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Chemical degradation is not coupled with toxicity reduction in gamma-ray treatment of phenol

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Abstract. Gamma-ray treatment of phenol was studied in terms of both chemical degradation and toxicity change. Phenol was efficiently removed by gamma-irradiation, but acute toxicity was dramatically increased due to formation of more toxic by-products such as hydroquinone, benzoquinone, resorcinol and catechol. Furthermore, the observed toxicity of gamma-ray treated phenol was well correlated with the one calculated from individual toxicity based on EC_{50} value of the by-products. Degradation of phenol in wastewater effluent was less than that in ultrapure water likely due to consumption of reactive radicals by dissolved organic matters in effluents. However, particularly for a dose of 1.0 kGy, toxicity of gamma-ray treated phenol in ultrapure water was higher than that in wastewater effluent though more phenol was removed. It was found that highly toxic by-products such as hydroquinone and benzoquinone were much more generated for the ultrapure water sample.

Keywords: acute toxicity, *Daphnia magna*, gamma rays, radiation treatment, titanium dioxide

1. Introduction

Chemical analysis alone is limited to assess ecological effects of toxic compounds in treated wastewaters [1]. As an alternative approach, the whole effluent toxicity (WET) test was recommended by the US Environmental Protection Agency (USEPA), which accounts for the toxic effects of unknown chemicals and for the interaction and bioavailability of toxic materials on aquatic systems [2]. Consequently, the Korea Ministry of Environment announced in 2007 that new permission criteria would be gradually effective starting from 2011 on the basis of *Daphnia magna* acute toxicity tests for wastewater effluents [3].

In line with these, a number of studies have documented toxicity of refractory pollutants and industrial wastewater treated by ionizing radiation [4-6]. Radiation treatment with gamma-rays or electron-beams has been found to be an efficient technology for degradation of a wide range of toxic organic contaminants [7]. Particularly, we found that toxicity of phenol and monochlorophenols was dramatically increased by gamma-ray treatment at a dose of as low as 1 kGy [8]. However, the previous work just investigated in pure aqueous solutions while degradation and toxicity change are likely influenced in complex systems such as industrial effluents. Thus, this study compared chemical degradation and toxicity change of phenol in different matrices such as ultrapure water and wastewater effluent by gamma-ray treatment. The phenol was used as a model compound.

2. Materials and Methods

2.1. Gamma-ray treatment

Phenol (≥ 99%) was purchased from Sigma-Aldrich Co. (USA), and used without further purification. Sample solutions for gamma irradiation were prepared in 5.0×10^{-4} M with ultrapure water with resistivity of 18.2 MΩ cm^{-1}, and with wastewater effluent collected from a sewage treatment facility. The effluents were

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used after filtration using a 0.45 μm GF/C filter (Advantec MFS, USA). Chemical properties of ultrapure water and effluent used in this study were summarized in Table 1. Gamma-ray treatment was performed at room temperature with a high-level ^{60}Co source (AECL IR79, Canada). Samples were prepared in 500 mL amber bottles and irradiated applying different absorbed doses of 1, 5 and 10 kGy.

Table 1. Chemical properties of ultrapure water (UW) and wastewater effluent (WE) used in this study.

Parameters	UW	WE
pH	5.60	6.89
DO (mg L^{-1})	6.69	6.30
DOC (mg L^{-1})	-[a]	22.06
48-h acute toxicity (TU)	NT[b]	NT

[a] Not determined; [b] Not toxic

2.2. Chemical analysis

Dissolve organic carbon (DOC) was analyzed using a Shimadzu TOC analyzer (model 5000A, Kyoto, Japan). Metals were analyzed using a Varian inductively coupled plasma-optical emission spectrophotometer (ICP-OES, Varian Vista PRO, CA, USA). Concentration of phenol and by-products was measured by HPLC (ACME 9000, Korea) with UV/Vis detector and Inertsil ODS2-C18 column (250 mm × 4.6 mm × 5μm, GL SCIENCE, Japan). The elution was performed with 3/7 or 4/6 water/acetonitrile volume ratios. The detection wavelengths were 254 or 276 nm.

2.3. Toxicity test

Acute toxicity tests were performed using *Daphnia magna* according to the Organization for Economic Co-operation and Development OECD standard procedures [9]. Daphnids were grown in the laboratory with 16 h light and 8 h dark periods at 20 ± 2°C. Toxicity tests were performed in quadruplicate with five daphnids (neonates less than 24 h old) in each 10 mL test solution. Immobilization data were used to calculate EC_{50} by US EPA Probit analysis. Toxic units (TU) were obtained by a relationship, $TU = 100/EC_{50}$. Standard reference toxicity tests were conducted with $K_2Cr_2O_7$ in between tests.

3. Results and discussion

3.1. Gamma-ray treatment of phenol

Removal of phenol in ultrapure water (UW) was more efficient than that of phenol in wastewater effluent (WE) by gamma-ray treatment (Fig. 1a). Considering DOC value of effluent (15.67 mg/L), dissolved organic matters that consumes highly reactive hydroxyl radicals were likely responsible for the difference in degradation [10]. Marci et al. [11] also demonstrated that photodegradation rate of phenol was largely influenced by the total amount of organic substrates present independently of their nature.

Toxicity change of phenol by gamma-ray treatment was greatly different from the results of chemical degradation. Toxicity of phenol in ultrapure water sample was dramatically increased for a dose of 1.0 kGy and then gradually decreased as absorbed dose was increased (Fig. 1b). However, the toxicity increase, in particular at 1.0 kGy, was less significant in the case of wastewater effluent, though less phenol was removed in that sample compared to gamma-ray treatment alone (Fig. 1a). Shim et al. [8] reported that gamma-irradiated phenol in ultrapure water significantly induced new aqueous toxicity due to formation of toxicity-causing by-products such as hydroquinone, benzoquinone, resorcinol and catechol. As indicated in the fact that phenol was not fully mineralized into carbon dioxide even for a dose of 10 kGy, suggesting formation of by-products by gamma-ray treatment.

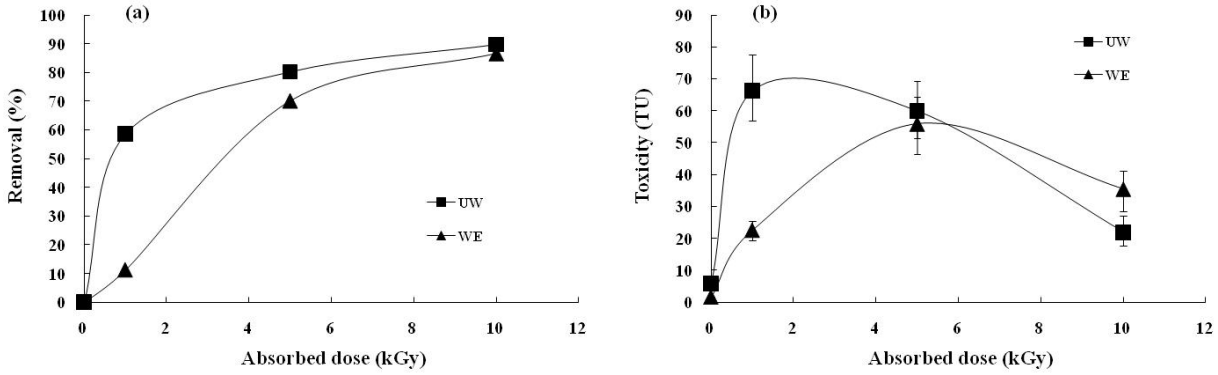

Fig. 1: (a) Removal and (b) change of 48-h acute toxicity toward *Daphnia magna* of phenol (5.0×10^{-4} M) in ultrapure water (UW) and in wastewater effluent (WE) by gamma-ray treatment.

3.2. By-products formation of phenol

By-products formation of phenol by gamma-ray treatment as a function of absorbed dose is given in Fig. 2. Hydroquinone, benzoquinone, resorcinol and catechol were generated in gamma-ray treatments of phenol dissolved in ultrapure water, while resorcinol was not found for phenol in wastewater effluent.

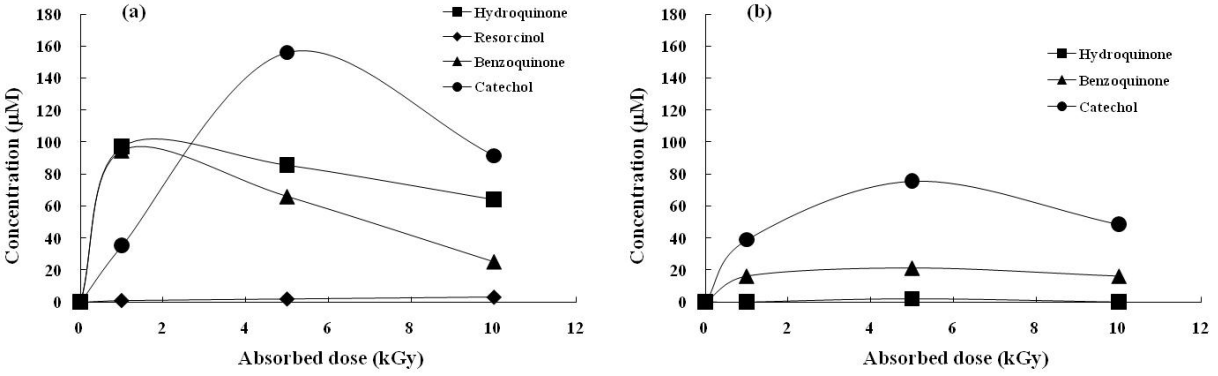

Fig. 2: Formation of by-products of phenol (5.0×10^{-4} M) in (a) ultrapure water and (b) wastewater effluent by gamma-ray treatment.

As indicated in Table 2, the by-products are much more toxic than the mother compound phenol, strongly suggesting that toxicity of phenol was increased due to formation of more toxic by-products by gamma-ray treatment. Additionally, the higher toxicity of gamma-ray treated phenol in ultrapure water at a dose of 1.0 kGy than that in wastewater effluent was due to greater production of highly toxic by-products such as hydroquinone and benzoquinone.

Table 2. 48-h acute toxicity of phenol and by-products toward *Daphnia magna*.

Chemical compounds	EC_{50} [a] (μM)
Phenol	85.38 (79.80 - 91.34)
Benzoquinone	0.55 (0.45 - 0.68)
Catechol	24.52 (20.79 - 28.91)
Hydroquinone	0.73 (0.68 - 0.78)
Resorcinol	3.85 (3.40 - 4.36)

[a] 50% effective concentration with 95% confidence limits

By using EC_{50} values and concentrations (conc.) of by-products, toxic unit (TU = conc./EC_{50}) of individual compounds was calculated. Assuming simple summation of individual toxicity, calculated toxicity

was compared with observed toxicity (Fig. 3). For ultrapure water sample, the calculated toxicity was much larger than the observed toxicity, but correlation between them was significant. In the case of wastewater effluent samples, calculated toxicity was well simulated observed toxicity. Guerra [11] reported that effluent toxicity toward *D. magna* was under- or over-estimated by summation of TUs of individual component, depending on types of effluents. This suggests that combined or joint toxicity of individual toxic by-products should be studied to predict toxicity of gamma-ray treated phenol successfully.

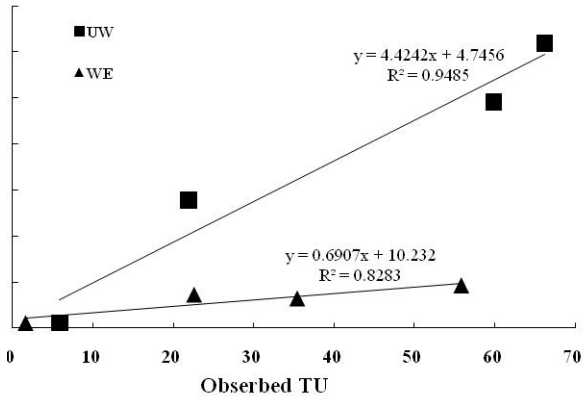

Fig. 3: Relationship between observed toxicity and calculated toxicity of gamma-ray treated phenol (5.0×10^{-4} M) in ultrapure water (UW) and wastewater effluent (WE).

4. Conclusions

Gamma-ray treatment seemed to be effective in degrading phenol, but acute toxicity of phenol was rather increased. Additionally, phenol degradation and toxicity change were largely influenced by chemical composition of background matrix (i.e. ultrapure water or wastewater effluent). We found that by-products formation plays important role in toxicity change by gamma-irradiation. However, the reaction mechanism and/or kinetics were not fully identified in this work, thus this should be further investigated.

5. Acknowledgement

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