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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 (H_2O_2) for alachlor degradation in an aqueous solution was first investigated in this study. The combination of gamma irradiation and H_2O_2 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 H_2O_2 concentrations of 0 and 0.1 μM, respectively. In addition, the TOC removal efficiencies of the alachlor under initial H_2O_2 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 H_2O_2 concentrations (greater than 1 μM), the alachlor degradation was reduced because $^{\bullet}OH$ radicals were scavenged by the H_2O_2. 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.

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, a 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 ($^{\bullet}OH$) for the removal of various organic pollutants from water and wastewater [8,9]. Various AOPs, such as ozonation [3], TiO_2 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 ($^{\bullet}OH$, e_{aq}^{-}, and $^{\bullet}H$) and molecular products (H_2, H_2O_2) are generated according to the following equation [18]:

$$H_2O \rightarrow 2.7e_{aq}^{-} + 0.6H^{\bullet} + 2.8^{\bullet}OH + 0.45H_2 + 0.7H_2O_2 + 3.2H_{aq}^{+} + 0.5OH_{aq}^{-} \quad (1)$$

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 ($^{\bullet}OH$, e_{aq}^{-}, and $^{\bullet}H$), particularly the $^{\bullet}OH$ 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 H_2O_2 to enhance alachlor degradation.

This study focused on the combination of gamma irradiation and H_2O_2 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 H_2O_2 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 (H_2O_2, 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 ^{60}Co 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 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).

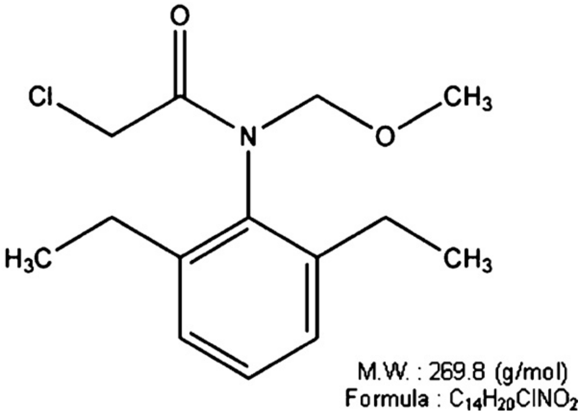

Fig. 1. Chemical structure of alachlor.

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 $^{\bullet}$OH radicals, e_{aq}^- and $^{\bullet}$H, produced from water radiolysis (Eq. (1)). H_2O_2 and H_2 do not take part in the degradation reactions because of their low reactivity and yields. In the presence of O_2, the reducing species, $^{\bullet}$H and e_{aq}^-, are converted into oxidizing species, $HO_2^{\bullet}$ and $O_2^{\bullet -}$, respectively (Eqs. (2)–(4)) [18,20,21].

$$H^{\bullet} + O_2 \rightarrow HO_2^{\bullet} \quad k = 2.1 \times 10^{10}\,M^{-1}\,s^{-1} \tag{2}$$

$$e_{aq}^- + O_2 \rightarrow O_2^{\bullet -} \quad k = 1.9 \times 10^{10}\,M^{-1}\,s^{-1} \tag{3}$$

$$HO_2^{\bullet} \leftrightarrow H^+ + O_2^{\bullet -} \quad pK = 4.7\text{–}4.8 \tag{4}$$

The concentration of $^{\bullet}$OH radicals is higher than that of $HO_2^{\bullet}$ and $O_2^{\bullet -}$. Thus, the $^{\bullet}$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]:

$$C = C_0 \exp(-dD) \tag{5}$$

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

where C_0 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.

$[\text{alachlor}]_0$ (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