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2,4-D Degradation by Electron Beam Irradiation: Influence of Oxygen Concentration

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2,4-D (2,4-dichlorophenoxyacetic acid) is a systemic herbicide used for weed control in cereals and crops. It is one of the herbicides most widely used around the world, and it is included in the so called "black list" of selected pesticides that can cause contamination of soils and waters due to its high solubility and persistence (Barceló 1993). In 1982, the World Health Organization considered 2,4-D as moderately toxic (Class Ⅱ) and recommended a maximum 2,4-D concentration of 100 ppb in drinking water. Its microbiological decomposition in fresh water is only practicable for concentrations below 1 ppm (Hoover et al. 1986). For an efficient treatment of natural waters contaminated with pollutants, a lot of advanced oxidation technologies (AOTs) are in use or under study.

High energy electron beam (E-beam) irradiation is emerging as an effective technology for destroying pollutants found in groundwater, industrial wastewaters and other contaminated media (sediments and sludges). This technology involves injecting high energy electrons into aqueous solutions of contaminants. Interaction of the highly energetic electrons and water results in the formation of highly reactive species including the reducing of aqueous electrons (e_{aq}^-), hydrogen atom (H), the oxidizing hydroxyl radical ($OH^\cdot$) and in some cases the molecular product hydrogen peroxide (H_2O_2). These reactive transient species in turn attack the organic solutes resulting in a series of reactions that may involve all of the primary radiation products, and given adequate energy, results in the decomposition of the parent molecules.

In this study, for the first time the effect of E-beam on the degradation of 2,4-D has been investigated. The objective was aimed at the irradiation-induced oxidation of 2,4-D and at the influence of oxygen concentration on the mineralization process.

MATERIALS AND METHODS

2,4-D (99% purity) supplied by Jingjiang pesticide factory in China. All other chemicals used herein were analytical grade or better. Solution of 2,4-D (100 ppm) were made in triple distilled water, used directly or saturated with air or oxygen during irradiation.

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Table 1. Estimated concentration (mM) of transient reactive species arising from high energy irradiation of water

Dose		e_{aq}^-	$H^{\bullet}$	$OH^{\bullet}$	H_2O_2
krad	kGy				
50	0.5	0.13	0.03	0.14	0.03
100	1	0.27	0.06	0.28	0.07
200	2	0.54	0.12	0.56	0.14
300	3	0.81	0.19	0.84	0.21
500	5	1.35	0.30	1.40	0.35

Note: The SI unit for dose is Gray (Gy), 1 rad=0.01Gy, where 1 Gray is defined in J/kg.

Yields of 2,4-D were determined by Hewlett-Packard series 1100; column: Spherisorb ODS 2 RP-18; temperature: 30℃; injection volume: 3μl; flow rate: 1ml/min; eluent H_2O (0.1% w/v phosphoric acid) / CH_3OH = 60/40 v/v; the absorption was measured at 210nm. Aliphatic acids and chloride were determined by Ion Chromatography (Dionex Series 4500i); columns: Dionex Ionpac ASII (4×250mm) and AGII (4×50mm); injection volume: 15μl; flow rate: 2ml/min; gradient: sodium hydroxide from 0.75 to 40 mM.

High energy electron accelerator (9 Mev) is manufactured by accelerator institute in Nanjing University. Total organic carbon (TOC) is determined by SHIMADZU TOC-5000 (made in Japan); pH: JENCO Model 6171 pH meter.

RESULTS AND DISCUSSION

Irradiation of water results in several radicals, ions and molecules and can be described as shown in equation (1) (Spinks And Woods 1990):

$$H_2O \rightarrow [2.6]e_{aq}^- + [0.6]H^{\bullet} + [2.7]OH^{\bullet} + [0.45]H_2 + [0.7]H_2O_2 + [2.7]H_3O^+ \qquad (1)$$

This equation describes the net reaction in pure water 10^{-7} s after an energetic electron has passed through the aqueous solution. The numbers in brackets [*G* values] indicate the relative number of each species formed per 100 eV absorbed energy. The three reactive species/radicals then react among themselves and with other ions and solutes present in water. Table 1 lists the initial concentration of the reactive species arising from irradiation of water. These are based on *G* values shown in equation (1). In addition to the organic solutes, there are other solutes, such as O_2, and Cl^- and reaction byproducts which also compete for the aqueous electrons and the other reactive species (Fei et al 1997).

Exposure of water or 2,4-D aqueous solutions to E-beam leads to the primary species e_{aq}^-, $H^{\bullet}$, $OH^{\bullet}$, H_2, H_2O_2 . In the presence of air (oxygen), the reducing $H^{\bullet}$ and e_{aq}^- are scavenged to form $HO_2^{\bullet}$ and $O_2^{\bullet-}$. Oxygen is further consumed by its addition to carbon centered radicals (in the case of aromatic compounds, these are hydroxycyclohexadienyl radicals, $^{\bullet}OH$-adducts, generated after diffusion controlled $^{\bullet}OH$-addition to the benzene ring system). The resulting isomeric hydroxycyclohexadienyl-peroxylradicals decay mainly by two competing pathways: $HO_2^{\bullet}$ elimination leading to hydroxylation (phenols), and ring fragmentation (aliphatic acids) (von and Schuchmann 1997).

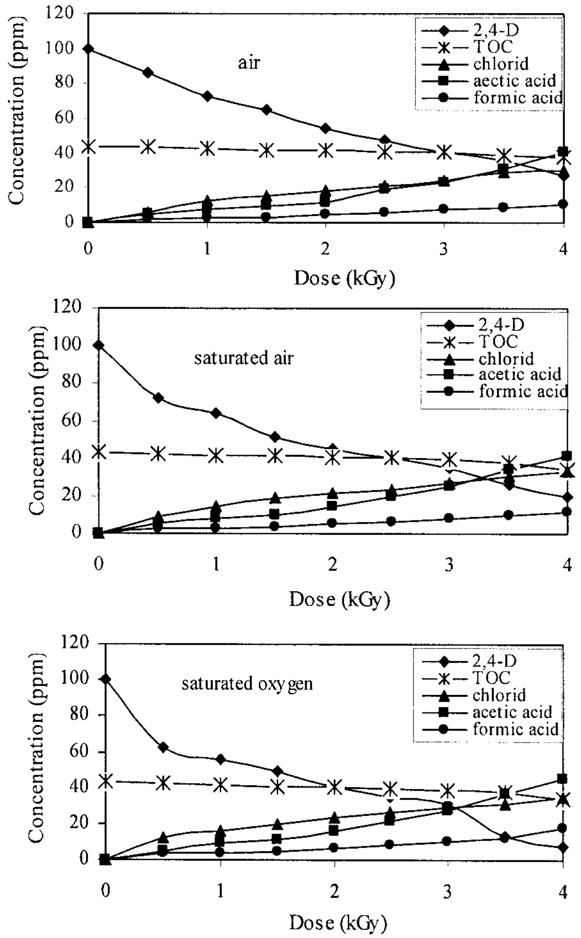

Figure 1. Degradation of 2,4-D and TOC and formation of chloride、 acetic acid and formic acid versus dose at different oxygen concentration. Solutions: 100ppm 2,4-D, pH 9.

2,4-D and TOC degradation and chloride formation at different oxygen concentration is presented as a function of dose in Fig. 1. From Fig. 1, it is observed that the degradation of 2,4-D and TOC increases with the increasing of dose and oxygen concentration. The curve of 2,4-D degradation at three oxygen concentrations is steep, and the amount of 2,4-D degradation is most when the oxygen in solutions is saturated, indicating that 2,4-D can be decomposed by E-beam process and high concentration oxygen accelerates its decomposition. 92.5% of 2,4-D can be removed when the solution is saturated with oxygen, and the irradiation dose is 4 kGy (Fig. 2). From Fig.2, the percentage of 2,4-D removal increases significantly as the oxygen concentration and irradiation dose increase. However in comparison with 2,4-D degradation, TOC degradation is low which indicates that only very small part of 2,4-D was completely mineralized. The percentage of ultimate mineralization is only 0.94-2.5% when the absorbed

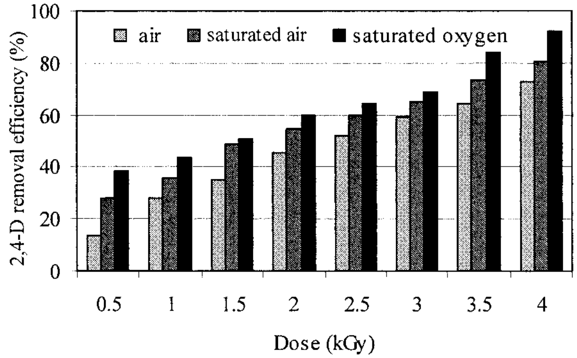

Figure 2. 2,4-D removal efficiency versus dose at different oxygen concentrations.

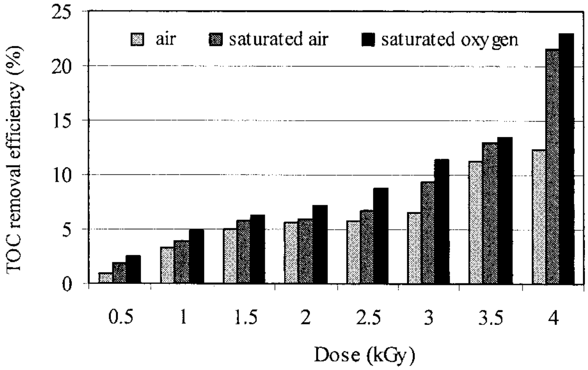

Figure 3. TOC removal efficiency versus dose at different oxygen concentrations.

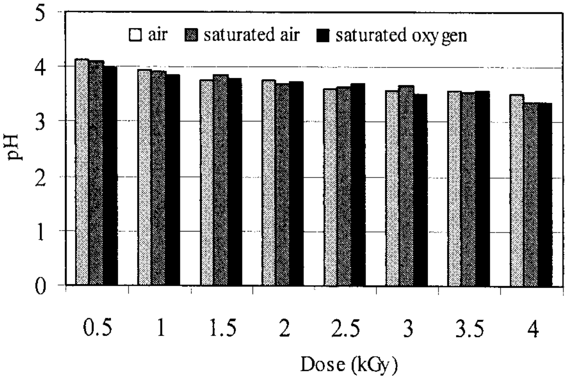

Figure 4. pH values after irradiation versus dose at different oxygen concentrations.

dose is 0.5 kGy, and improves with the dose and oxygen concentration (Fig. 3). The highest TOC removal efficiency achieves 22.9% when the irradiation dose is 4 kGy and oxygen concentration is at saturation. The results show that the oxygen plays a great role during the irradiation. The soluble oxygen in water can rapidly react with e_{aq}^- produced during the irradiation as follows equations (2) and (3):

$$e_{aq}^- + O_2 \rightarrow O_2^- \quad k = 1.9\times10^{10}\ (\mathrm{L\ mol^{-1}\ s^{-1}}) \qquad (2)$$

$$O_2 + H^\cdot \rightarrow HO_2^\cdot \quad k = 2.1\times10^{10}\ (\mathrm{L\ mol^{-1}\ s^{-1}}) \qquad (3)$$

The products O_2^- and $HO_2^\cdot$ can further react with the contaminant and reduce the contaminant concentration. By increasing the level of soluble oxygen in solutions, the reaction processes of (2) and (3) will be intensified and the reaction efficiency can be markedly enhanced. So when oxygen participates in the reaction, the contamination can achieve small part of ultimate mineralization, indicating that the mineralization process has a close correlation with the soluble oxygen level in solution.

Chloride and aliphatic acids were determined by ion chromatography. The production of chloride can reach over 30ppm when the dose is more than 3 kGy at three kinds of oxygen concentration (Fig.1), indicating that many intermediates are produced after irradiation, such as 2,4-DCP, chlorophenols and so on. These intermediates are under validation.

The production of acetic acid starts immediately after irradiation. It increases within a dose of 1 kGy to about 7.65-9.48ppm at different oxygen levels (Fig.1). Compared to 28-44ppm decomposed 2,4-D, almost half of the degraded substrate underwent a cleavage of acetic acid, indicating that its formation results from primary reaction steps. Due to the electrophilic nature of the $^\cdot$OH radicals, the $^\cdot$OH adducts on position 6 of 2,4-D are to be expected as main primary transients. This reaction has to compete with the addition of oxygen. Since hydroxycyclohexadienyl radicals, having electron-withdrawing substituted groups like chlorine or nitrile, have been found to react poorly towards oxygen (Fang et al. 1995), such a competition is conceivable. Acetic acid can compete successfully for $^\cdot$OH radicals only if it is present in high concentration. Reaction of $^\cdot$OH with acetate results partly in decarboxylation. Formic acid represents the last step before mineralization (Buxton et al. 1988, Buxton 1987):

$$HCOO^{\cdot-} + {}^\cdot OH \rightarrow H_2O + CO_2^{\cdot-} \quad k = 3.2\ \times10^{9}/\mathrm{M\ s}. \qquad (4)$$

$$CO_2^{\cdot-} + O_2 \rightarrow CO_2 + O_2^{\cdot-} \quad k = 4.2\ \times10^{9}/\mathrm{M\ s}. \qquad (5)$$

High energy electron irradiation can produce a number of H_3O^+ (Equation 1), leading to the increase of H_3O^+ concentration in water and the sharp decrease of pH (Fig. 4). The pH of system seems independent of the irradiation dose and oxygen concentration, and can reduce to about 4 in all samples.

High energy electron irradiation effectively decomposed 2,4-D in this study. For complete removal of 92.5ppm, a dose of 4kGy was required. At this dose the chloride release was between 30-35.4ppm, and TOC could achieve removal of 22.9%, depending on the oxygen concentration.

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