



## Radiation removals of low-concentration halomethanes in drinking water

Zhaobing Guo<sup>a,\*</sup>, Zheng Zheng<sup>b</sup>, Chunhui Gu<sup>b</sup>, Dengyong Tang<sup>a</sup>

<sup>a</sup> School of Environmental Science & Engineering, Nanjing University of Information Science & Technology, Nanjing 210044, PR China

<sup>b</sup> State Key Laboratory of Pollution Control and Resource Reuse, School of Environment, Nanjing University, Nanjing 210093, PR China

### ARTICLE INFO

#### Article history:

Received 26 March 2008

Received in revised form 24 August 2008

Accepted 26 August 2008

Available online 30 August 2008

#### Keywords:

Gamma radiation

Halomethanes

Drinking water

### ABSTRACT

Gamma radiation induced removals of four halomethanes, with low initial concentrations in drinking water were investigated. The results show that absorbed dose and solution pH are important factors in affecting halomethanes removals. High-absorbed dose and solution pH drive halomethanes removals. The reactions of halomethanes with  $e_{aq}^-$  play a crucial role in their removal processes. Halomethanes removal during the radiation follow a pseudo-first-order kinetics model. Gamma radiation results in a slight decrease in pH and TOC values of drinking water.

© 2008 Elsevier B.V. All rights reserved.

### 1. Introduction

Chlorine is widely applied to disinfection in drinking water, which inevitably produces several disinfection by-products (DBPs), such as halomethanes and haloalkenes [1]. Consumption of such drinking water is associated with increasing cancer risk of urinary and gastrointestinal tracts [2]. Many countries have formulated a strict DBPs standard in drinking water [3,4].

Some efforts have been devoted to DBPs removals from aqueous solution. It is inefficient for most DBPs removals using conventionally biological techniques. While air stripping and activated carbon adsorption may efficiently remove DBPs from aqueous solution, this is only a pollutant transfer process without ultimately solving DBPs pollution problem. Ozone oxidation of DBPs in drinking water is environmentally sound, but money consuming [5]. Recently, ultrasound has been proposed to decompose halomethane mixtures in drinking water, but their removal efficiencies need to be further improved [6]. Therefore, an alternative technique is required for treating low-concentration halomethanes in drinking water.

There have been a few studies on radiolytic decomposition of organic pollutants in aqueous solution [7–10]. In particular, some investigations are involved in radiolytic destruction of THMs from water [11–17]. Unfortunately, the majorities of these studies are not of representative significance because they

failed to mirror actual compositions of chlorinated drinking water, which typically consists of DBPs mixtures with a low concentration. In this study, therefore, gamma radiation induced degradation of low-concentration halomethanes in drinking water (pH = 7.13,  $\text{NO}_3^- = 1.3 \text{ mg/L}$ ,  $\text{Cl}^- = 36.1 \text{ mg/L}$ ) was carried out. The target compounds are involved in carbon tetrachloride ( $\text{CCl}_4$ ), chloroform ( $\text{CHCl}_3$ ), bromodichloromethane ( $\text{CHBrCl}_2$ ) and dibromochloromethane ( $\text{CHBr}_2\text{Cl}$ ) with an initial concentration of 10.4, 15.8, 3.2 and 4.7  $\mu\text{g/L}$ , respectively. We evaluate the possibility of gamma radiation in drinking water treatment under different absorbed doses and solution pH values.

### 2. Materials and methods

#### 2.1. Materials

Drinking water was collected from Science Building in Nanjing University. Chromatographic grade hexane is a MEDIA product and standard sample of Halogenated Volatiles Mix 551A was purchased from Supelco. pH value of drinking water was adjusted using diluted HCl and NaOH solution.

#### 2.2. Radiation process

Radiation was conducted by a  $^{60}\text{Co}$  source ( $1.85 \times 10^{16} \text{ Bq}$ ). Samples (25 mL each) were conserved in 50 mL airtight glass vessels, which were placed in the radiation field to a specific distance from the source to achieve the desired series of absorbed doses.

\* Corresponding author. Tel.: +86 25 58731090; fax: +86 25 58731090.  
E-mail address: [guozbnuist@163.com](mailto:guozbnuist@163.com) (Z. Guo).

Absorbed doses were determined by silver dichromate dosimeter [18].

### 2.3. Analysis

Four halomethanes in drinking water were extracted with hexane. Concentrations of halomethanes were determined using gas chromatograph (GC, Agilent 6890) equipped with electron capture detector (ECD). Carrier gas: helium; HP-5 capillary column: 28.5 m × 0.45 mm × 0.42 μm; GC oven temperature is held constant at 35 °C for the first 4 min, then increases up to 220 °C with a rate of 5 °C/min [6].

Digital pH monitor (JENCO Medel6171) and TOC measuring instrument (Shimadzu-TOC 5000) were used to analyze water qualities before and after gamma radiation.

All the experiments in this study were carried out in duplicate; the averages were calculated to describe the removals of four halomethanes in drinking water.

## 3. Results and discussion

### 3.1. Radiation removal of four halomethanes

#### 3.1.1. Removal efficiency

Gamma radiation of four halomethanes in drinking water was conducted at absorbed doses of 0.5, 1.0, 1.5, 2.0 and 3.0 kGy, respectively. The concentration variations of four halomethanes with increasing absorbed doses at pH 7.13 are compared in Fig. 1. It can be observed that the initial concentrations of CHCl<sub>3</sub>, CCl<sub>4</sub>, CHBrCl<sub>2</sub>, and CHBr<sub>2</sub>Cl in drinking water are 15.8, 10.4, 3.2 and 4.7 μg/L, respectively. At absorbed dose of 3.0 kGy, the residual concentrations of CHCl<sub>3</sub>, CCl<sub>4</sub>, CHBrCl<sub>2</sub> and CHBr<sub>2</sub>Cl decreased to 7.3, 0.8, 0.1, and 0.15 μg/L, about 53.8% CHCl<sub>3</sub>, 92.3% CCl<sub>4</sub>, 96.9% CHBrCl<sub>2</sub> and 96.8% CHBr<sub>2</sub>Cl were removed, respectively. It is indicative of an effective method to remove low-concentration halomethane mixtures from drinking water by using gamma radiation. Besides, we studied the radiation removals of four halomethanes with the same initial concentrations (20 μg/L) in an aqueous solution, and found that the removal percentages of CHCl<sub>3</sub>, CCl<sub>4</sub>, CHBrCl<sub>2</sub> and CHBr<sub>2</sub>Cl at 3.0 kGy were 51.3%, 89.7%, 92.6% and 92.9%, respectively. This increasing order is generally in agreement with that of four halomethanes in drinking water, although the increase in initial concentrations of four halomethanes decreases their removal percentages to some degree.

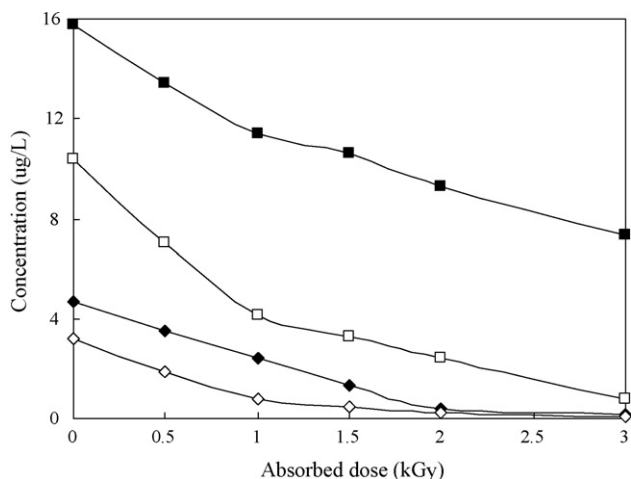


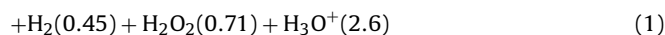
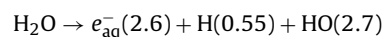
Fig. 1. Removals of four halomethanes under different absorbed doses. pH 7.13; (■) CHCl<sub>3</sub>; (□) CCl<sub>4</sub>; (◆) CHBrCl<sub>2</sub>; and (◇) CHBr<sub>2</sub>Cl.

Table 1

G values of four halomethanes removals under different absorbed doses ( $\times 10^{-5}$  molecules/(100 eV))

| Absorbed dose (kGy) | CHCl <sub>3</sub> | CCl <sub>4</sub> | CHCl <sub>2</sub> Br | CHClBr <sub>2</sub> |
|---------------------|-------------------|------------------|----------------------|---------------------|
| 0.5                 | 38.8              | 42.6             | 15.3                 | 11.1                |
| 1.0                 | 35.5              | 39.5             | 14.1                 | 10.6                |
| 1.5                 | 28.0              | 29.7             | 10.6                 | 10.5                |
| 2.0                 | 26.2              | 25.1             | 8.8                  | 9.9                 |
| 3.0                 | 22.9              | 20               | 6.1                  | 7.0                 |

In diluted solution, gamma radiation of water produces some active species, such as solvated electrons  $e_{aq}^-$ , hydrogen atoms H· and hydroxyl radicals ·OH, which can be described in formula (1) (numbers in the brackets present the amount of produced radicals/100 eV energy) [19]. According to reaction rate constants of halomethanes with the three active species, it can be speculated that reactions between individual halomethanes and  $e_{aq}^-$  play a significant role in halomethanes removals [20].



It is noteworthy from Fig. 1 that residual concentrations of four halomethanes decrease with increasing absorbed doses. A measurement of single halomethane removal efficiency during gamma radiation is generally described by G value. G value can be calculated by the following equation [21]:

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

where  $\Delta R$  is the amount of reduced pollutants (mol/L);  $N_A$  is Avogadro constant,  $6.02 \times 10^{23}$  (molecules/mol);  $D$  is radiation dose ( $10^{-2}$  kGy);  $6.24 \times 10^{19}$  is conversion constant from kGy to 100 eV/L (100 eV/(L kGy));  $G$  is specific removal efficiency (molecules/(100 eV)).

G values of four halomethanes at different absorbed doses are shown in Table 1. It is found that removal efficiencies (G values) of four halomethanes decrease with increasing absorbed doses, which is in agreement with those reported by Mak et al. [14] and Basfar et al. [16]. The decrease in G value possibly results from intermediate reaction by-products and their competitions with parent compounds for the active species at high-absorbed dose.

#### 3.1.2. Removal kinetics

Based on the plots of  $\ln(R_D/R_0)$  versus absorbed dose compiled in Fig. 2, it can be inferred that removals of four halomethanes follow

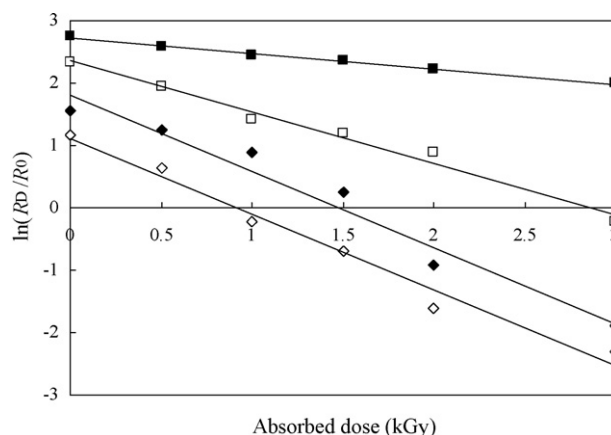


Fig. 2. Determination of degradation kinetics of four halomethanes during gamma irradiation. pH 7.13; (■) CHCl<sub>3</sub>; (□) CCl<sub>4</sub>; (◆) CHBrCl<sub>2</sub>; and (◇) CHBr<sub>2</sub>Cl.

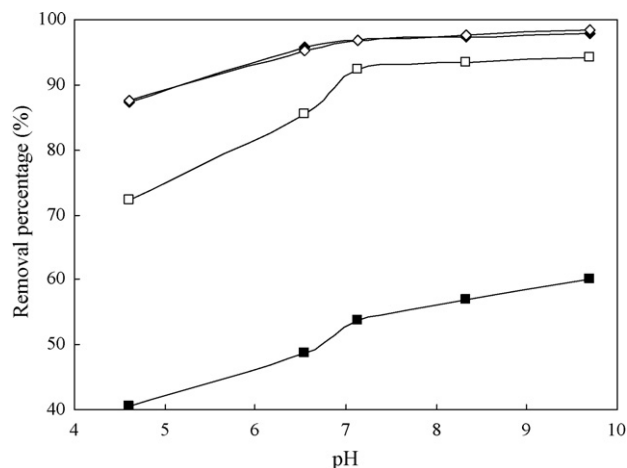


Fig. 3. Removals of four halomethanes under different solution pH values. absorbed dose: 3.0 kGy; (■) CHCl<sub>3</sub>; (□) CCl<sub>4</sub>; (◆) CHBr<sub>2</sub>Cl; and (◇) CHBrCl<sub>2</sub>.

a pseudo-first-order kinetic model with respect to absorbed dose, which can be described by the following equation [22]:

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

where  $R_D$  is residual concentration of halomethanes at different absorbed doses ( $\mu\text{g/L}$ );  $D$  is absorbed dose (kGy);  $R_0$  is initial concentration of halomethanes ( $\mu\text{g/L}$ ); and  $k$  is rate constant (1/kGy).

Rate constants ( $k$ ) of CHCl<sub>3</sub>, CCl<sub>4</sub>, CHBrCl<sub>2</sub> and CHBr<sub>2</sub>Cl removals are 0.25, 0.82, 1.21 and 1.22 kGy<sup>-1</sup>, respectively, and their corresponding correlation coefficients are above 0.97. CHCl<sub>3</sub> shows the slowest removal rate constant, followed by an increasing order of CCl<sub>4</sub>, CHBrCl<sub>2</sub> and CHBr<sub>2</sub>Cl. Removal rate constant of CHBrCl<sub>2</sub> is comparable to that of CHBr<sub>2</sub>Cl in drinking water. This order is exactly consistent with that of reaction rate constants between single halomethane and  $e_{\text{aq}}^-$ , demonstrating the importance of  $e_{\text{aq}}^-$  in removing low-concentration halomethane mixtures during gamma radiation. Besides, removal rate constants of single halomethane are also in dependence on bonds stability. Based on the fact that bond dissociation energy between carbon and bromine atoms (293 kJ/mol) is much smaller compared to those between carbon and chlorine atoms (351 kJ/mol) and carbon and hydrogen atoms (413 kJ/mol), rate constants of four halomethanes removal should follow an increasing order of CHCl<sub>3</sub> < CCl<sub>4</sub> < CHBrCl<sub>2</sub> < CHBr<sub>2</sub>Cl. Our experimental result is nicely in agreement with this order.

### 3.2. Effect of pH on removal of four halomethanes

As Fig. 3 shows, four halomethanes removals are associated with solution pH during gamma radiation. Removals of four halomethanes increase with increasing pH values at absorbed dose of 3.0 kGy. However, a distinct increase in CHBr<sub>2</sub>Cl and CHBrCl<sub>2</sub> removals is not observed, which is probably attributed to their inclusive C–Br bonds and high removal percentages under different pH values. Similar to removal percentages,  $G$  values and pseudo-first-order rate constants of four halomethanes become higher at high pH compared to those at low pH (Tables 2 and 3).

Removal efficiencies of pollutants during gamma radiation are in dependence on the kind of active species [23]. The predominant species from water radiolysis vary with solution pH. In acidic solution,  $e_{\text{aq}}^-$  is likely to react with  $\text{H}_3\text{O}^+$  to generate  $\text{H}^\cdot$  ( $k = 2.3 \times 10^{10} \text{ L}/(\text{mol s})$ ), thereby decreasing the concentration of  $e_{\text{aq}}^-$  to react with halomethanes. In alkaline solution,  $\text{HO}^\cdot$  easily reacts with  $\text{HO}^-$  ( $k = 1.3 \times 10^{10} \text{ L}/(\text{mol s})$ ), thereby decreasing the

Table 2

$G$  values of four halomethanes removals under different solution pH ( $\times 10^{-5}$  molecules/(100 eV))

| pH   | CHCl <sub>3</sub> | CCl <sub>4</sub> | CHCl <sub>2</sub> Br | CHClBr <sub>2</sub> |
|------|-------------------|------------------|----------------------|---------------------|
| 4.61 | 17.2              | 15.7             | 5.5                  | 6.3                 |
| 6.55 | 20.7              | 18.9             | 5.9                  | 6.9                 |
| 7.13 | 22.9              | 20               | 6.1                  | 7.0                 |
| 8.32 | 24.2              | 20.3             | 6.1                  | 7.1                 |
| 9.69 | 25.6              | 20.5             | 6.2                  | 7.1                 |

Table 3

Rate constants ( $k$ ) of four halomethanes removals under different solution pH (1/kGy)

| pH   | CHCl <sub>3</sub> | CCl <sub>4</sub> | CHCl <sub>2</sub> Br | CHClBr <sub>2</sub> |
|------|-------------------|------------------|----------------------|---------------------|
| 4.61 | 0.18              | 0.45             | 0.73                 | 0.71                |
| 6.55 | 0.22              | 0.64             | 1.07                 | 1.11                |
| 7.13 | 0.25              | 0.82             | 1.21                 | 1.22                |
| 8.32 | 0.27              | 0.85             | 1.24                 | 1.28                |
| 9.69 | 0.30              | 0.95             | 1.31                 | 1.33                |

recombination probability between  $\text{HO}^\cdot$  and  $e_{\text{aq}}^-$ . The decreased removal percentage at low pH and the increased removal percentage at high pH of four halomethanes further demonstrate the importance of  $e_{\text{aq}}^-$  in their degradation during gamma radiation.

### 3.3. Variation of solution pH and TOC during the radiation

Fig. 4 describes pH values of drinking water before and after gamma radiation. It is noteworthy that solution pH decreases during gamma radiation. Higher absorbed dose results in a more distinct decrease in pH value. pH values decrease from 7.13 to 7.02, 6.91, 6.88, 6.82 and 6.70 at absorbed doses of 0.5, 1.0, 1.5, 2.0 and 3.0 kGy. The decrease of solution pH values is most possibly the result of formation of organic acids during solution radiolysis. pH values of drinking water after gamma radiation are still at the permitted range of drinking water (6.5–8.5) stipulated by China. This indicates that it is feasible to apply gamma radiation to remove halomethanes in drinking water in our study.

TOC values of drinking water are approximate two orders of magnitude larger than carbon concentrations from four halomethanes (Fig. 5), which indicates the existence of other organic matters in drinking water. TOC value in drinking water gradually decreases during gamma radiation, suggesting that gamma radiation leads to both removals of halomethanes and partial mineralization of other organic matters in drinking water.

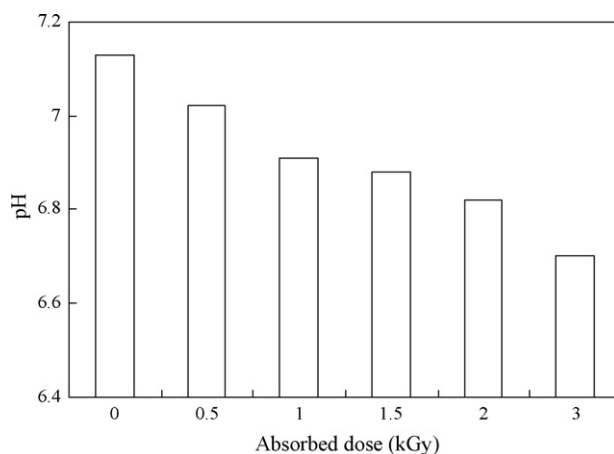


Fig. 4. pH value variations of drinking water before and after gamma irradiation.

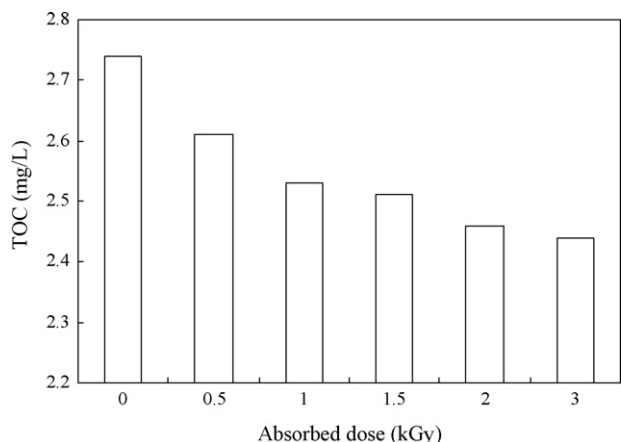


Fig. 5. TOC value variations of drinking water before and after gamma irradiation, pH 7.13.

#### 3.4. Comparison of halomethanes removals using gamma ray and ultrasonic wave

Based on our investigations on the removals of four halomethanes in drinking water using gamma radiation and ultrasonic irradiation [6], we find that these two techniques are feasible for removing low-concentration halomethanes in drinking water. Gamma radiation induced removals of halomethanes in drinking water seem to be more effective than ultrasonic irradiation in our studies. This provides an insight into the removals of trace organic pollutants in aqueous solution using gamma radiation. The removals of halomethanes in drinking water by gamma ray and ultrasonic wave are both associated with molecular polarities. In addition, gamma radiation removals of halomethanes are mainly originated from the reductive reactions of  $e_{aq}^-$ . However, ultrasonic degradation of halomethanes in drinking water is related to the pyrolysis and  $\cdot\text{OH}$  radical oxidation.

#### 4. Conclusion

Gamma radiation is proved to be an effective method to remove low-concentration halomethanes from drinking water. Gamma radiation induced reactions of four halomethanes are chiefly controlled by  $e_{aq}^-$  and follow a pseudo-first-order kinetic model. A slight decrease in pH value of drinking water demonstrates that gamma radiation is achievable in the treatment of halomethanes from chlorinated drinking water.

#### Acknowledgements

We gratefully acknowledge financial supports from State Key Laboratory of Pollution Control and Resource Reuse (PCRRF07010), Jiangsu Provincial Key Laboratory of Coastal Wetland Bioresources and Environmental Protection (JLCBE07004), research fund of Nanjing University of Information Science & Technology (QD54) and

project on Natural Science Foundation Research of Jiangsu Colleges (No. 07KJD610135). We also thank the editor and the anonymous reviewers for improvements to original manuscript.

#### References

- [1] J. Gibbons, S. Laha, Water purification systems: a comparative analysis based on the occurrence of disinfection by-products, *Environ. Pollut.* 106 (1999) 425–428.
- [2] K.T. Cantor, Drinking water and cancer, *Cancer Causes Contr.* 8 (1997) 292–308.
- [3] Sanitary criterion of drinking water, Ministry of Health, People's Republic of China, Beijing, 2001, 1–8 (in Chinese).
- [4] EPA Document, No. 815-F-98-010, US Environmental Protection Agency, GPO, Washington DC, 1998.
- [5] W.Z. Tang, S. Tasso, Oxidation kinetics and mechanism of trihalomethanes by Fenton's reagent, *Water Res.* 31 (1997) 1117–1125.
- [6] Z.B. Guo, C.H. Gu, Z. Zheng, R. Feng, F. Jiang, Sonodegradation of halomethane mixtures in chlorinated drinking water, *Ultrason. Sonochem.* 13 (2006) 487–492.
- [7] T. Miyazaki, Y. Katsumura, M.Z. Lin, Y. Muroya, H. Kudo, M. Taguchi, M. Asano, M. Yoshida, Radiolysis of phenol in aqueous solution at elevated temperatures, *Radiat. Phys. Chem.* 75 (2006) 408–415.
- [8] M.T. Radoiu, D.I. Martin, I. Calinescu, H. Iovu, Preparation of polyelectrolytes for wastewater treatment, *J. Hazard. Mater.* 106 (2004) 27–37.
- [9] J.B. Zhang, Z. Zheng, J.F. Luan, G.J. Yang, W.H. Song, Y. Zhong, Z.C. Xie, Degradation of hexachlorobenzene by electron beam irradiation, *J. Hazard. Mater.* 142 (2007) 431–436.
- [10] Z.B. Guo, Z. Zheng, C.H. Gu, Y.F. Zheng, Gamma irradiation-induced removal of low-concentration nitrite in aqueous solution, *Radiat. Phys. Chem.* 77 (2008) 702–707.
- [11] P. Gehringer, E. Proksch, W. Szinovatz, H. Eschweiler, Decomposition of trichloroethylene and tetrachloroethylene in drinking water by a combined radiation/ozone treatment, *Water Res.* 225 (1988) 645–646.
- [12] P. Gehringer, Advances in radiation processing of wastewater—basics of the process, IAEA-TECDOC-1407 (2004) 7–18.
- [13] W.J. Cooper, E. Cadavid, M.G. Nickelsen, K. Lin, C.N. Kurucz, T.D. Waite, Removing THMS from drinking water using high-energy electron-beam irradiation, *J. Am. Water Works Assoc.* 85 (1993) 106–112.
- [14] F.T. Mak, S. Zele, W.J. Cooper, C.N. Kurucz, T.D. Waite, M.G. Nickelsen, Kinetic modeling of carbon tetrachloride, chloroform and methylene chloride removal from aqueous solution using the electron beam process, *Water Res.* 31 (1997) 219–228.
- [15] T. Tobien, W.J. Cooper, K.D. Asmus, Removal simulation for the radiation-induced degradation of the disinfection by-product chloroform, in: S.E. Barrett, S.W. Krasner, G.L. Amy (Eds.), *Natural Organic Matter and Disinfection By-products: Characterization and Control in Drinking Water*, vol. 761, American Chemical Society, Washington, DC, 2000, pp. 270–281.
- [16] A.A. Basfar, H.M. Khan, A.A. Al-Shahrani, Trihalomethane treatment using gamma irradiation: kinetic modeling of single solute and mixtures, *Radiat. Phys. Chem.* 72 (2005) 555–563.
- [17] C.H. Gu, Z. Zheng, G.J. Yang, W.H. Song, D.S. Hang, Study on degradation of disinfection by-products of chlorination in drinking water by irradiation, *Environ. Sci. Technol.* 2 (8.) (2005) 3–5 (in Chinese).
- [18] J.B. Zhang, Z. Zheng, T. Zhao, Y.F. Zhao, L.H. Wang, Y. Zhong, Y. Xu, Radiation-induced reduction of diuron by gamma-ray irradiation, *J. Hazard. Mater.* 151 (2008) 465–472.
- [19] N. Getoff, Factors influencing of radiation-induced degradation of water pollutants, *Radiat. Phys. Chem.* 65 (2002) 437–446.
- [20] J.W.T. Spinks, R.W. Woods, *An Introduction to Radiation Chemistry*, Wiley, New York, 1990.
- [21] K. Junko, Enhancement of wastewater and sludge treatment by ionizing radiation, in: *Proceedings of the Workshop on the Potential for Engineering-Scale Processing of Waste Treatment Streams by Electron-Beam Irradiation*. USA: University of Miami, (1997) 30–172.
- [22] M.G. Nickelsen, W.J. Cooper, K. Lin, High energy electron beam generation of oxidants for the treatment of benzene and toluene in the presence of radical scavengers, *Water Res.* 28 (1994) 1227–1237.
- [23] L. Wojnárovits, T. Pálfi, E. Takács, Kinetics and mechanism of azo dye destruction in advanced oxidation processes, *Radiat. Phys. Chem.* 76 (2007) 1497–1501.