



Gamma radiolysis of alachlor aqueous solutions in the presence of hydrogen peroxide

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ABSTRACT

The enhanced effect of gamma irradiation with hydrogen peroxide (H₂O₂) for alachlor degradation in an aqueous solution was first investigated in this study. The combination of gamma irradiation and H₂O₂ led to an enhanced effect, which remarkably increased the degradation efficiency of alachlor and the total organic carbon (TOC) removal. At a dose of 200 Gy, the degradation degree of the alachlor solution reached 81.7 and 99.2% under H₂O₂ concentrations of 0 and 0.1 μM, respectively. In addition, the TOC removal efficiencies of the alachlor under initial H₂O₂ concentrations of 0, 0.5 and 1.0 μM were 59.5, 74.8 and 83.8%, respectively, at an absorbed dose of 20 kGy. However, for higher H₂O₂ concentrations (greater than 1 μM), the alachlor degradation was reduced because •OH radicals were scavenged by the H₂O₂. The biodegradability of alachlor solutions prior to and after treatment by gamma irradiation was also assessed using the Closed Bottle Test (CBT). The results showed enhanced biodegradability of alachlor with increasing absorbed doses.

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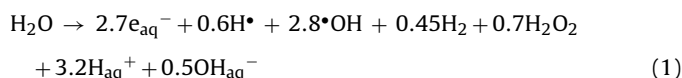
1. Introduction

The increasing production and extensive use of chemical herbicides in agriculture has become an important issue due to their persistent recurrence in various sectors of our environment. The herbicide alachlor (2-chloro-2',6'-diethyl-N-methoxymethylacetanilide) is widely used to control broadleaf and grass weeds in agricultural crops [1,2]. It has been detected from 0.1 to 10 μg/L in groundwater and surface water in the United States, Europe, Japan, and China [3,4]. Due to its toxicity, recalcitrance, and potential adverse health effects, alachlor has been classified as a B2 carcinogen by the U.S. Environmental Protection Agency (USEPA) and is one of the priority substances (PS) listed by the European Commission (EC) [2,3,5]. Alachlor, an extremely toxic endocrine disruptor, has been restricted to a maximum of 2 μg/L in drinking water by the USEPA [3,4,6].

Alachlor is a persistent organic pollutant with high toxicity to many organisms due to its strong aromaticity and high chemical stability. Conventional biological and physico-chemical processes are inadequate for its degradation in contaminated water [2,7]. Therefore, efficient and cost effective treatment methods to remove refractory organic pollutants have been suggested. In recent years, advanced oxidation processes (AOPs) have received significant

attention because they are based on the generation and use of highly reactive hydroxyl radicals (•OH) for the removal of various organic pollutants from water and wastewater [8,9]. Various AOPs, such as ozonation [3], TiO₂ and UV process [10,11], photo-Fenton oxidation [4,5], ferrate oxidation [12], and ultrasonic treatment [13], have been proposed for the removal of alachlor. These processes still have limitations such as low removal efficiency and high operational cost. Gamma irradiation is considered to be an effective process for removal of refractory organic pollutants.

Gamma irradiation has proved to be a promising solution for the degradation of refractory substances such as fluorine [14], methyl tert-butyl ether (MTBE) [15], nitrobenzene [16] and cefaclor [17]. As a consequence of the interaction between the gamma irradiation and the aqueous solution, the primary species (•OH, e_{aq}⁻, and •H) and molecular products (H₂, H₂O₂) are generated according to the following equation [18]:



The numbers in Eq. (1) are the G-values (#species/100 eV) of each species. These reactive species and radicals react with the target compounds and decompose of the solutes present in wastewater. The chemical reactions of the three reactive species (•OH, e_{aq}⁻, and •H), particularly the •OH radicals, are highly reactive and are key importance with regard to gamma radiation and electron beam processes in aqueous solutions. Recently, Da Silva and Vieira [6] reported on their study of radiolytic degradation

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of alachlor in aqueous solution by gamma radiation. The result showed that gamma radiation was effective for alachlor degradation in an aqueous solution. However, a high dose of 5.0 kGy was required for the degradation of alachlor. This called for an innovative means of reducing the absorbed dose for practical use. Thus, we employ the combination process of gamma irradiation and H₂O₂ to enhance alachlor degradation.

This study focused on the combination of gamma irradiation and H₂O₂ as an effective treatment method for the degrading of alachlor found in the environment. The main objectives were (1) to study the degradation kinetics of alachlor; (2) to investigate the enhanced effect of gamma irradiation and H₂O₂ on the radiolytic decomposition and mineralization of alachlor in aqueous solutions; (3) to evaluate the biodegradability of the irradiated solutions after gamma irradiation.

2. Materials and methods

2.1. Chemicals

Alachlor (99.2%, HPLC grade), the structure of which is shown in Fig. 1, was obtained from Sulpelco Inc. (Bellefonte, PA, USA). Hydrogen peroxide (H₂O₂, Showa Chemical Co., Ltd., Japan) was used as a 30% (w/w) solution. Acetonitrile used for HPLC analysis was of HPLC grade and purchased from J.T. Baker (USA). All the solutions were prepared using Milli-Q purified water (Millipore Inc., USA).

2.2. Irradiation sources

Gamma irradiation was performed with a high-activity ⁶⁰Co source (Nordion Inc., Canada) at the Korea Atomic Energy Research Institute (Jeongeup, Korea). The radioactivity of the source was around 9.85×10^{15} Bq (= 266,200 Ci). Aqueous alachlor solutions were irradiated in 15 mL screw-cap-bottles without any headspace. The solutions were prepared 24 h prior to irradiation, sealed with screw caps to avoid contact with air and stored at 4 °C. All the samples were allowed to reach equilibrium at atmospheric pressure and room temperature (20 ± 2 °C) before being irradiated.

2.3. Analytical methods

The concentration of alachlor in the aqueous solution was measured using high performance liquid chromatography, using an Agilent 1200 Series HPLC (Agilent Technologies, Santa Clara, CA, USA), equipped with a UV absorbance detector and a Discovery C18, 5 μm, 150 mm × 4 mm column (Supelco, USA). The eluent consisted of acetonitrile/distilled water (60/40, v/v) and the flow rate was 1.0 mL/min. The wavelength for alachlor was set at 230 nm and

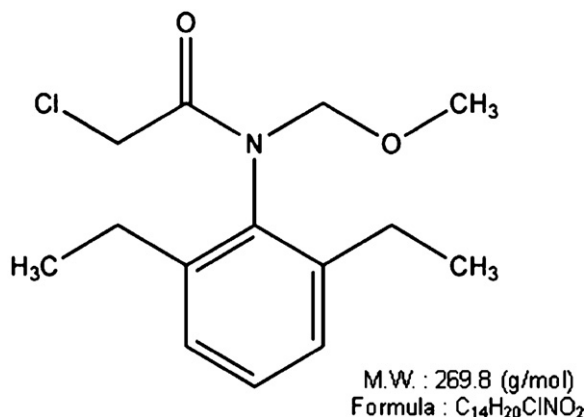


Fig. 1. Chemical structure of alachlor.

the column temperature was kept at 30 °C. The total organic carbon (TOC) in the aqueous samples was determined using a Shimadzu TOC-VCPH analyzer (Shimadzu Co., Japan).

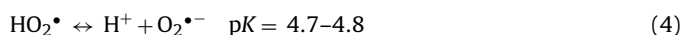
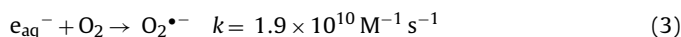
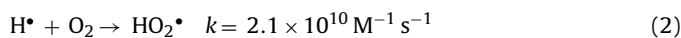
2.4. Biodegradability in the Closed Bottle Test (OECD 301 D)

The CBT (Closed Bottled Test) is recommended as a first, simple test for the assessment of the biodegradability of organic compounds [19]. It was performed with distilled water at room temperature (20 ± 2 °C), according to test guidelines [19]. The inoculum was taken from the effluent of a municipal wastewater treatment plant (Jeongeup, Korea). During the CBT, the incubated alachlor samples were monitored by measuring the oxygen concentration (OxiTop, WTW Weilheim, Germany).

3. Results and discussion

3.1. Degradation kinetics of alachlor

Radiation-induced degradation of organic pollutants is initiated by primary species or radicals such as •OH radicals, e_{aq}⁻ and •H, produced from water radiolysis (Eq. (1)). H₂O₂ and H₂ do not take part in the degradation reactions because of their low reactivity and yields. In the presence of O₂, the reducing species, •H and e_{aq}⁻, are converted into oxidizing species, HO₂• and O₂•⁻, respectively (Eqs. (2)–(4)) [18,20,21].



The concentration of •OH radicals is higher than that of HO₂• and O₂•⁻. Thus, the •OH radicals present in aerated solutions have been shown to contribute significantly to the radiolytic degradation of alachlor.

In this study, alachlor aqueous solutions of 11.5, 18.9, 29.0 and 45.4 μM were irradiated at 0–500 Gy. The results showed that the concentration of alachlor decreased exponentially with the increase of the absorbed doses, indicating that alachlor degradation followed a pseudo-first-order kinetic model, which can be described by the following equations [22,23]:

$$C = C_0 \exp(-dD) \quad (5)$$

$$-\ln \left(\frac{C}{C_0} \right) = dD, \quad (6)$$

where C₀ is the initial concentration of the alachlor before irradiation; C is the concentration after irradiation; d is the dose constant in units of a reciprocal dose; and D is the absorbed dose.

Fig. 2 shows the degradation of alachlor at different initial concentrations with increasing absorbed doses. Alachlor decreased with increasing absorbed dose. For a dose of 150 Gy, the removal efficiencies for initial aqueous alachlor concentrations of 11.5, 18.9, 29.0 and 45.4 μM were 97.7, 91.2, 79.2 and 69.3%, respectively. Fig. 3 and Table 1 show the radiolytic degradation rate constants of alachlor at different initial concentrations, indicating a dependence on the initial alachlor concentration. The dose constant increased with decreasing initial concentrations of alachlor. The relationship

Table 1
Change in dose constant (d) with increasing the initial concentration of alachlor.

[alachlor] ₀ (μM)	Dose constant, d (Gy ⁻¹)	R ²
11.5	0.0242	0.9915
18.9	0.0173	0.9855
29.0	0.0108	0.9980
45.4	0.0084	0.9951

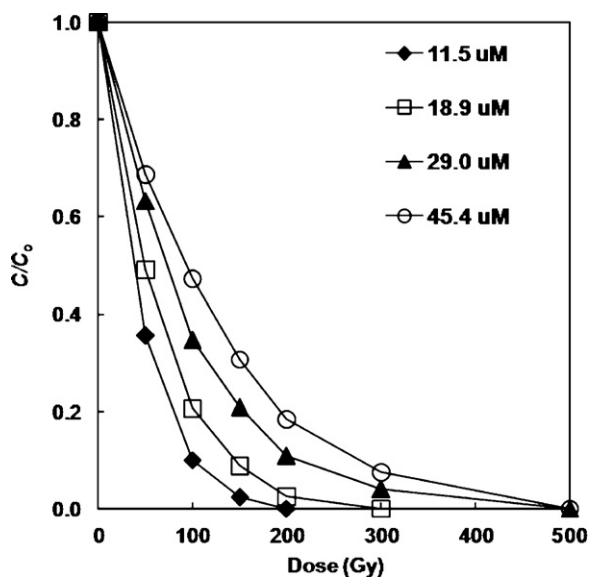


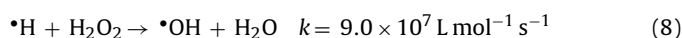
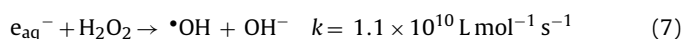
Fig. 2. Radiolytic degradation of alachlor at different initial concentrations with increasing absorbed doses.

between the dose constant and the initial concentrations of the pollutants was also observed in the study of gamma radiolysis for pentachlorophenol by Xue and Wang [23] and of PCB by Mincher

et al. [24]. Therefore, the absorbed dose required to remove the alachlor concentration in aqueous solution under the same experimental conditions can be easily calculated.

3.2. The effect of added H_2O_2 on alachlor degradation

H_2O_2 is a well-known source of $\cdot OH$ radicals, which is widely used to remove refractory organic pollutants in wastewater [25,26]. The effect of H_2O_2 on alachlor ($40 \mu M$) degradation was investigated for the different absorbed doses. Fig. 4 shows the concentration of residual alachlor as the efficacy of the concentration of H_2O_2 on the absorbed doses. The concentrations of added H_2O_2 were varied from 0 to $10 \mu M$. As shown in Fig. 4, the residual alachlor concentration had decreased significantly as the concentration of H_2O_2 increased up to $1.0 \mu M$, but as more H_2O_2 was added, the residual alachlor concentration gradually increased. H_2O_2 can react with the e_{aq}^- and $\cdot H$ produced by the water radiolysis (Eq. (1)), converting them into more $\cdot OH$ radicals, as shown in Eqs. (7) and (8) [26,27].



Thus, the combination of H_2O_2 with gamma radiation could significantly enhance the degradation of alachlor. However, further increase of H_2O_2 ($>1.0 \mu M$) could compete with organic compounds for $\cdot OH$ radicals (Eqs. (9) and (10)) and therefore increase the resid-

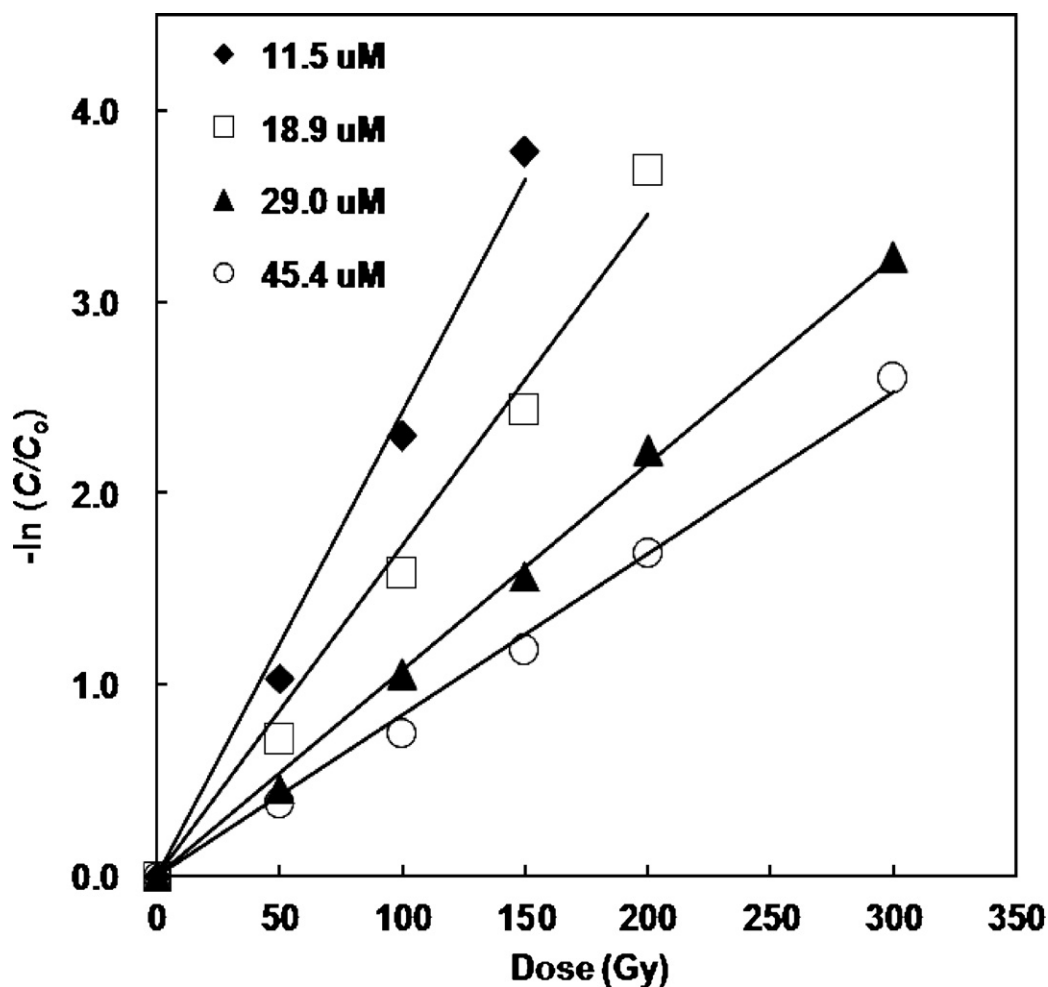


Fig. 3. Initial concentration dependency of the radiolytic degradation rate constant (dose constant) by gamma irradiation.

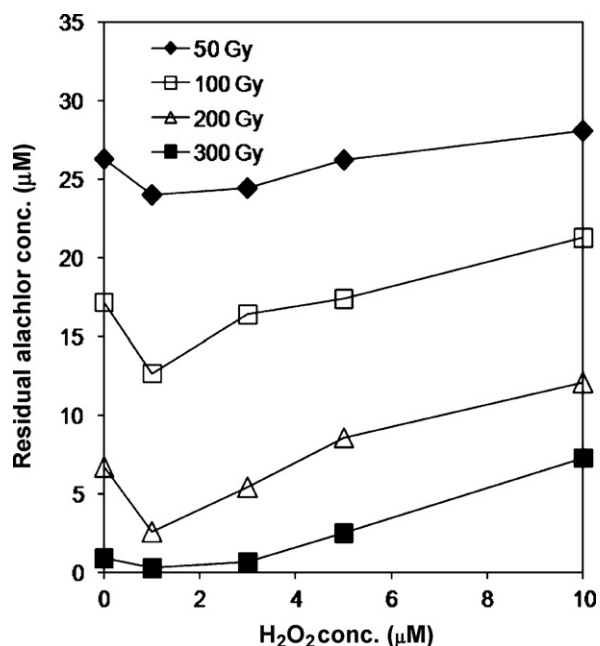
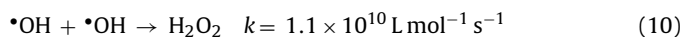
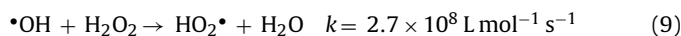


Fig. 4. Residual alachlor after gamma irradiation with H_2O_2 ($[\text{alachlor}]_0 = 40 \mu\text{M}$, $[\text{H}_2\text{O}_2]_0 = 0\text{--}10 \mu\text{M}$).

ual concentration of alachlor (Fig. 4) [26,28].



The relationship between gamma radiation and H_2O_2 on the degradation effect of the target organic pollutants (*p*-nitrophenol, dyes (red KE-3B and blue XBR)) has been reported previously by Yu et al. [29] and Wang et al. [27]. The radiolytic degradation efficiencies of the pollutants increased with the increasing initial H_2O_2 concentration, consistent with our experimental results. However, an optimal ratio of H_2O_2 concentration for alachlor degradation was observed in our study. When H_2O_2 concentration exceeds the optimal ratio, it could play an important role as a $\bullet\text{OH}$ radical scavenger as shown in Eqs. (9) and (10).

3.3. TOC removal of alachlor

In order to investigate the effects of H_2O_2 on the mineralization of alachlor by gamma irradiation, the TOC values of the irradiated solutions were analyzed. Fig. 5 shows the TOC removal with increasing absorbed doses at different initial H_2O_2 concentrations. When the initial H_2O_2 concentrations were in the range of 0–1.0 μM , more TOC was removed as the concentration of H_2O_2 increased. For an absorbed dose of 20 kGy, the TOC removal rates from the alachlor solutions with initial H_2O_2 concentrations of 0, 0.5 and 1.0 μM were approximately 59.5, 74.8 and 83.8%, respectively. When irradiated with the same absorbed doses, a higher H_2O_2 concentration in the solution showed more effective TOC removal efficiency. Similar results were reported for the TOC removal of chlorophenols [25] and *p*-nitrophenol [29]. As shown in Eqs. (7) and (8), this could be due to H_2O_2 promoting the mineralization of alachlor. However, the TOC in the irradiated alachlor solutions with different initial H_2O_2 concentrations was not completely removed even for an absorbed dose of 20 kGy (Fig. 5). Li et al. [3] and Qiang et al. [30] reported that organic acids such as formic, acetic, oxalic and propionic acid were produced as organic by-products after degradation of alachlor by $\text{O}_3/\text{H}_2\text{O}_2$ and O_3 . It is suggested that the reduction of the TOC removal efficiency could be due to the

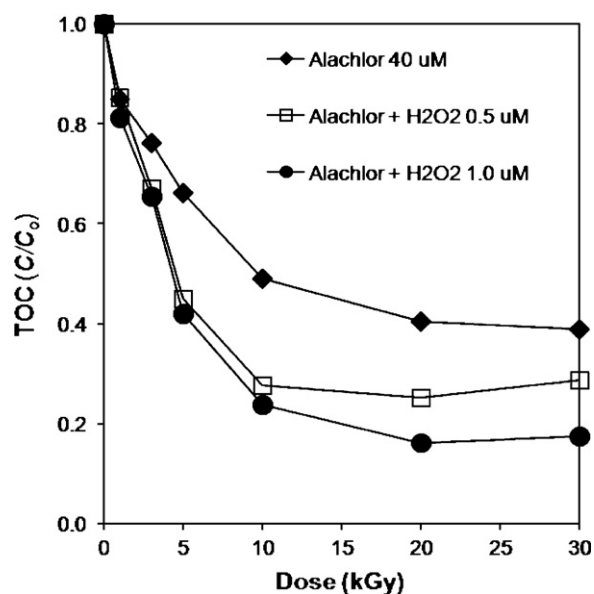


Fig. 5. TOC removal efficiencies of alachlor (40 μM) with increasing absorbed doses at different initial H_2O_2 concentrations.

remaining organic by-products produced from the alachlor decomposition. These by-products were not completely mineralized.

3.4. Biodegradability of alachlor

The biodegradability of alachlor solutions (40 μM) prior to and after treatment by gamma irradiation was assessed according to the CBT (Closed Bottled Test). Aqueous solutions of 40 μM alachlor were irradiated with doses of 0, 200, 400 and 1000 Gy, and the biodegradability results are shown in Fig. 6. Note that 'Control' of Fig. 6 says 40 μM alachlor solutions without inoculums. As shown in Fig. 6, the tested alachlor was readily biodegraded in the CBT and the biodegradability of the irradiated solutions were enhanced as the absorbed doses were increased. The irradiated alachlor solutions had been biodegraded by 63.1–72.0% during the test period of 28 days. Thus, they can all be classified as readily biodegradable. Torres

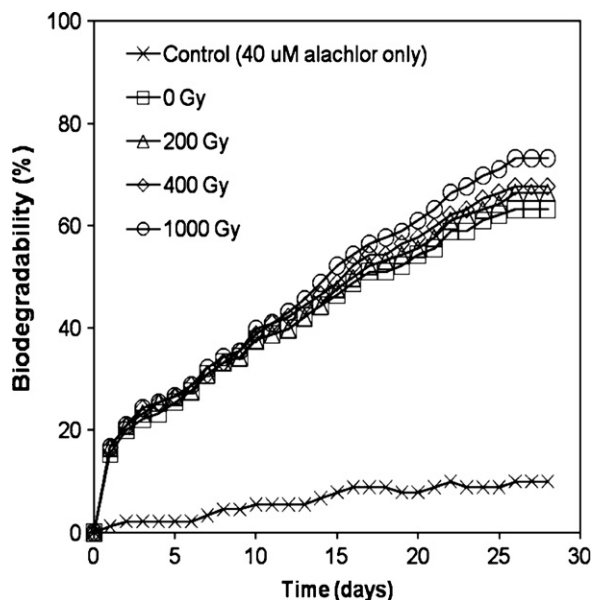


Fig. 6. Biodegradability of alachlor aqueous solutions (40 μM) irradiated by gamma irradiation; 'Control': 40 μM alachlor solutions without inoculum.

et al. [13] also reported that the biodegradability test (BOD₅/COD) results showed a significant enhancement in the biodegradability of the alachlor solution after ultrasonic treatment. Therefore, our experimental results indicate that the gamma irradiation process transforms alachlor into more biodegradable and less toxic by-product.

4. Conclusions

Based on the experiments on the radiolytic degradation of alachlor and on the effect of H₂O₂, we can conclude this study with the following points:

- (1) Alachlor was effectively degraded by gamma irradiation. Its degradation followed pseudo-first-order kinetic model, and the dose constant *d* increased with decreasing initial concentrations of alachlor.
- (2) An enhanced effect was found on the degradation of alachlor by gamma irradiation with H₂O₂. However, increasing the initial concentration of H₂O₂ in the solution reduced the alachlor degradation efficiency because H₂O₂ acted as a scavenger of the •OH radicals at high H₂O₂ concentrations.
- (3) In the presence of H₂O₂, the removal efficiency of TOC was enhanced significantly as the absorbed dose was increased. At an absorbed dose of 20 kGy, TOC removal efficiency of the alachlor with initial H₂O₂ concentration of 1.0 μM was approximately 83.8%.
- (4) The biodegradability of irradiated alachlor samples was enhanced with increasing absorbed doses, indicating that a significant portion of the non-biodegradable alachlor is transformed into biodegradable by-products by gamma irradiation.

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