaOH and 1 N H_2SO_4 . The solutions were prepared and added to Pyrex petri dishes, which were sealed with Parafilm (Bemis NA, Neenah, WI, USA). The diameters for the petri dish bottom and cover were 95 mm and 100 mm respectively. The solution volume was 30 ml, and the depth of the water in the dishes was about 4 mm. The sealed petri dishes were placed in resealable bags before being taken out of the anaerobic chamber for irradiation.

2.3. EBeam irradiation

All irradiation experiments were conducted at the NCEBR. The samples were placed on the conveyance system to be irradiated and its speed was adjusted to achieve the desired doses. 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 at 5 °C for about 12 h until analysis.

2.4. 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. The relationship between the dose on top of petri dish and the dose on top of solution was determined in the same systems, and the results showed that the dose delivered to the solution was 1.144 times that at the top of petri dish (see [Supplementary information](#)). The dose delivered to the solution was calculated accordingly.

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 aforementioned relationship.

2.5. Sample analysis

2.5.1. Bromate-spiked samples

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- μL injection loop so that it could detect very low concentrations of BrO_3^- and Br^- . The initial concentration of BrO_3^- was about 100 $\mu\text{g/L}$. The method detection limits (MDLs) 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.

2.5.2. PFOA-spiked samples

The concentration of stock PFOA solution was measured with an Agilent 8453 UV-Vis spectrometry. An IonPac AS11 HC was employed to analyze the concentration of F^- after irradiation. The eluent was 10 mM NaOH, and the injection loop was 1000 μL . The MDL was determined as 0.46 $\mu\text{g/L}$. Defluorination efficiency was calculated as follows:

$$\text{Defluorination efficiency} = C_{\text{F}^-} / (C_0 * 15) \times 100\% \quad (2)$$

where C_{F^-} is the molar concentration of free fluoride ions, C_0 is the initial molar concentration of PFOA. The factor of 15 arises from the number of fluorine atoms in the PFOA molecule. Defluorination efficiency is found to be related to the decomposition of PFOA [32,33,35,51], and thus it is used as the parameter evaluating PFOA degradation.

3. Results and discussion

3.1. Removal of bromate in absence of oxygen

3.1.1. Model for effect of dose on bromate concentration in presence of scavenger

A model was developed to describe the relationship between contaminant removal and eBeam dose in the presence of a scavenger. Bromate removal is accomplished by highly reactive species

Table 1
Radical reactions for bromate removal.

	Reaction	Rate
(a)	$T + e_{\text{aq}}^- \xrightarrow{k_1} P_1$	$r_1 = k_1 * [T] * [e_{\text{aq}}^-]$
(b)	$S + e_{\text{aq}}^- \xrightarrow{k_2} P_2$	$r_2 = k_2 * [S] * [e_{\text{aq}}^-]$
(c)	$\text{H}_2\text{O} \xrightarrow{\text{irradiation}} e_{\text{aq}}^-$	$r_3 = r_{\text{dose}} * g_e * \rho$

Nomenclature: T = target compound (BrO_3^-); e_{aq}^- = aqueous electron; S = scavengers toward active radicals; P_1, P_2 = products; r_1, r_2, r_3 = reaction rates of reactions (a)–(c); k_1, k_2 = second order rate constants of reaction (a)–(c); r_{dose} = dose rate defined as the dose absorbed per unit time; g_e is the yield for e_{aq}^- ; ρ = the density of the irradiated solution.

in solution and the aqueous electron is believed to be the most important one. Two reactions of the aqueous electron are considered: the reaction with the target (BrO_3^-) and reaction with a generalized scavenger, which could be a compound such as nitrate. These simple reactions combined with the reaction that produces aqueous electrons are summarized in Table 1, and a detailed derivation of the model is shown in Supplementary information.

This model is derived under the assumption that the reactions are extremely fast, and therefore the derivatives of the concentration of the aqueous electron with time is negligible compared to the rates of the other reactions. This is because the aqueous electron reacts with targets and scavengers soon after they are produced, so the concentration of aqueous electron remains very low, which means that the derivative of the concentration would also be very low. The relationship between the concentration of target compound (BrO_3^-) and the absorbed dose can be expressed as:

$$[T] = [T]_0 \exp(-kD) \quad (3)$$

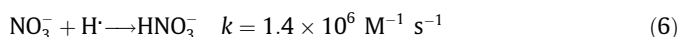
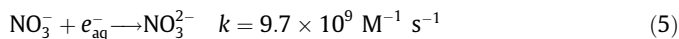
where $[T]_0$ and $[T]$ are the initial bromate concentration and the concentration at dose D , respectively. The dose constant (k) for removal of the target compound can be related to the concentration of primary scavenger ($[S]$) that can also react with the reactive species produced by the eBeam (derivation in Supplementary information).

$$k = \frac{a}{[S] + b} \quad (4)$$

where a and b are constants that depend on rate constants and other variables (Supplemental information).

3.1.2. Effect of nitrate on bromate removal

Nitrate is a universally present radical scavenger in surface water and groundwater and is known to react very rapidly with e_{aq}^- ($k = 9.7 \times 10^9 \text{ mol}^{-1} \text{ s}^{-1}$) and H^\cdot ($k = 1.4 \times 10^6 \text{ mol}^{-1} \text{ s}^{-1}$) [52]. Many studies have concluded that the presence of NO_3^- significantly inhibits reduction processes induced by e_{aq}^- and H^\cdot radicals [41,53]. The related reactions include:



Increasing NO_3^- concentration slowed down BrO_3^- degradation as shown in Fig 1(a). Dose constants (k) were determined for BrO_3^- degradation by nonlinear regression on experimental using 'cftool' in Matlab and are shown as a function of nitrate concentration in Fig 1(b). Although nitrate inhibited bromate degradation, a dose constant of 0.35 kGy^{-1} was still obtained when 20 mg/L NO_3^- was used. This indicates that BrO_3^- and its intermediate degradation products are highly reactive with e_{aq}^- and H^\cdot . The second-order rate 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 for NO_3^- and its radicals [10,41,42]. In addition, reactivity of 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.

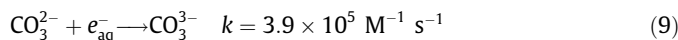
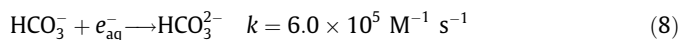
Assuming that NO_3^- is the primary scavenger, Eq. (4) can be applied to describe the effect of nitrate on the dose constant.

$$k = \frac{a}{[\text{NO}_3^-] + b} \quad (7)$$

To evaluate the feasibility of this simple model, the MATLAB tool "cftool" was used to fit Eq. (7) to the data for dose constant obtained at different nitrate concentrations and the results are shown in Fig 1(b). 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). A value for R^2 of 0.9903 was obtained for this fit. This 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. The ability of a known scavenger of aqueous electrons like nitrate to inhibit bromate reduction is evidence that bromate is being degraded by the aqueous electron.

3.1.3. Effect of alkalinity on bromate removal

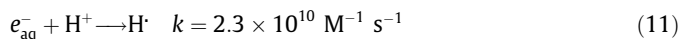
The effect of alkalinity on dose constant of BrO_3^- removal is shown in Fig 2. Since the pH was buffered around neutrality (pH 7.3), alkalinity was primarily in the form of bicarbonate (HCO_3^-). Visual Minteq showed that HCO_3^- accounted for 93% of total carbonate at pH 7.3. HCO_3^- is a scavenger for e_{aq}^- , but the rate constants are much lower than that for bromate [52].



As we can see, e_{aq}^- is five orders more active with bromate than with bicarbonate/carbonate, which explains why the dose constant barely changes with alkalinity.

3.1.4. Effect of pH on bromate removal

Experiments with three levels of pH (5.0, 7.3 and 9.0) were conducted to probe its influence on BrO_3^- removal and the results are shown in Fig 3. The dose constant increased from 0.45 kGy^{-1} to 0.69 kGy^{-1} as pH changed from 5.0 to 7.3. The effect of pH could be simply ascribed to the reactions of H^+ and OH^- . At the lower pH, more hydrogen ions (H^+) exist, which could scavenge e_{aq}^- according to Eq. (11).



The rates for both reactions (Eqs. (10) and (11)) can be calculated and compared by assuming concentrations of BrO_3^- (1.1 E-6M) and H^+ ($10^{-5}, 10^{-7.3} \text{ M}$). At pH 7.3, the aqueous electron reacts with bromate about three times the rate of reaction with hydrogen ion. However, at pH 5, the reaction with hydrogen ion is almost 60 times as fast as that with bromate. Therefore, scavenging of aqueous electron by hydrogen ions is probably the reason for decrease in bromate removal at pH 5. As pH increased to 9.0, the rate of reaction with bromate was nearly three orders larger than with hydrogen ion, so the scavenging of e_{aq}^- 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.

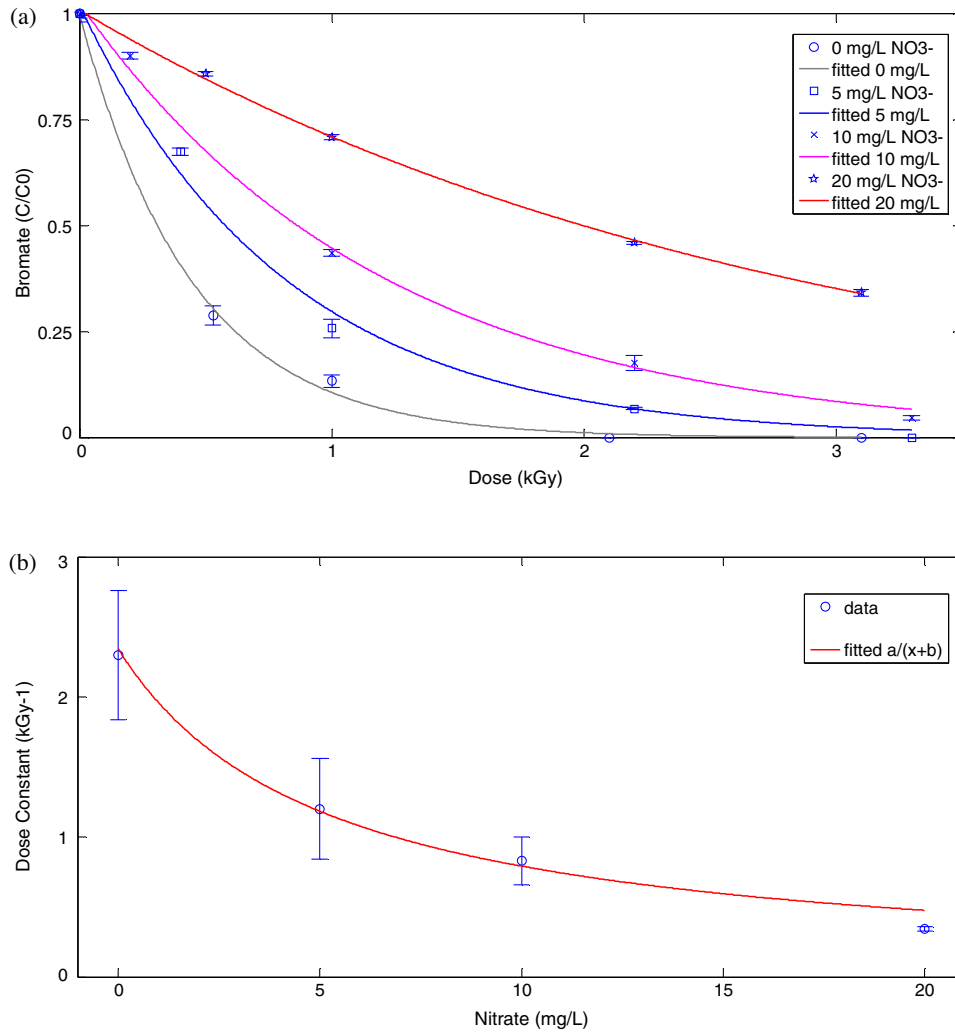


Fig. 1. (a) Effect of eBeam dose on BrO_3^- removal at various NO_3^- concentrations. Error bars indicate the standard deviation of triplicate samples. Initial BrO_3^- concentration: $99.8 \pm 1.0 \mu\text{g/L}$; pH: 7.3; FA: $50 \mu\text{g-C/L}$; Alkalinity: $50 \text{ mg-CaCO}_3/\text{L}$; EBeam power: 10 MeV. (b) Dose constant (kGy^{-1}) as a function of NO_3^- concentration (mg/L). Error bars indicate 95% confidence intervals. Line represents model prediction.

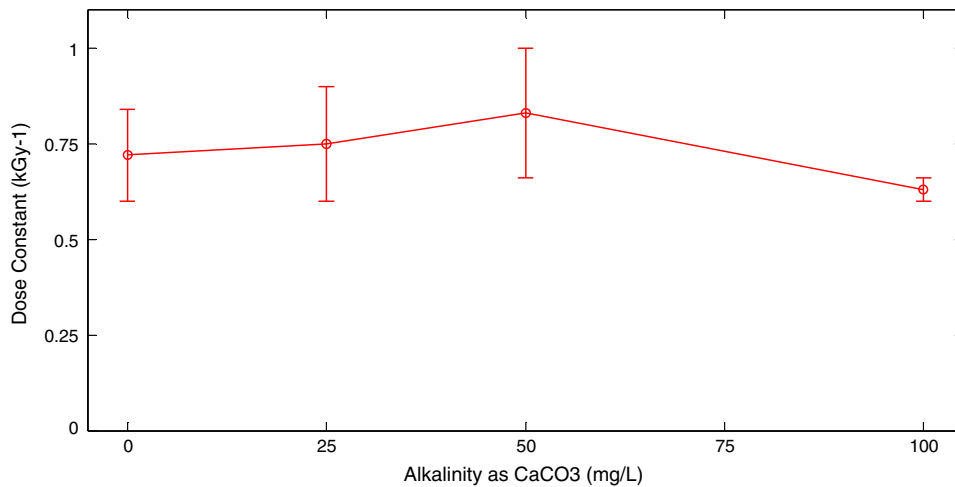


Fig. 2. Dose constant (kGy^{-1}) as a function of alkalinity concentration as CaCO_3 (mg/L). Error bars indicate 95% confidence intervals. Initial BrO_3^- concentration: $101 \pm 1.1 \mu\text{g/L}$; NO_3^- : 10 mg/L ; pH: 7.3; FA: $50 \mu\text{g-C/L}$; EBeam power: 10 MeV.

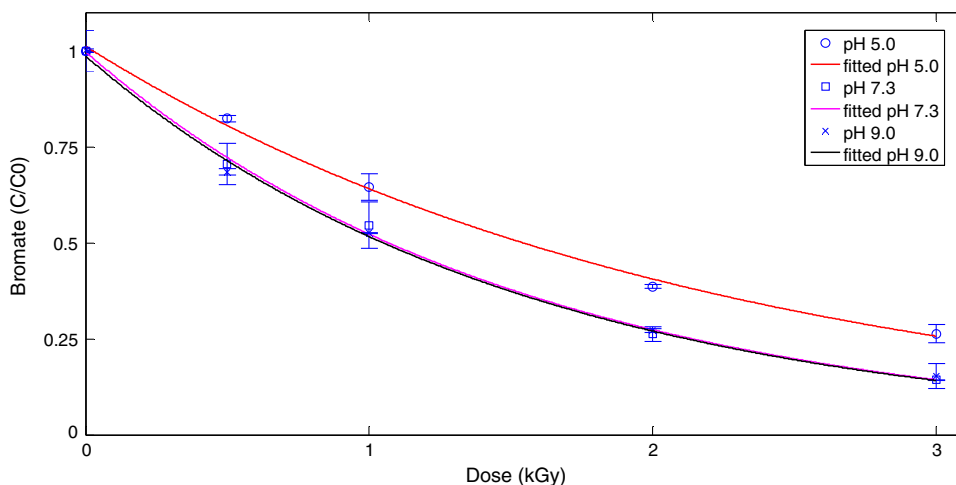


Fig. 3. Effect of eBeam dose on BrO_3^- removal for different pH. Error bars indicate standard deviation. Initial BrO_3^- concentration: $98.5 \pm 4.3 \mu\text{g/L}$; NO_3^- : 10 mg/L; FA: 50 $\mu\text{g-C/L}$; Alkalinity: 50 mg- CaCO_3/L ; EBeam power: 8.5 MeV.

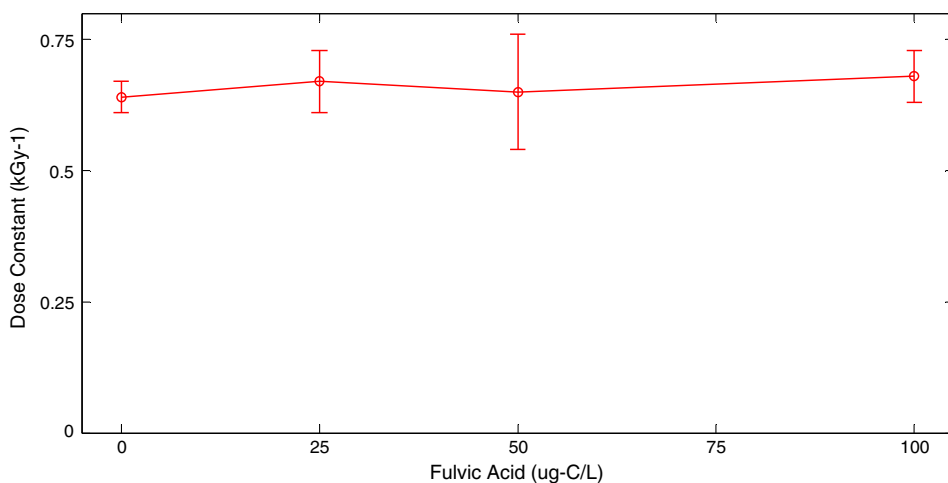


Fig. 4. Dose constant (kGy^{-1}) as a function of FA concentration ($\mu\text{g-C/L}$). Error bars indicate 95% confidence intervals. Initial BrO_3^- concentration: $102 \pm 1.4 \mu\text{g/L}$; NO_3^- : 10 mg/L; pH: 7.3; Alkalinity: 50 mg- CaCO_3/L ; EBeam power: 8.5 MeV.

3.1.5. Effect of fulvic acid on bromate removal

As a ubiquitous constituent in aquatic systems, the influence of NOM on degradation processes has been tested in many studies. However, the effects of fulvic acid on BrO_3^- degradation through radical reactions have not been investigated. The effect of four levels of fulvic acid (0, 25, 50 and 100 $\mu\text{g-C/L}$) on BrO_3^- reduction is shown in Fig 4. As fulvic acid concentration increased from 0 $\mu\text{g/L}$ to 100 $\mu\text{g/L}$, the degradation of BrO_3^- does not appear to be influenced. Fulvic acid is more likely to exist in a reduced form so it is more active in scavenging oxidants such as $\cdot\text{OH}$, than in scavenging reducing radicals such as e_{aq}^- and $\text{H}\cdot$. The lack of effect of fulvic acid on bromate removal is consistent with the hypothesis that the reduction of BrO_3^- is primarily carried out by e_{aq}^- and $\text{H}\cdot$ radicals.

3.2. Defluorination of PFOA in absence of oxygen

3.2.1. Model for defluorination of PFOA

The eBeam irradiation experiments of aqueous PFOA solutions were conducted under different conditions to investigate the effects of water quality parameters such as nitrate, alkalinity and fulvic acid. A model that assumes defluorination of PFOA occurs by production of partially defluorinated intermediates was used to evaluate effects of the experimental variables on defluorination of PFOA. This model substantially simplifies the degradation pathways of PFOA into a two-step mechanism (Fig 5) in which the first step is the degradation of PFOA into two intermediates (I_1 , I_2). A fraction (f) of the PFOA that is degraded forms the intermediate (I_1) that is susceptible to complete defluorination, while the rest of the PFOA degrades to the intermediate (I_2) that cannot be further defluorinated. In the second step, the degradable intermediate (I_1) is completely defluorinated. The rates of each step are assumed to be proportional to the concentration of the reactant (PFOA or I_1) and the dose rate, which is the rate of energy absorption of the eBeam per mass of solution. The dose rate strongly affects the degradation rate because it is proportional to the rate of production of reactive species such as e_{aq}^- . The model also assumes that reactions generating different intermediates in the first step have

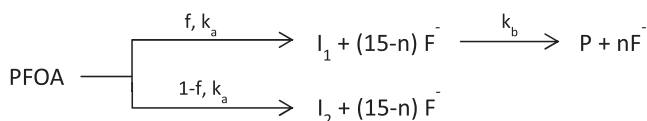


Fig. 5. Scheme of the simplified PFOA degradation pathways.

the same rate constant, and that both intermediates contain the same number of fluoride atoms. The detailed derivation of this model can be found in [Supplementary information](#). When this simple model is applied to a batch reactor, the concentration of fluoride in solution at different times can be described as:

$$F = 15 * [\text{PFOA}]_0 - 15 * [\text{PFOA}]_0 * \exp(-k_a * D) - n * \frac{f * k_a * [\text{PFOA}]_0}{k_b - k_a} * [\exp(-k_a * D) - \exp(-k_b * D)] - n * (1 - f) * [\text{PFOA}]_0 * [1 - \exp(-k_a * D)] \quad (12)$$

where $[\text{PFOA}]_0$ is the initial molar concentration of PFOA, k_a and k_b are the dose constants for the first and second step, respectively; and n is the number of fluorine atoms in the partially defluorinated intermediates. A series of nonlinear regressions was conducted with 'cftool' in Matlab using measured values of fluoride ion concentration and selected integral values of n to determine values of the dose coefficients (k_a , k_b). Each regression was conducted with a different integer values of n and the value of 7 was found to give the lowest sum of squared errors considering all of the regressions. Therefore, that value of n and the values of k_a and k_b obtained from individual regressions were used in the model that evaluate defluorination of PFOA by eBeam irradiation.

3.2.2. Effect of nitrate on PFOA degradation

The effect of nitrate on defluorination efficiency by eBeam irradiation is shown in [Fig 6](#) and the final defluorination efficiency, k_a and k_b are shown in [Table 2](#). As nitrate concentration increases, the maximum defluorination efficiency observed increases rapidly at low nitrate concentration and then more slowly at higher concentrations. At the nitrate level of 20 mg/L, nearly all PFOA was defluorinated. Accordingly, k_a and k_b tend to be larger in the presence of nitrate. Therefore, the addition of nitrate not only speeds up the degradation reaction but increases the production of degradable intermediates. Higher dose constants and higher defluorination efficiencies indicate that the addition of nitrate improves degradation of PFOA and its intermediates.

It is well-known that nitrate scavenges e_{aq}^- and generates the nitrate radical ($\text{NO}_3^{\cdot-}$) (Eq. (5)), which has been found to reduce various organic compounds [54]. Moreover, the nitrate radical could react with water to form the nitrogen dioxide radical (NO_2^{\cdot}) [55], which can also react with organics [56]. These radicals are likely formed during eBeam irradiation and could play a role in defluorinating PFOA, but direct evidence of that mechanism is not available. Detailed investigation on this is needed to elucidate the mechanisms of PFOA degradation in the presence of nitrate.

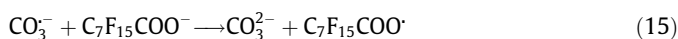
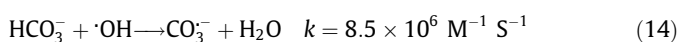
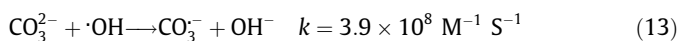
Table 2
Defluorination efficiency and dose constants for PFOA degradation.

Parameters	Final defluorination efficiency (%)	a (kGy ⁻¹)	b (kGy ⁻¹)	f	R^2	
Nitrate (mg/L)	0	34.6	0.20	-0.14	0.18	0.9911
	5	70.1	0.70	1.45	0.38	0.9872
	10	77.0	0.52	2.07	0.50	0.9957
	20	93.3	0.58	0.30	0.95	0.9995
Alkalinity (mg/L as CaCO ₃)	0	53.8	0.37	0.01	0.42	0.9977
	25	72.4	0.58	1.21	0.45	0.9802
	50	77.0	0.52	2.07	0.50	0.9957
Fulvic acid (μg-C/L)	0	100	0.68	1.10	1	0.9801
	25	90.0	0.57	1.53	0.78	0.998
	50	77.0	0.52	2.07	0.50	0.9957
	100	75.4	0.59	2.28	0.45	0.9936

3.2.3. Effect of alkalinity on PFOA degradation

[Fig 7](#) shows the effect of alkalinity on defluorination efficiency of PFOA and [Table 2](#) provides values for final defluorination efficiency and the dose constants. The defluorination efficiencies and both dose constants (k_a and k_b) increase as alkalinity increases. In addition, the degradable fraction rises as well.

The enhancement of defluorination efficiency at higher alkalinity can be attributed to the formation of the carbonate radical ($\text{CO}_3^{\cdot-}$) as shown in Eqs. (13) and (14). The carbonate radical is an oxidant and could react with the PFOA anion ($\text{C}_7\text{H}_{15}\text{COO}^-$) according to the Eq. (15) [32,35]. Although bicarbonate/carbonate can also react with e_{aq}^- (Eqs. (8) and (9)), it does so much more slowly than with $\cdot\text{OH}$.



The anion radical produced by this reaction can undergo further degradation processes [32]. Higher alkalinity would produce more carbonate radicals, which would accelerate these processes and result in a higher defluorination efficiency. Both values for k_a and k_b increased as alkalinity increased, which indicates that the

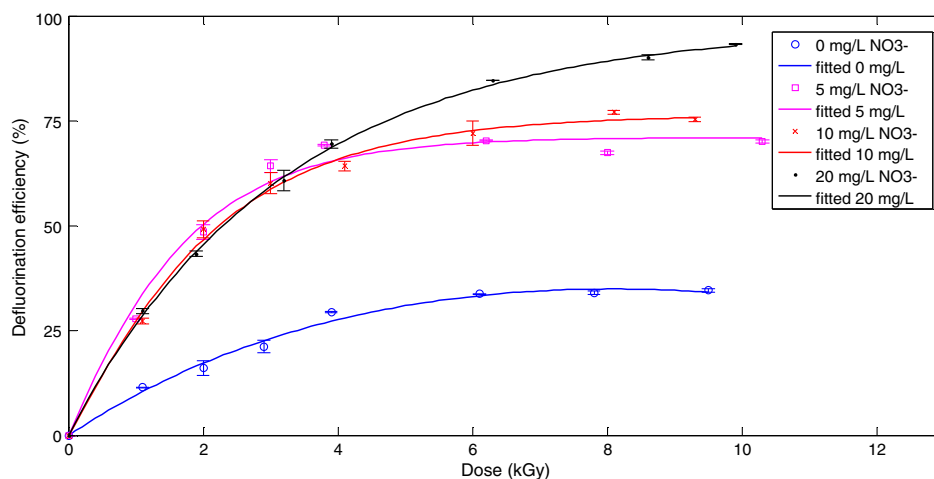


Fig. 6. Defluorination efficiency of PFOA with different nitrate concentrations. Initial PFOA concentration: 500 μg/L. Error bars indicate standard deviation.

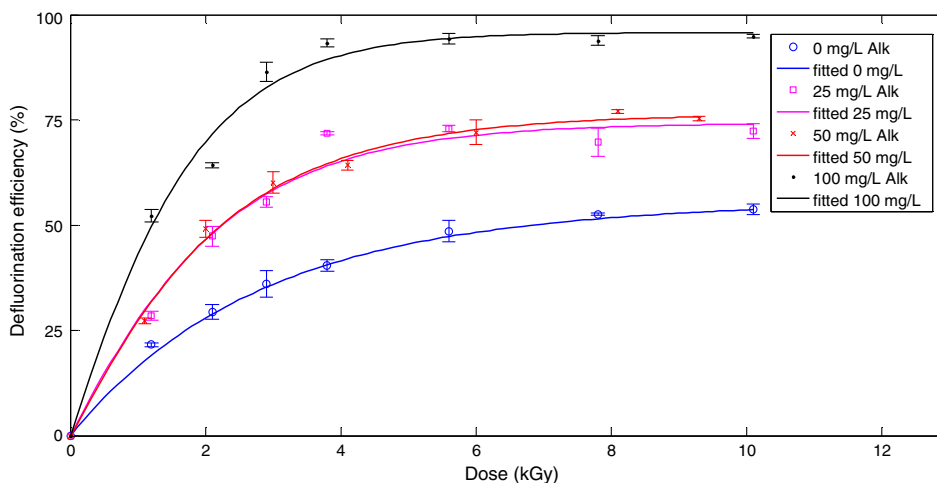


Fig. 7. Defluorination efficiency of PFOA with different alkalinity levels. Initial PFOA concentration: 515 $\mu\text{g/L}$. Error bars indicate standard deviation.

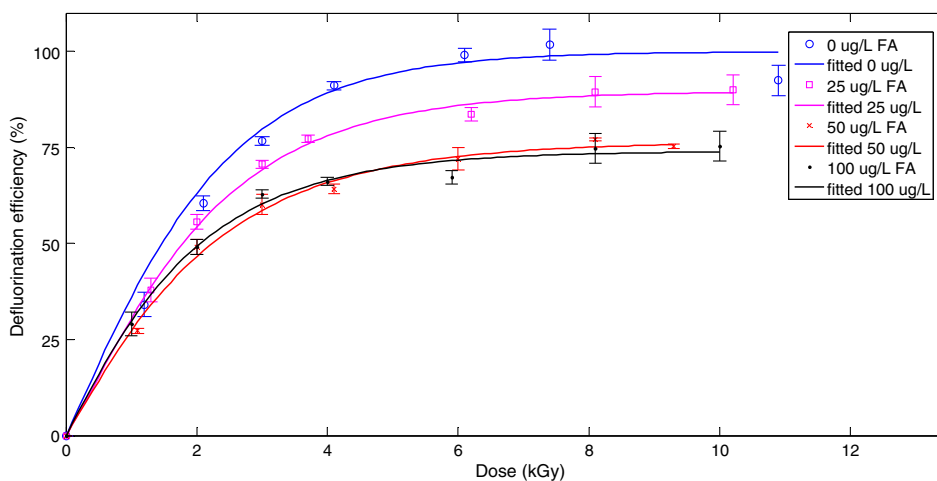


Fig. 8. Defluorination efficiency of PFOA with different fulvic acid concentrations. Initial PFOA concentration: 527 $\mu\text{g/L}$. Error bars indicate standard deviation.

overall processes for PFOA degradation was improved with higher alkalinity. When 100 mg/L alkalinity as CaCO_3 was present, an almost complete mineralization of PFOA was obtained and 94.9% of fluoride was released.

3.2.4. Effect of fulvic acid on PFOA degradation

The effect of fulvic acid on defluorination of PFOA by eBeam irradiation was investigated and the results are shown in Fig. 8 and Table 2. Fig. 8 shows that the final defluorination efficiency diminishes as fulvic acid concentration increases, possibly as the result of the scavenging effect of fulvic acid on $\cdot\text{OH}$. $\cdot\text{OH}$ is critical in defluorination because it can break the C–F bond [37], so the effect of FA in reducing the extent of defluorination may be due to such scavenging. Based on the slight decrease in k_a and the stronger decrease in f with fulvic acid concentration, it can be observed that the rate and extent of producing degradable fluorinated intermediates diminished as fulvic acid level increased. However, k_b tended to increase with fulvic acid concentration, which may imply that fulvic acid accelerates degradation of short-chain fluorinated intermediates.

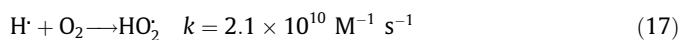
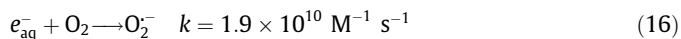
3.3. Removal of bromate in presence of oxygen

The effect of dissolved oxygen (DO) on eBeam irradiation is of interest, because it will often be present in waters being treated.

The effect was evaluated by conducting experiments with water in equilibrium with air, resulting in a DO concentration of 8.4 mg/L.

Fig. 9(a) shows that BrO_3^- was degraded very differently when DO was present. BrO_3^- concentration in the presence of DO decreased with increasing dose at low doses (0–2 kGy), but increased at higher doses (3–4 kGy) and then fell at doses above 6.0 kGy.

The presence of DO would scavenge the reducing radicals (e_{aq}^- and $\text{H}\cdot$) as described by the following reactions [57,58]:



Therefore, the concentrations of e_{aq}^- and $\text{H}\cdot$ available for reaction with bromate and PFOA should be decreased in the presence of oxygen. Scavenging of radical reductants could explain the higher bromate concentrations observed at low doses, but would not explain the subsequent increase. That increase might be due to formation of oxidizing radicals from the superoxide produced by the oxygen scavenging reactions (Eqs. (16) and (17)) that could oxidize intermediate bromate reduction products back into bromate. The subsequent decrease in bromate concentrations shown in

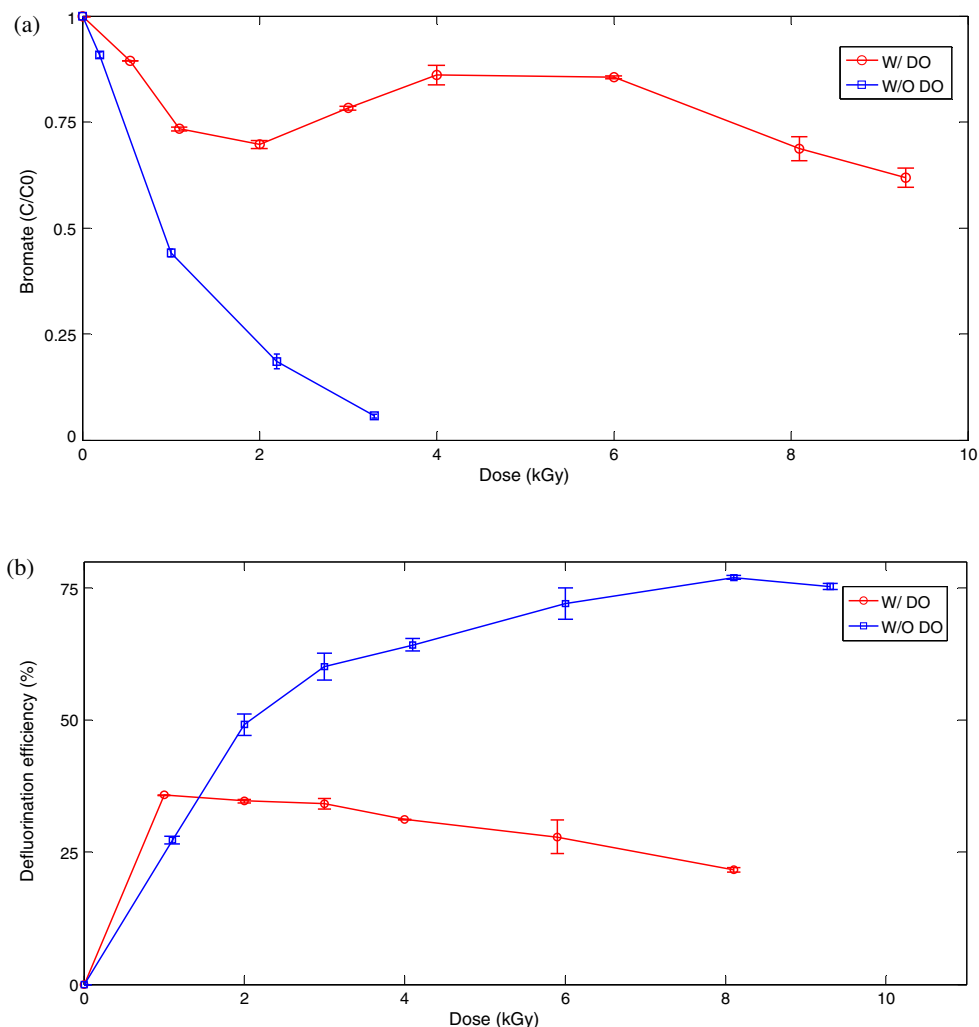


Fig. 9. EBeam treatment in presence of dissolved oxygen: (a) Bromate reduction in presence and absence of dissolved oxygen; (b) defluorination of PFOA in presence of dissolved oxygen.

Fig. 9(a) could be the result of oxygen being depleted, resulting in no further formation of oxidizing radicals. Doses between 0.8 and 3.2 kGy would be able to produce sufficient reducing radicals to react with all oxygen present (8.4 mg/L), assuming that between 1 and 4 mol radicals would be required per mole oxygen. The response of bromate concentration to dose above 6 kGy looks more like the typical relationship, so a dose constant of 0.10 (0.09–0.11) kGy⁻¹ was calculated. This dose constant was used to calculate a dose of 29 kGy being required to achieve 90% bromate removal.

3.4. Defluorination of PFOA in presence of oxygen

The presence of DO also affected defluorination of PFOA as shown in Fig 9(b). The defluorination efficiency reached a maximum of 36% at the lowest measured dose (1 kGy) and decreased at higher doses. The maximum defluorination efficiency was about half of that observed under anaerobic conditions. Much of the reduced defluorination efficiency could be due to the scavenging of e_{aq}^- by oxygen. However, the behavior of bromate is consistent with oxygen being consumed at a dose around 6 kGy and there is no improvement observed in PFOA defluorination about that dose. This could be due to formation of more stable partially defluorinated intermediates [59] or to more complex reactions of superoxide and other radicals formed in the presence of oxygen.

4. Conclusion

The eBeam irradiation was effective in removing BrO_3^- and defluorinating PFOA in the absence of oxygen. Degradation of these oxidized compounds is probably the result of reaction with reducing radicals such as e_{aq}^- and H that are produced by eBeam irradiation. The more complex behavior of PFOA indicates that other radicals such as $\cdot OH$ and $CO_3\cdot^-$ could be important in degrading PFOA. The degradation of BrO_3^- could be described by an exponential function of dose.

The effects of major water quality parameters (i.e. NO_3^- , alkalinity and pH) on BrO_3^- and PFOA degradation were studied in a matrix of synthesized reclaimed wastewater. Dissolved oxygen negatively influenced BrO_3^- and PFOA degradation. Deoxygenation may be recommended prior to application of eBeam irradiation.

In this study, both degradation of BrO_3^- and defluorination of PFOA were only investigated in synthetic treated wastewater. The presence of some wastewater constituents resulted in substantial changes in the patterns of degradation of BrO_3^- and PFOA, so further research regarding this aspect of treatment by radical-based methods should be carried out in future for a wider range of target compounds.

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 that require large amounts of reagents and/or produce undesirable secondary wastes.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.cej.2016.05.034>.

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