Degradation of p-nitrophenol by Gamma Irradiation

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Abstract − Degradation of p-nitrophenol has been carried out using only gamma irradiation or gamma irradiation with H_2O_2 or $Na_2S_2O_8$. Effects of different operating parameters such as initial concentration (50 mg l^{-1}, 100 mg l^{-1}, 200 mg l^{-1}, 300 mg l^{-1}, 400 mg l^{-1}, 500 mg l^{-1} and 600 mg l^{-1}) on the extent of degradation has been investigated. At 5 kGy, 50 mg l^{-1} p-nitrophenol was completely degraded, and the radiolytic degradation of p-nitrophenol was described by the pseudo-first-order kinetic model. The combination of gamma irradiation with H_2O_2 or $Na_2S_2O_8$ leads to an enhanced effect, which remarkably increased the degradation efficiency of p-nitrophenol and TOC removal. However, at high H_2O_2 concentration, the efficacy of p-nitrophenol degradation is reduced because ·OH radicals are scavenged by H_2O_2 and $Na_2S_2O_8$.

Key words : Gamma irradiation, p-nitrophenol, Degradation

INTRODUCTION

p-Nitrophenol (PNP) is used for the synthesis of medicines, dyes, explosives, leather coloring agents, and it is also generated during the photodegradation of pesticides that contain the nitrophenol moiety (Uberoi and Bhattacharya 1997; Kidak and Ince 2006). Consequently, PNP occurs widely in industrial and agricultural wastewater, rivers and soils (Dieckmann and Gray 1996; Oturan *et al.* 2000). The presence of substitute groups, e.g., nitro and chloro groups, on phenols increases the toxic effects on ecosystem and human health due to their persistence in the environment. Therefore, PNP are notified as priority organic pollutants by the United States Environmental Protection Agency (EPA 2008). Phenolic hydrocabons including nitrophenols are widely used in pharmaceutical, petrochemical, and other chemical manufacturing processes. Because of their harmful effects, wastewaters containing phenolic compounds must be treated before being discharged into receiving water bodies. The methods to treat wastewaters containing phenolic compounds can be classified into biological metods (Wan *et al*. 2007; Qiu *et al.* 2007), physical methods (Chern and Chien 2002) and chemical methods (Pintar and Levec 1994). The reaction rate of the biological methods are usually slow. Thus new waste disposal problems are generated. Among the many chemical methods, the advanced oxidation process (AOP) using the hydroxyl radical (·OH) has been recognized as a promising technology to treat wastewaters containing refractory organic compounds. There are various advanced oxidation processes that can produce hydroxyl radicals, such as hydrogen peroxide (H_2O_2), and persulfate reagent (Chang *et al*. 2008). Gamma irradiation has proven to be promising for the degradation of refractory substances such as fluorine (Popov and Getoff 2004), and nitrobenzene (Zhang *et al.* 2007). As a consequence of the interaction between gamma irradiation and aqueous solution, the primary species (·OH,e_{aq}^- and ·H) and molecular products (H_2O_2) are generated by the following equation (Getoff 1996): The che-

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mical reactions by the three reactive species (·OH, e_{aq}^-, and ·H), especially ·OH radicals, are very reactive and are principal important with respect to gamma irradiation or electron beam processes in aqueous solutions.

This study focused on the combination of gamma irradiation, $Na_2S_2O_8$ and H_2O_2 as an effective treatment method for degrading p-nitrophenol found in the environment. The main objectives were (1) to study the degradation of p-nitrophenol, (2) to investigate the enhanced effect of gamma irradiation, $Na_2S_2O_8$ and H_2O_2 for radiolytic decomposition and mineralization of p-nirophenol in aqueous solutions.

MATERIALS AND METHODS

1. Chemicals

p-nitrophenol (≥99% purity) and sodium persulfate ($Na_2S_2O_8$, ≥99%) were purchased from Aldrich-Sigma Chemicals Co. Hydrogen peroxide (H_2O_2, Showa Chemical Co., Ltd., Japan) and was used as a 30% (w/w) solution. Acetonitrile used for HPLC analysis was a HPLC grade and purchased from J.T. Baker (USA). All solutions were prepared using Milli-Q purified water (MilliporeInc., USA).

2. Irradiation sources

Gamma irradiation was performed with a high-level ^{60}CO source (NordionInc., Canada) at the Korea Atomic Energy Research Institute (Jeongeup, Korea). The radioactivity of the source was around 9.85×10^{15} Bq (=266200 Ci). Aqueous p-nitrophenol solutions were irradiated in 15 ml screw-cap-bottles without any headspace. The solutions were prepared 24 hrs 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°C ± 2) before being irradiated.

3. Analytical methods

The concentration of p-nitrophenol 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 an UV absorbance detector and a Discovery C18, 5 μm, 4.6 × 150 mm column (Zorbax 300SB). The eluent consisted of acetonitrile/distilled water (15/85, v/v) and flowrate was 0.7 ml min^{-1}. The wavelength for p-nitrphenol was set at 290 nm and the column temperature was kept at 40°C. The total organic carbon (TOC) in the aqueous samples was determined using a Shimadzu TOC-VCPH analyzer (Shimadzu Co., Japan).

RESULTS AND DISCUSSION

1. Degradation of p-nitrophenol

Radiolytic decomposition of organic pollutants is initiated by primary species produced from water radiolysis in the bulk of the solution. The radiolytic degradation of PNP in aqueous solutions was investigated. Fig. 1 shows the degradation of PNP at different initial concentrations with increasing absorbed doses. Concentration of PNP was decreased with increasing absorbed dosage. At the dose of 5 kGy, the removal efficiencies for initial aqueous PNP concentrations of 0.36, 0.72, 1.44, 2.15, 2.87, 3.59 and 4.31 μM were 98, 81, 59, 55, 37, 31 and 27%, respectively. Fig. 2 and Table 1 show the radiolytic degradation rate constants of PNP at different initial concentrations, indicating a dependence on the initial PNP concentration. It was found that the concentration of PNP decreased exponentially with the absorbed doses, indicating that PNP degradation followed a pseudo-first-order kinetic model, which can be described by Eq. (1) and (2):

$$C = C_o \exp(-dD) \tag{1}$$

$$-\ln\left(\frac{C}{C_o}\right) = dD \tag{2}$$

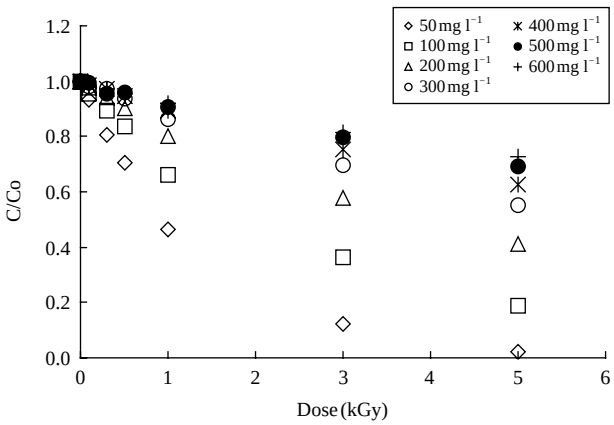

Fig. 1. Radiolytic degradation of PNP at different initial concentrations with increasing absorbed dose.

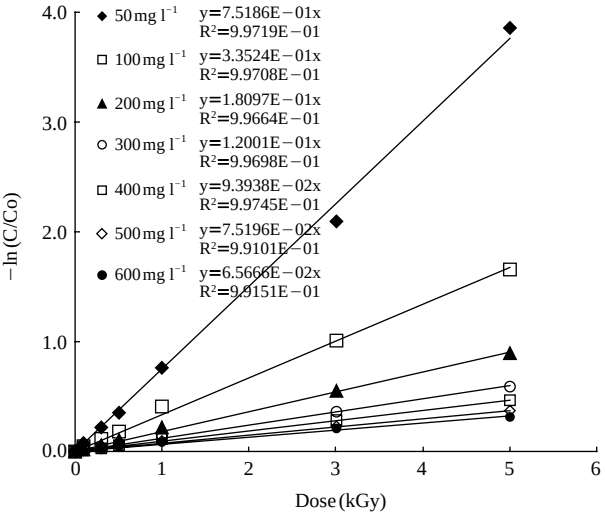

Fig. 2. Initial concentration dependency of the radiolytic degradation rate constant (dose constant) by gamma irradiation.

Table 1. Change in dose constant (d) with increasing initial concentration of p-nitrophenol

$[PNP]_o$ (μM)	Dose constant (d) (Gy^{-1})	R^2
0.36	0.07	0.9972
0.72	0.05	0.9971
1.44	0.02	0.9966
2.15	0.02	0.9969
2.87	0.01	0.9974
3.59	0.01	0.9910
4.31	0.01	0.9915

Where C_o is the initial concentration of the PNP 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 (Mincher and Curry 2000; Xue and Wang 2008).

The dose constant increased with decreasing initial concentrations of PNP, which is consistent with the results reported recently for the PCB by Mincher *et al.* (2002) and pentachlorophenol of Xue and Wang (2008). Therefore, the absorbed dose requirements to remove the PNP concentration in aqueous solution under the same experimental conditions can be calculated easily.

2. The effect of H_2O_2 and $Na_2S_2O_8$ on p-nitrophenol decomposition

H_2O_2 is a well-known source of ·OH radicals, which is widely used to remove refractory organic pollutants in wastewater (Hu and Wang 2007; Kwon *et al.* 2009). The effect of H_2O_2 on PNP (=0.36 μM) degradation was investigated by

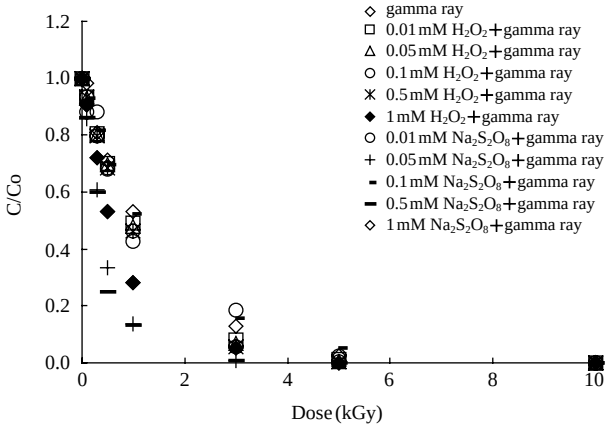

Fig. 3. Residual PNP after gamma irradiation with H_2O_2 and $Na_2S_2O_8$ concentration according to the absorbed doses ($[PNP]_o$=0.36 μM, $[H_2O_2]_o$=0～10 μM, $[Na_2S_2O_8]_o$=0～10 μM).

the different absorbed doses. Fig. 4 shows the concentration of residual PNP as the efficacy of the concentration of H_2O_2 and $Na_2S_2O_8$ on the absorbed doses. The concentrations of added H_2O_2 and $Na_2S_2O_8$ were varied with from 0 to 1 mM. As shown in Fig. 4, the residual PNP concentration had remarkably decreased as the concentration of H_2O_2 and $Na_2S_2O_8$ increased up to 1.0 mM, while its residual concentration had gradually increased as more H_2O_2 and $Na_2S_2O_8$ was added. H_2O_2 can react with $_{aq}^-$ and ·H produced by water radiolysis, converting them in to much more ·OH radicals, as shown in Eq. (3), (4) (Wang *et al.* 2006; Kwon *et al.* 2009).

$$e^-_{aq}+H_2O_2 \rightarrow \cdot OH+OH^- \quad k=1.1\times10^{10}\,lmol^{-1}s^{-1} \qquad (3)$$

$$\cdot H+H_2O_2 \rightarrow \cdot OH+H_2O \quad k=9.0\times10^{7}\,lmol^{-1}s^{-1} \qquad (4)$$

Thus, the combination of H_2O_2 with gamma irradiation could remarkably enhance the degradation of PNP. However, further increase of H_2O_2 (>1.0 mM) could compete with organic compounds for ·OH radical (Eq. (5), (6)) and therefore increased the residual concentration of PNP (Fig. 3) (Gao *et al.* 2009; Kwon *et al.* 2009).

$$\cdot OH+H_2O_2 \rightarrow HO\cdot_2+H_2O \quad k=2.7\times10^{8}\,lmol^{-1}s^{-1} \qquad (5)$$

$$\cdot OH+\cdot OH \rightarrow H_2O_2 \quad k=1.1\times10^{10}\,lmol^{-1}s^{-1} \qquad (6)$$

3. The effect of H_2O_2 and $Na_2S_2O_8$ on mineralization p-nitrophenol

The TOC values of the irradiated solutions were analyzed

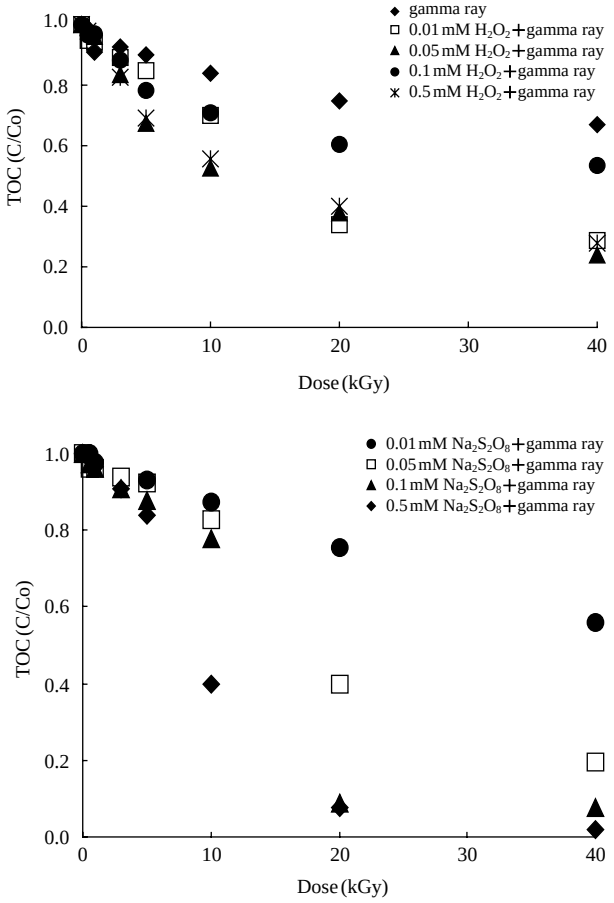

Fig. 4. TOC removal efficiencies of PNP (=0.36 μM) with increasing absorbed dose at different initial H_2O_2 and $Na_2S_2O_8$ concentration.

to evaluate the effects of H_2O_2 and $Na_2S_2O_8$ on the mineralization of PNP under gamma irradiation. Fig. 4 shows the TOC removal with increasing absorbed dose at different initial H_2O_2 and $Na_2S_2O_8$ concentrations. When the initial H_2O_2 and $Na_2S_2O_8$ concentrations were in the range of 0 ~ 1 mM, TOC was removed more remarkably at a higher concentration of H_2O_2 and $Na_2S_2O_8$. At 1 kGy of an absorbed dose, the TOC removal efficiencies of the PNP solutions with initial H_2O_2 concentrations of 0.01 and 1.0 mM were approximately 50, 52.7, 55.5, 58.3 and 72.2%, respectively. When irradiated to 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 (Hu and Wang 2007) and *p*-nitrophenol (Yu *et al.* 2010). By reason that, as mentioned equation above (Eq. (3), (4)), the presence of H_2O_2 promoted the mineralization of PNP. However, as previously reported results by Hu and wang (2007) and Yu *et al.* (2010), the TOC in the irradiated PNP solutions with different initial H_2O_2 concentrations was not removal completely even after absorbed dose of 20 kGy (Fig. 4). It could be suggested that the reduction of TOC removal efficiency is probably due to the remaining organic by-products produced from PNP decomposition. These by-products were not completely mineralized.

CONCLUSION

Based on the experiments on the radiolytic degradation of p-nitrophenol and the effect of H_2O_2 and $Na_2S_2O_8$ on PNP degradation, it is concluded that: p-nitrophenol was effectively degraded by gamma irradiation with H_2O_2 or $Na_2S_2O_8$.

(1) An enhanced effect was found on the degradation of p-nitrophenol by gamma irradiation with H_2O_2. And the removal efficiency of TOC was enhanced significantly with increasing absorbed dose. At an absorbed dose of 5 kGy, degradation efficiency of the p-nitrophenol with initial H_2O_2 concentration of 0.5 mM was approximately 99.99%.

(2) The addition of $Na_2S_2O_8$ as additives increased the degradation efficiency to 99.99% ($Na_2S_2O_8$: 0.05 mM). Therefore, the addition of H_2O_2 or $Na_2S_2O_8$ with radiation technology such as gamma irradiation has been promised as an effective process for the degradation of p-nitrophenol.

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