



# 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  $0.45 \text{ kGy}^{-1}$  to  $0.69 \text{ kGy}^{-1}$ , 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

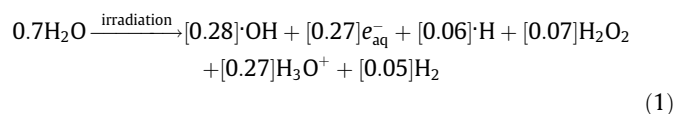
$a$	dose constant for first step of PFOA degradation ( $\text{kGy}^{-1}$ )	$k_1$	second order rate constant between target and aqueous electron ( $\text{mmol}^{-1} \text{L s}^{-1}$ )
$b$	dose constant for second step of PFOA degradation ( $\text{kGy}^{-1}$ )	$k_2$	second order rate constant between scavengers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

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 ( $\text{OBr}^-$ ). 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  $1 \text{kGy}$  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  $92 \text{ ng/L}$ , and  $2.3$  to  $84 \text{ ng/L}$  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  $0.47$ – $60 \text{ ng/L}$  [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  $1.3$ – $135 \text{ ng/L}$  and  $3.8$ – $104 \text{ ng/L}$  in effluents. In recycled water from four California wastewater treatment plants, PFOA was detected to be  $10$ – $190 \text{ ng/L}$  [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 ( $116 \text{ kcal/mol}$ ), 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 ( $\text{CO}_3^{2-}$ ) [32], sulfite ( $\text{SO}_3^{2-}$ ) [33] and iodine ( $\text{I}^-$ ) [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  $\gamma$ -ray with a  $^{60}\text{Co}$  source achieved a complete mineralization of PFOA in a  $\text{N}_2$ -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  $10 \text{ MeV}$ ,  $18 \text{ kW}$  Electron Beam Linear

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