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Effect of Titanium Dioxide Nanoparticles on Gamma-Ray Treatment of Phenol in Different Matrices: Implications in Toxicity Toward *Daphnia magna*

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Abstract Gamma-ray treatment of phenol was studied in terms of both chemical degradation and toxicological change. About 90 % of phenol (5.0×10^{-4} M) in ultrapure water (UW) was eliminated by gamma-irradiation at a dose of 10 kGy, but acute toxicity was dramatically increased, particularly for dose of 1 kGy, due to the formation of more toxic by-products such as hydroquinone, benzoquinone, resorcinol and catechol. The addition of TiO_2 nanoparticles had little effect on the removal of phenol in UW, but substantially enhanced the mineralization of phenol compared with gamma-irradiation alone. Additionally, degradation of phenol by gamma-irradiation was inhibited in a wastewater effluent (WE) matrix, likely due to the presence of dissolved organic carbon (22.06 mg L^{-1}). Furthermore, lower concentrations of toxic by-products were generated both in WE and in the presence of TiO_2 nanoparticles, resulting in reduction of toxicity increase by gamma-irradiation. Meanwhile, the toxicity of gamma-ray treated phenol in WE was well estimated with simple summation of individual toxicity of phenol and by-products ($R^2 = 0.9678$).

Keywords Acute toxicity · *Daphnia magna* · Effluent · Gamma rays · Radiation treatment · Titanium dioxide

Recently, advanced oxidation processes (AOPs), such as the Fenton reaction, UV photocatalysis, ozonation, and ionizing radiation, have emerged as effective methods of removing non-biodegradable substances (Oller et al. 2011). Radiation treatment with gamma-rays or electron-beams has been found to be a particularly efficient technology for the degradation of a wide range of toxic organic contaminants (Pikaev 1994).

Additonally, metal oxides such as TiO_2, Al_2O_3 etc. have been used to enhance the degradation of organic pollutants (Krapfenbauer and Getoff 1999; Gonzalez-Juares and Jimenez-Becerril 2006; Follut and Karpel Vel Leitner 2007). In the previous work, we found that TiO_2 (Degussa P25) and bentonite exhibited a catalytic activity in the radiation treatment of trichloroethylene (TCE) and perchloroethylene (PCE) (Jung et al. 2002; Jung and Lee 2002). However, unlike photocatalysis, the mechanism of radiocatalysis is not well understood.

Toxicity assessments are generaly recommended to account for the toxic effects of unknown chemicals, including the interaction and bioavailability of toxic materials in industrial wastewaters (USEPA 2000; Yi et al. 2011). Several studies have documented the treatment of industrial wastewater and refractory pollutants, using ionizing radiation to reduce toxicity (Borrely et al. 2004; Jo et al. 2006, 2008). However, in a previous study, we found that the toxicity of phenol and monochlorophenols was dramatically increased by gamma-ray treatment doses as low as 1 kGy (Shim et al. 2009; Kang et al. 2011). Hence, this study aims to evaluate the effect of a nano-sized TiO_2 catalyst on chemcial degradation and toxicity change of phenol in different matrices by gamma-irradiation.

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Materials and Methods

Phenol (≥99 %), benzoquinone (98 %), catechol (≥99 %) and resorcinol (99 %) were purchased from Sigma-Aldrich Co. (USA), and hydroquinone (AnalaR grade) was obtained from BDH Co. (England). All these chemicals were used without further purification. Nanoparticles of TiO_2 (P25) were a mixture of anatase (80 %) and rutile (20 %), and were obtained from Degussa Co. (USA). The nominal average size was stated to be 21 nm, and the specific surface area about 50 m^2 g^{-1}. Sample solutions for gamma-irradiation were prepared in 5.0×10^{-4} M, using ultrapure water (UW) with a resistivity of 18.2 MΩ cm^{-1} (Puris, Esse-UP Water System, Mirae St Co., Korea), and with wastewater effluent (WE) from a wastewater treatment plant (WWTP). The WWTP treats about 279,000 m^3/day (industrial wastewater of 189,000 m^3/day and sewage of 90,000 m^3/day) using primary sedimentation, aerobic bioreaction, secondary sedimentation, and rapid sand filtration (Kang et al. 2011). The effluents were filtered using a 0.45 µm GF/C filter (Advantec MFS, USA) prior to use in this study.

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, without replication, and irradiated applying different absorbed doses of 1, 5 and 10 kGy. For gamma-ray treatment in the presence of a catalyst, TiO_2 nanoparticles were dispersed in the solution to a concentration of 1.00 g L^{-1} and were allowed to stand 24 h in order to reach equilibrium.

Dissolved organic carbon (DOC) was analyzed using a Shimadzu TOC analyzer (5000A, Kyoto, Japan). Metals were analyzed using a Varian inductively coupled plasma-optical emission spectrophotometer (ICP-OES; Varian Vista PRO, USA). Concentration of phenol was measured by a high performance liquid chromatography (HPLC; ACME 9000, Korea) with UV/Vis detector, using a Unison US-C18 (250 mm × 4.6 mm × 5 µm) column. A mixture of water and acetonitrile (20/80 v/v) was used as the eluent. The flow rate was 1 mL/min, and the detection wavelength was 254 nm. Concentrations of by-products generated by gamma-irradiation were determined by HPLC (Waters 515, USA) with a photodiode array detector (Waters 2996) and Unison US-C18 (250 mm × 4.6 mm × 5 µm) column. A mixture of water and methanol (60/40 v/v) was used as the eluent, and the flow rate was 0.8 mL/min.

Acute toxicity tests were performed using *Daphnia magna* according to the Organization for Economic Co-operation and Development standard procedures (OECD 2004). Daphnids were grown in the laboratory with 16 h light and 8 h dark periods at 20 ± 2°C in Elendt M4 medium. Each toxicity test consisted of five dilutions (100 %, 50 %, 25 %, 12.5 % and 6.25 %) and one control with four replicates per treatment, and each test vessel contained 10 mL of test solution and five individuals (≤24 h old). Dilution and control water (pH = 7.8 ± 0.1 and hardness = 250 ± 25 mg L^{-1} as $CaCO_3$) was prepared as described by the International Organization for Standardization (ISO 1996). Immobilization data (48 h) were used to calculate EC_{50} (50 % effective concentration) 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 and compared with a control chart. The control chart was prepared by calculating the mean (1.00 mg L^{-1}) and upper (1.47 mg L^{-1}) and lower (0.54 mg L^{-1}) control limits (±2S) using the 20 most recent data (USEPA 2002).

Results and Discussion

The removal of phenol in UW by gamma-irradiation was found to be more efficient than that of phenol in WE (Fig. 1). As indicated in Table 1, WE sample contained appreciable amounts of dissolved organic matters (DOMs), which can consume highly reactive hydroxyl radicals (Kang et al. 2011). Westerhoff et al. (2007) have demonstrated that DOMs are responsible for the inhibition of chemical degradation in radiation treatments.

The effect of TiO_2 nanoparticles on the gamma-ray treatment of phenol was not found to be pronounced, but instead, seemed to be primarily dependent on the matrix to which radiation was applied (Fig. 1). The addition of TiO_2 catalyst decreased removal of phenol when applied to UW, whereas it increased phenol removal when applied to WE. However, the concentration of DOC in UW was substantially decreased for all absorbed doses by gamma-irradiation in the presence of TiO_2 nanoparticles (Fig. 2), indicating more mineralization of phenol than that by

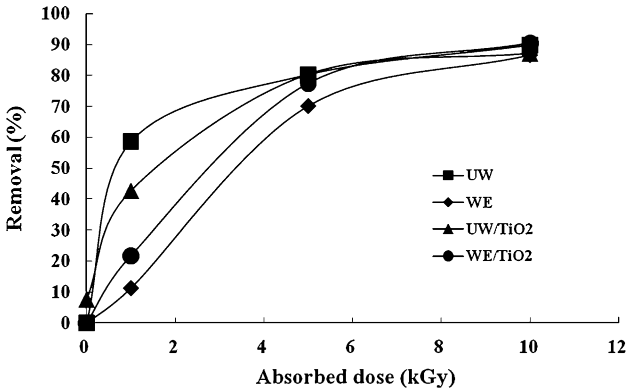

Fig. 1 Removal of phenol (5.0×10^{-4} M) in ultrapure water (*UW*) and wastewater effluent (*WE*) with and without TiO_2 nanoparticles (1.00 g L^{-1}) by gamma-ray treatment

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
Acute toxicity (TU)	NT[b]	NT

[a] Not analyzed

[b] Not toxic

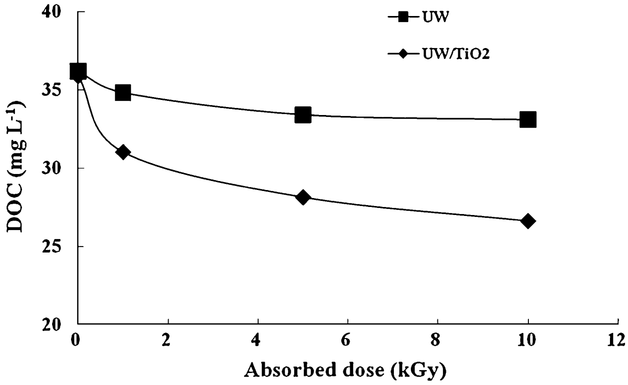

Fig. 2 Change of dissolved organic carbon (*DOC*) concentration in gamma-ray treatment of phenol (5.0×10^{-4} M) in ultrapure water (*UW*) with and without TiO_2 nanoparticles (1.00 g L^{-1})

gamma-ray treatment alone. Chitose et al. (2003) reported that TiO_2 had no significant effect on phenol decomposition by gamma-ray treatment while DOC removal was greatly increased.

Gonzalez-Juares and Jimenez-Becerril (2006) demonstrated that the degradation of 4-chlorophenol (CP) was increased by the radiocatalytic effects of commercial SiO_2, TiO_2 and Al_2O_3. However, Follut and Karpel Vel Leitner (2007) demonstrated that the improved removal of 4-nitrophenol by electron-beam irradiation in the presence of TiO_2 or Al_2O_3 nanoparticles was due to adsorption rather than catalysis. Together these findings indicate that the catalytic effects of metal oxides used in radiolytic degradation of organic compounds are inconsistent.

Although phenol was largely eliminated by gamma-irradiation, the toxicity of the products of degradation was dramatically increased when compared to that of phenol, gradually decreasing when the absorbed dose was increased (Fig. 3). Shim et al. (2009) demonstrated that the gamma-irradiation of phenol and monochlorophenols in UW significantly induced aqueous toxicity toward *D. magna* due to the formation of toxic by-products. Zazo et al. (2007) also reported that Fenton's oxidation of phenol induced the evolution of toxicity to *Vibrio fisheri*, which was also caused by the formation of more toxic intermediates.

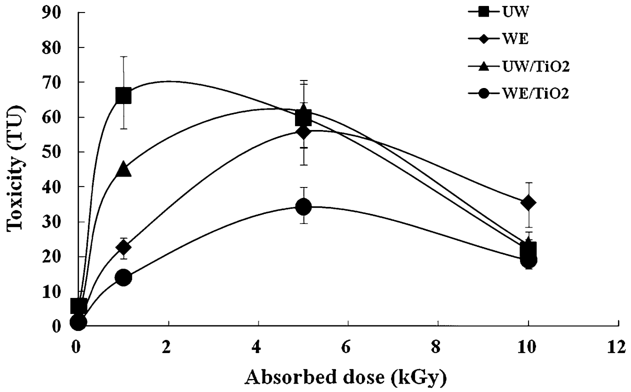

Fig. 3 Change of acute toxicity (48 h) toward *D. magna* of phenol (5.0×10^{-4} M) in ultrapure water (*UW*) and wastewater effluent (*WE*) with and without TiO_2 nanoparticles (1.00 g L^{-1}) by gamma-ray treatment

Considering that phenol was not fully mineralized even when a dose of 10 kGy was applied (Fig. 2), the formation of by-products by gamma-ray treatment is evidently a consequence. As shown in Fig. 4, hydroquinone, benzoquinone, resorcinol and catechol were generated during the gamma-ray treatment of phenol. Moreover, since the intermediate by-products of its degradation are generally much more toxic than phenol (Table 2), it is highly likely that the observed increase in toxicity was due to the formation of such by-products by gamma-ray treatment.

The toxicity increase observed for gamma-ray treated phenol in WE was less than that in UW (Fig. 3). Furthermore the presence of TiO_2 nanoparticles reduced the production of highly toxic by-products such as hydroquinone and benzoquinone (Fig. 4). Kang et al. (2011) demonstrated that toxicity reduction of 4-CP by gamma-irradiation (in an industrial effluent) was substantially enhanced in the presence of ZrO_2 nanoparticles, mostly due to adsorption of 4-CP on the nanoparticles.

The toxic unit (TU) of individual compounds was calculated by dividing their concentrations by their EC_{50} values, and simply summated to compare with observed toxicity (Fig. 5). The calculated toxicity was much higher than the observed toxicity for UW samples, but two values were comparable for WE samples both in the presence and absence of the presence of TiO_2 nanoparticles. Guerra (2001) reported that the simple summation of TUs of phenolic compounds in industrial effluents under- or overestimated whole effluent toxicity, depending on the types of effluent and test organisms used. These findings suggest that interactions among such toxic by-products should be

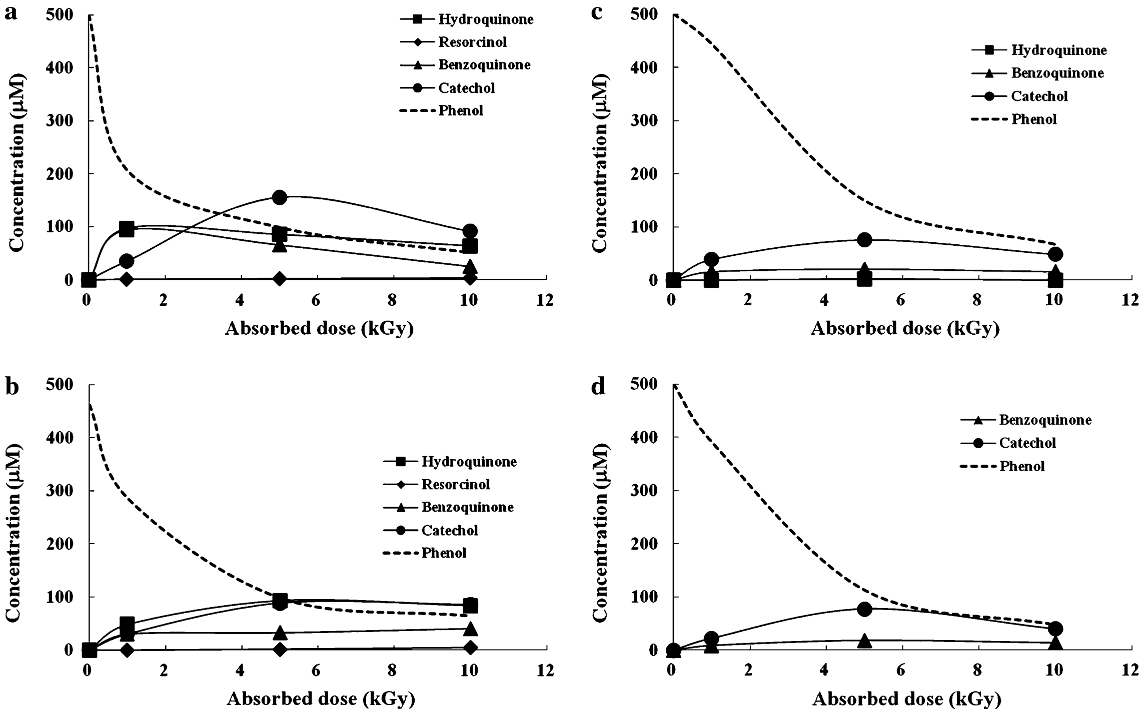

Fig. 4 Formation of by-products of phenol (5.0×10^{-4} M) in ultrapure water (*UW*) **a** without and **b** with TiO_2 nanoparticles (1.00 g L^{-1}), and in wastewater effluent (*WE*) **c** without and **d** with TiO_2 nanoparticles (1.00 g L^{-1}) by gamma-ray treatment

Table 2 Acute toxicity (48 h) of phenol and by-products toward *D. 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 from the study of Shim et al. (2009)

further studied in order to more successfully predict their antagonistic/synergistic toxicity.

In conclusion, gamma-ray treatment proved to be effective in degrading phenol, but largely increased the acute toxicity due to by-products of degradation being more toxic than the parent compound. These findings suggest that gamma-ray treatment should not be advised for phenol in aqueous media since it makes more toxic intermediates. Additionally, phenol degradation and its ultimate toxicity were influenced by both background matrix and TiO_2 catalyst. However, the reaction mechanism of the gamma-ray treatment of phenol was not fully identified in this work, and should be further investigated.

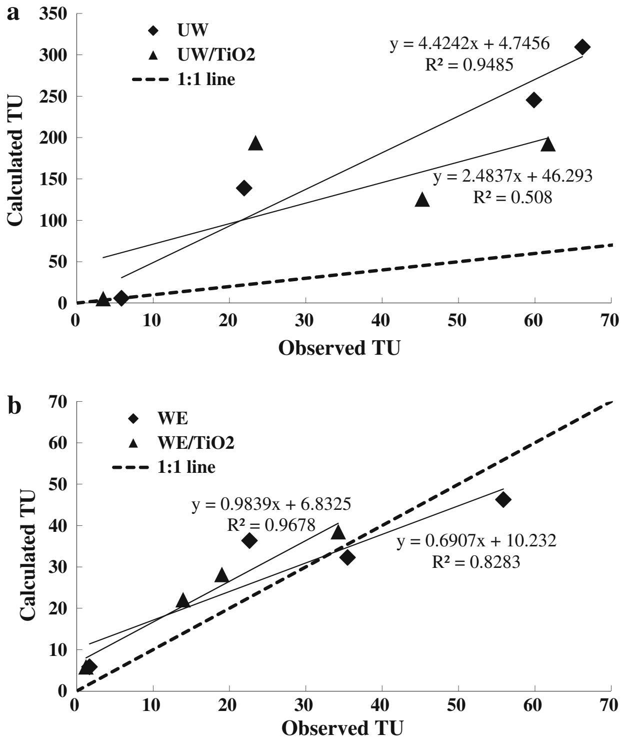

Fig. 5 Relationship between observed toxicity and calculated toxicity of gamma-ray treated phenol (5.0×10^{-4} M) in **a** ultrapure water (*UW*) and **b** wastewater effluent (*WE*) with and without TiO_2 nanoparticles (1.00 g L^{-1})

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