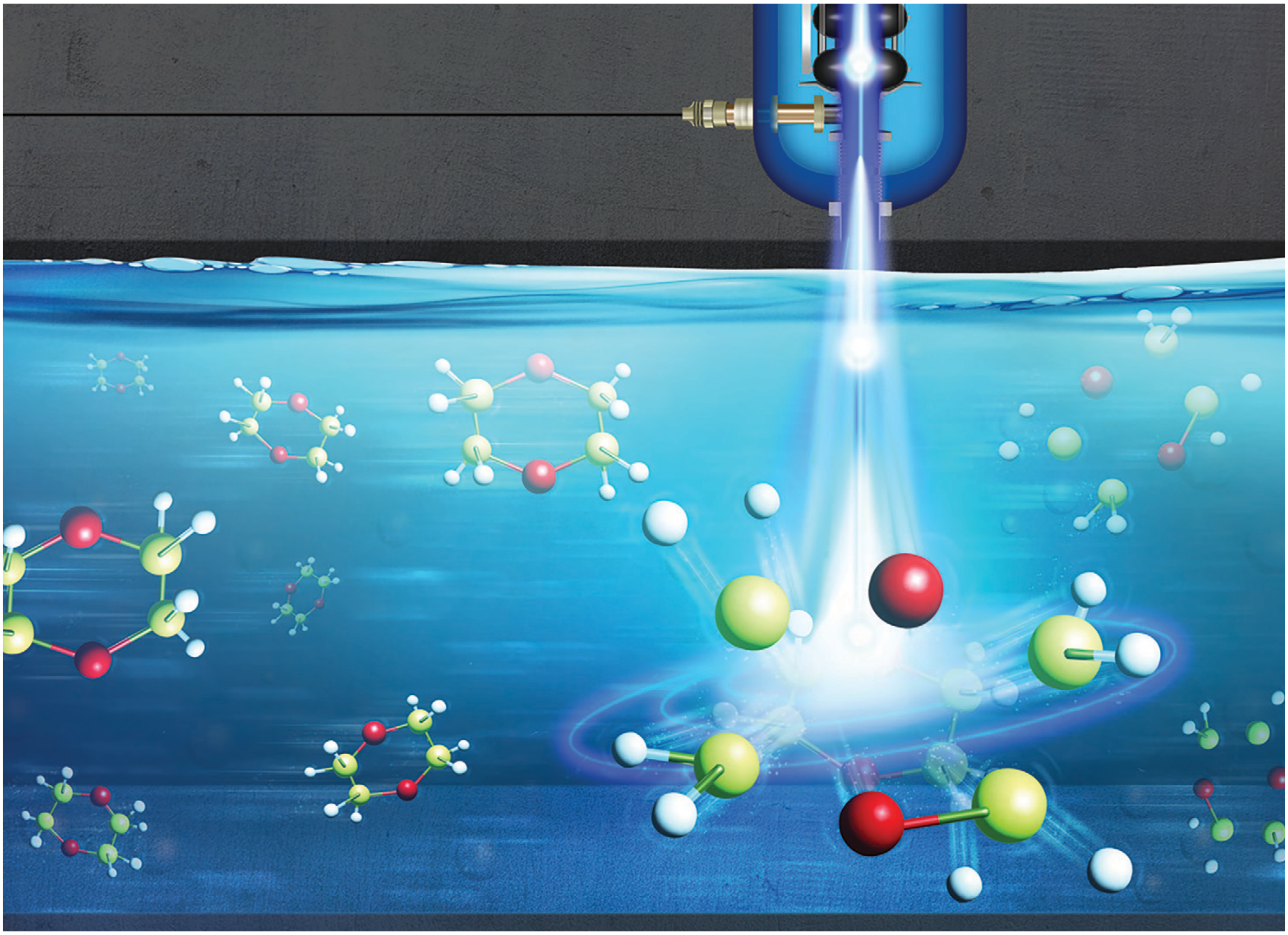

Featuring work from Arjun Research Lab, which focuses on the occurrence, fate and treatment of emerging contaminants. Dr. Venkatesan is currently an Associate Professor of Civil & Environmental Engineering at New Jersey Institute of Technology.

Emerging investigator series: low doses of electron beam irradiation effectively degrade 1,4-dioxane in water within a few seconds

Electron beam water radiolysis is highly effective in the treatment of 1,4-dioxane. Complete destruction is achieved within a few seconds without the addition of chemicals, making it a promising alternative to conventional processes for the treatment of 1,4-dioxane-containing wastes.

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Emerging investigator series: low doses of electron beam irradiation effectively degrade 1,4-dioxane in water within a few seconds†

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The application of electron beam (e-beam) technology for water treatment has been proposed to be a faster and safer approach to decomposing persistent contaminants in water, because of its ability to rapidly generate high amounts of both oxidizing and reducing reactive species without the addition of chemicals. In this study, we utilized a lab-scale 9 MeV e-beam accelerator to investigate the feasibility of treating 1,4-dioxane in various water matrices in batches with low sample volumes (<90 mL). Very low doses (<5 kGy) and treatment times (<5 s) were sufficient to degrade >98% of 1,4-dioxane within the range of environmentally relevant concentrations (0.1–10 mg L^{-1}), without the need for any sample modification or pH adjustment. Low dissolved oxygen in the solution enhanced the degradation efficiency by 21–23% when treating 1000 mg L^{-1} of 1,4-dioxane, presumably because of the increased $H^{\bullet}$ and $O^{\bullet-}$ that can react with 1,4-dioxane. Although the degrading intermediates were not fully mineralized to carbon dioxide at the tested doses, the detected intermediates, such as aldehydes and organic acids, were not as persistent as 1,4-dioxane and were more vulnerable to conventional treatment methods and natural attenuation. The slowest reaction rate constant was observed when treating wastewater samples (k = 0.13–0.62 kGy^{-1}), followed by contaminated groundwater (k = 0.16–1.4 kGy^{-1}), suggesting other organics and ions could scavenge the generated reactive species. The electrical energy per order (EE/O) ranged from 0.39 (DI water) to 6.3 (wastewater) kWh m^{-3} per order, depending on the initial concentration of 1,4-dioxane and water matrix. The EE/O values were comparable to other traditional advanced oxidation processes (AOPs) to treat 1,4-dioxane, suggesting the feasibility of utilizing e-beam to treat contaminated waters. The organic carbon content of the sample positively correlated (R^2 >0.9) with the EE/O values and thus can be utilized to predict e-beam treatment performance. Our results show that e-beam radiolysis is a promising technology to treat 1,4-dioxane and could potentially outperform other AOPs and 1,4-dioxane disposal methods (*e.g.*, incineration) in terms of energy consumption and treatment time, leaving no trace of oxidants.

Water impact

1,4-Dioxane is a likely human carcinogen and a widespread water contaminant across the U.S. Electron beam irradiation can rapidly and efficiently degrade 1,4-dioxane in water within seconds, without the need for sample modification and chemical addition (oxidants), making it a promising alternative to current treatment and disposal methods for 1,4-dioxane.

1. Introduction

1,4-Dioxane is a widespread contaminant of emerging concern, a likely human carcinogen, and the main route of exposure to humans is *via* contaminated drinking water. It occurs in industrial wastewater because it is a commonly used solvent stabilizer in the chlorinated solvent industry and a byproduct of plastic (polyethylene terephthalate, PET) manufacturing.[1–3] It can also be present as an impurity in many household products and cosmetics at parts-per-million

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(ppm) levels,[4] resulting in an unintentional discharge of 1,4-dioxane into surface water and groundwater *via* municipal wastewater[5] or septic systems.[6] The USEPA'S Third Unregulated Contaminant Monitoring Rule (UCMR3) study revealed the widespread contamination of 1,4-dioxane in water supplies throughout the U.S. Over 4000 sites have detectable 1,4-dioxane levels, with over 600 sites having concentrations higher than 0.35 $\mu g\ L^{-1}$, the level in drinking water representing one-in-a-million cancer risk.[7] So far, there is no federal regulation for 1,4-dioxane; however, a few states have implemented their maximum contaminant level (MCL) for 1,4-dioxane. For example, New York State has adopted an MCL of 1 $\mu g\ L^{-1}$ for 1,4-dioxane in drinking water.

1,4-Dioxane is highly soluble in water, not volatile, has low sorption affinity, and is highly resistant to natural degradation processes. As a result, conventional water/wastewater treatment approaches like air stripping, filtration (*e.g.*, granular activated carbon (GAC), reverse osmosis and nanofiltration), coagulation/flocculation, and activated sludge are not effective in the removal of 1,4-dioxane.[8] Technologies for 1,4-dioxane biodegradation have grown significantly in recent years,[6,9,10] but the efficiency in terms of treatment time is still not able to compete with chemical degradation such as advanced oxidation processes (AOPs). 1,4-Dioxane can be readily destroyed by hydroxyl radicals ($OH^{\bullet}$) generated *via* AOPs. Various AOP configurations such as UV/hydrogen peroxide, UV/chlorine, UV/titanium dioxide, UV/persulfate, UV/chloramine, and peroxone (ozone/hydrogen peroxide) have been successfully applied to remove 1,4-dioxane in water from bench-scale to full-scale systems.[11–19] Although these technologies show promising results, concerns have arisen because of the presence of residual chemicals/catalysts used for $OH^{\bullet}$ generation in treated water, the formation of disinfection byproducts, and higher operating and maintenance costs.[20,21]

Electron beam (e-beam) radiolysis is an advanced oxidation–reduction process utilizing ionizing radiation to break down recalcitrant chemicals. One of the most attractive features of e-beam is that it generates not only oxidizing ($HO^{\bullet}$, $HO_2^{\bullet}$, O, $O^{\bullet-}$, $O_2^{\bullet-}$, $O_3^{\bullet-}$, H_2O_2, $HO_3^{\bullet}$, *etc.*) but also reducing (e_{aq}^{-}, $H^{\bullet}$) reactive species during water radiolysis, whereas other destructive technologies are not able to do both.[22] The accelerated electrons can penetrate the water column to decompose both dissolved and suspended pollutants. The generated high concentration of short-lived reactive species can rapidly decompose pollutants, and the excess reactive species and radicals are converted back to water and hydrogen. An important advantage of e-beam is that it does not require the addition of chemicals to generate radicals and hence does not require additional polishing treatment steps to remove chemical residues. Modern e-beam radiolysis is claimed to be an effective, high-speed, well-reproducible, energy-efficient technology.[23,24] It also has advantages such as compactness and a high degree of automation to couple with traditional water treatment methods.[24–26]

Several studies have investigated e-beam radiolysis on the degradation of various contaminants in water, including chlorinated solvents, pharmaceuticals, and per- and polyfluoroalkyl substances (PFAS).[22,27–31] For recalcitrant pollutants, such as PFAS, the energy requirement of e-beam is often comparable and much lower than other destructive techniques like activated persulfate, plasma, ultrasound, and photochemical and electrochemical oxidation.[22] To the best of our knowledge, to date there are only two studies applying e-beam radiolysis to degrade 1,4-dioxane in water. Li *et al.*[32] used 1,4-dioxane as a model compound to design and commission the e-beam facility and reported that about 95% of 1,4-dioxane in pure water (with initial concentrations of 8.1 and 78.5 $\mu g\ L^{-1}$) can be removed with a dose of 1 kGy. A recent follow-up study from the same group reported the removal of 1,4-dioxane (0.48 to 85 $\mu g\ L^{-1}$) in pure water and secondary effluent by e-beam irradiation with slow dose rates to study the removal kinetics.[33] They obtained >94% removal efficiency with the calculated electrical energy per order (EE/O) values ranging from 0.08 to 0.53 kWh m^{-3} per order. These studies, however, did not treat raw groundwater and influent wastewater, study the impact of initial concentrations of 1,4-dioxane, or assess the formation of byproducts during treatment. 1,4-Dioxane concentrations in contaminated waters can vary a wide range. The average concentration of 1,4-dioxane in wastewater and contaminated groundwater reported in the literature was often around low parts-per-billion (ppb, or $\mu g\ L^{-1}$) levels.[34,35] A few reported cases can exceed 10 $\mu g\ L^{-1}$, and the extreme ones can sometimes go beyond 100 $\mu g\ L^{-1}$.[5,36–38] Landfill leachate usually contains a higher level of 1,4-dioxane than wastewater and the concentration as high as ~22 mg L^{-1} has been reported.[5] Whether e-beam technology can successfully degrade high levels of 1,4-dioxane without any traces of concerning byproducts in these matrices remains unanswered and is merited to be tested.

Given that 1,4-dioxane has often been found as a co-contaminant along with other pollutants in surface water, groundwater, and wastewater, and considering that e-beam technology is claimed a fast-growing and promising "green method" to treat contaminated water,[23] it is merited to study 1,4-dioxane removal in water by e-beam irradiation. The goal of this study was to (i) investigate the effectiveness of e-beam technology in treating 1,4-dioxane (0.1 to 1000 mg L^{-1}) in different water matrices (pure water, contaminated groundwater, and wastewater), (ii) evaluate the impacts of sample modification (*e.g.*, varying pH and dissolved O_2 levels) and water quality on the removal performance, (iii) assess byproduct formation resulting from 1,4-dioxane degradation, and (iv) estimate the energy demands of the e-beam technology.

2. Materials and methods

2.1 Sample preparation

Pure standards of 1,4-dioxane, 1,4-dioxane-d_8, and tetrahydrofuran-d_8 (THF-d_8) were purchased from Sigma-Aldrich. GC-MS grade methanol (MeOH) and dichloromethane (DCM) were purchased from Fisher Scientific. All other chemicals (*e.g.*, acid and base) used in this study, without specifically mentioning here, were of either ACS reagent grade or analytical grade with high purity and were purchased from Sigma-Aldrich and Fisher Scientific. Ultrapure Milli-Q® water (18.2MΩ cm, MQW) was used throughout the experiments. Samples were prepared in borosilicate glass jars capped with plastic lids, with volumes of 15 or 90 mL, depending on experimental needs. For most of the samples, different concentrations of 1,4-dioxane solutions (0.1–1000 mg L^{-1}) were directly prepared in pure water without any modification or adjustment. For acidic and basic test samples, nitric acid and sodium hydroxide were used to adjust the solution pH to 4, 8, and 13. The pH values were measured by a portable pH meter (sensION+ MM150, Hach Company, Loveland, CO). Several blanks (without 1,4-dioxane addition) and controls (without e-beam treatment) in each treatment batch were prepared accordingly to track any potential loss or contamination of 1,4-dioxane during the sample processing and transportation. Contaminated groundwater (GW) was acquired from a military site, and its background water quality parameters are listed in Table S1.† Raw wastewater (WW) was obtained from the Wastewater Research and Innovation Facility (WRIF) in Suffolk County, NY. Each sample was prepared in triplicate.

2.2 Electron beam device configurations and treatment

Fermilab houses a demonstration accelerator (accelerator application development and demonstration, A2D2) that enables proof-of-concept studies. A2D2 is a 9 MeV electron accelerator and is provided by a repurposed teletherapy linac. It is a normal conducting multi-cell 2.85 GHz accelerator structure. Electrons are generated by a thermionic electron gun and are powered by a classic klystron amplifier. Once the electrons are accelerated, they are collimated by thin slits and a 270-degree bending magnet. When combined, these electrons have a narrow momentum spread and are well-focused, leaving the vacuum window. With variable settings, the machine can provide a maximum of 1.2 kW of beam power and electron kinetic energy of 9 MeV.

Dosimetry is provided by a NIST-certified dosimetry system that is available to measure/verify the amount of total dose given to each sample. For all samples to be placed in the electron beam, an optical density film is placed alongside the sample. The dosimetry method used to measure absorbed dose for e-beam irradiations is far west film dosimetry (FWT-60, Far West Technology, Inc., Goleta, CA). These 44.5 μm thin radiochromic films are derivatives of the family of aminotriphenyl-methane dyes that gradually change from colorless to a deeply colored state as a function of the absorbed dose. Specifically, these dosimeters use a hexa(hydroxyethyl) aminotriphenylacetonitrile (HHEVC) dye. Their absorbed radiation dose range is 0.5 to 200 kGy and they are measured by observing the color change at a wavelength of 510 nm or 600 nm by photometer or spectrophotometer. The dose received by the film can be considered approximate to the dose received by the sample with comparable density.

The samples were treated as batch systems using the 9 MeV electron beam located at Fermilab. Samples were treated in sealed containers as received, except for few samples requiring low oxygen conditions, which needed to be opened and purged with high-purity N_2 gas to attain final dissolved oxygen (DO) concentration of ∼2 mg L^{-1} prior to treatment. The oxygen level was measured by a portable DO meter (sensION+ DO6, Hach Company, Loveland, CO). The dose rate was fixed at 1.2 kGy s^{-1}, and the e-beam irradiation time determined the applied dose (from 2.5 to 25 kGy in this study). The sample depth in each container was carefully chosen to match the penetration depth of the e-beam (3 cm). To maximize the usefulness of A2D2 beam time, samples were treated in a set of six for each irradiation. For dose uniformity, the samples were placed in a revolving hexagonal-shaped sample holder. After sample treatment, the samples were confirmed sealed and were shipped on ice back to Stony Brook University for chemical analysis.

2.3 Analysis of 1,4-dioxane and other byproducts

1,4-Dioxane in solutions was extracted by small volume liquid–liquid extraction. About 800 μL of the sample solution was transferred to a 2 mL centrifuge tube and fortified with a deuterated surrogate (SUR) 1,4-dioxane-d_8. DCM (800 μL) containing the internal standard THF-d_8 was then added into the tube, capped firmly, shaken vigorously for 2 minutes, and frozen at −80 °C for half hour. The upper frozen aqueous phase layer was discarded and the bottom organic layer was collected for subsequent analysis. The mean extraction yield of SUR was 98 ± 6% (n = 103) throughout the experiments.

1,4-Dioxane was analyzed using an Agilent 7890/5975 gas chromatography-mass spectrometer (GC/MS). Data analysis was performed by Agilent ChemStation. For samples with a very high initial 1,4-dioxane concentration (*i.e.*, 1000 ppm), the analysis was done by an Agilent 7890B GC equipped with a flame ionization detector (FID). The detection limit for GC/MS and GC-FID was 1 μg L^{-1} and 1 mg L^{-1}, respectively. Aldehydes (formaldehyde, acetaldehyde, and glyoxal) were analyzed using the 2,4-dinitrophenylhydrazine (DNPH) derivatization method followed by HPLC-UV detection (Shimadzu Prominence). Analysis of organic acids (formic, acetic, and oxalic acids) was performed using ion chromatography (Metrohm 930 Compact IC Flex). Total organic carbon (TOC) was measured by a Shimadzu TOC-L analyzer. Instrument settings are shown in Table S2.†

3. Results and discussion

3.1 Degradation of 1,4-dioxane with varying initial concentration and pH

Firstly, we conducted a preliminary experiment where we fixed the dose at 5 kGy (irradiation time of ∼4.2 s at a dose rate of 1.2 kGy s^{-1}) and varied the initial concentration of 1,4-dioxane (0.10 to 1000 mg L^{-1} prepared in pure water) to determine the degree of degradation. Table 1 summarizes the degradation results. The dose of 5 kGy was enough to

Table 1 Degradation of 1,4-dioxane in ultrapure water at 5–25 kGy irradiation as a function of initial concentration. C_0 = initial concentration of 1,4-dioxane

Target C_0 (mg L^{-1})	Measured C_0 (mg L^{-1})	Dose (kGy)	pH	N_2 purging (DO <2 mg L^{-1})	Degradation (%)
0.10	0.09	5.0	Neutral	N	>99.9%
0.50	0.46	5.0	Neutral	N	>99.9%
1.0	0.97	5.0	Neutral	N	>99.9%
1.0	0.97	5.0	Neutral	Y	>99.9%
1.0	0.97	5.0	pH 4	N	>99.9%
1.0	0.97	5.0	pH 8	N	>99.9%
1.0	0.97	5.0	pH 13	N	>99.9%
10	9.81	5.0	Neutral	N	>99.9%
100	100.7	5.0	Neutral	N	59 ± 4.7%
1000	1029	5.0	Neutral	N	16 ± 5.3%
1000	1029	15	Neutral	N	24 ± 3.5%
1000	1029	15	Neutral	Y	29 ± 0.2%
1000	1029	25	Neutral	N	38 ± 2.6%
1000	1029	25	Neutral	Y	46 ± 3.2%

degrade 10 mg L^{-1} of 1,4-dioxane to below the detection limit (<1 μg L^{-1}). The degree of degradation in response to the total dose given was comparable to previous studies conducted by Li *et al.*[32] and Pearce *et al.*,[33] where they reported >95% of 1,4-dioxane (initial concentrations ranging from 8.1 to 78.5 μg L^{-1} in pure water) degradation by e-beam irradiation with a dose of ~1 kGy. However, the dose rate they used was 0.54 kGy min^{-1} which was two orders of magnitude lower than this study. Incomplete degradation at 5 kGy was observed only when the initial concentration was increased to >100 mg L^{-1}, presumably because of excess 1,4-dioxane molecules in the solution, and the number of reactive species became the rate-limiting factor. pH can influence the abundance of reactive species generated *via* e-beam irradiation, altering the dominance of oxidizing or reducing capability. For example, under alkaline conditions (*e.g.*, pH ~12), $HO^{\bullet}$ would be deprotonated to form less reactive oxide radical anions ($O^{\bullet-}$)[39,40] and hydrogen radicals ($H^{\bullet}$) would be converted to e_{aq}^{-}.[41] Under acidic conditions, e_{aq}^{-} would be consumed by protons to form $H^{\bullet}$.[41] Our result indicates that varying pH (pH 4 and 13, 1,4-dioxane = 1 mg L^{-1}) did not show any adverse impacts on the degradation. This may be due to the abundant reactive species constantly generated by e-beam irradiation. Although the concentration of reactive species such as $HO^{\bullet}$ decreased with elevated pH, there was still enough $HO^{\bullet}$ available to decompose 1,4-dioxane (1 mg L^{-1}) rapidly. This implies that pH adjustment can be minimal or neglected while treating 1,4-dioxane with environmentally relevant concentrations in contaminated water.

Degradation byproducts were detected after the complete treatment of 1,4-dioxane at low concentrations (0.1, 0.5, 1 mg L^{-1}). Three known byproducts of 1,4-dioxane, reported for reactions with hydroxyl radicals,[12] was measured in this study. Oxalic, acetic, and formic acids were detected and accounted for the overall carbon mass of 15 ± 2%, 8.2 ± 0.7%, and 1.9 ± 0.2% (for all three initial concentrations), respectively. Because of the high detection limit of the TOC instrument (~0.5 mg L^{-1}), the remaining total organic carbon mass was not determined. Detection of these byproducts suggested that reaction with hydroxyl radicals was the dominant pathway for the degradation of 1,4-dioxane. Additional irradiation may help eliminate these intermediates, but some known intermediates are less reactive with $HO^{\bullet}$,[42] reducing the overall treatment efficiency in converting 1,4-dioxane into CO_2.

3.2 Effect of dissolved oxygen on 1,4-dioxane degradation

The reducing reactive species such as e_{aq}^{-} and $H^{\bullet}$ can be rapidly scavenged by dissolved oxygen (DO), lowering the equilibrium concentration of e_{aq}^{-} and $H^{\bullet}$ to react with pollutants. Therefore, purging the solution with inert gas may help to create a low-oxygen or oxygen-free environment to generate sufficient reducing reactive species by e-beam irradiation to break down certain target compounds (*e.g.*, per- and polyfluorinated compounds). To the best of our knowledge, reductive degradation is not a preferred pathway to degrade 1,4-dioxane and is scarcely reported in the literature. Here we purged 1000 mg L^{-1} of 1,4-dioxane solutions with N_2 to achieve a low DO environment (~2 mg O_2 L^{-1}) to observe whether abundant reducing species generated by e-beam irradiation could impact 1,4-dioxane degradation. We intentionally increased the initial concentration of 1,4-dioxane because incomplete degradation was required to evaluate DO's impact. Our results show that 1,4-dioxane degradation was enhanced under low DO conditions, with an increase of 21% and 23% (calculated by the decreased mass of 1,4-dioxane) at 15 and 25 kGy, respectively (Table 1 and Fig. S1†). It is known that $OH^{\bullet}$ is the major oxidizing agent to react with 1,4-dioxane ($k_{OH^{\bullet}} = 2.8 \times 10^9$ M^{-1} s^{-1}) during e-beam treatment.[33] From our observation, $OH^{\bullet}$ was still likely the dominant reactive species to degrade 1,4-dioxane even when the DO level was low, as the production yield of $OH^{\bullet}$ does not seem to be impacted by

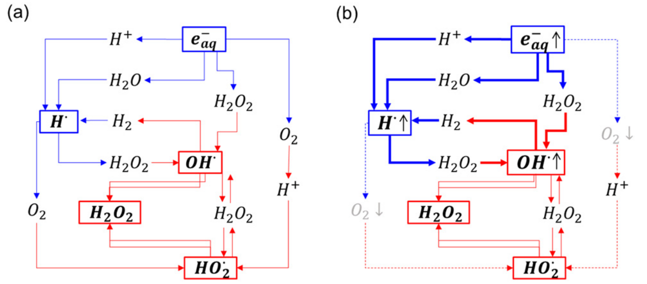

Fig. 1 A schematic diagram of interconversion between reactive species during water radiolysis by e-beam irradiation (modified from Ponomarev and Ershov[23]) under (a) oxic and (b) suboxic/anoxic conditions. Blue and red lines represent the pathways involving reducing and oxidizing reactive species, respectively. Bold and dashed lines indicate potentially enhanced and declined reactions, respectively, at low DO conditions.

DO. The reason for this enhanced degradation, however, needs further investigation.

There was no information to suggest that e_{aq}^- and 1,4-dioxane could react with each other. This is attributed to the high reduction potential of −2.9 eV of e_{aq}^-, enabling them to degrade reactants susceptible to reduction. The reactivity of e_{aq}^- with ether (–O–) functional groups was low.[23] In contrast, another reducing reactive species, $H^\cdot$ has greater reactivity, and the reaction rate constant between $H^\cdot$ and 1,4-dioxane was reported in a previous study ($k_{H^\cdot} = \sim 1.0 \times 10^7$ M^{-1} s^{-1}).[42,43] Thus, the enhanced degradation of 1,4-dioxane may be partially contributed by the elevated reducing species $H^\cdot$ in solution under low DO conditions. Nevertheless, because $k_{H^\cdot}$ is about two orders of magnitude lower than $k_{OH^\cdot}$, there were other factors that increased the degradation percentage by 21–23%. One of the reactive oxidizing species, oxide anion radicals ($O^{\cdot-}$), would not be scavenged by DO ($O^{\cdot-} + O_2 \rightarrow O_3^-$, $k = 3.6 \times 10^9$ M^{-1} s^{-1}) as DO decreases. Although the general reactivity of $O^{\cdot-}$ with organics is considered much slower than $OH^\cdot$,[42] the increased $O^{\cdot-}$ might still partially assist with 1,4-dioxane degradation. Overall, varying DO may influence the interconversion of oxidative and reductive intermediate products during water radiolysis by e-beam irradiation (Fig. 1). Suboxic and anoxic environments may be in favor of certain reactions, resulting in a higher equilibrium concentration of reactive species (*i.e.*, $OH^\cdot$ and $H^\cdot$) that can enhance the degradation of 1,4-dioxane.

3.3 Kinetics of 1,4-dioxane degradation and byproduct formation

To study degradation kinetics, degradation curves were established with increasing doses for high 1,4-dioxane initial concentrations of 10, 100, and 1000 mg L^{-1} (Fig. 2a). The final concentration for the samples with 10 mg L^{-1} initial concentration was 0.030 mg L^{-1} (99.7% removal) after receiving 2.5 kGy irradiation and became undetectable (<0.001 mg L^{-1}) beyond 5 kGy. A near-complete degradation curve was observed for C_0 = 100 mg L^{-1}, following the first-order-like curve down to 1.1 mg L^{-1} at 25 kGy (98.9% removal). C_0 = 1000 mg L^{-1} samples (actual mean C_0 = 1029 mg L^{-1}) were degraded to 638 mg L^{-1} (38% removal) at 25 kGy with the degradation curve following a zero-order reaction, which is probably because the 1,4-dioxane concentration greatly exceeded the amount of reactive species in the solution. We further calculated the pseudo-first-order reaction rate constant for each treatment (Fig. 2b). The calculated rate constant (2.31 for 10 mg L^{-1}, 0.178 for 100 mg L^{-1}, and 0.0186 for 1000 mg L^{-1}; unit = kGy^{-1}) decreased as the initial concentration increased. This observation agreed with the previous studies in which water radiolysis was used to treat perfluoroalkyl compounds,[41,44] endosulfan,[45] and 2,3,7,8-tetracholorodibenzo-*p*-dioxin (TCCD).[46] Because the degradation byproducts of 1,4-dioxane were likely to increase with the increasing initial concentration, it would consequently lead to greater competition for reactive species to thus lower their reaction probability with 1,4-dioxane.

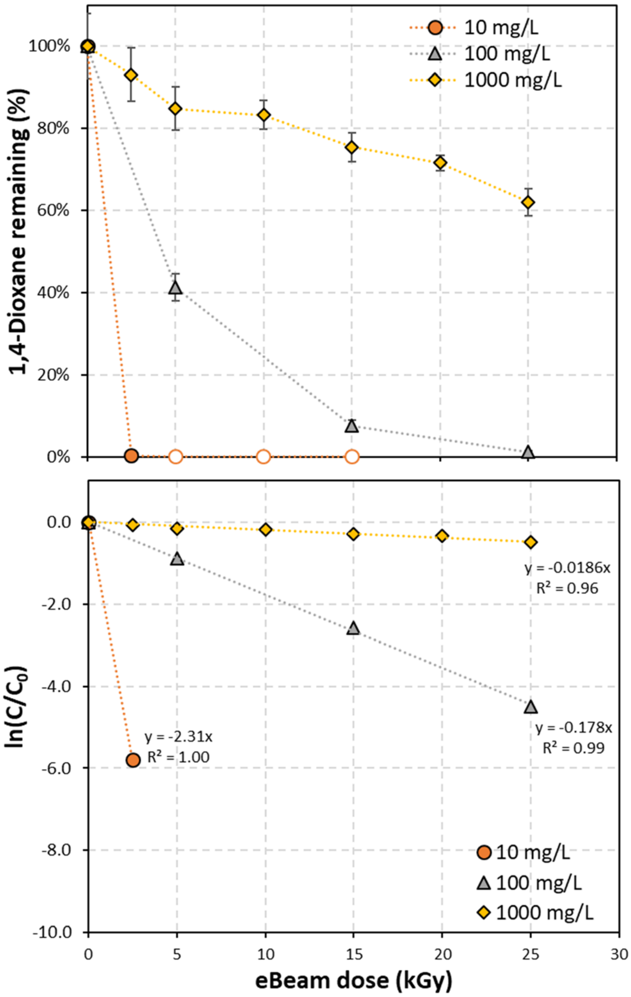

Fig. 2 Degradation of 1,4-dioxane as a function of the e-beam dose. Error bars represent the standard error of two replicate measurements. The open circle indicates below the detection limit. Average measured initial concentration: $[C_{0,\ 10mg\ L^{-1}}]$ = 9.81 mg L^{-1}, $[C_{0,\ 100mg\ L^{-1}}]$ = 100.7 mg L^{-1}, and $[C_{0,\ 1000mg\ L^{-1}}]$ = 1029 mg L^{-1}.

Selected known byproducts were measured in both 10 mg L^{-1} and 100 mg L^{-1} degradation kinetics experiments (Fig. 3).

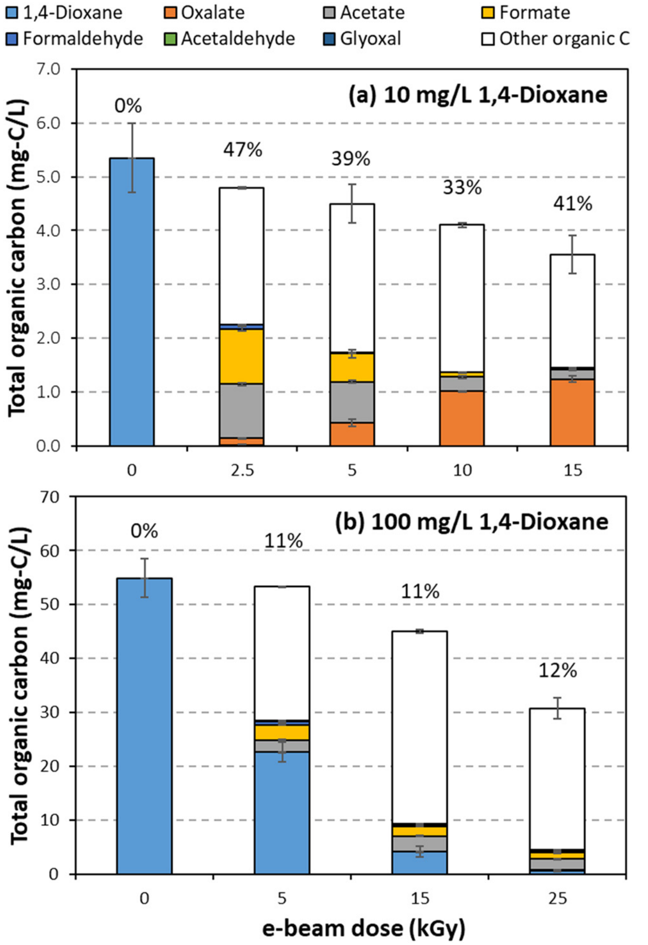

Fig. 3 Byproduct formation as a function of e-beam dose at two initial 1,4-dioxane concentrations: (a) 10 mg L^{-1} (~5.45 mg-C L^{-1}) and (b) 100 mg L^{-1} (~54.5 mg-C L^{-1}); [other organic carbon] = [total organic carbon] − ∑[measured byproducts]. The value above each bar represents the percentage of measured byproducts (in C mass) out of total organic carbon.

For 10 mg L^{-1} of 1,4-dioxane treatment, formate, acetate, and oxalate were found to be the major byproducts (Fig. 3a). When the dose was increased from 2.5 to 15 kGy, the formate and acetate concentrations dropped, whereas the oxalate concentration increased. Very low formaldehyde (0.18 and 0.06 mg L^{-1}) was only detected at 2.5 and 5 kGy; whereas acetaldehyde and glyoxal were not detected during the entire treatment of 10 mg L^{-1} 1,4-dioxane. The TOC result indicated that the measured byproducts accounted for <50% of the carbon mass balance, suggesting a significant amount of other unknown intermediates remained in the solution. 1,2-Ethanediol diformate (EGDF) is likely the primary intermediate produced after 1,4-dioxane oxidation,[12,19] but it was not measured in this study. Only about 39% of TOC was fully mineralized to CO_2 after 15 kGy irradiation. For the treatment of 100 mg L^{-1} 1,4-dioxane (Fig. 3b), all six known byproducts were detected. Their concentrations as a function of the e-beam dose reflected their reactivity with radicals and the continuous generation of byproducts from 1,4-dioxane degradation. For example, formaldehyde and formate were found to be highest at 5 kGy and then declined rapidly over time, probably due to their higher reactivity with $OH^{•}$ ($k_{OH^{•}}$ = 1.0 × 10^9 for formaldehyde and 3.2 × 10^9 for formate).[42] The other byproducts did not vary greatly or even increase over time. This is likely because they were not preferably reacted with $OH^{•}$ ($k_{OH^{•}}$ = 7.7 × 10^6 for oxalate, 8.5 × 10^7 for acetate, 6.6 × 10^7 for glyoxal, 7.3 × 10^8 for acetaldehyde)[42] compared to 1,4-dioxane. At 25 kGy, about 46% of TOC was degraded and the majority of the remaining carbon mass (86%) was other intermediates. Overall, we expect that increasing irradiation should eventually remove these intermediates. Alternatively, these intermediates are more vulnerable to traditional treatment methods or natural attenuation processes (*e.g.*, biodegradation) and hence can be easily removed in the following treatment stages. For instance, air-stripping process is useful to remove volatile organics (*e.g.*, aldehydes and EGDF), adsorption by activated carbon can help remove organic acids,[47] and aldehydes and organic acids both have high biodegradation potential to be degraded in biologically active filtration and activated sludge systems.[48]

3.4 Effect of water matrix during the treatment of contaminated groundwater and wastewater

Coexisting organic/inorganic compounds and ions in real water can scavenge reactive species and reduce the removal efficiency of target contaminants during e-beam treatment. Here we explored the impact of groundwater and wastewater matrix on the degradation kinetics of 1,4-dioxane. Two different initial concentrations (10 and 100 mg L^{-1}) of 1,4-dioxane solutions were prepared in the three types of water matrices: Milli-Q water (MQW), groundwater (GW), and wastewater (WW). The calculated pseudo-first-order reaction rate constant followed the trend of $k_{MQW} > k_{GW} > k_{WW}$ (Fig. 4) as expected. This was due to the presence of higher organic content in WW and GW compared to MQW as the TOC concentration for WW (31 mg-C L^{-1}) > GW (5.1 mg-C L^{-1}) > MQW (<0.5 mg-C L^{-1}).

A greater decline of the rate constant between the three water types (k_{MQW} = 2.31; k_{GW} = 1.39; k_{WW} = 0.62; unit = kGy^{-1}) was observed in the more diluted 1,4-dioxane solution (10 mg L^{-1}), where 1,4-dioxane initially made up 100% (MQW), 53.2% (GW), and 14.8% (WW) of TOC. With the 1,4-dioxane concentration increased from 10 to 100 mg L^{-1}, 1,4-dioxane became the primary dominant species of TOC in the solutions, accounting for 100% (MQW), 91.2% (GW), and 64.7% (WW) of organic carbon mass. Therefore, the impact of the water matrix on the reaction rate constant became less prominent (k_{MQW} = 0.18; k_{GW} = 0.16; k_{WW} = 0.13; unit = kGy^{-1}) (Fig. 5b). This suggests that the removal efficiency is vulnerable to the water matrix when the concentration of 1,4-dioxane is low (or accounts for a small fraction of TOC). The corresponding energy demand would also be impacted and is discussed in the next section.

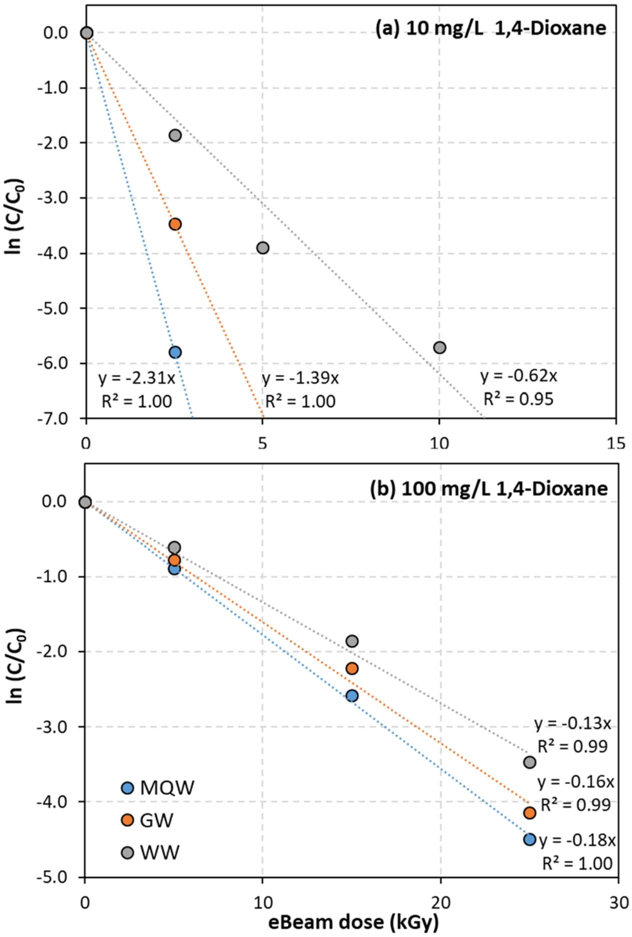

Fig. 4 Degradation kinetics with the initial 1,4-dioxane concentration of (a) 10 mg L^{-1} and (b) 100 mg L^{-1} in pure water (MQW), contaminated groundwater (GW), and wastewater (WW). Average measured initial 1,4-dioxane concentration: [$C_{0,\ 10\text{mg L}^{-1}\text{MQW}}$] = 9.81 mg L^{-1}, [$C_{0,\ 10\text{mg L}^{-1}\text{GW}}$] = 10.1 mg L^{-1}, [$C_{0,\ 10\text{mg L}^{-1}\text{WW}}$] = 10.0 mg L^{-1}, [$C_{0,\ 100\text{mg L}^{-1}\text{MQW}}$] = 100.7 mg L^{-1}, [$C_{0,\ 100\text{mg L}^{-1}\text{GW}}$] = 96.1 mg L^{-1}, [$C_{0,\ 100\text{mg L}^{-1}\text{WW}}$] = 102.9 mg L^{-1}.

3.5 Energy demand for e-beam treatment

Electrical energy per order (EE/O) is often used to represent the energy efficiency of a treatment technique that needs external energy input (*e.g.*, UV-based AOPs). It is defined as the energy required for one log reduction (*i.e.*, 90% removal) of a pollutant in a unit volume of water. With this parameter, a comparison in terms of energy demand between different treatment technologies can be achieved. Here we used the equation derived by Londhe *et al.*[22] to calculate EE/O for e-beam radiolysis,

$$\mathrm{EE/O}\ \left(\mathrm{kWh\ m^{-3}\ per\ order}\right)\ \text{for e-beam} = \frac{\mathrm{Dose(kGy)}}{3.6\times\log\left(\frac{[\mathrm{C}]_{\mathrm{in}}}{[\mathrm{C}]_{\mathrm{out}}}\right)}$$

where Dose is the e-beam dose delivered to the sample; $[\mathrm{C}]_{\mathrm{in}}$ and $[\mathrm{C}]_{\mathrm{out}}$ are 1,4-dioxane concentrations before and after treatment. To calculate EE/O values in this study, we used the data from the experiments of 1, 10, and 100 mg L^{-1} of 1,4-dioxane because >90% removal was achieved in these experiments. Summarized EE/O values are shown in Table 2. The energy transfer/generation efficiency was ~80% for the e-beam accelerator in this study, and the estimated EE/O values ranged from 0.39 to 6.3 kWh m^{-3} per order (all three water matrices) while the initial 1,4-dioxane concentrations varied from 1 to 100 mg L^{-1}. The values calculated from 1–10 mg L^{-1} initial dioxane concentrations agree with previous studies.[32,33] Although Pearce *et al.*[33] reported an EE/O value of 0.08 kWh m^{-3} per order in pure water, it should be noted that EE/O values would be overestimated when the initial concentration was low and no detection after treatment (*i.e.*,

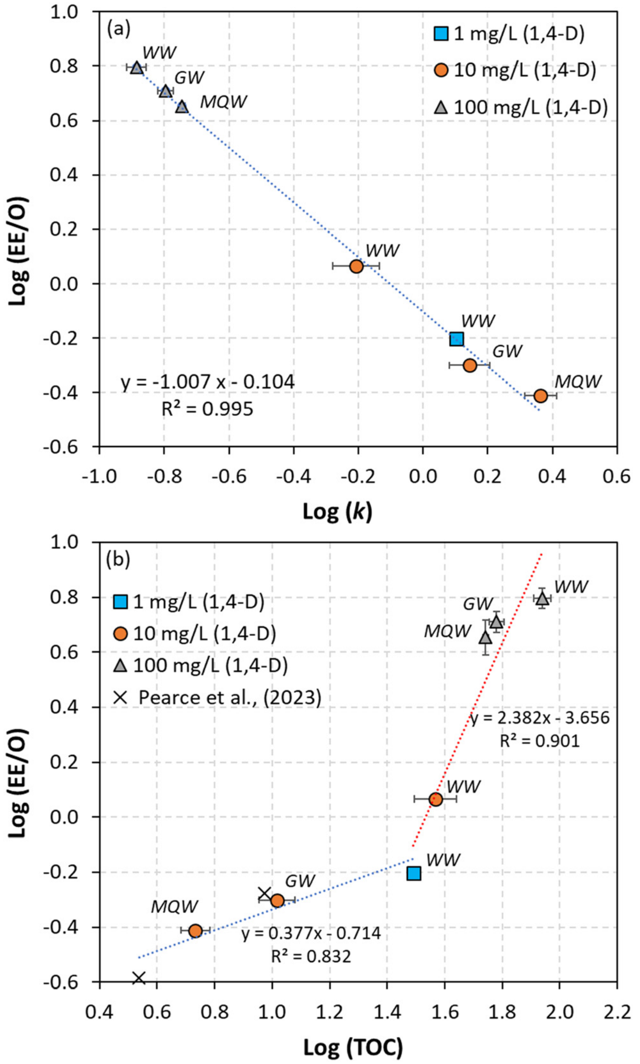

Fig. 5 Relationship (log–log) between calculated EE/O values (kWh m^{-3} per order) and (a) pseudo-first-order reaction rate constants (kGy^{-1}) and (b) TOC concentrations. Marker shapes represent different targeted initial 1,4-dioxane concentrations (1 to 100 mg L^{-1}) and the type of water matrix (MQW, GW, and WW) is denoted next to each data point. The background TOC value in GW and WW was ~5.1 mg-C L^{-1} and ~31 mg-C L^{-1}, respectively. Two data points (cross) are acquired from Pearce *et al.*[33] in panel (b).

Table 2 Estimated EE/O values for different technologies to remove 1,4-dioxane in water

1,4-Dioxane (mg L^{-1})	Water matrix	EE/O (kWh m^{-3} per order)	Technology	Reference
1.0	MQW	0.58[a]	e-beam	This study
	GW	0.59[a]		
	WW	0.63		
10	MQW	0.39 ± 0.05	e-beam	This study
	GW	0.50 ± 0.08		
	WW	1.16 ± 0.20		
100	MQW	4.5 ± 0.13	e-beam	This study
	GW	5.1 ± 0.25		
	WW	6.3 ± 0.38		
0.0081/0.0785	MQW	0.30[c]	e-beam	Li *et al.*[32]
0.00048–0.085	Purewater WW	0.08–0.53	e-beam	Pearce *et al.*[33]
0.10	MQW GW	0.13–0.20	UV/H_2O_2	Lee *et al.*[11]
0.20	MQW Tap water	0.45–1.67	UV/H_2O_2	Antoniou and Anderson[13]
0.20	Surface water	0.6–3[b]	UV/H_2O_2	Martijn *et al.*[49]
100–450	Tap water Contaminated water	3.2–7.4	UV/H_2O_2	Safarzadeh-Amiri *et al.*[50]
0.036–0.10	GW Synthetic water	3–15[b]	Vacuum UV (VUV)	Shi *et al.*[53]
0.88	GW	0.2–0.6	Electrochemical advanced oxidation process (EAOP)	Li *et al.*[54]
3.5	MQW	1.6	UV/ZnO/CNF	Dehghani *et al.*[66]
0.85	WW	1.9	UV/TiO_2	Lee *et al.*[52]
0.050	Tap water	0.58–11	UV, VUV, UV/TiO_2, VUV/TiO_2	Matsushita *et al.*[51]
0.10	GW	0.29–0.85	UV/H_2O_2, VUV/H_2O_2	Matsushita *et al.*[51]
220	n/a	30[b]	Ozone/UV	Kishimoto and Nakamura[55]
150	Purewater + WW	108–134[b]	Ozone/UV	Takahashi *et al.*[56]
0.213	GW	<10	Ozone/UV Ozone/H_2O_2/UV	Ikehata *et al.*[57]
0.020	Synthetic GW	5	Non-thermal plasma	Xiong *et al.*[58]
n/a	n/a	1.8–2.1	Non-thermal plasma	Solnik *et al.*[59]
0.018	GW	1.93–2.75	Non-thermal plasma	Even-Ezra *et al.*[60]

[a] Underestimated value (calculated by the method detection limit (0.001 mg L^{-1})). [b] Raw data not provided, values estimated from the figures. [c] Calculated from the information provided in the text; assuming 70% transfer efficiency.

values with the asterisk in Table 2). The water with a complex matrix (*i.e.*, GW, WW) required higher energy to achieve one log removal of 1,4-dioxane, and the EE/O value was inversely correlated with the pseudo-first-order rate constant (Fig. 5a). The energy consumption required to degrade 10 mg L^{-1} of 1,4-dioxane in GW and WW was 29% and 300%, respectively, greater than in MQW. In contrast, only 14% (GW) and 39% (WW) increase in EE/O was observed for the treatment with the initial concentration of 100 mg L^{-1} compared to MQW. This again reflects the strong negative influence of complex matrices in terms of removal efficiency as well as increased energy demand if the initial concentration of the target contaminant is relatively low. Fig. 5b summarizes the relationship between the EE/O values and the TOC concentrations in this study. Two extra data points from Pearce *et al.*[33] were included and fitted very well. The EE/O and TOC show a positive non-linear correlation, with a breakpoint around 30 mg-C L^{-1}. This suggests a threshold TOC concentration for e-beam radiolysis exists with the e-beam configuration used in this study, and treatment performance would have deteriorated greatly if the TOC concentration had gone beyond the threshold under the conditions tested. The concept of this threshold TOC concentrations came from our observations of a significant difference in EE/O values between high and low TOC background concentrations. We hypothesize that the amount of reactive species generated in a given time was stable but much less than the organics present in the sample, and therefore the reaction acted like a zero-order reaction instead of a pseudo-first-order reaction. The threshold TOC concentration depends on the e-beam system configuration, and theoretically, if the dose rate increases, this threshold concentration should become lower.

EE/O values reported from other types of advanced treatment, such as UV/H_2O_2,[11,13,49–51] UV/TiO_2,[51,52] vacuum UV,[51,53] electrochemical oxidation,[54] ozone-based AOP,[55–57] and non-thermal plasma,[58–60] were, in general, ranging from 0.13 to 134 kWh m^{-3} per order (Table 2). It should be noted that for a few non-UV-based AOPs, such as ozone/H_2O_2 (peroxone), the system's overall energy consumption (*e.g.*, for O_2/O_3 production) is usually not revealed in the text. Therefore, their EE/O values were not able to calculate. Without considering water matrices and initial concentrations tested, UV/H_2O_2 systems usually performed the best, followed by electrochemical oxidation, UV/

TiO_2 and non-thermal plasma, and direct UV/VUV photolysis.[22] The EE/O values for e-beam treatment from our study were comparable to those reported from UV/H_2O_2 systems. Moreover, our values were calculated with the initial 1,4-dioxane concentration which is at the upper limit of the environmentally relevant concentration. We expect the actual energy demand should be much lower when treating 1,4-dioxane concentration at sub-parts-per-billion levels.

3.6 Implications on future applications of e-beam

According to EPA, 2017, ~700 000 pounds (16.7% of total production related waste) of industrial 1,4-dioxane in the U.S. was released to the environment. The current disposal method of 1,4-dioxane in the industry is primarily *via* incineration.[61,62] The stack air and fugitive air releases, along with the disposal of incineration residues (landfill), result in the release of 1,4-dioxane to the environment.[62] For example, Fujiwara *et al.*[63] reported high levels of 1,4-dioxane (up to 340 μg L^{-1}) in landfill leachate in Japan and concluded the source to be the fly ash produced by solid waste incinerators. Using e-beam irradiation to treat high levels of 1,4-dioxane waste on-site could be an efficient, economical, and sustainable way to reduce its release to the environment.

A few papers have already reported a successful scale-up of the e-beam technology for treating dyeing wastewater with installation in the existing treatment process. For example, one study in Korea developed an industrial-scale e-beam device to treat ~2.6 million gallons per day (MGD) of dyeing wastewater.[64] In a recent study in China, multiple e-beam accelerators were installed to comprise a full-scale treatment system capable of treating ~7.9 MGD of dyeing wastewater.[65] Lastly, a mobile e-beam treatment plant developed in Korea demonstrated its capacity for on-site treatment and could treat up to 0.13 MGD of liquid waste.[25] Experimental work from this study was done on an electron beam accelerator that delivers 1.2 kW of power only. Commercial accelerators, and the accelerator being developed at Fermilab, can deliver 100 s of kWs of power. Assuming a dose of 10 kGy is needed to destroy the 1,4-dioxane, a 200 kW accelerator can treat 15 000 gallons of water per hour, equivalent to 0.36 MGD. With the recent advancement in e-beam technology and the existing successful examples, we do not expect issues in scaling the technology.

The typical concentration of 1,4-dioxane observed in waters (*e.g.*, surface water, groundwater, and wastewater) can be easily decomposed by e-beam with very low doses (<5 kGy). The EE/O values obtained in this study for 1,4-dioxane are comparable to values calculated for other persistent organic pollutants such as chlortetracycline (~0.04 kWh m^{-3} per order), tetrachloroethylene (~0.17 kWh m^{-3} per order), bromodichloromethane (~0.45 kWh m^{-3} per order) and 4-chlorophenol (~1.1 kWh m^{-3} per order).[22] Higher e-beam doses (8–2000 kGy) have been utilized to degrade more persistent contaminants, resulting in higher EE/O values of ~248, 381, and 464 kWh m^{-3} per order calculated for 2,3,7,8-PCDD/Fs, perfluorooctanoic acid (PFOA), and perfluorooctanesulfonic acid (PFOS)[22] in aqueous matrices, respectively. Thus, if e-beam technology was used to degrade these more persistent contaminants at higher doses, we hypothesize that this technology would also be able to simultaneously degrade contaminants such as 1,4-dioxane and tetrachloroethylene if they were present in the sample as co-contaminants. Although competition between co-contaminants to react with reactive species could occur, abundant reductive/oxidative species produced by water radiolysis are supposed to preferentially and rapidly degrade co-contaminants that have lower resistance to degradation. Thus, e-beam technology, unlike other technologies that require a treatment train approach, is capable of simultaneously treating a suite of persistent organic pollutants. It is merited to explore the optimal configurations of how e-beam can either act as a stand-alone treatment process or align with the existing treatment approaches to deal with various types of pollutants in diverse water matrices.

4. Conclusions

The feasibility of e-beam irradiation to degrade 1,4-dioxane in water was successfully demonstrated in this study. The approach is highly effective in degrading 1,4-dioxane to below detection from an initial concentration ranging from 0.1 to 1 mg L^{-1} at 5 kGy, without the need for any sample modification and pH adjustment. Even with the initial concentration of 10 mg L^{-1}, 5 kGy irradiation was sufficient to achieve >99.9% (ultrapure water and contaminated groundwater) and 98% (wastewater) removal of 1,4-dioxane. Low DO in water can enhance 1,4-dioxane removal efficiency by 21–23%, which was likely due to the increased reactive species ($H^{\bullet}$ and $O^{\bullet-}$) that were not scavenged by DO. However, the enhanced efficiency of the process at lower DO levels may not justify the need for additional energy of purging when treating environmentally relevant concentrations since a low treatment dose was sufficient to achieve complete degradation of 1,4-dioxane.

1,4-Dioxane was rapidly removed by e-beam water radiolysis but was not fully mineralized. Intermediates and degradation byproducts are less reactive and need additional energy and time to accomplish full mineralization. Instead, these byproducts could easily be removed by conventional treatment methods.[47] Either additional treatment time should be applied by e-beam irradiation or coupling the e-beam technology with conventional water treatment methods need to be carefully evaluated depending on the required treated water quality.

The calculated EE/O values from using the e-beam technique in this study are low (<1.0 kWh m^{-3} per order) and comparable to traditionally used AOPs for 1,4-dioxane treatment like UV/H_2O_2 systems. In addition, one notable advantage of using e-beam over other AOPs for 1,4-dioxane treatment is that it does not require any chemical additions, and the generated oxidizing and reducing reactive species do not last in the solution. Traditional AOPs relying on oxidants require excess dosing of chemicals to generate a sufficient amount of hydroxyl radicals and hence require additional polishing filters to remove the residual oxidants in the treated water. While AOPs usually require a contact time of tens to hundreds of seconds in the reactor,[67–69] the e-beam technique needs only a few seconds (with a high dose rate) to achieve complete degradation of target contaminants.

Conflicts of interest

There are no conflicts to declare.

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