Modeling of Radiolytic Degradation of Cefaclor by Ionizing Energy

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1. Introduction

Recently, many researches have been conducted on the treatments of antibiotics found in groundwater, surface water, and wastewater. Ingerslev et al. [1] showed that antibiotics under aerobic and anaerobic conditions were not readily biodegradable. Advanced oxidation processes (AOPs) have been suggested in recent years as a suitable alternative for the removal of refractory organic compounds found in a variety of environment. AOPs by using free radicals such as the hydroxyl radical (·OH) include ozone, ozone/UV, TiO_2 photo catalysis, fenton's reaction, H_2O_2/UV, H_2O_2/O_3 and ionizing radiation [2, 3, 4].

Herein are reported the results of the radiolytic degradation of cefaclor. This study focused on the use of gamma radiation as an AOP for the complete mineralization of antibiotics. Among the many kinds of antibiotics, the target antibiotic in this study was cefaclor, which a β–lactam antibiotic widely used for the medical treatment of microbial infective diseases.

The objectives of this study were: 1) to investigate the decomposition and mineralization of cefaclor using gamma irradiation; 2) to study the decomposition kinetics of cefaclor; and 3) to simulate radiolytic decomposition of cefaclor with experimentally measured kinetic parameters.

2. Methods and Results

2.1 Irradiation Source

Gamma irradiation were performed with a high-level ^{60}CO source (Nordion Inc., Canada) at the Korea Atomic Energy Research Institute (Jeongup, Korea). The radioactivity of the source was around 1.47 X 10^{17} Bq (= 397949 Ci). Aqueous antibiotics solutions were irradiated in 50 mL screw cap bottles and 2 mL septa-capped vial without any headspace. The solutions were prepared 24 hrs prior to irradiation and stored at 4℃. All the samples were prepared in equilibrium with an atmospheric pressure and room temperature (22℃±2) before irradiated, and were sealed with screw caps to avoid the contact with air.

2.2 Analytical Methods

Cefaclor concentrations in the aqueous samples were determined using high performance liquid chromatography (HPLC), using an Agilent 1200 Series HPLC (Agilent Technologies, Santa Clara, CA, USA), equipped with an UV absorbance detector operated at 254 nm. Separation of cefaclor was achieved using a Phenomenex Syrnergi 4μ Polar-RP column (150 × 4.6 mm), with 20 mM ammonium formate adjusted to pH 3.5/methanol (65:35 ratio) as an eluent, at a flow rate of 1.0 mL/min.

2.3 Model Development

The models were solved using STELLA (isee systems) using independently measured kinetic parameters and compared with the experimental data.

2.4 Decomposition of Cefaclor by Gamma Irradiation

A typical decomposition curve of cefaclor by gamma radiation is shown in Figure 1. Experiments were conducted in quintuplicate to ensure the reproducibility of the kinetic results for each tested dose. Aqueous solutions of 30 mg/L cefaclor were irradiated with doses of 0, 100, 200, 300, 400, 600, 800 and 1000 Gy in batch bottles, without any head space (total volume = 150 mL). As shown in Figure 1, the cefaclor concentrations decreased with increasing absorbed dose. Thirty mg/L of cefaclor was completely degraded after 1000 Gy of irradiation.

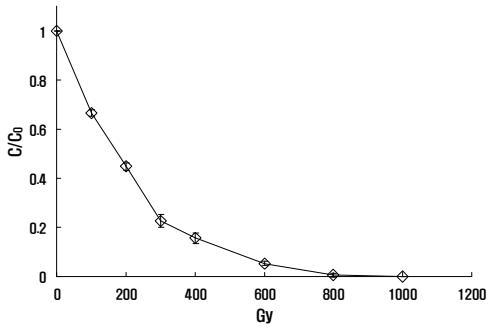

Fig1. Radiolytic decomposition of cefaclor in an aqueous solution (= 30mg L^{-1}) using gamma radiation.

2.5 Kinetic Study for a Radiolytic Decomposition of Cefaclor

In most radiolytic decompositions, the concentration of the targeted organic compound decreases exponentially with the absorbed doses, as shown in Figure 2, which can be represented by equation (1) [5, 6].

$$C = C_0 e^{-kD} \quad (1)$$

where C is the aqueous concentration of cefaclor after irradiation, C_0 the initial concentration of cefaclor, k the

dose constant in reciprocal dose rather than reciprocal time units, and *D* the absorbed dose.

Figure 2 shows the results of the radiolytic decomposition of cefaclor at different initial aqueous concentrations. The kinetic experiments were performed in duplicate, which revealed almost identical results. At lower concentrations, the decomposition rates (based on C/C_0) were faster, as shown in Figure 2 (a). More than 90% of the initial cefaclor concentrations were degraded with less than 600 Gy. All the experimental data (Figure 2 (b)) fitted the pseudo first-order reaction model, and showed statistically reliable results (R^2 values higher than 0.995). Figures 2 (b) and (c) show that the dose constants increased with lower initial cefaclor concentrations, which was consistent with the findings for the radiolytic decomposition of the individual PCB congeners of Mincher et al. [7] and TNT of Lee and Lee [5]. As shown in Figure 2 (c), a strong initial concentration dependency on a dose constant can be expressed in the form of a power function: $k = 0.0815C_0^{-0.9255}$, with R^2 = 0.9955.

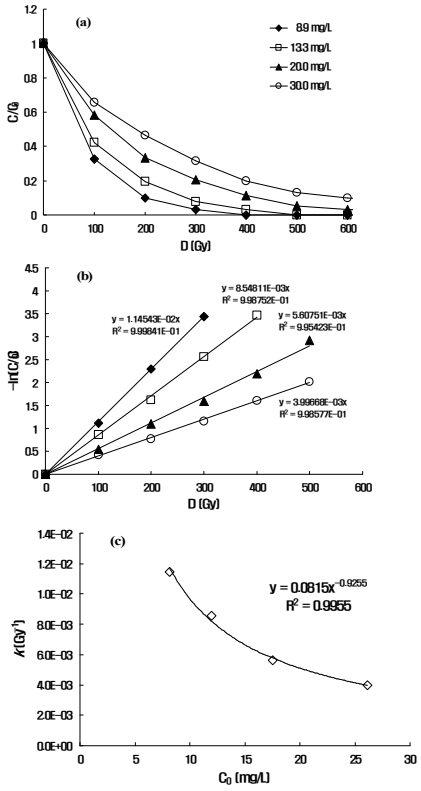

Fig 2. Kinetic results for the radiolytic decomposition of cefaclor at different initial aqueous concentrations. (a) Removal of cefaclor at different initial conc. vs. irradiation doses and (b) the corresponding rate constants and (c) dependency of the initial concentration on the dose constant

2.6 Modeling of Radiolytic Decomposition of Cefaclor

The results of the radiolytic decomposition of cefaclor at different initial concentrations were shown in Figure 3. The lines shown in the figure represent model simulations using equation 1. The model simulations showed good agreement with the experimental results at different concentrations of cefaclor, indicating that radiolytic decomposition of cefaclor follows the pseudo first-order reaction model, which is used for the calculation of the required radiation doses.

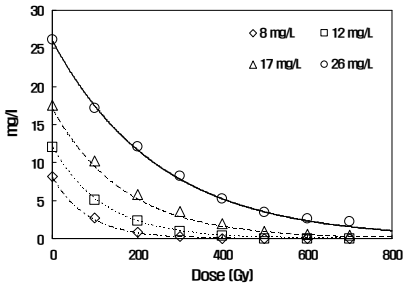

Fig 3. Radiolytic decomposition kinetics at different initial cefaclor concentrations. The lines represent model simulations.

3. Conclusions

The radiation technology was very effective for the complete decomposition of cefaclor. A kinetic model employing the pseudo first-order reaction model simulated well the radiolytic decomposition of cefaclor over a wide range of concentrations.

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