Removal of iopromide and degradation characteristics in electron beam irradiation process

Minhwan Kwon\textsuperscript{a}, Yeojoon Yoon\textsuperscript{a}, Eunha Cho\textsuperscript{a}, Youmi Jung\textsuperscript{a}, Byung-Cheol Lee\textsuperscript{b}, Ki-Jung Paeng\textsuperscript{c}, Joon-Wun Kang\textsuperscript{a,}\textsuperscript{*}

\textsuperscript{a} Department of Environmental Engineering (VIEST), Yonsei University, 234 Maeji, Heungup, Wonju 220–710, Republic of Korea
\textsuperscript{b} Quantum Optics Laboratory, Korea Atomic Energy Research Institute, 1045, Daejeok-dong, Yuseong-gu, Daejeon 305–353, Republic of Korea
\textsuperscript{c} Department of Chemistry, Yonsei University, 234 Maeji, Heungup, Wonju 220–710, Republic of Korea

HIGHLIGHTS

$\blacktriangle$ The second-order kinetic was fitted in overall removal tendency of iopromide.
$\blacktriangle$ In the electron beam/H$_2$O$_2$ process, enhanced removal rate of iopromide was observed.
$\blacktriangle$ The iopromide removal rate increased in the presence of OH$^*$ scavengers.
$\blacktriangle$ The mineralization was mainly performed in the electron beam/H$_2$O$_2$ condition.
$\blacktriangle$ The e$_{aq}^-$ mainly attacks the iodo-group, whereas the OH$^*$ reacts non-selectively.

ARTICLE INFO

Article history:
Received 30 January 2012
Received in revised form 4 May 2012
Accepted 5 May 2012
Available online 14 May 2012

Keywords:
Advanced oxidation process
Electron beam
Hydrogen peroxide
Iodinated contrast media
Iopromide

ABSTRACT

The aim of this study is to evaluate the removal efficiency of iopromide using electron beam (E-beam) irradiation technology, and its degradation characteristics with hydroxyl radical (OH$^*$) and hydrated electron (e$_{aq}^-$). Studies are conducted with different initial concentrations of iopromide in pure water and in the presence of hydrogen peroxide, bicarbonate ion, or sulfite ion. E-beam absorbed dose of 19.6 kGy was required to achieve 90% degradation of 100 μM iopromide and the E-beam/H$_2$O$_2$ system increased the removal efficiency by an amount of OH$^*$ generation. In the presence of OH$^*$ scavengers (10 mM sulfite ion), the required dose for 90% removal of 100 μM iopromide was only 0.9 kGy. This greatly enhanced removal was achieved in the presence of OH$^*$ scavengers, which was rather unexpected and unlike the results obtained from most advanced oxidation process (AOP) experiments. The reasons for this enhancement can be explained by a kinetic study using the bimolecular rate constants of each reaction species. To explore the reaction scheme of iopromide with OH$^*$ or e$_{aq}^-$ and the percent of mineralization for the two reaction paths, the total organic carbon (TOC), released iodide, and intermediates were analyzed.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

A substantial number of emerging contaminants (pharmaceuticals and personal care products (PPCPs), endocrine disrupting chemicals (EDCs), surfactants, and other chemicals) are continuously being released into the environment, and have been detected in various aquatic environments. According to recent research, about 31 species of EDCs and PPCPs were detected in the Han River of Korea [1], iopromide (IPM) was the major species among the identified species. IPM is an iodinated X-ray contrast media compound (ICM) and is one of the widely used pharmaceutical agents in Korean hospitals. It is used for imaging of organs or blood vessels during diagnostic tests, and it is designed to be resistant to human metabolism; therefore, the admitted agent is mostly eliminated via urine or feces without transforming to another metabolite [2,3]. Steger-Hartmann et al. [4] reported that no toxic effects of IPM were observed in both short-term and chronic toxicity tests. However, the environmental safety of IPM cannot be guaranteed [2,5], since the side effects and toxic effects on renal cells by IPM have been consistently reported. Recently, IPM is known to induce the vacuolization and apoptosis of tubular cells, and endothelial dysfunction leading to kidney injury [6]. Since the IPM is resistant in the conventional wastewater treatment processes [7,8], the detected concentration of IPM in wastewater effluent, surface water, and even in treated tap water is relatively high in comparison to other PPCPs and EDCs [9,10]; therefore, more effective processes to remove the IPM in wastewater and drinking water treatment are urgently needed.
Some studies on IPM removal using ozonation, photocatalytic activity of TiO₂, UV/H₂O₂, and other advanced oxidation processes (AOPs) have been reported [11–14]. However, the removal scheme of these processes relies on the oxidizing agents such as OH⁻ and/or O₃, but not on the reducing scheme. It should be noted that the halogenated compounds have high reactivity toward reducing agents such as e⁻. Since the electron beam (E-beam) irradiation process in water can induce not only oxidation but also reduction reaction, this technology can be advantageous if the contaminant can be removed via both an oxidation and reduction scheme. In addition many researchers have proposed some combined systems such as the addition of a catalyst of reactive oxidants before the irradiation of E-beam to improve its removal efficiency [17,18]. The irradiation of E-beam in water results in the production of several radicals, ions, and molecules [19], and can be described as the following Eq. (1):

\[
\text{H}_2\text{O} \rightarrow [2.7]\text{OH}^+ + [2.6]\text{e}_\text{aq} + [0.6]\text{H}^+ + [0.7]\text{H}_2\text{O} + [2.6]\text{H}_3\text{O}^+ \\
+ [0.45]\text{H}_2
\]

(1)

where the numerical values in [ ] are the G values, which refer to the yield of each species per 100 eV of absorbed dose.

Of the three radicals species (hydrated electrons (eₐq), hydroxyl radicals (OH⁺) and hydrogen radicals (H⁺)) produced by E-beam irradiation, the species eₐq and OH⁺, were regarded as important reactive species in degrading IPM. The H⁺ is also known to be a reactive reducing species, but its contribution in IPM degradation was neglected since it has a considerably lower reactivity toward IPM compared to eₐq and a lower G value (=0.6) H⁺ as compared to other species. Table 1 lists the major reactions that might occur in the E-beam irradiation process in pure water and IPM contained aqueous solutions. Jeong et al. investigated the IPM removal with γ-irradiation [20], focusing on the degradation mechanisms in an attempt to elucidate the structures of major by-products. The aim of our study is also to investigate IPM removal by E-beam, but our study focuses on the detailed radical reaction schemes of eₐq and OH⁺ with IPM, the matrix (or scavenger) effect of removal enhancement, and the role of eₐq and OH⁺ in the partial or complete mineralization of IPM. Overall, our utmost aim is to explore a method to enhance IPM removal in the E-beam process.

2. Experimental methods

2.1. Solution preparation

All of the solutions were prepared using 18 MΩ deionized distilled water. A reagent grade (pure material) of IPM (C₁₁₂H₁₄₂I₃N₃O₈; MW 791.11) was purchased from U.S. Pharmacopeia. H₂O₂ solutions were prepared from Sigma–Aldrich® (30 wt%) solution, and were added before E-beam irradiation for the E-beam/H₂O₂ process. Quenching reagents of OH⁺ were prepared with the sodium sulfite (Na₂SO₃, 95.0%, SHINYO Pure Chemicals Co.) and sodium bicarbonate (NaHCO₃, 99.5%, Sigma–Aldrich®).

2.2. Electron-beam irradiation

All E-beam irradiation experiments were performed using an electron accelerator made by EB TECH Co. (ELV-8, 2.5 MeV, 100 kW, Korea). The samples were prepared with 50 mL in a polyethylene-packet and were placed on the moving and irradiated so that the absorbed dose would be from 0.5 to 50 kGy.

2.3. Analysis

The IPM concentration in solution was measured with a high performance liquid chromatography (HPLC) system (Gilson Inc., USA) equipped with a reverse phase column (Waters 5 μm ODS2 4.6×250 mm, C₁₈) and a variable UV–vis wavelength detector (242 nm wavelength). An elution was performed with 10 mM phosphoric acid/acetonitrile (60/20, v/v) at a flow rate of 1 mL/min.

The total organic carbon (TOC) contents of samples were measured to investigate the degree of mineralization using a TQC analyzer–TOC–VCPHOCF (Shimadzu Co., Japan). To measure the released iodide ion, ion chromatography (IC) was employed using an IC (DX-120, Dionex) equipped with a Dionex Ion Pac AS 16 anion column (4 mm×250 mm, Dionex) and a conductivity detector. To investigate some of the fragmented IPM breakdown products and degradation path, the samples were analyzed with a LC/IT-ESI-MS (LCQ Advantage, Thermo Finnigan) by direct injection.

3. Result and discussion

3.1. Degradation of IPM by E-beam irradiation

Fig. 1A shows the degradation profile of IPM as a function of absorbed dose (from 0 to 25 kGy) for varied IPM initial concentrations (10, 50, and 100 μM). In a 10 μM of initial IPM added solution, rapid degradation of IPM was observed by E-beam irradiation. However, the degradation rate was slower with the increase of the initial IPM concentration; therefore, higher doses were required for complete removal of IPM (e.g. 3, 10, and >25 kGy required for 95% removal of 10, 50, and 100 μM of initial IPM, respectively). The first-order kinetic is common for most of the E-beam irradiation for contaminant removal [21,22], in which the half-life of the contaminant should be constant throughout the reaction. In this study, IPM seems to be also removed by first-order kinetic (R² = 0.85), but the second-order kinetic (R² = 0.98) was better fitted in overall removal tendency, which reveals a rapid removal followed by a rather retarded degradation profile. The second-order kinetic equation was represented at Eq. (2).

\[
\frac{1}{C} - \frac{1}{C_0} = kD
\]

(2)

where C is the residual concentration of IPM in μM, C₀ is the initial concentration of IPM in μM, D is the absorbed dose in kGy, and k is the second-order rate constant in μM⁻¹ kGy⁻¹. The inserted
The calculated $D_{0.9}$ for 10, 50, and 100 µM of IPM were 2.3, 6.5, 19.6 kGy, respectively, with the respective $k$ values of 0.3977, 0.0279, and 0.0046 µM$^{-1}$ kGy$^{-1}$.

The observed kinetic characteristics can be explained as follows. (1) The parent compound, IPM, has a high reactivity toward key reactive species, OH$^*$ and $e_{aq}$ generated by the E-beam process (Eqs. (B.1) and (B.2), Table 1). The key reactive species could also be reactive toward intermediate IPM reaction products, degrading them to smaller products and eventually leading to the mineralized end products. Fig. 1B demonstrates the absorption spectra of the treated IPM solution. As the peak of IPM (wavelength at 242 nm) decreases, one of its notable by-product peaks (wavelength at 225 nm) appeared at 1 kGy and increased with the increase of dose to 10 kGy, but the peak almost disappeared with a further increase of radiation dose to 25 kGy. These results imply that the key reactive species react not only with the parent compound, IPM, but also with its reaction intermediates for further breakdown. Actually, under a lower irradiation dose, the IPM rapidly degrades under the intermediate free matrix conditions, but the IPM degradation rate could be lowered as the run proceeds due to the buildup of intermediate products during reaction. The supporting evidence for this interpretation is revealed in Fig. 1C, showing TOC removal (%) versus IPM removal (%). Until 80% of IPM removal, the TOC removal (%) was substantially low and linear with respect to IPM removal (%). However, a significant increase in TOC removal (%) was observed after achieving significant removal of the parent compound, which implies that the key reactants would preferably react with the parent compound, and then the reactants will continuously react with the intermediate products. (2) Another plausible reason for the retarded reaction at higher doses, which is the cause of the second-order degradation kinetics of IPM, is the radical-radical recombination reactions among the primary radicals (e.g. Eq. (A.2)).
and (A.4), etc., some of which could be competitive with the IPM removal reaction. Mak et al. also observed similar phenomena in their work with chlorinated compounds [23,24].

3.2. E-beam/hydrogen peroxide (H₂O₂) process

In AOPs such as the UV/H₂O₂ process and O₃/H₂O₂ process, H₂O₂ is frequently added to generate additional OH* [25]. The E-beam/H₂O₂ process is also known to induce the synergy effect in removing contaminants, generating additional OH* [26].

In order to observe any enhancement of IPM removal in the E-beam/H₂O₂ process, H₂O₂ was initially added from 0 to 8 mM before irradiation. In this set of H₂O₂ added cases, enhanced removal rate of IPM was observed from an increase of 1.70 to 3.47 times with reference to the E-beam alone process (Fig. 2 and Table 2). The reason for this enhancement can be attributed to the additional OH* production due to the reaction of H₂O₂ and e⁻[aq] (Eq. (A.1), Table 1) or H⁺ (Eq. (A.15), Table 1) in the E-beam/H₂O₂ process.

Maximum enhancement was observed at [H₂O₂] = 2 mM, but the rate of enhancement decreased with the increase of H₂O₂. This is because the excess amount of H₂O₂ could scavenge OH* as given by the reaction (Eq. (A.8), Table 1), which will lower the net OH* concentration [27]. Similar results of negative effects on substrate removal by excessive H₂O₂ addition were reported in other H₂O₂ involved AOPs [28,29]. In fact, an optimum level of H₂O₂ addition is also required in the E-beam/H₂O₂ process, and a 2 mM of H₂O₂ dose is suggested in removing IPM ([IPM]₀ = 100 μM).

3.3. Effect of OH* scavenger on IPM removal

In the E-beam process, both OH* and e⁻[aq] are important reactive species for IPM removal. To investigate the relative contribution of each in IPM removal, an OH* quenching study was performed using SO₃²⁻ (sulfite). Since the sulfite slowly reacts with e⁻[aq] \( (k_\text{sulfite/e}^{-}[aq] = < 1.5 \times 10^6 \text{ M}^{-1} \text{s}^{-1} \) [19]), whereas it quickly reacts with OH* (\( k_\text{sulfite/OH}^* = 5.5 \times 10^9 \text{ M}^{-1} \text{s}^{-1} \)) [19], the sulfite was recommended as a suitable OH* scavenger in the E-beam process [30]. Recently, sulfate radical (SO₄^•−) was received attention because of its high reactivity of organic pollutants including pharmaceuticals [31–33], but the possibility of generating the sulfate radical is remote in E-beam/sulfite condition. Fig. 3 shows the change of IPM removal rates by E-beam irradiation in varied sulfite concentrations ([sulfite]₀ = 2, 10, and 20 mM). The IPM removal rate increased in the sulfite added condition. IPM removal was only 43% without sulfite addition, whereas, a considerably increased IPM removal was observed with increasing sulfite (82%, 93%, and 96% of IPM removal in 2, 10, and 20 mM sulfite concentration, respectively) under the same irradiation dose of 1 kGy.

A possible interpretation could be that even though both OH* and e⁻[aq] are reactive species degrading IPM, the bimolecular reaction rate constant of IPM with e⁻[aq] \( (k_{IPM/e}^{-}[aq] = 3.25 \times 10^{10} \text{ M}^{-1} \text{s}^{-1} \) Table 1) is one order greater than the IPM with OH* \( (k_{IPM/OH}^* = 3.3 \times 10^9 \text{ M}^{-1} \text{s}^{-1} \) Table 1). According to a recently research by Jeong et al. [20], the IPM degradation efficiency with e⁻[aq] is greater than with OH*. It should also be noted that the two reactive species, OH* and e⁻[aq], could rapidly react with each other by radical-radical recombination reaction \( (k_{OH^*/e}^{-}[aq] = 3.0 \times 10^{10} \text{ M}^{-1} \text{s}^{-1} \) Table 1) in the absence of each background scavenger. In this sulfite added experimental condition, a greater concentration of e⁻[aq] could be maintained, suppressing the radical-radical recombination reaction by scavenging OH*; therefore, the reaction opportunity of more reactive species, e⁻[aq], with IPM could be increased. Similar results were reported by Cooper et al. in removing chloroform, which is also more reactive toward e⁻[aq] than OH* \( (k_{chloroform/e}^{-}[aq] = 1.1 \times 10^{10} \text{ M}^{-1} \text{s}^{-1} , k_{chloroform/OH}^* = 5.4 \times 10^7 \text{ M}^{-1} \text{s}^{-1} ) \) [23,34,35].

To confirm the enhanced IPM removal in the presence of the OH* scavenger, other scavenging experiment was performed using bicarbonate. In a natural aquatic system, bicarbonate ion is always present and is known to trap OH* \( (k_{bicarbonate/OH}^* = 1.0 \times 10^7 \text{ M}^{-1} \text{s}^{-1} \) [19]). As shown in Fig. 4, an enhanced removal of IPM was also observed as the bicarbonate concentration increases from 2 to 16 mM; even the smaller enhancement was observed compared with experiments observed in the sulfite added case. This is because the second-order rate constant value of OH* with sulfite is
significantly greater than the value of OH• with bicarbonate ($k_{\text{H}_2\text{O}_2/\text{OH}•} = 5.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1} > k_{\text{bicarbonate/OH}•} = 1.0 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$) [19]. Table 2 lists the second-order rate constant values, rate of enhancement, and corresponding $D_{0.9}$ values determined in all different matrix conditions. Under the E-beam/sulfite condition, the $e_{aq}$, which is the single dominant major reacting species, only contributes to the dehalogenation of IPM not forming any various intermediates; therefore, the removal tendency is suitable for the first-order kinetic equation. In Table 2, we cannot compare the rate constants between second-order and first-order rate constants, but the $D_{0.9}$ value (calculated by each rate constant) could be substituted to compare the removal efficiency of each condition. In all matrix conditions, the enhanced removals of IPM were observed. However, it should be noted that the enhancement mechanism of the E-beam/H$_2$O$_2$ process must differ from the cases of E-beam/sulfite and E-beam/bicarbonate. Compared to E-beam/sulfite and E-beam/bicarbonate, the E-beam/H$_2$O$_2$ process maintains a lower concentration of $e_{aq}$ but a higher concentration of OH•. This is undesirable in increasing IPM removal since $e_{aq}$ is more reactive toward IPM than OH•. However, some enhancements were observed in reality. Plausible interpretations even with the unfavorable distribution of the reactive species between OH• and $e_{aq}$ are: (1) the E-beam/H$_2$O$_2$ process can generate a greater amount of OH• than the E-beam alone, because the reaction between the H$_2$O$_2$ and $e_{aq}$ or H• produces additional OH•, and (2) the H$_2$O$_2$ addition can suppress the radical-radical recombination between $e_{aq}$ and OH•, leading to the significantly greater concentration of OH•, which contributed to the overall net reaction increase.

To confirm the previously discussed IPM removal mechanism and the IPM removal enhancement for the E-beam/sulfite condition with respect to the E-beam alone, a simple calculation approach was conducted using an equation proposed as given by Eq. (4):

$$\text{Enhanced removal} = \frac{(\Delta [\text{IPM}] / \Delta k_{\text{Gy}})_{\text{sulfite}}}{(\Delta [\text{IPM}] / \Delta k_{\text{Gy}})_{\text{alone}}} = \frac{(k_{\text{IPM/\text{OH}•}}[\text{IPM}] + k_{\text{IPM/\text{e}_{aq}}} [\text{IPM}])_{\text{sulfite}}}{(k_{\text{IPM/\text{OH}•}}[\text{IPM}] + k_{\text{IPM/\text{e}_{aq}}} [\text{IPM}])_{\text{alone}}}$$

(4)

where $\Delta [\text{IPM}] / \Delta k_{\text{Gy}}$ is the removed IPM per given absorbed dose. $k$ is the second-order rate constant value of IPM with OH• or $e_{aq}$, $[\text{OH}•]_{\text{IPM}}, [\text{OH}•]_{\text{IPM}}, [\text{e}_{aq}]_{\text{IPM}}$, and $[\text{e}_{aq}]_{\text{IPM}}$ are the concentration of each reacted species used for IPM removal in the E-beam alone and E-beam/sulfite condition. As previously described, the mole concentration of the key reacting species, OH• and $e_{aq}$, would be changed upon the addition of OH• scavengers.

In the E-beam alone process, the concentration of each reacting species used for IPM removal, $[\text{OH}•]_{\text{IPM}}$ and $[\text{e}_{aq}]_{\text{IPM}}$ can be calculated as the equation given by Eqs. (5) and (6):

$$[\text{OH}•]_{\text{IPM/alone}} = G([\text{OH}•]) \times \frac{k_{\text{IPM/\text{OH}•}} [\text{IPM}]}{k_{\text{IPM/\text{OH}•}} [\text{IPM}] + k_{\text{e}_{aq}/\text{OH}•} G([\text{e}_{aq}])}$$

(5)

$$[\text{e}_{aq}]_{\text{IPM/alone}} = G([\text{e}_{aq}]) \times \frac{k_{\text{IPM/\text{e}_{aq}}} [\text{IPM}]}{k_{\text{IPM/\text{e}_{aq}}} [\text{IPM}] + k_{\text{OH}•/\text{e}_{aq}} G([\text{OH}•])}$$

(6)

which is the fractional distribution of each species reacted with IPM considering reactions (A.2), (B.1) and (B.2) as the key reactions of the all reactions in Table 1. The G value of each species ($G([\text{OH}•])$ and $G([\text{e}_{aq}])$) is the mole concentration of the reacting species initially generated upon E-beam irradiation, which can be calculated from G values given in Eq. (1). Under the E-beam sulfite condition (Fig. 3), the initial slope (below 1 kGy) was calculated to know the removal tendency of IPM; therefore, the initial concentrations of OH• and $e_{aq}$ calculated by the G value at 0.5 kGy were $G([\text{OH}•]) = 0.141$ mM and $G([\text{e}_{aq}]) = 0.136$ mM, respectively.

For the case of E-beam/sulfite radiation, the added sulfite will preferentially react with OH• owing to the high
reactivity ($k_{SO_3^{2-}/OH^*} = 5.5 \times 10^9 \text{ M}^{-1} \text{s}^{-1}$ [19]), and the radical-radical recombination reaction ($k_{OH^*/e_{aq}^-}$) would be decreased. In fact, $e_{aq}^-$ will be the major reacting species used for IPM removal. In the sulfite added case of E-beam irradiation, the reacted species with IPM, $[OH^*]_{IPM,sulfite}$ and $[e_{aq}^-]_{IPM,sulfite}$, can be expressed by Eqs. (7) and (8):

$$[OH^*]_{IPM,sulfite} = G([OH^*]) \times \frac{k_{IPM,OH^*}[IPM]}{k_{IPM,OH^*}[IPM] + k_{e_{aq}^-/OH^*}G([e_{aq}^-]) + k_{SO_3^{2-}/OH^*}[SO_3^{2-}]}$$

(7)

$$[e_{aq}^-]_{IPM,sulfite} = G([e_{aq}^-]) \times \frac{k_{IPM,e_{aq}^-}[IPM]}{k_{IPM,e_{aq}^-}[IPM] + k_{OH^*/e_{aq}^-} + [OH^*]_{IPM}}$$

(8)

where $[OH^*]_{e_{aq}^-}$ is given by Eq. (9):

$$[OH^*]_{e_{aq}^-} = G([OH^*]) \times \frac{k_{e_{aq}^-/OH^*}G([e_{aq}^-])}{k_{IPM,OH^*}[IPM] + k_{e_{aq}^-/OH^*}G([e_{aq}^-]) + k_{SO_3^{2-}/OH^*}[SO_3^{2-}]}$$

(9)

Comparing the concentrations of the reacted species with IPM in E-beam alone and in E-beam/sulfite, the OH* concentration in E-beam/sulfite is smaller than that in E-beam alone ($[OH^*]_{IPM,alone} > [OH^*]_{IPM,sulfite}$) but the $e_{aq}^-$ concentration in E-beam/sulfite will be considerably greater than that in E-beam alone ($[e_{aq}^-]_{IPM,sulfite} > [e_{aq}^-]_{IPM,alone}$). Since IPM is more reactive with $e_{aq}^-$, the IPM removal enhancement can be observed in the sulfite added solution. Plugging Eqs. (5)–(8) with known second-order rate constant values of IPM with reacting species into Eq. (4), the enhancement removal (%) can be calculated. In Table 3, the calculated values were compared with the experimental results determined with the initial data points observed under 1 kGy of irradiation dose (Fig. 3), which shows a good agreement between the two.

Even though the above modeling approach is useful in explaining the enhanced removal of a compound such as IPM, it should be noted that this approach is limited to a simple matrix and early reaction phase. For the case of E-beam/H$_2$O$_2$ process, radical reactions associated with the key reacting species, OH* and $e_{aq}^-$, are significantly complicated and interconnected to each other with chain reactions. In fact, the above approach is inapplicable to the E-beam/H$_2$O$_2$ process due to the difficulty of prediction of the key reacting species in the H$_2$O$_2$ spiked water matrix condition. Even though the lack of precise model equation for every water matrix conditions, the reaction schemes of IPM with the key reacting species in the three different conditions (E-beam alone, E-beam/sulfite, E-beam/H$_2$O$_2$) can be (Fig. 5). The solid lines represent the major or increased reactions occurring in a reference (Fig. 5A) or a changing matrix condition, and the dotted lines are the decreased reaction opportunities in the presence of the OH* scavenger (Fig. 5B) and H$_2$O$_2$ (Fig. 5C). In Fig. 5B, compared to the reactions in Fig. 5A, the reaction opportunities of IPM with $e_{aq}^-$ will be increased, whereas the reactions of IPM with OH* and $e_{aq}^-$ with OH* decrease in the presence of sulfite of bicarbonate. Fig. 5C

![Fig. 5. Reaction scheme of iopromide with key reacting species (A), and change of major reaction path in addition of sulfite (B) and H$_2$O$_2$ (C) (solid line represents key or increased reaction opportunities; dotted line represent decreased reactions in a changing water matrix conditions).](image-url)
suggestions why the enhanced IPM removal could be observed in the H$_2$O$_2$ added condition, even though the reaction opportunity of IPM with $e_{aq}$ was decreased. This is because the reaction opportunities between IPM and OH$^*$ could be greatly increased as shown in path (1) and (2) by adding H$_2$O$_2$. Considering that the reaction path (1) (reaction between IPM and OH$^*$) is dominant in E-beam/H$_2$O$_2$, the initially added H$_2$O$_2$ will scavenge $e_{aq}$ with a rapid reaction rate (path (3)), producing additional OH$^*$. The reaction path (2) represents the reaction between IPM with the secondarily formed OH$^*$. It should be noted that H$_2$O$_2$ itself can act as an OH$^*$ scavenger (path (4)), but it will eventually transform back to OH$^*$ by the reaction of $e_{aq}$ and H$_2$O$_2$. The excess amount of H$_2$O$_2$, which could scavenge the OH$^*$, is greater for the lower dose; therefore, the initial slope could not reflect the overall removal rate and the model is inapplicable to the E-beam/H$_2$O$_2$ condition.

3.4. Mineralization

The mineralization extent was investigated for each different test condition (E-beam alone, E-beam/H$_2$O$_2$, E-beam/sulfite) to explore the major reacting species involved in IPM mineralization. As discussed previously in Section 3.1 with Fig. 1C, low TOC removal was observed even with the high E-beam irradiation dose. Fig. 6 compares the %TOC removal of IPM as function of the absorbed dose for the tested conditions.

Several interesting features can be observed in this set of experiments: (1) In E-beam alone without any scavenger addition ([IPM]$_0$ = 100 $\mu$M), the %TOC removal was approximately 40% at a 50 kGy absorbed dose. For the case of E-beam/H$_2$O$_2$, a rather enhanced TOC removal was observed. The %TOC removal increased from 40% in the blank solution to 50 and 60% in the 0.05 and 1.47 mM H$_2$O$_2$ added solution at a 50 kGy absorbed dose, respectively. In this case of the H$_2$O$_2$ added condition, it should be remembered that the increased IPM removal observed and the degree of mineralization also increased along with the enhanced IPM removal in the E-beam/H$_2$O$_2$ process. (2) For the case in E-beam/sulfite, it is interesting to observe that the %TOC removal decreased compared to the E-beam alone, even though we observed a significantly enhanced IPM removal with the increase of sulfite addition (Fig. 3). The %TOC removal was only 3% or less even for the complete removal of IPM with E-beam/sulfite at a low irradiation dose (5 kGy). (3) The above mineralization data could support our previous interpretation on the major reacting species between $e_{aq}$ and OH$^*$ for both of the runs, E-beam/sulfite and E-beam/H$_2$O$_2$, in which total enhanced IPM degradation was observed. The E-beam/sulfite condition is efficient in the removal of IPM since a greater amount of $e_{aq}$, which is considerably more reactive toward IPM, could be maintained in this sulfite added matrix condition. However, the lower mineralized results in this process are due to the key reacting species, $e_{aq}$, which is limited only to attack the iodo-group of IPM and its intermediates, but not to the carbon containing intermediates. OH$^*$ is known to be non-selective when reacting with various compounds having diverse functional groups, and in fact, the further reaction of OH$^*$ with IPM intermediates will eventually lead to the complete mineralization. The enhanced TOC removal in this E-beam/H$_2$O$_2$ process indirectly supports the previous mechanistic interpretation of the IPM removal enhancement due to the additional OH$^*$ production in the E-beam/H$_2$O$_2$ process.

3.5. Deiodination of IPM

To confirm the reaction schemes of the reacting species (OH$^*$ and $e_{aq}$) with IPM in detail, the samples were analyzed by IC for the released iodide (I$^-$) and MS for the key intermediates. In general, the halogen substituents have an electron-attracting characteristic; therefore, the IPM carrying iodides could be resistant to an oxidation process [36], and the role of OH$^*$ would be minimal, whereas, since an electron affinity to halogen atoms is high [37], the IPM will favorably react with $e_{aq}$.

Fig. 7A shows the %iodide release from degraded IPM for the three tested processes, E-beam alone, E-beam/H$_2$O$_2$, and
E-beam/sulfite. For three case conditions, the released iodide concentration rapidly reaches maximum level at around 5 kGy of radiation dose, and stays almost constant, followed by a slight decrease, with an increase of the radiation dose. One possible explanation for the decrease of iodide after reaching the maximum is the reaction between OH$^+$ and I$^-$ (OH$^+$ + I$^-$ → HOI$^-$, $k = 1.1 \times 10^{10} M^{-1} s^{-1}$ [19]). The maximum %yield of iodide release was highest (93%) in E-beam/sulfite and lowest (30%) in the E-beam/H$_2$O$_2$. The lowest iodide release in the E-beam/H$_2$O$_2$ process is understandable since the deiodination reaction by e$_{aq}^-$ could be reduced because H$_2$O$_2$ scavenges e$_{aq}^-$. In the E-beam/sulfite process, the released iodide reached almost close to the level of complete deiodination, in which a sufficient concentration of e$_{aq}^-$ must have been maintained. This result also supports the previously described reaction scheme of IPM by OH$^+$ and e$_{aq}^-$ for the tested processes. To investigate the portion of deiodination reaction of the total IPM removal, the released % iodide from the removed IPM was replotted with respect to % IPM removal (Fig. 7B). In the E-beam/sulfite (≈2 mM) process, the IPM removal (%) was almost equivalent to the released iodide (%), which implies that IPM removal is mainly governed by the deiodination reaction path by e$_{aq}^-$. These results also concurred with the lower mineralization rate (<3% TOC removal) observed in this condition (Fig. 6). In the E-beam/H$_2$O$_2$ process, the slope of IPM removal (%) versus released iodide (%) is about three, implying that the deiodination reaction path by e$_{aq}^-$ contributes about 1/3 of the total IPM removal. Unlike the previous two processes, in the case of E-beam alone, the portion of deiodination reaction changes as the reaction proceeds. The slope between IPM removal (%) and released iodide (%) was about two until 40% of IPM removal, but then approached one. This slope change implies that at the initial reaction period, both e$_{aq}^-$ (by deiodination path) and OH$^+$ (by oxidation reaction path) equally contribute to the IPM removal. However, as the reaction proceeds further, the role of e$_{aq}^-$ becomes dominant over OH$^+$ because the attack of e$_{aq}^-$ to the iodogroup of fragmented intermediates could become easier after the breakdown of the parent IPM into smaller fragments by OH$^+$. To confirm the deiodination reaction scheme of IPM, irradiated samples taken from the E-beam alone and the E-beam/sulfite (2 mM) process were analyzed by a mass spectrometer (MS). To capture the initial deiodination reaction path with the MS, the IPM contained solutions were irradiated at relatively lower doses of 1 and 3 kGy. Fig. 8 shows and compares the MS spectrum of two different samples, one without sulfite (Fig. 8A) and the other with sulfite (Fig. 8B). It should be noted that the mass to charge ratio (m/z) values of the same species are greater in Fig. 8B than the value showed in Fig. 8A due to the contribution of the m/z value of Na (m/z = 23) to the fragment under the MS analysis of the sample containing Na$_2$SO$_3$ (≈2 mM). In both runs, the MS spectrums of the deiodinated compounds corresponding to one to three iodide released fragments of IPM were all observed. However, comparing the two spectrums of the samples irradiated at the lowest dose, 1 kGy, the completely deiodinated peaks (m/z = 552 and 449) were detected in the E-beam/sulfite condition rather than in E-beam alone, although iodide contained fragments still appear in the E-beam alone process. Table 4 lists the m/z values of the deiodination reaction products, and also compares the peaks detected in the result of the deiodination favorable reaction for the two test conditions. The sulfite added condition is significantly favorable to the deiodination reaction since the number of peaks corresponding to the three iodide released fragments is more dominant.

| Adsorbed dose | E-beam alone | E-beam/sulfite (≈2 mM Na$_2$SO$_3$)
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>0 kGy</td>
<td>791</td>
<td>791</td>
</tr>
<tr>
<td>1 kGy</td>
<td>791</td>
<td>591*</td>
</tr>
<tr>
<td></td>
<td>682***</td>
<td>554***</td>
</tr>
<tr>
<td></td>
<td>664*</td>
<td>427***</td>
</tr>
<tr>
<td>3 kGy</td>
<td>554**</td>
<td>427***</td>
</tr>
<tr>
<td></td>
<td>444***</td>
<td>553***</td>
</tr>
<tr>
<td></td>
<td>664*</td>
<td>591*</td>
</tr>
</tbody>
</table>

*a m/z number in E-beam/sulfite was adjusted excluding m/z value of Na (≈23).

The number of released iodide.

Fig. 8. MS spectrum of IPM reaction products. (A) E-beam alone (No scavenger); (B) E-beam/sulfite (≈2 mM Na$_2$SO$_3$).
than the peaks observed in the sulfite absence case. This result again suggests that the $e_{aq}$ involved deiodination reaction is significantly favored in the E-beam/sulfite process compared with E-beam alone. This MS analysis was limited to the qualitative analysis only observing deiodination scheme; therefore, more detailed analysis employing quantitative analysis needs to follow.

4. Conclusion

From this study, it appears that the E-beam process can effectively remove IPM. The E-beam absorbed dose of 20 kGy was required to achieve the 90% removal of 100 μM IPM, and the E-beam/H$_2$O$_2$ system increased the removal efficiency by an amount of OH$^-$ generation. On the contrary, the OH$^-$ quenching test also increased the removal efficiency by the induction of many more $e_{aq}$ reactions, which was unexpected for most advanced oxidation processes (AOPs). In this regard, the E-beam process may be proposed as a strong candidate among AOPs for removing the reactive pharmaceuticals simultaneously present with a high level OH$^-$ scavenger such as alkalinity, which is the case for the municipal wastewater and livestock wastewater. Furthermore, the E-beam/H$_2$O$_2$ process could be designed according to the water condition. The mineralization was improved when the OH$^-$ was a major reactant, but it was decreased when $e_{aq}$ was a major reactant. This is the reason why each reactant has a different reaction preference. The $e_{aq}$ mainly attacks the iodo-group, whereas the OH$^-$ non-selectively reacts with the side chains of the benzene ring rather than the iodo-group. These results will provide better estimates of the removal efficiencies according to the target compound.

Acknowledgments

This work was supported by BK21 Program and Nuclear Research & Development Program of the Korea Science and Engineering Foundation (KOSEF) grant funded by the Korean government (MEST).

References