



Computer-simulated degradation of CF_3Cl , CF_2Cl_2 , and CFCl_3 under electron beam irradiation

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Abstract. Electron beam treatment technologies should be versatile in the removal of chlorofluorocarbons (CFCs) owing to their exceptional cross sections for the thermal electrons generated in the radiolysis of air. Humidity, dose rates, O_2 concentration, and CFC concentration influence the efficiency of the destruction process under electron beam treatment. Computer simulations have been used to theoretically demonstrate the destruction of chlorotrifluoromethane (CF_3Cl), dichlorodifluoromethane (CF_2Cl_2), and trichlorofluoromethane (CFCl_3) in the air ($\text{N}_2 + \text{O}_2$: 80% + 20%) in room temperature up to a dose of 13 kGy. Under these conditions, it is predicted that the removal efficiency is in the order CF_3Cl (0.1%) < CF_2Cl_2 (7%) < CFCl_3 (34%), which shows the dependence of the process on the number of substituted Cl atoms. Dissociative electron attachment with the release of Cl^- is the primary process initiating the destruction of CFCs from the air stream. Reactions with the first excited state of oxygen, namely, $\text{O}(^1\text{D})$, and charge-transfer reactions further promote the degradation process. The degradation products can be further degraded to CO_2 , Cl_2 , and F_2 by prolonged radiation treatment. Other predicted products can also be removed through chemical processes.

Keywords: Chlorofluorocarbons (CFCs) • Computer simulation • Electron beam • Mechanism

Introduction

Global interest in the reduction of carbon emissions and substances that deplete the ozone layer to the detriment of the environment has sparked the development of technologies to mitigate the release of these substances or otherwise degrade them into more-labile species. Persistent and stable organic pollutants generated by human socioeconomic activities pose a substantial environmental threat owing to their wide applications in industrial and consumer goods [1–4]. Landfills, wastewater treatment plants, and incineration are the conventional disposal practices for wastes accruing from the utilization of these chemicals. However, these methods are reported to concentrate pollutants, transport them between sites, or make them highly mobile [5]. Removal technologies, such as adsorption (e.g., granular activated carbon), ion exchange, reverse osmosis, and domestic water treatment systems, are prone to producing perfluoroalkyl substance (PFAS)-laden wastes from common consumer products. These disposal methods can inadvertently lead to the gasification of volatile waste constituents, culminating in the release of harmful air pollutants into the atmosphere [6, 7]. The incineration of PFASs as a method of disposal releases ozone-depleting chlorofluorocarbons (CFCs), fluorinated greenhouse

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gases, aromatic compounds, and perfluorinated carboxylic acids. Adsorption on activated carbon or combustion is predominantly used for volatile organic compound (VOC) removal. However, the adsorbed VOCs are not changed into nontoxic substances and are therefore able to cause other types of pollution at different places from the point sources [8]. Thermal reactivation of granular activated carbon with absorbed perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS), common in polymers and coatings, leads to the conversion of these compounds to volatile species. Similarly, CFCs released from the use or disposal of CFC-containing products act as Cl reservoirs in the atmosphere and release Cl atoms and halogenated radicals into the stratosphere by photolysis and oxidation. Through the reactions of these derivatives, CFCs indirectly affect the environment and human health. Therefore, their elimination from exhaust gas streams is vital.

Ionizing radiation is observed to effectively and efficiently destroy a wide variety of organic pollutants both in water and gases [9, 10]. Plasmas have been used to degrade persistent pollutants or mixtures, thereby offering an alternative process to incineration and absorption [11]. The irradiation of a simple gas generates excited states, ions, molecular fragments, and low-energy electrons. Energetic secondary electrons are slowed down in successive inelastic collisions, and these transfer their energy to the components of the medium, thus generating a wide range of reactive chemical moieties useful in waste treatment applications [12, 13]. Electron beam (EB) treatment is progressively being found to be effective for the destruction of CFCs both in liquid and gaseous matrices. EB technology is energy saving and has better handling and operational characteristics compared to gamma rays and therefore is more widely used even though gamma rays have higher penetration. The rate of imparted energy is higher than that of electromagnetic radiations corresponding to higher absorbed dose rates due to higher directivity to the direction of acceleration [14, 15]. Low-energy electrons are very reactive and efficiently captured by CFCs, which have very large cross sections compared to ionization or excitation and subsequently lead to rapid unimolecular decompositions of the CFCs [16, 17]. EB technology is a promising method for the treatment of aromatics and aliphatics [18–20]. In this work, the kinetic and Gear methods are used to simulate the destruction of trichlorofluoromethane (CFCl₃), dichlorodifluoromethane (CF₂Cl₂), and chlorotrifluoromethane (CF₃Cl) in humid air (20% O₂, 80% N₂) under an EB. Reactions and their corresponding reaction rates are sourced from the literature to simulate the irradiation treatment of VOCs with increasing absorbed dose.

Methodology

The theoretical model of CFC decomposition in humid air under the influence of EB irradiation was based on the reactions in Eqs. (1)–(16), among other

reactions from the literature on atmospheric chemistry reactions. Primary processes in EB irradiation of N₂ and O₂, ion-molecular reactions of positive and negative charge transfer, ion recombination reactions, neutral species reactions, and free radical reactions are considered. Reversible and irreversible reactions of the different chemical species, expressed as differential equations for the conservation of mass and the formation and destruction of chemical species, were also computed. The reactions induced by the EB will only be active during the residence time of the gas in the beam.

The computer code “kinetic” and Gear method are used to calculate the time evolution of the different main species involved in the kinetic reaction system at constant pressure and temperature. The reaction system is considered self-contained and closed and obeys the principle of mass balance and charge balance. The kinetic reaction system is mathematically described by the system of ordinary differential equations (ODEs). The “kinetic” code used the Gear algorithm for the numerical integration of the stiff systems of ODEs.

The “kinetic” code applied to study CFC decomposition in air under EB irradiation in this work involves calculating the rate of W_j of j -type species (molecules·cm⁻³·s⁻¹) generated from a matrix with k -type molecules according to Eq. (1) [21]:

$$(1) \quad W_j = \Sigma G_{jk} \cdot I \cdot \rho_k / \rho$$

where G_{jk} is the chemical yield of the j -type species from the k -type matrix following irradiation, also referred to as the G-value or radiation chemical yield; I is the dose rate (in kGy/s); ρ_k is the gas phase density of the matrix (in g/cm³); and ρ is the overall density of the gas phase (in g/cm³) when the dose is expressed in ρ^{-1} ·eV·cm⁻³.

Accordingly, 330 kinetic reactions and 80 kinds of species were included. Most calculations were made in the following gas mixtures: N₂ (80%) + O₂ (20%) + CFC (300–10 000 parts per million [ppm]) + H₂O (300 ppm), respectively. The calculation input values included the following: initial concentrations of O₂, N₂, CF_xCl_y, and H₂O; temperature, pressure, dose rate, and irradiation time.

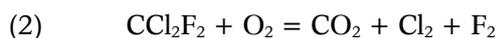
Results and discussion

CFCs such as CF₂Cl₂, CF₃Cl, and CFCl₃ are extensively used as refrigerants and propellants due to their remarkable chemical and photochemical stability, exceptional vaporization temperature (243 K), high latent heat, nontoxicity, and inertness [22–25]. However, their inertness perpetuates their transport as an intact molecule into the stratosphere, where absorption by ultraviolet (UV) photons (>5.5 eV) induces the release of Cl radicals that are involved in a catalytic cycle of decomposition of ozone [26, 27]. Environmentally benign materials, i.e., hydrochlorofluorocarbons (HCFCs) (susceptible to OH attack at the C–H bond), exhibit reduced ozone depletion potential and are therefore preferred in the place of

CFCs [27]. The abstraction of Cl or F from CFCs by the OH radical is endothermic and therefore considered negligible compared to the exothermic abstraction of H in HCFCs. However, there remain reservations about the use of these substitutes.

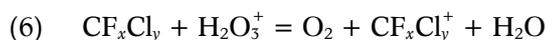
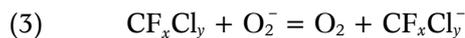
Gas-phase advanced oxidation (GPAO) processes, synonymous with the natural self-cleaning processes occurring in the Earth's atmosphere, generate hydroxyl radicals that initiate the oxidation of pollutants with considerable efficiency. GPAO is energy efficient and applicable to pollutants from diverse sources. Similarly, the low-energy secondary electrons generated by the interaction of cosmic rays with matter in the atmosphere have the potential to influence the chemistry of atmospheric halocarbons [28]. However, their contribution to halocarbon decomposition in the stratosphere is uncertain owing to the low free electron density in the stratosphere because the electrons are quickly captured by abundant molecules, in particular, O₂ [29]. The low-energy electrons transfer rapidly to CFCs, causing dissociation of CFCs to produce chloride ions, and photo-detachment of these chloride ions subsequently yields chlorine atoms that destroy ozone [30].

Complete oxidation of CF₂Cl₂ (CFC-12) in the air can be globally represented by the following process:

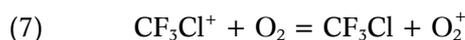


A similar process is implied for the complete mineralization of other CFCs. Photon-induced dissociation is the natural process for the decomposition of CFCs in the troposphere. Similarly, EB bombardment breaks down complex molecular structures and is therefore proposed in the destruction of CFCs and other VOCs in air streams [1, 31, 32]. However, the cross sections for electron-induced dissociation of CFCs are several orders of magnitude higher than those of photon-induced dissociation. Oxidizing free radicals, O₃, ions, and secondary hot electrons are produced by EB irradiation through the dissociation and ionization of the components of air [8]. These reactive species react with pollutants in the air stream, leading to their decomposition.

Hydroxyl radicals, formed through the scavenging of positive ions by H₂O molecules in humid air and thermalized electron precursors of secondary hot electrons, react with molecules present in the air stream [21, 33]. Similarly, charge-transfer reactions are additional major reaction mechanisms. The charge is transferred from the host gas to the constituent gas with the lowest ionization potential (IP). VOCs most frequently have sufficiently lower IP than the donor ions in the air. Nitrogen (15.58 eV) has a considerably higher IP than most VOCs. The energy required to form an ion pair is 33.85 eV, which is higher than the IPs for both nitrogen and oxygen, allowing the formation of ion pairs and excited molecules. Ion pairs undergo charge-transfer reactions with the VOCs, yielding free radicals that react with the excited molecules and form VOC-removal agents, which then react with the VOCs and destroy them. The proposed charge-transfer reactions are as follows, where CF_xCl_y represents the CFCs.



CF₃Cl has an IP of 12.6 eV; therefore, the charge-transfer reaction with O₂⁺ (12.06 eV), as portrayed in Eq. (4), is unlikely. However, CF₃Cl⁺ will transfer the charge to O₂ according to Eq. (7):



Most of the negative ions formed following the impact of low-energy electrons with CFCs (CF₂Cl₂, CF₃Cl, and CFCl₃) are a result of the dissociative attachment process [34–36]. Experiments using CCl₄ suggest dissociative electron attachment (DEA) as the initiating decomposition mechanism in the context of chlorinated methanes. EB destruction of dilute concentrations of trichloromethane (CHCl₃) in air yielded similar results. The attachment of electrons to molecules can occur through both non-dissociative attachment and dissociative attachment mechanisms [37]. Fast electrons have a limited penetration range in matter and are therefore preferable in the processing of low-density gases (three orders of magnitude lower than that of liquids or solids). The energy of electrons determines their penetration range; in air, 1 MeV, 3 MeV, and 10 MeV electrons penetrate 405 cm, 1400 cm, and 4200 cm, respectively. Electrons dissipate their energy through interactions with the orbital electrons of light nuclei within the medium, causing ionization or excitation along the electron track and eventually forming secondary electrons [2]. Based on calculated and experimental results, Gal *et al.* [38] deduced that high-energy plasma electrons' encounter with CFC was responsible for its decomposition rather than energy transfer from electronically excited species. The corresponding rates for DEA are presented in Table 1. Thermal electron-induced dissociation of CFCs via DEA is represented by Eq. (8):



where *x* and *y* represent the number of F and Cl atoms, respectively; *x* + *y* = 4, and *z* = *y* - 1. CF_xCl_y = CFCl₃, CF₂Cl₂, CF₃Cl and CF_xCl_z^{*} are the corresponding halomethyl radicals following DEA. The capture of low-energy electrons results in a negative ion resonance that dissociates into neutral and negatively charged fragments. The dissociation can be initiated by 0 eV electrons owing to the high electron affinity of halogens and, conversely, large cross sections (E) for DEA even at zero electron energy. This efficiently produces halogen anions, halogen atoms, or halogen-containing radicals, which are important precursors for further reactions. The DEA reaction of CFCs produces a halomethyl

Table 1. Reaction rates at 298 K of different reactive species with selected chlorofluorocarbons and IP (in electronvolts)

Compound	e_{thr}^- ($\text{cm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$)	OH ($\text{cm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$)	O(^1D) ($\text{cm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$)	IP (eV)	References
CFCl ₃	2.40×10^{-7}	4.79×10^{-18}	2.00×10^{-10}	11.77 ± 0.02	34, 39–41
CF ₂ Cl ₂	1.90×10^{-9}	6.93×10^{-18}	1.40×10^{-10}	12.05 ± 0.24	29, 34, 41
CF ₃ Cl	4.20×10^{-13}	7.01×10^{-18}	4.00×10^{-10}	12.60 ± 0.20	34
CF ₄	Not available	2.00×10^{-18}	1.40×10^{-16}		

radical with Cl⁻ as the dominant anion formed [29, 42]. It is difficult to decompose CF₄ in nonthermal plasma because the electron energy is too low to break the C–F bond. However, this has been achieved in thermal plasma [43].

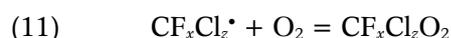
The electron cross sections for CFCl₃, CF₂Cl₂, and CF₃Cl between 0.6 eV and 50 eV have positive electron affinities and efficiently capture low-energy electrons. The cross sections are in the following order: CFCl₃ > CF₂Cl₂ > CF₃Cl [17]. The OH radical and the O radical are produced from humid air through the dissociation and/or excitation of N₂ and O₂ molecules by EB irradiation [8]. Hydroxyl ($\cdot\text{OH}$) radical reactions may be an additional sink for fluorocarbons in the troposphere and stratosphere [44]. Additionally, reactions with Cl atoms in the troposphere can remove these molecules. Cl radicals, in addition to the OH radicals produced in humid air, have been reported to accelerate the degradation of trichloroethylene in both humid and dry air [21, 45]. CFCs may be removed from the stratosphere by their reaction with O₂, and gas-phase reactions with the first excited state of oxygen, namely, O(^1D). The sum of the rates of DEA, OH reaction, and O₂ reaction determines the rate of removal of these species [46].

As already discussed, in contrast to the stratosphere, where UV photolysis is the initiating reaction for CFC decomposition, under EB treatment, DEA is the predominant reaction leading to the formation of halomethyl radicals as in Eq. (8). Additionally, the rate constants for the reaction of hydroxyl radicals with CFCs have been reported previously [40].



Similar observations have been made in the photolysis and oxidation of single-carbon CFCs, which produce halomethyl radicals that are further oxidized to release Cl atoms that react to destroy ozone.

The carbon-centered halomethyl radical (CF_xCl_z \cdot) is oxidized to form a halomethyl peroxy radical. Reactions with tropospheric oxidants, such as NO₃ and O₃, are very slow and therefore insignificant [44, 46, 47]. Due to the relative abundance of oxygen (O₂) in the atmosphere, reactions between the halomethyl radical and molecular oxygen are the predominant reactions [48].



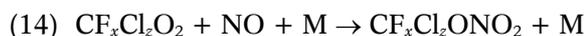
In the stratosphere, halomethyl peroxy radicals react mainly with NO and NO₂, leading in the first case to the formation of the halomethoxy radical [26]. Therefore, under high-NO_x conditions, CF_xCl_zO₂ radicals predominantly react with NO to form a halogenated alkoxy radical (CF_xCl_zO).



Another possible reaction involving NO would lead to the formation of CF₂O (reactions involving CF₂Cl) or COFCl (reactions involving CFCl₂). The halomethoxy radical releases a chlorine atom. It is also suggested that an exothermic unimolecular decay of CF₂ClO would lead to the CF₂O being in an excited vibrational state.



The formation of a halogenated nitrate is a minor channel for small molecules (<C3):



The reaction with NO₂ leads directly to the formation of a stable product, namely, CF_xCl_zOONO₂ [44, 48, 49]:



The generated peroxyxynitrate, CF_xCl_zOONO₂, is a temporary reservoir for the reactive halogen and NO_x. The CF_xCl_zOONO₂ molecule decomposes back to the reactants by cleavage of the weak O–O bond. In the atmosphere, the lifetime of CF_xCl_zOONO₂ is dependent on its thermal decomposition and UV photolysis governed by temperature and pressure.



The literature further alludes to the further decomposing of the carbonyl fluoride (CF₂O) and phosgene/carbonyl chloride (COCl₂) products formed to form carbon dioxide, fluorine gas, or chlorine gas [41]. The scheme for the destruction of CFCs can be diagrammatically represented as in Fig. 1.

Degradation products

Figures 2–4 show the simulated decomposition of CFCl₃, CF₂Cl₂, and CF₃Cl respectively under EB irradiation in air and the by-products of the process. According to the schematic in Fig. 1, the degradation products of CFCl₃, CF₂Cl₂, and CF₃Cl decomposition under a simulated O₂–N₂ atmosphere were predicted to be COFCl, COF₂, and COCl₂, similar to products from laboratory experiments reported in the literature [25]. These would undergo further degradation to form Cl₂, F₂, and CO₂. However, in the present simulation, owing to the less-ideal efficiency (34% and 7%), only COFCl and COF₂ could be determined

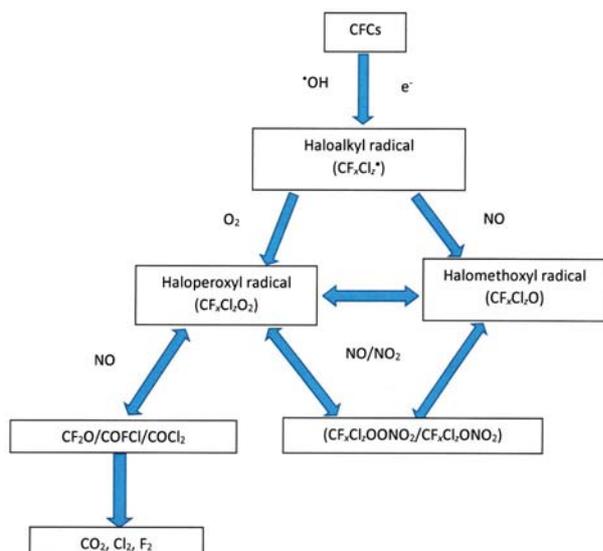


Fig. 1. Schematic diagram for the degradation of chlorofluoromethanes under electron beam treatment in wet air ($\text{N}_2\text{-O}_2$).

for CFCl_3 and CF_2Cl_2 degradation under EB irradiation (Figs. 2 and 3), alongside Cl_2 gas.

The amount of ozone produced by the EB can be mitigated using catalysts [19, 50, 51]. Increased buildup of ozone was observed in the simulated destruction of CF_2Cl_2 and CF_3Cl (Figs. 3 and 4, respectively) compared to the CFCl_3 simulation.

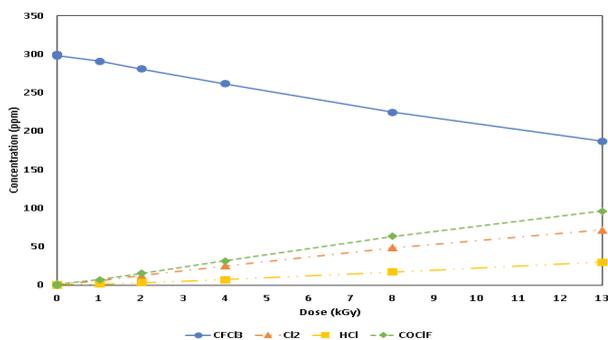


Fig. 2. Degradation of 300 ppm CFCl_3 under an electron beam in humid air: $\text{O}_2\text{-N}_2 = 1:4$, $\text{H}_2\text{O} = 300$ ppm.

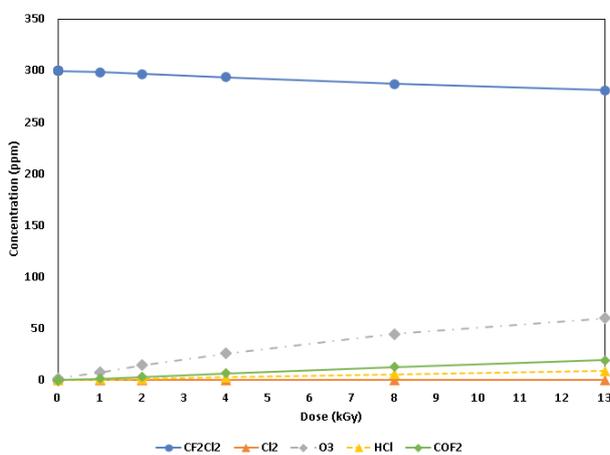


Fig. 3. Degradation of 300 ppm CF_2Cl_2 under an electron beam in humid air: $\text{O}_2\text{-N}_2 = 1:4$, $\text{H}_2\text{O} = 300$ ppm.

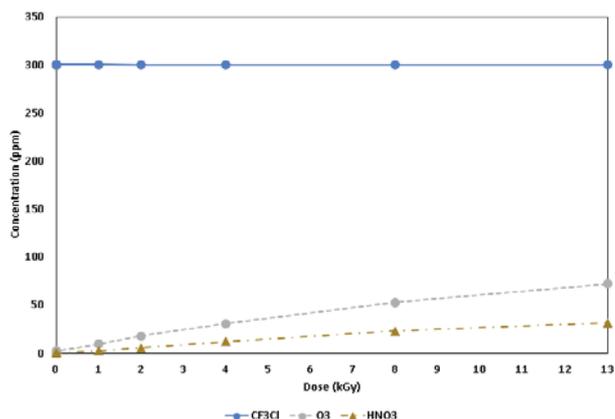


Fig. 4. Degradation of 300 ppm CF_3Cl under an electron beam in humid air: $\text{O}_2\text{-N}_2 = 1:4$, $\text{H}_2\text{O} = 300$ ppm.

Effects of target pollutant concentration

With increasing concentrations of the target compounds, the removal efficiency dropped. For CFCl_3 , the removal efficiency dropped from 37% at 300 ppm to $<5\%$ at 2000 ppm. Similar observations were made for the other CFCs at different concentrations. However, as can be seen in Figs. 5a–5c, the removal efficiency increased with the absorbed dose. Similar observations in simulations involving aromatic VOCs have been made. Chlorinated aliphatic substances and VOCs have shown better degradation efficiencies compared to nonchlorinated adducts [52–54].

Effects of water concentration

Humidity has been reported to have a positive effect on the decomposition of organic pollutants during EB treatment. Hydroxyl radicals produced from radiolysis of wet air ($\text{H}_2\text{O} \rightarrow \text{OH} + \text{H}$) increase with increasing humidity and facilitate the degradation process.

Experiments in humid air and dry air have shown similar tendencies, with higher doses achieved in the humid air as compared to the results in dry air [8, 9, 21, 55, 56]. From the simulation, it was observed that the contribution of the DEA reaction to the degradation of CFC increased with increasing water concentration, whereas the contribution of charge-transfer reactions decreased. Penetrante *et al.* concluded that in humid mixtures, the $\cdot\text{OH}$ oxidation only becomes significant after the depletion of secondary electrons available and therefore DEA will be the more preferred decomposition process [57].

Electron impact ionization rates have been reported to increase with increasing humidity in atmospheric pressure plasma jets. However, a decline in the formation of reactive oxygen and nitrogen species with increasing humidity has been also reported. N_2^+ ions react with H_2O ($\text{IP} = 9.9$ eV) to form H_2O^+ , which would reduce the charge-transfer reactions targeting CFCs. Additionally, the depletion of high-energy electrons by inelastic collisions with H_2O decreases the rate of electron impact excitation of N_2 [58, 59]. Humidity has been found to have

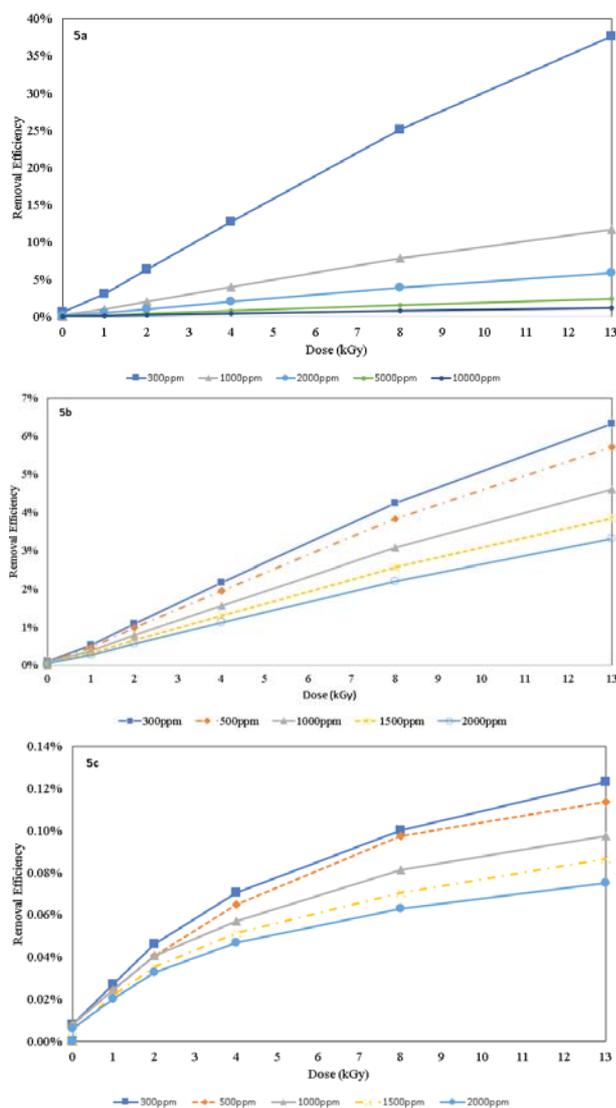


Fig. 5. Effect of pollutant concentration on its removal efficiency in the air under EB irradiation: (a) CF₂Cl₂, (b) CF₂Cl₂, and (c) CF₃Cl.

a negative impact on the decomposition of CCl₄. A similar slight suppression was observed for CF₂Cl₂ (Fig. 7a). Additionally, humidity enhances the attachment of electrons to O₂, which subsequently decreases the decomposition efficiency of CCl₄.

The addition of water vapor during EB decomposition of aromatic VOCs in batch and flow systems in previous studies resulted in a 5–10% and 15–20% increase, respectively, in decomposition efficiencies [10]. In the current simulation, the effect of water concentration on the decomposition of CFCl₃ (Fig. 6), CF₂Cl₂, and CF₃Cl (Fig. 7) was observed to be negligible. Rate constants for reactions of the hydroxyl radical with the investigated CFCs were in the order of 10⁻¹⁸. Hydroxyl radical is considered to play an important role in the removal reaction of chlorinated VOCs [52, 60, 61]; the rate constants for reactions of the hydroxyl radical with the chlorinated VOCs were in the order of 10⁻¹². It is also reported that in humid air, comparatively lower doses are needed to obtain the desired removal efficiency, as opposed to dry air, for the same initial

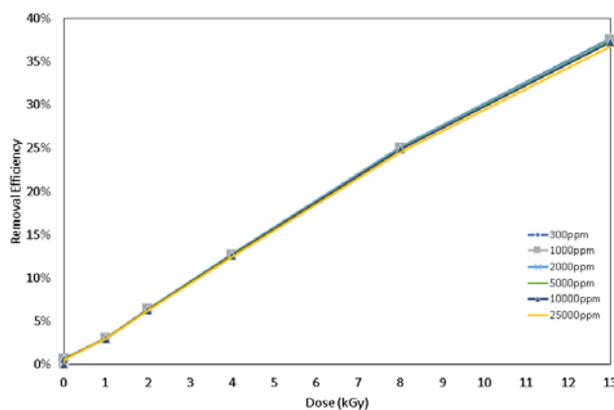


Fig. 6. Effect of increasing humidity (water concentration) on the removal efficiency of 300 ppm CF₂Cl₂ under EB irradiation in simulated air.

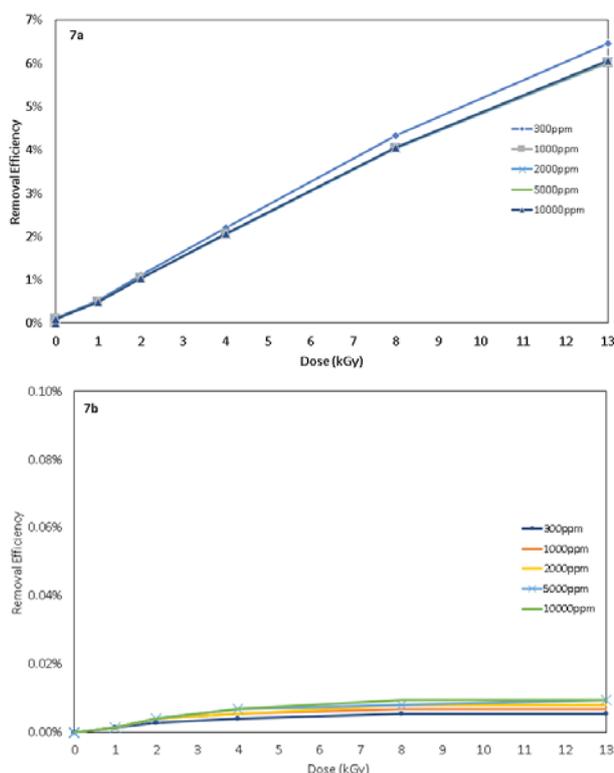


Fig. 7. Effect of water concentration on the removal efficiency of 300 ppm CF_xCl_x in simulated air under EB irradiation: (a) CF₂Cl₂, (b) CF₃Cl.

concentrations of pollutants [21]. Both the dose rate and water vapor in humid air are believed to significantly influence the degradation efficiency of chlorinated VOCs under EB treatment.

Effects of dose rates

The removal efficiency for the carbon-centered halo-methane is predicted to decrease with an increasing dose rate. From the literature, this is attributed to the recombination of radicals with an increase in the rate of their formation. In this simulation, dose rates of the system were increased and removal efficiency of CFC was collected after a dose of 13 kGy had been achieved. Figure 8 shows the decrease in removal efficiency with increasing dose rates.

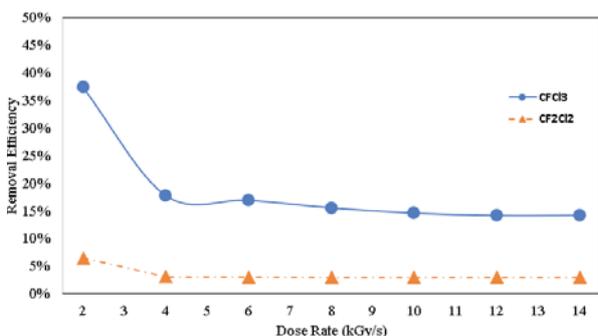


Fig. 8. Predicted effect of dose rates on the removal efficiency of 300 ppm CFC at 13 kGy absorbed dose.

Effects of oxygen concentration

Oxygen has large cross sections for low-energy electrons in the atmosphere [29], and being more abundant, it impedes the availability of low-energy electrons to react with atmospheric CFCs. A similar decrease in degradation efficiency was observed by other researchers [25]. The decomposition of CHF₃ and CHClF₂ was found to decrease with increasing O₂ concentration in nonthermal plasma decomposition of halides under an O₂-N₂ atmosphere with increased CO₂ generation as the O₂ concentration increased. Similar decreases in efficiency with increasing O₂ concentration according to Figs. 9a and 9b were observed during the current simulation.

In the presence of O₂, O[•] radicals are generated by a reaction of the O₂ molecule with an electron, leading to the formation of O₃. Therefore, a significant portion of the input energy is consumed for the

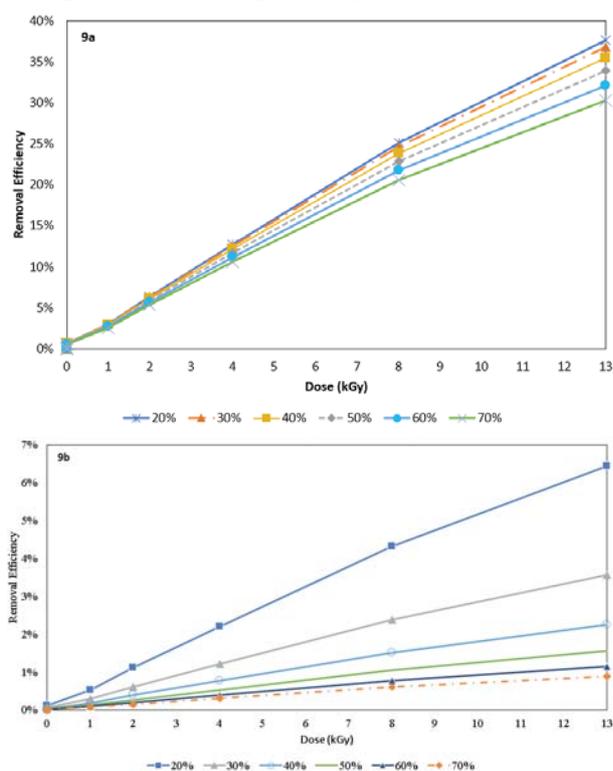


Fig. 9. The removal efficiency of 300 ppm CFCl₃ (a) and CF₂Cl₂ (b) decreases progressively with increasing O₂ concentration (from 20% to 70%), N₂ is the remaining gas.

excitation and dissociation of O₂ molecules, which leads to a decrease in the decomposition efficiency of halide gases [25, 43].

Conclusions

Computer simulations have been carried out to demonstrate the degradation of CFCs using EB treatment. The degradation of chlorofluoromethanes is dependent on the number of chlorine atoms attached to the carbon. Based on already conducted research and the simulation results presented herein, the order of degradation efficiency of chlorofluoromethanes under EB treatment is CCl₄ > CFCl₃ > CF₂Cl₂ > CFCl₃ > CF₄. Under similar irradiation conditions, CFCl₃ had the highest removal efficiency (35%) in simulated conditions (300 ppm H₂O and CFCs, 80% N₂, and 20% O₂, 2.083 kGy·s⁻¹ dose rate, and 13 kGy absorbed dose). Increasing the dose further results in an increase in the removal efficiency. It is also observed that dose rates play a major role in degradation efficiency under EB irradiation. From the simulation, an increase in the dose rates resulted in a drop in the removal efficiency at a target dose (13 kGy) with other conditions maintained. This reaction has been attributed by other researchers to ion recombination reactions. Under humid conditions, no improvements in the removal efficiency were observed, which is attributed to the low rate constants of reactions between hydroxyl radicals and the selected CFCs. The simulation on the effects of O₂ concentrations on degradation efficiency showed that higher O₂ concentrations were accompanied by reduced degradation efficiency, which is attributed to the reaction of the thermal electrons with the more-abundant O₂ molecules, therefore reducing the concentration of thermal electrons available for DEA reactions.

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