

## Radiation-induced reduction of diuron by gamma-ray irradiation

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### Abstract

Diuron degradation efficiencies and the proposed mechanism by gamma-ray irradiation were investigated. Several factors that might affect the degradation values were further examined. The UV absorbances at 200–400 nm and diuron concentration decreased with the increase of radiation dose. When diuron initial concentration was 18.5 mg L<sup>-1</sup> and 1.0 kGy was selected as the radiation dose, diuron removal value and loss of total organic carbon were 100 and 34.1%, respectively. However, the concentration of Cl<sup>-</sup> ion increased with the increase of radiation dose. The process could be depicted by first order reaction kinetics and the reaction was mainly caused by the reaction of diuron with •OH and e<sub>aq</sub><sup>-</sup>. The degradation efficiency decreased with the increase of initial concentration at the same radiation dose. H<sub>2</sub>O<sub>2</sub>, HCO<sub>3</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>, CH<sub>3</sub>OH and humic acid as additives reduced the degradation efficiency. Furthermore, the increase of NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>, CH<sub>3</sub>OH and humic acid would result in the decrease of the degradation values. The pH value could affect the removal efficiency and the degradation process was enhanced in acid condition. The pH value became lower with increasing radiation dose after gamma-ray irradiation.

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**Keywords:** Degradation; Diuron; Gamma-ray irradiation; Mechanism

### 1. Introduction

Diuron, a herbicide belonging to the *phenylurea* family, is chemically stable [1] and considered priority substances by the European Union Water Framework Directive (Directive 2000/60/EC) [2]. It could pollute water bodies through agricultural runoffs and wastewaters generated from diuron manufacturing plants [3]. Due to its high persistence (one month to one year) [4], groundwater contamination with it became a serious problem. Up to now, a lot of researches have been carried out to remove diuron.

Adsorption of diuron from aqueous solution onto activated carbon-cloth had been studied [5] and the effect of ozonation on the competitor effect of humic and fulvic acids against diuron in adsorption on activated carbon in drinking water process was also studied [6]. The ozone dose of 1.3 mg L<sup>-1</sup> did not cause significant transformations of humic and fulvic acids. Diuron

could be completely mineralised by electrochemical technology and passivation of the electrode surface was not observed [7]. Photocatalytic methods and photo-Fenton were used by many researchers to remove diuron [1,8–18]. 100% of chlorine could be recovered as chloride and 90% of mineralization was reached. The toxicity was reduced to below the threshold (EC<sub>50</sub>) in a short time. But it was entirely possible that a photochemical intermediate was more toxic than diuron [18]. Recently, solar photo-Fenton degradation of diuron was also examined [2,19]. Laser-flash photolysis and pulse radiolysis were also able to degrade diuron [20].

The degradation of diuron by biological ways were also tested. Isolate D47 hydrolysed the urea side chain at the carbonyl group of diuron [21] and *Pseudomonas* sp., *Bjerkandera adusta* and *Oxysporus* s.p, were also able to detoxicate the herbicide diuron [22,23]. Gamma-ray irradiation is considered to be an effective way to degrade organic compounds by chemical oxidation processes [24]. But decomposition of diuron by gamma-ray irradiation has not yet been studied.

The purpose of the present study was to investigate the possibility of diuron degradation from aqueous solution

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by gamma-ray irradiation and the possible mechanism was proposed. Furthermore, some factors that might affect the degradation efficiency were examined.

## 2. Experimental

### 2.1. Chemicals and reagents

Standard diuron was purchased from Sigma-Aldrich and methanol used in the analysis was HPLC grade. The other reagents were all analytical-grade.

### 2.2. Sample preparation

Diuron solutions at different initial concentration were prepared and different additives of different concentrations were added into  $18.5 \text{ mg L}^{-1}$  diuron solution to examine their effects on degradation. HCl and NaOH were put into  $18.5 \text{ mg L}^{-1}$  diuron solution to test the effect of pH value on reduction efficiency.

### 2.3. Irradiation process

Gamma-ray was obtained from  $^{60}\text{Co}$  source ( $1.85 \times 10^{16} \text{ Bq}$ ), which was located in Institute of Atomic Energy, Jiangsu Academy of Agriculture Sciences, People's Republic of China. Aqueous solutions (25 mL each) were placed in 50 mL

airtight glass vessels, which were placed in radiation field to a specific distance from the source. 0, 0.2, 0.6, 0.8 and 1.0 kGy were adopted as the radiation doses. Irradiation process lasted about 5 h. The doses that samples absorbed were determined with silver dichromate dosimeter. Silver dichromate dosimeters used in the study were prepared by following the ASTM Standards. Doubly-distilled water and analytical grade reagents of silver dichromate and perchloric acid were used without further purification.  $0.5 \text{ mmol L}^{-1} \text{ Ag}_2\text{Cr}_2\text{O}_7$  in  $0.1 \text{ mol L}^{-1} \text{ HClO}_4$  was prepared and the measurement wavelength was 350 nm. The absorbed dose was determined by the calibration curve.

### 2.4. Analysis

The UV absorbances at 200–400 nm were measured by UV spectrophotometer (Shimadzu, UV-2450). The concentration of diuron was determined using a HPLC system (Agilent, USA, 1200 Series high-performance liquid chromatography) equipped with Hypersil ODS HPLC column (250 mm  $\times$  4.6 mm i.d.,  $5 \mu\text{m}$ , Agilent, USA), a multiple wavelength UV diode array detector and an auto sampler controlling under a Chemstation data acquisition system. The eluent consisted of 70% methanol and 30% water and the flow rate was  $1.0 \text{ mL min}^{-1}$ . The determination wavelength for diuron was set at 254 nm and the column temperature was kept at  $30^\circ\text{C}$ . Retention time of diuron was 5.31 min in the above conditions. The degradation efficiency for

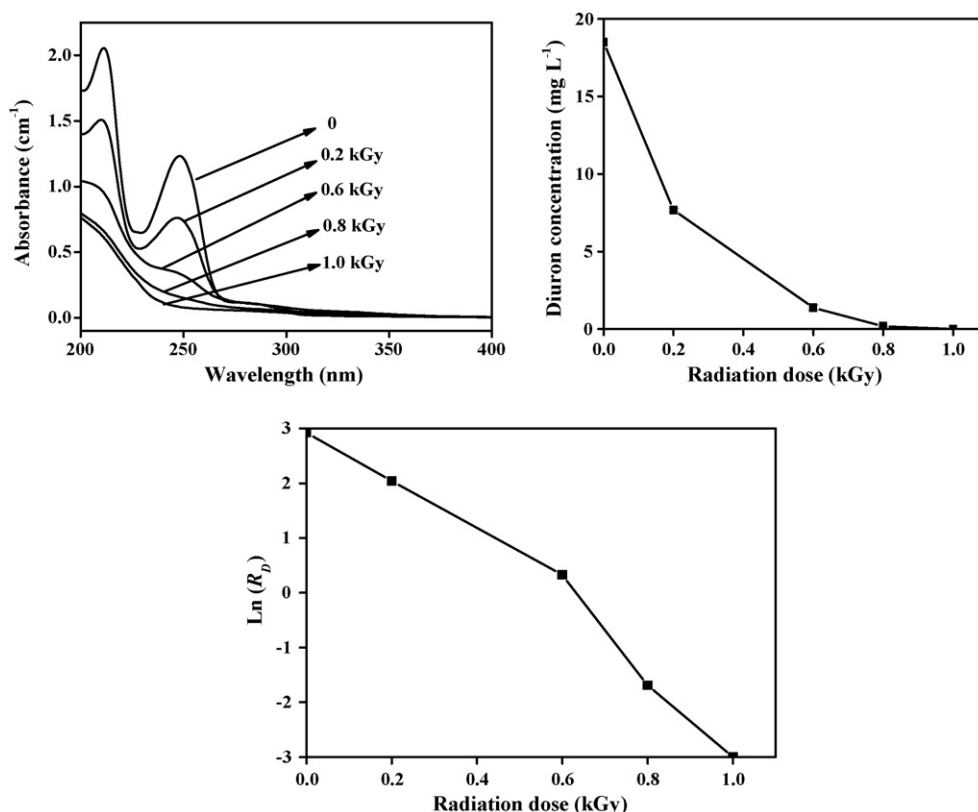


Fig. 1. The UV absorbances at 200–400 nm and diuron concentration after gamma-ray irradiation.

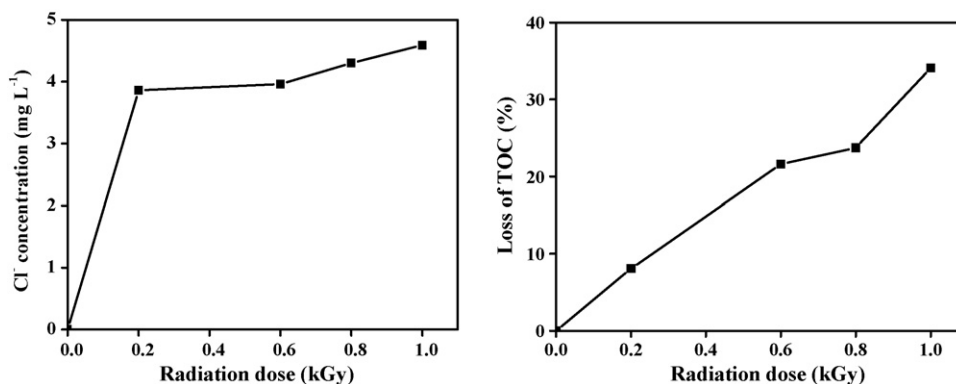


Fig. 2. Concentration of Cl<sup>-</sup> ion and loss of TOC after gamma-ray irradiation.

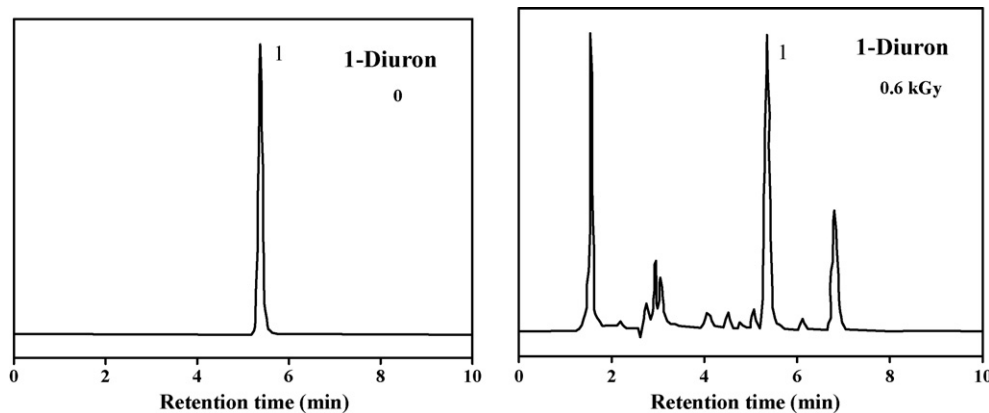


Fig. 3. HPLC chromatograms of diuron solution before and after gamma-ray irradiation.

each sample was calculated from the following Eq. (1):

$$\eta = \left( \frac{R_0 - R_D}{R_0} \right) \times 100\% \quad (1)$$

where  $\eta$  was the degradation efficiency of diuron (%);  $R_D$  was the residual concentration of diuron after gamma-ray irradiation (mg L<sup>-1</sup>);  $R_0$  was the initial concentration of diuron before gamma-ray irradiation (mg L<sup>-1</sup>).

Total organic carbon (TOC) was determined by TOC analyzer (Shimadzu, TOC-5000A). Formation of Cl<sup>-</sup> ion was followed by LC-IC (ICS-2000, anions column ASII-HC, 250 mm long), equipped with conductivity detector. The ion-chromatographic determinations were carried out at 30 °C with 30 mmol L<sup>-1</sup> KOH as the eluent solution and the flow rate was 1.0 mL min<sup>-1</sup>. Retention time of Cl<sup>-</sup> ion was 3.76 min at the above conditions.

The identification of diuron and its degradation products was first performed by LC-MS (ThermoQuestLCQ Duo, USA) with Beta Basic-C<sub>18</sub> HPLC column (150 mm × 2.1 mm i.d., 5 μm, Finnigan, Thermo, USA). 20 μL of diuron solution after gamma-ray irradiation was injected automatically into the LC-MS system. The flow rate was 0.2 mL min<sup>-1</sup>. The other LC conditions were the same as the conditions used in determining diuron concentration. MS conditions were as follows: the electrospray ionization interface was selected. The capillary temperature was set to 275 °C with a voltage of 19.00 V. The spray voltage was 5000 V and the sheath gas flow rate was 18 arb.

The spectra were acquired in the negative scan mode, over the  $m/z$  range 50–600. The pH value was measured by pH monitor (Shanghai Kangyi Instrument Co., Ltd. China, PHS-2C).

### 3. Results and discussion

#### 3.1. Radiation-induced reduction of diuron by gamma-ray irradiation

Fig. 1 shows the UV absorbances at 200–400 nm and diuron concentration after gamma-ray irradiation. The results showed that the UV absorbances at 200–400 nm and diuron concentration decreased with increase of radiation dose. At 0.2 kGy, the degradation efficiency was only 58.5%. The total disappearance of diuron was obtained when 1.0 kGy was adopted as the radiation dose.

Fig. 2 shows the concentration of Cl<sup>-</sup> ion and loss of TOC after gamma-ray irradiation. The results showed that the concentration of Cl<sup>-</sup> ion was becoming higher with increase of radiation dose, while it was contrary for TOC. The concentration of Cl<sup>-</sup> ion was 4.59 mg L<sup>-1</sup> when 1.0 kGy was selected as

Table 1  
The  $G$  values of diuron by gamma-ray irradiation

Radiation dose (kGy)	0.2	0.6	0.8	1.0
$G$ (molecules (100 eV) <sup>-1</sup> )	2.2	1.2	0.9	0.8

the radiation dose. So loss of the chlorine atoms was realized on diuron. At 0.2 kGy, loss of TOC was only 8.1%. Loss of TOC was 34.1% when 1.0 kGy was selected. The loss value of TOC was lower than diuron degradation value at the same dose. So only small part of diuron was mineralized.

Under different conditions, the amount of diuron reduced from per unit dose, i.e. specific reduction efficiency, was different. Generally,  $G$  value could be used to express this parameter (Eq. (2)) [25].

$$G = \frac{(\Delta R)(N_A)}{(D)(6.24 \times 10^{19})} \quad (2)$$

$\Delta R$  – the amount of reduced diuron ( $\text{mol L}^{-1}$ );  $N_A$  – Avogadro constant,  $6.02 \times 10^{23}$  (molecules  $\text{mol}^{-1}$ );  $D$  – Radiation dose ( $10^{-2}$  kGy);  $6.24 \times 10^{19}$  – Conversion constant from kGy to  $100 \text{ eV L}^{-1}$  ( $100 \text{ eV L}^{-1} \text{ kGy}^{-1}$ );  $G$  – specific reduction efficiency (molecules ( $100 \text{ eV}$ ) $^{-1}$ ).

According to Eq. (2),  $G$  values of diuron were obtained, as shown in Table 1. The results showed that  $G$  values decreased with the enhancement of radiation dose. At the higher dose, the relative concentration of active radicals is lower.

By plotting the natural logarithm of residual concentration as a function of radiation dose, a linear relationship could be derived ( $R^2 = 0.9739$ ). This indicated that the degradation of diuron was first-order one with respect to radiation dose and could be described by Eq. (3) [26].

$$R_D = R_0 e^{-kD} \quad (3)$$

$R_D$  – the residual concentration of diuron at any radiation dose ( $\text{mg L}^{-1}$ );  $D$  – radiation dose (kGy);  $R_0$  – the initial concentration of diuron ( $\text{mg L}^{-1}$ );  $k$  – kinetics constant ( $\text{kGy}^{-1}$ ).

The equation  $R_D = 18.52e^{-4.4511D}$  ( $R^2 = 0.9993$ ) could be used to depict the degradation process of diuron by gamma-ray irradiation. Using Eq. (3),  $D_{0.99}$ , the required radiation dose to reduce 99% of initial concentration (i.e. where  $R_D = 0.01R_0$ ) was obtained (Eq. (4)).

$$D_{0.99} = \frac{\ln 0.01}{-k} \quad (4)$$

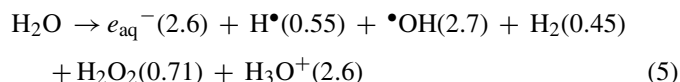
Using Eq. (4),  $D_{0.99}$  of diuron degradation by gamma-ray irradiation was 1.0 kGy.

### 3.2. Identification of degradation products

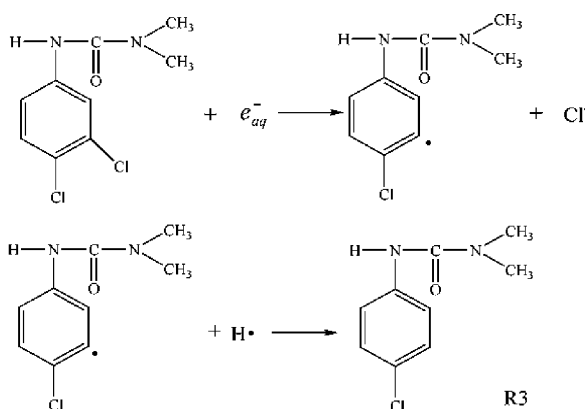
In the present work, we focused mainly on the mechanism of diuron degradation with particular care in the identification of degradation products. Fig. 3 shows HPLC chromatograms of diuron solution before and after gamma-ray irradiation. It could be seen from Fig. 3 that the retention time of almost all degradation products was shorter than diuron. As a result, diuron was decomposed into compounds of small molecules. Diuron and the degradation products were analysed by LC–MS and listed in Table 2.

During gamma-ray irradiation, water radiolysis happened within about  $10^{-7}$  s. Three reactive species, such as hydrogen atoms  $\text{H}^\bullet$ ; hydrated electrons  $e_{\text{aq}}^-$ ; and hydroxyl radicals  $\bullet\text{OH}$ ,

as well as the less reactive species  $\text{H}_3\text{O}^+$ , which could be seen in Eq. (5) (The numbers in the brackets present the amount of the produced radicals ( $100 \text{ eV energy}^{-1}$ ) [24], were produced.



According to the analysis of LC–MS, R6, R8, R11, R13 and R14 as degradation products were produced, which was in accordance with the previous studies [10,15]. R2 was possibly produced by the attack hydroxyl radical on the aromatic ring of R8, with subsequent loss of two chlorine atoms. R15 was the product of the attack of the hydroxyl radical on R13. R7 might be produced by the attack hydroxyl radical on the aromatic ring of diuron, with subsequent loss of a chlorine atom [15].  $e_{\text{aq}}^-$  and  $\text{H}^\bullet$  could react with diuron and the intermediate product as follows:



Based on the identification of intermediate products, the corresponding degradation pathway of diuron by gamma-ray irradiation was proposed in Fig. 4.

### 3.3. The factors affecting degradation efficiency of diuron

#### 3.3.1. Effect of initial concentration of diuron

Fig. 5 shows the effect of initial concentration on diuron degradation by gamma-ray irradiation. As shown in Fig. 5, the degradation rates were decreased with the increasing of initial concentration. It indicated that initial concentration greatly affected the degradation of diuron. When the initial concentration of diuron was  $9.2 \text{ mg L}^{-1}$ , the kinetics constant was  $6.10 \text{ kGy}^{-1}$  and diuron was completely removed at the radiation dose of 0.6 kGy. However, when the initial concentrations were 18.5 and  $27.8 \text{ mg L}^{-1}$ , the kinetics constants were 4.45 and  $3.05 \text{ kGy}^{-1}$ , respectively. Complete removal of diuron at the initial concentration of  $27.8 \text{ mg L}^{-1}$  was achieved when 1.0 kGy was selected as the radiation dose.

#### 3.3.2. Effect of $\text{H}_2\text{O}_2$ and $\text{HCO}_3^-$ on diuron degradation by gamma-ray irradiation

Fig. 6 shows the effect of 1.5%  $\text{H}_2\text{O}_2$  and  $0.24 \text{ mmol L}^{-1}$   $\text{HCO}_3^-$  on diuron degradation by gamma-ray irradiation. The results showed that the degradation value in the presence or absence of additives improved with increasing radiation dose.

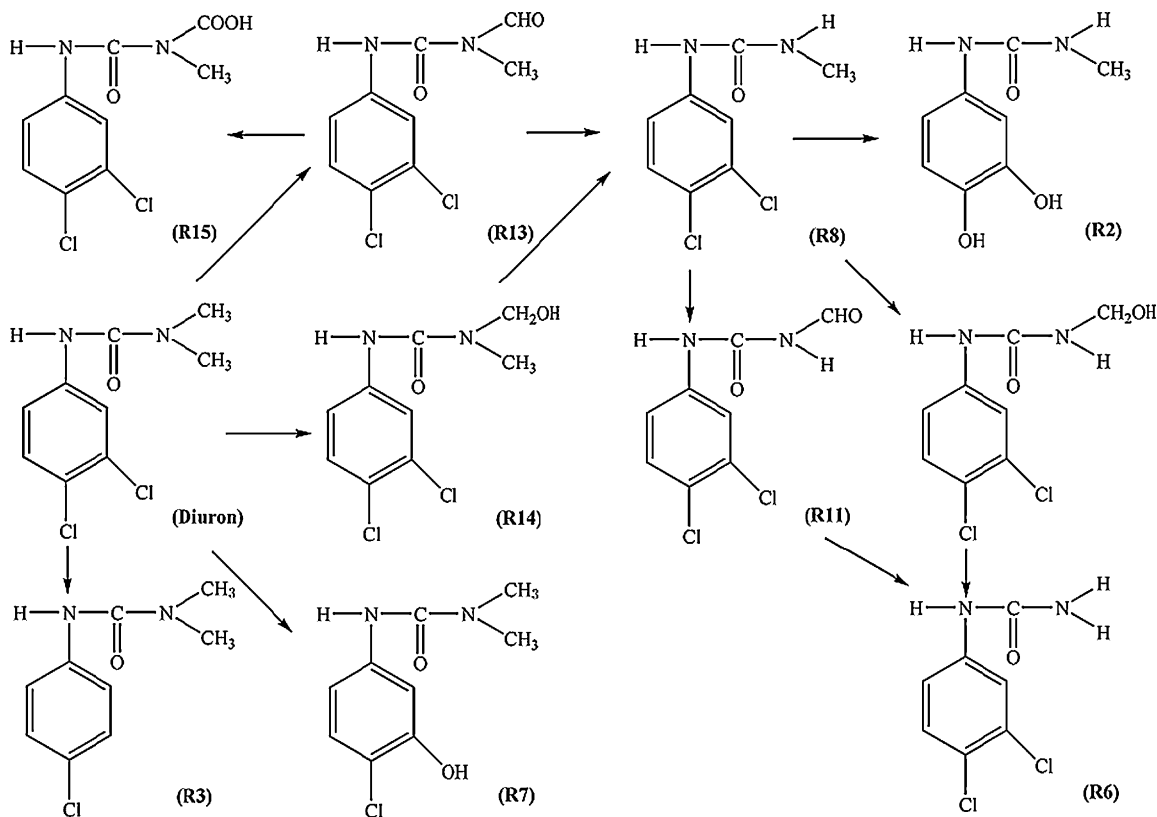


Fig. 4. Degradation pathway of diuron by gamma-ray irradiation.

As shown in Fig. 6, at the same radiation dose the removal efficiency was lower in the presence of H<sub>2</sub>O<sub>2</sub> and HCO<sub>3</sub><sup>-</sup> than that in the absence of them. The kinetics constants in the presence of H<sub>2</sub>O<sub>2</sub> and HCO<sub>3</sub><sup>-</sup> were only 1.77 and 2.90 kGy<sup>-1</sup>, respectively

and they were lower than that in the absence of them (4.45 kGy<sup>-1</sup>). This result also indicated that the degradation of diuron by gamma-ray irradiation was inhibited when H<sub>2</sub>O<sub>2</sub> and HCO<sub>3</sub><sup>-</sup> were added. It might be the reason that the hydroxyl

Table 2  
Structures, retention time of diuron and degradation products by gamma-ray irradiation

	<i>m/z</i>	Retention time (min)	X	Y	Z	W
Diuron	231	5.38	Cl	Cl	CH <sub>3</sub>	CH <sub>3</sub>
R1	179	2.03	-	-	-	-
R2	181	2.02	HO	HO	CH <sub>3</sub>	H
R3	197	2.66	Cl	H	CH <sub>3</sub>	CH <sub>3</sub>
R4	201	6.07	-	-	-	-
R5	202	6.13	-	-	-	-
R6	203	5.94	Cl	Cl	H	H
R7	213	2.76	Cl	HO	CH <sub>3</sub>	CH <sub>3</sub>
R8	217	5.22	Cl	Cl	CH <sub>3</sub>	H
R9	219	2.06	-	-	-	-
R10	227	2.96	-	-	-	-
R11	231	5.25	Cl	Cl	CHO	H
R12	233	4.25	-	-	-	-
R13	245	7.18	Cl	Cl	CHO	CH <sub>3</sub>
R14	247	7.18	Cl	Cl	CH <sub>2</sub> OH	CH <sub>3</sub>
R15	261	4.88	Cl	Cl	COOH	CH <sub>3</sub>

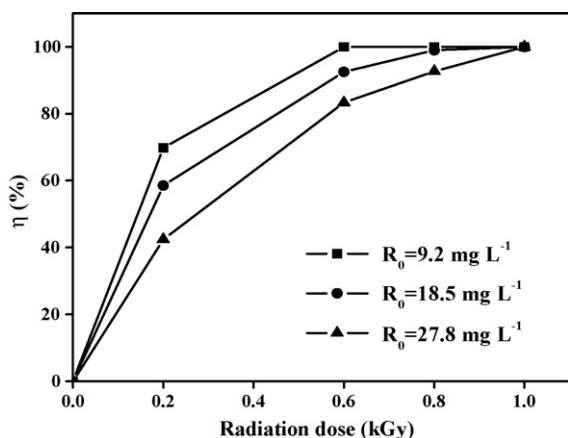


Fig. 5. Effect of initial concentration on diuron degradation by gamma-ray irradiation.

radicals generated in the radiolysis process of water produced hydroperoxyl radicals ( $\text{HO}_2^\bullet$ ) in the presence of a local excess of  $\text{H}_2\text{O}_2$  [27,28]. In the presence of  $\text{HCO}_3^-$ ,  $\bullet\text{OH}$  could be scavenged by it [24]:  $\bullet\text{OH} + \text{HCO}_3^- \rightarrow \text{CO}_3^{\bullet-} + \text{H}_2\text{O}$  (rate constant was  $8.5 \times 10^6 \text{ mol (L S)}^{-1}$ ).

### 3.3.3. Effect of $\text{NO}_3^-$ , $\text{NO}_2^-$ , $\text{CH}_3\text{OH}$ and humic acid on diuron degradation by gamma-ray irradiation

Fig. 7 shows the effect of  $\text{NO}_3^-$  and  $\text{NO}_2^-$  on diuron degradation by gamma-ray irradiation. The results showed that the degradation efficiency in the presence or absence of  $\text{NO}_3^-$  and  $\text{NO}_2^-$  improved with increasing radiation dose. When  $\text{NO}_3^-$  and  $\text{NO}_2^-$  were added, the removal value of diuron was lower in the presence of  $\text{NO}_3^-$  and  $\text{NO}_2^-$  than that in the absence of them at the same radiation dose. Furthermore, the increase of these additives would result in the decrease of the degradation efficiency. These results could also be concluded from the kinetics constant under each condition. It might be the reason that  $e_{\text{aq}}^-$  was quickly cleared by  $\text{NO}_3^-$  and  $\text{NO}_2^-$  [29] and  $\bullet\text{OH}$  was scavenged by  $\text{NO}_2^-$  [30].

Fig. 8 shows the effect of  $\text{CH}_3\text{OH}$  and humic acid on diuron degradation by gamma-ray irradiation. The results showed that the degradation efficiency in the presence or absence

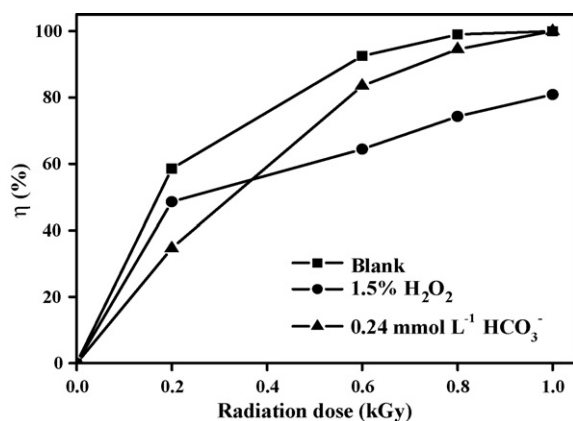


Fig. 6. Effect of  $\text{H}_2\text{O}_2$  and  $\text{HCO}_3^-$  on diuron degradation by gamma-ray irradiation.

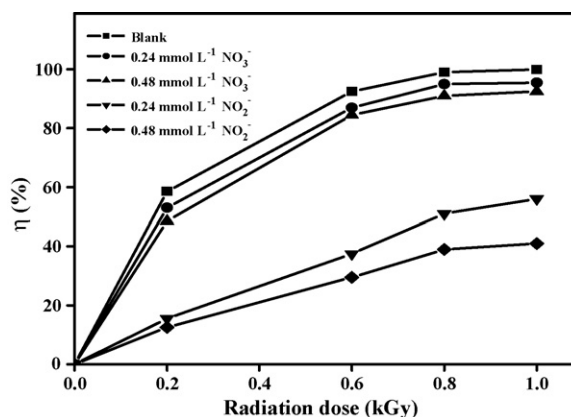


Fig. 7. Effect of  $\text{NO}_3^-$  and  $\text{NO}_2^-$  on diuron degradation by gamma-ray irradiation.

of additives improved with increasing radiation dose. When  $\text{CH}_3\text{OH}$  and humic acid were added, the removal efficiency of diuron was lower than that in the absence of them when the same radiation dose was selected. Furthermore, the increase of these two additives would result in the decrease of the degradation value. Maybe this reason was that methanol reacted quickly with  $\bullet\text{OH}$  and to a lesser extent with  $e_{\text{aq}}^-$  in aqueous solution [24]:  $\bullet\text{OH} + \text{CH}_3\text{OH} \rightarrow \text{H}_2\text{O} + \bullet\text{CH}_2\text{OH}$  (93%) +  $\text{CH}_3\text{O}^\bullet$  (rate constant was  $4.7 \times 10^8 \text{ mol (L S)}^{-1}$ );  $e_{\text{aq}}^- + \text{CH}_3\text{OH} \rightarrow \text{H}^\bullet + \text{CH}_3\text{O}^-$  (rate constant was  $1.0 \times 10^4 \text{ mol (L S)}^{-1}$ ). The addition of humic acid resulted in reducing the removal value since  $\bullet\text{OH}$  was scavenged by humic acid.

Fig. 9 shows the HPLC chromatogram of diuron solution by gamma-ray irradiation when  $\text{CH}_3\text{OH}$  was added. The result showed that only one new peak was detected. By LC-MS, only one of the degradation products R3 was detected. Under this condition, diuron was removed only by loss of the chlorine atom.

### 3.3.4. Effect of pH value on diuron degradation by gamma-ray irradiation

Fig. 10 shows the effect of pH value on diuron degradation by gamma-ray irradiation. The results showed that the pH value was an important factor that might affect the removal efficiency.

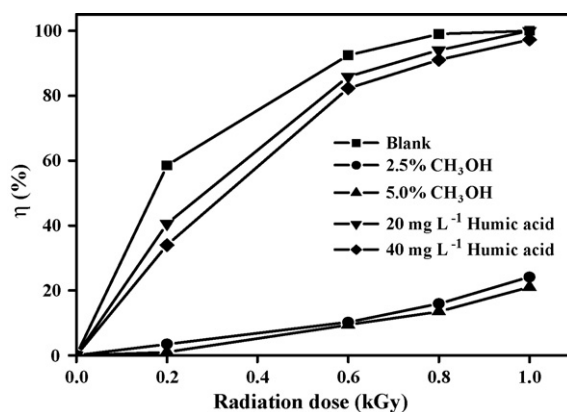


Fig. 8. Effect of  $\text{CH}_3\text{OH}$  and humic acid on diuron degradation by gamma-ray irradiation.

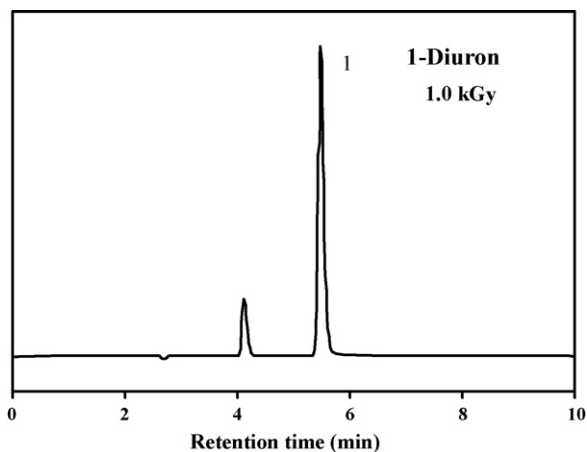


Fig. 9. HPLC chromatogram of diuron solution by gamma-ray irradiation when  $\text{CH}_3\text{OH}$  was added.

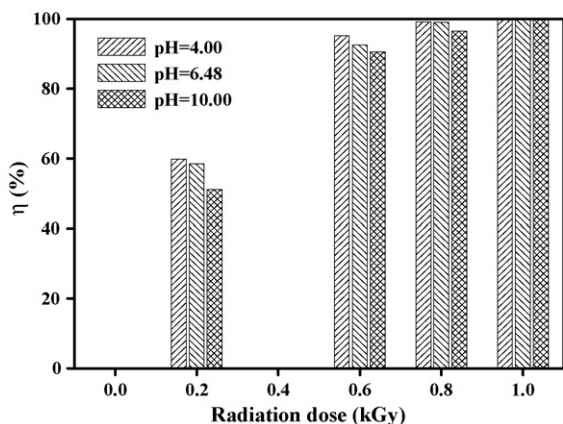


Fig. 10. Effect of pH value on diuron degradation by gamma-ray irradiation.

The degradation efficiency was enhanced in acid condition. At pH 4.00, a reduction of 99.2% was achieved at 0.8 kGy, while at the same radiation dose, at pH 6.46 and 10.00, the degradation efficiencies were 99.0 and 96.5%, respectively. The change of pH value resulted in concentration change of  $[\text{H}^+]$  and  $[\text{OH}^-]$ . As we knew,  $e_{\text{aq}}^- + \text{H}^+ \rightarrow \text{H}^\bullet$  (with rate constant of  $2.3 \times 10^{10} \text{ L (L S)}^{-1}$ ). As a result, the relative concentration of  $\bullet\text{OH}$  was

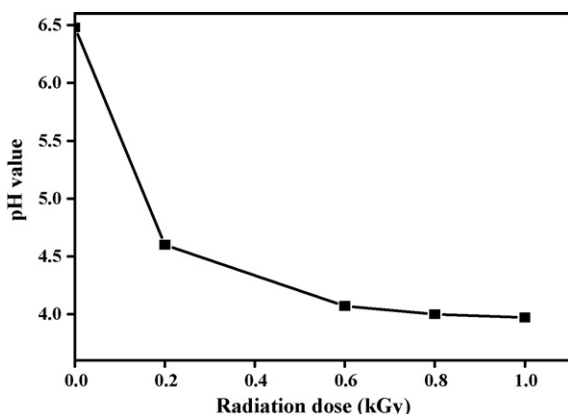


Fig. 11. Change of pH value after gamma-ray irradiation.

higher in acid condition and change of pH value could accelerate  $\bullet\text{OH}$  reacting with diuron.

### 3.4. Change of pH value

Fig. 11 shows the effect of gamma-ray irradiation on pH value. The results showed that the pH value decreased with increasing radiation dose due to lots of  $\text{H}_3\text{O}^+$  produced in the irradiation process (in Eq. (5)) and R15 produced in the degradation process.

## 4. Conclusions

Gamma-ray irradiation could effectively degrade diuron. The UV absorbances at 200–400 nm and diuron concentration decreased with the increase of radiation dose. At the radiation dose of 1.0 kGy, diuron degradation efficiency was 100%. The reaction could be depicted by first order reaction kinetics and the process was possibly because of  $\bullet\text{OH}$  and solvated electrons reacting with diuron. Loss of the chlorine atoms was realized on diuron.

The addition of  $\text{H}_2\text{O}_2$ ,  $\text{HCO}_3^-$ ,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{CH}_3\text{OH}$  and humic acid reduced the degradation efficiency. Furthermore, the increase of  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{CH}_3\text{OH}$  and humic acid would result in the decrease of the removal values.

The pH value could affect the degradation efficiency. Degradation value of diuron was enhanced in acid condition. Based on the experimental results above, gamma-ray irradiation was an effective method to decompose diuron.

Gamma-ray irradiation could be utilized in combination with conventional methods (biological, floatation, adsorption, aerosolization and so on) for the purification of water and wastewater. This technology was used as an additional and/or facilitating process for the removal of pollutants.

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