Decomposition of Oxalic Acid by Gamma-ray Irradiation

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1. Introduction

Recalcitrant organic compounds are used to decontaminate oxide films or oxide deposits in various nuclear power systems. Oxalic acid was usually used for decontamination of water-cooled reactors such as pressurized power reactor and boiled water reactor. To remove chemical agents, advanced oxidation processes by radicals were used [1, 2]. This study focused on radiolytic decomposition of oxalic acid by gamma irradiation.

2. Materials and Methods

2.1 Chemicals

All of chemicals were high-purity analytical grade. The initial concentrations of oxalic acid prepared at 1, 2, 5 and 10 mM. The initial pH was 3-4 at each test condition.

2.2 Irradiation

Gamma irradiation was performed using a high-level ^{60}Co source at the Korea Atomic Energy Research Institute. The radiation activity of source was 1.47×10^{17} Bq with dose rate of 10 kGy/hr. Absorbed doses were 5, 10, 20, 30 and 50 kGy, and measured by the alanine-EPR dosimetry system. All tests were carried out at room temperature.

3. Results and Discussion

3.1 Radiolytic decomposition of oxalic acid

Degradation of contaminants by ionizing radiation is initiated by the primary products of water radiolysis. The efficiency of gamma irradiation in the degradation of oxalic acid was compared between percentage removal and G-value. The results obtained are shown in Fig. 1. The G-Values for radiolytic decomposition of oxalic acid at 10 mM were 19.3, 9.7, 4.8, 3.2, and 1.9 for absorbed dose of 5, 10, 20, 30, and 50 kGy, respectively. The G-value increased with the initial concentration of oxalic acid. Interestingly, the G-value decreased with accumulated radiation dose but the removal increased. The removal of oxalic acid at 10 mM was 16.6, 36.5, 69.5, 83.4, and 92.2% for absorbed dose of 5, 10, 20, 30, and 50 kGy, respectively. According to these results, the efficiency of gamma irradiation process decreases with longer gamma exposure time.

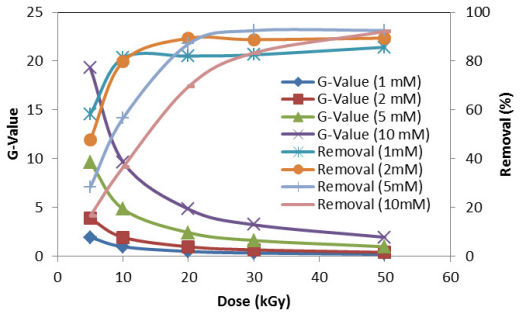

Fig. 1. G-Value and removal of oxalic acid using gamma irradiation.

3.2 Decomposition characteristics of oxalic acid

The dose constant, k, at different initial concentration was shown in Fig. 2. Oxalic acid removal efficiency can be quantitatively described in terms of two parameters, G-value and k. The G-values at 50 kGy were proportional to oxalic acid concentration. The G-values for radiolytic decomposition of oxalic acid at 50 kGy were 0.2, 0.4, 1.0, and 1.9 for initial concentration of 1, 2, 5, and 10 mM, respectively. Meanwhile, dose constant decreased with G-value. Dose constants for initial concentration of 1, 2, 5, and 10 mM were 0.1695, 0.1221, 0.0904, and 0.0536 kGy^{-1}, respectively.

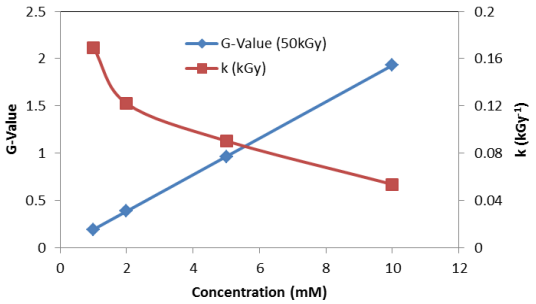

Fig. 2. Oxalic acid gamma irradiation at different initial concentrations.

The dose constant, k, was used to calculate the dose required to produce 50% and 90% oxalic acid degradation ($D_{0.5}$ and $D_{0.9}$ values). The variation of $D_{0.5}$ values was not too high. $D_{0.5}$ values increased from 4.1 to 12.9 kGy for initial concentration of 1 to 10 mM. Meanwhile, To obtain 90% removal at oxalic acid 10mM, 43.0 kGy was required. $D_{0.9}$ - $D_{0.5}$ values for initial concentration of 1, 2, 5, and 10 mM were 9.5, 13.2, 17.8, and 30.0 kGy, respectively. This shows that the mineralization of oxalic acid at higher concentration was difficult more than that at lower concentration because of a great number of generated intermediates.

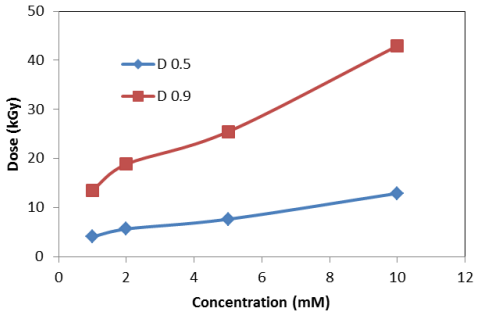

Fig. 3. D_{50} and D_{90} of oxalic acid gamma irradiation at different initial concentrations.

4. Conclusions

Oxalic acid was successfully degraded by gamma irradiation. 92% removal was obtained at initial concentration of 10 mM. Dose constant ranged from 0.1695 to 0.0536 kGy^{-1} at different initial concentrations. G-value was inversely proportional to dose constant.

ACKNOWLEDGEMENT

This work was supported by a Nuclear Research & Development Program through an NRF grant funded.

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