

Removal of chlorinated hydrocarbons from waters by means of gamma irradiation

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The paper presents the applicability of gamma-irradiation for degradation of chlorinated hydrocarbons generated during chlorination in water. Deionized water was laboratory-contaminated with a mixture of trichloromethane, bromodichloromethane, tribromomethane, dibromochloromethane, trichloroethene, tetrachloroethene and 1,2-dichloroethane at concentrations between 75 and 750 ppb and exposed to gamma-irradiation with absorbed doses of 5.8 kGy, 10.9 kGy, 20 kGy and 27 kGy. Dose rate of 1.01 kGy/h was applied. Analysis of the concentrations of organic pollutants was performed by GC-MS. Removal percentages and radiation-chemical yields (G-values) were determined. The obtained results showed that the radiation exposure with a dose of 5.8 kGy led to a significant degradation of the organic pollutants trichloromethane, bromodichloromethane, tribromomethane, dibromochloromethane, trichloroethene and tetrachloroethene and reached their concentration limit values defined according to the Bulgarian legislation. Dose of 27 kGy was needed to reach 99 % degradation of 1,2-dichloroethane. The calculated G-values were found to vary from 6×10^{-3} $\mu\text{mol/J}$ to 2×10^{-4} $\mu\text{mol/J}$ and decreased in the order: trichloromethane > dibromochloromethane > tribromomethane > trichloroethene > tetrachloroethene > 1,2-dichloroethane.

Keywords: chloroorganic pollutants, water decontamination, gamma radiation, radiolysis, radiation chemical yield

INTRODUCTION

The need for clean drinking water increases with population growth and plays a key role in human health. At the same time, the growth of industrialization, the application of a large amount of diverse and difficult to decompose chemical substances in nature, and the indiscriminate and unreasonable disposal of waste in rivers, seas and oceans presents humanity with a serious challenge to purify water for its needs [1]. Organic pollutants such as halogenated hydrocarbons can be obtained as by-products in the chlorination of water if it contains organic compounds such as microorganisms, algae, humic and fulvic substances [1, 2]. They are dangerous to health because they may have toxic and carcinogenic effects [3]. The use of gamma radiation to destroy hazardous, toxic and biologically persistent organic substances has been proven to be an effective method [1, 4-7]. The effectiveness of gamma irradiation for the removal of organochlorine hydrocarbons has been investigated and evaluated by various research groups [1, 8-10].

Given the harmful biological impact of this type of pollutants, low concentration levels at which they can be present in drinking water have been approved [11]. The effectiveness of the removal of chloroorganic pollutants from drinking water was

found to depend on the concentration of the pollutants, the dose rate, presence of oxygen, temperature, acidity, as well as the by-products present in the system [12].

In this study, gamma irradiation was applied to water artificially contaminated with seven organochlorine substances by applying doses from 5.8 kGy to 27 kGy. The efficiency of the destruction method for trichloromethane, bromodichloromethane, tribromomethane, dibromochloromethane, trichloroethene, tetrachloroethene and 1,2-dichloroethane, contained in a mixed aqueous solution, was evaluated by calculating the destruction percentages and radiochemical yields.

MATERIALS AND METHODS.

Materials

Deionized water was contaminated with a mixture of highly volatile organic pollutants (trichloromethane, bromodichloromethane, dibromochloromethane, tribromomethane, trichloroethene, tetrachloroethene and 1,2-dichloroethane) by the use of a mixed certified reference material (CRM) of CPChem company, Lot №:637094. Table 1 presents the concentrations of the chlorinated hydrocarbons in the CRM.

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Table 1. Mean values of the concentrations [$\mu\text{g/mL}$] and standard uncertainties of the used certified reference material (CRM).

Compound	Concentration [$\mu\text{g/mL}$]
Trichloromethane	1007.1 \pm 9.7
Bromodichloromethane	1009.4 \pm 9.7
Dibromochloromethane	1011.1 \pm 9.7
Tribromomethane	1009.9 \pm 9.7
1,2-Dichloroethane	100.20 \pm 0.99
Trichloroethene	102.73 \pm 1.17
Tetrachloroethene	99.89 \pm 1.21

To create calibration curves needed for analysis of the contaminated water samples, the following solutions were prepared:

Stock solution: from the CPM with a concentration of 1000/100 $\mu\text{g/mL}$ (Table 1), 0.10 mL was pipetted into a 100 mL Class A volumetric flask and diluted with methanol (high purity grade). Thus, a solution with a concentration of 1000/100 $\mu\text{g/L}$ was obtained. It was stored in the dark at 4 °C. Two series of mixed standard solutions were freshly prepared by diluting aliquots from the stock solution with ultrapure water to the required concentrations as follows:

Calibration curve 1: Five solutions with concentration levels from 20/2 to 800/80 $\mu\text{g/L}$.

Calibration curve 2: Five solutions with concentration levels from 2/0.2 to 40/4 $\mu\text{g/L}$.

Four quality control, solutions with concentration ranges of the studied chlorinated hydrocarbons varying from 10/1 to 600/60 $\mu\text{g/L}$ were prepared and recovery rates from 97.5 to 99 % were measured. Aliquots of the contaminated water were taken and irradiated with four different doses of gamma radiation. Six parallel samples were prepared for each absorbed dose of ionizing radiation. The initial concentrations of the chlorinated hydrocarbons are presented in Table 2.

Table 2. Mean values of the concentrations [$\mu\text{g/L}$] and standard uncertainties of the examined halogenated organic pollutants before and after gamma irradiation and the limit values of the concentrations of the pollutants, according to the Bulgarian legislation [11].

Compound	Concentrations [$\mu\text{g/L}$] before and after the absorbed doses					Limit value [$\mu\text{g/L}$]
	0 kGy	5.8 kGy	10.9 kGy	20 kGy	27 kGy	
1,2-Dichloroethane	74.8 \pm 9.42	32.1 \pm 4.56	13.4 \pm 4.30	1.92 \pm 0.41	0.74 \pm 0.16	3
Bromodichloromethane	747 \pm 68.7	< 2.38***	< 2.38	< 2.38	< 2.38	100*
Tribromomethane	750 \pm 75.0	1.94 \pm 0.21	< 1.32***	< 1.32	< 1.32	
Trichloromethane	738 \pm 62	17.5 \pm 3.92	1.17 \pm 0.35	0.47 \pm 0.19	0.48 \pm 0.04	
Dibromochloromethane	744 \pm 40.2	0.25 \pm 0.12	< 0.05***	< 0.05	< 0.05	
Tetrachloroethene	74.7 \pm 8.96	0.58 \pm 0.14	< 0.46***	< 0.46	< 0.46	10**
Trichloroethene	73.9 \pm 8.43	3.75 \pm 1.43	< 0.82***	< 0.82	< 0.82	

* Sum of the reaction products in drinking water that result from water disinfection or oxidation: trichloromethane, bromodichloromethane, dibromochloromethane and tribromomethane; ** Sum of the detected and quantified concentrations of individual substances; *** Limits of quantification (LOQ) of the studied compounds.

Methods

- *Sample preparation.* Samples were prepared for analysis by placing 2 g of anhydrous sodium sulfate in headspace vials. 5.0 mL of the water sample were pipetted out, transferred to the vial, after which it was sealed hermetically with a hand press.

- *Gamma irradiation.* Gamma-irradiation was performed with an industrial gamma-irradiator BULGAMMA based on JS-850 ^{60}Co type gamma-irradiator at Sopharma AD. Irradiation with 5.8 kGy, 10.9 kGy, 20 kGy and 27 kGy was performed. The dose rate was 1.01 kGy/h. The absorbed dose distributions were measured with ethanol chlorobenzene routing dosimeters. All the experiments were performed at room temperature (25 ± 1 °C).

- *Gas chromatography.* The concentrations of the chloroorganic pollutants in the water samples were determined on a gas chromatograph type "GC System 6890N" manufactured by Agilent Technologies, Germany, with a mass detector type "5975 Mass Selective Detector" and a headspace system type "G 1888 Headspace Sampler". The analysis was performed according to BDS EN ISO 10301: 1997: "Water quality. Determination of highly volatile halogenated hydrocarbons - gas chromatographic methods". The samples were analyzed under the following operating conditions: column DB-642, model J&W 122-1334 with dimensions 30.0 m \times 250 μm \times 1.40 μm and maximum temperature 260°C; carrier gas helium 5.0; constant gas flow with carrier gas velocity 1.2 mL/min; split ratio 10:1; volume of the injected sample 1.0 μL ; make-up gas (helium) flow 30 mL/min; injector temperature 220°C; column temperature 50°C; oven temperature 50°C (20 min) to 220°C (15 min) at 25°C/min; transfer line temperature 240°C.

Headspace conditions: loop 60°C, transfer line 70°C, carrier pressure 12.4 psi, vial pressure 24.7 psi.

- *The effect of gamma-irradiation* on the pH of the studied contaminated water samples was measured by using a portable pH-meter Milwaukee, Smart pH Meter, MW 102.

- *The analysis of pH* before and after gamma radiation treatment of the solutions was carried out according to the standardized method BDS 3424:1981 „Drinking water. Method for determination of pH”. A portable pH meter Milwaukee, Smart pH Meter, MW 102 was used which was calibrated by standard buffer solutions.

- *Determination of removal percentage and radiation chemical yield (G-value).* The efficiency of the applied gamma irradiation treatment for decomposition of the studied organic pollutants was evaluated, based on the removal percentage (Eq. 1) and radiation chemical yield (G-value), using Eq. 2. The G-value is defined as the number of molecules of a compound formed or destroyed per 100 eV of absorbed energy.

$$\% \text{ Removal} = \frac{(C_0 - C_i)}{C_i} \times 100 \quad (1)$$

$$G = \frac{(C_0 - C_i) \times N_A}{D \times 6.24 \times 10^{16}} \quad (2)$$

where C_0 is the concentration of the initial contaminant (mol/L) before irradiation (non-irradiated samples) while C_i is the contaminant concentration (mol/L) after irradiation, D is the absorbed dose (Gy), N_A is the Avogadro number (6.023×10^{23} molecules/mol), 6.24×10^{16} is the conversion factor of Gy at 100 eV/L. G-values are expressed in $\mu\text{mol/J}$, considering $1 \text{ molecule} \times (100 \text{ eV})^{-1} = 0.10364 \mu\text{mol/J}$.

RESULTS AND DISCUSSION

Table 2 presents the mean values from six parallel samples with the corresponding calculated standard uncertainties, before and after the absorbed gamma radiation doses. The limits of the concentrations of the pollutants in drinking water according to the Bulgarian legislation are also included. The obtained results show that gamma irradiation with a dose of 5.8 kGy leads to a significant destruction of the organic pollutants trichloromethane, bromodichloromethane, tribromo methane, dibromochloromethane, trichloroethene and tetrachloroethene, reaching their maximum permissible concentrations determined according to the Bulgarian legislation [11].

The lowest dose of 5.8 kGy was sufficient to destroy more than 99% of bromodichloromethane, tetrachloroethene, dibromochloromethane and

tribromomethane (Fig. 1). Bromodichloromethane was found to be completely destroyed even at the lowest absorbed dose, while 100% destruction of the other three compounds was observed after a dose of 10.90 kGy. Trichloromethane and trichloroethene, as shown in Fig. 1, were also removed by more than 90% at the lowest dose applied. Trichloromethane did not reach 100% decay, unlike trichloroethene, which was decomposed up to 100% after 10.90 kGy. The most persistent among the seven pollutants studied in terms of gamma radiation was shown to be 1,2-dichloroethane. At the lowest dose it decays by 57%, and even a dose of 27 kGy did not destroy it completely.

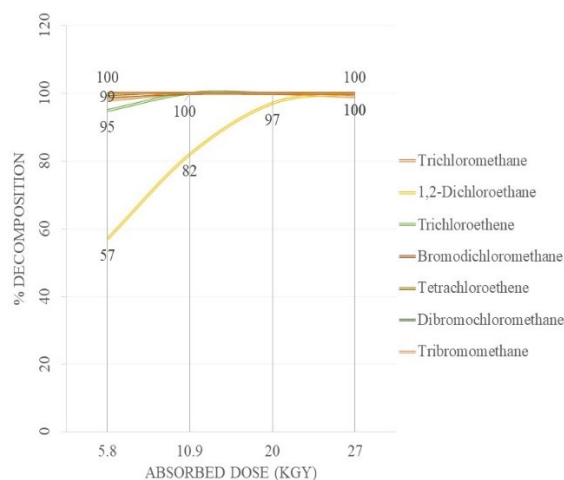


Fig. 1. Removal (in %) of trichloromethane, bromodichloromethane, tribromomethane, dibromochloromethane, trichloroethene, tetrachloroethene and 1,2-dichloroethane as a function of absorbed dose.

To determine the dose needed for decomposition of 1,2-dichloroethane present in the current model system to the maximum permissible concentration in drinking water, the concentration of the pollutant was plotted against the applied doses, as shown on Fig. 2. Polynomial regression of third order was used to derive an equation describing the dependence of the pollutant concentration on the absorbed dose.

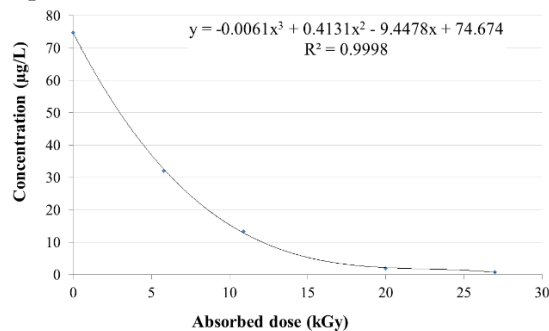
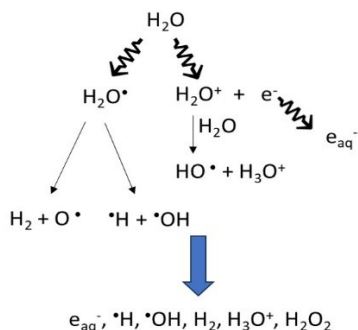


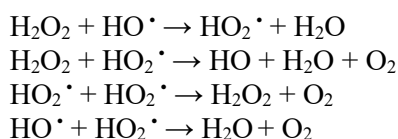
Fig. 2. Decrease of the concentration [$\mu\text{g/L}$] of 1,2-dichloroethane in the mixed water solution with the increase of the absorbed dose, at 1.01 kGy/h dose rate.

The calculations performed using the equation on Fig. 2. showed that absorbed dose of 17.8 kGy was required to remove 1,2-dichloroethane to concentrations below the acceptable concentration level of 3 µg/L.

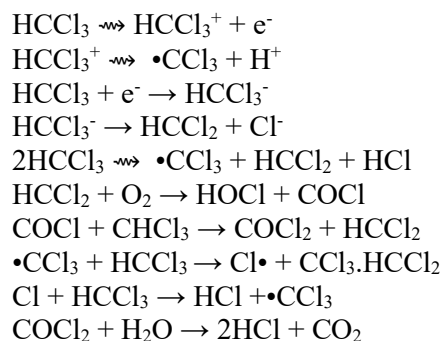


Scheme 1. Products of water radiolysis.

Radiolysis of water, as the main component of aqueous solutions, is accompanied by the formation of H_2O_2 and OH-radicals [1, 13]. The interaction of the generated molecular products and free radicals results in the formation of oxygen and oxidizing radicals, which are attributed to the degradation of organic pollutants.



The radiation-chemical transformations that take place with various hydrocarbons and their halogen derivatives have been the subject of research in previous experiments. For example, the processes that take place with trichloromethane under the action of gamma radiation were described by Hummel *et al.* [9]:



In the presence of oxygen, $HCCl_3 + O_2 \rightarrow Cl_3COOH$ [14, 15].

The G-values of the chlorinated hydrocarbons after irradiation in a mixed water solution with different absorbed doses are presented on Figs. 3, 4. The total decomposition of bromodichloromethane after the lowest applied dose of 5.8 kGy, marked as concentration < LOQ, as shown on Table 2, does not allow the G-value to be calculated precisely. However, it can be assessed to be higher than $7.57E-03 \mu\text{mol/J}$.

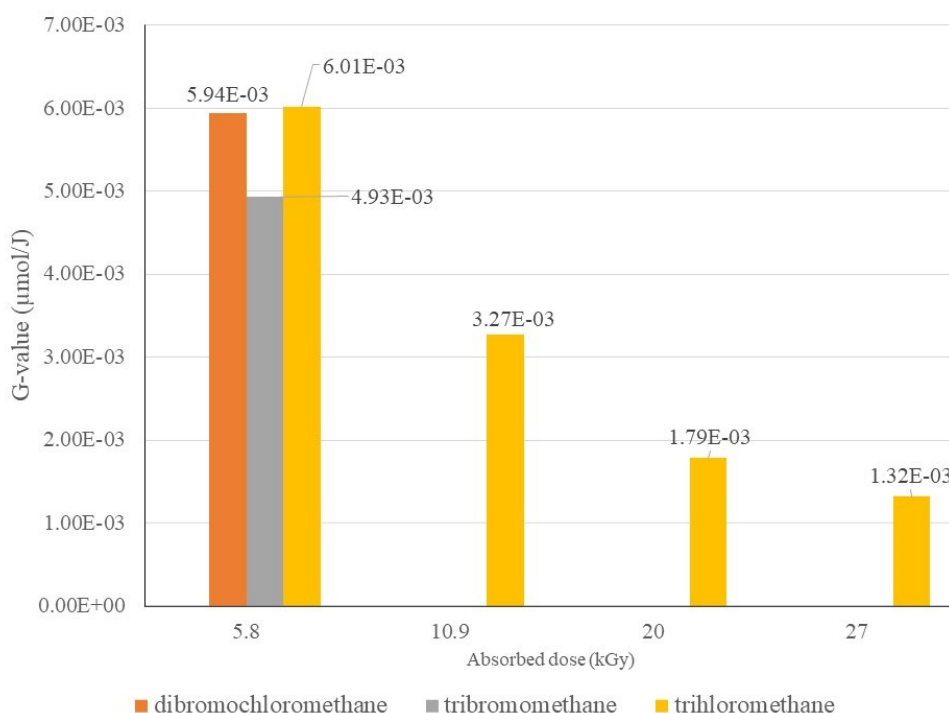


Fig. 3. Radiation chemical yields (G-values) of dibromochloromethane, tribromomethane and trichloromethane as a function of the applied gamma irradiation doses.

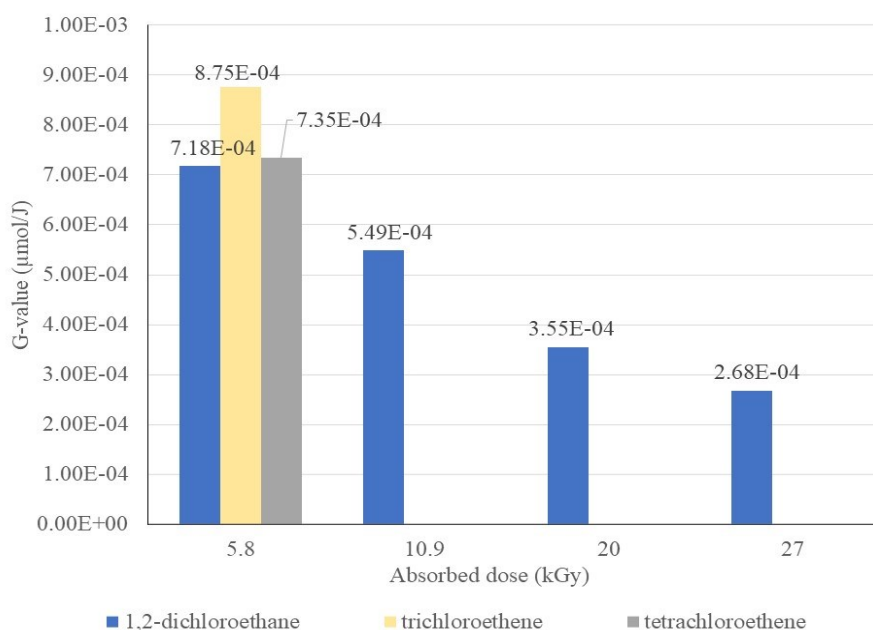


Fig. 4. Radiation chemical yields (G-values) of 1, 2-dichloroethane, trichloroethene and tetrachloroethene as a function of the applied gamma irradiation doses.

It can be seen that the G-values of trichloromethane (Fig. 3) and 1,2-dichloroethane (Fig. 4) decreased with the increase in the absorbed doses. Such an effect was reported for most organic systems in other studies [10, 16]. The radiochemical yield is a function of the dose rate, the absorbed dose, the temperature, and the concentrations of the substances in the irradiated system. For example, it has been reported that the higher dose rates result in a higher concentration of reactive species in the solutions, which leads to increased radical recombination [10].

G-values were found to decrease in the following order: trichloromethane > dibromochloromethane > tribromomethane > trichloroethene > tetrachloroethene > 1,2-dichloroethane.

The influence of gamma irradiation on the pH values of the samples was also evaluated. The analysis showed that gamma radiation has a strong influence on the acidity of the solution. The measured values are presented in Table 3.

Table 3. pH values in deionized water, contaminated with the studied halogenated hydrocarbons non-irradiated water sample and samples irradiated with doses from 5.8 to 27 kGy

Water sample	pH
Deionized water	6.55 ± 0.026
Contaminated, non-irradiated	7.58 ± 0.030
Irradiated with 5.8 kGy	3.91 ± 0.031
Irradiated with 10.9 kGy	4.00 ± 0.032
Irradiated with 20.0 kGy	3.89 ± 0.031
Irradiated with 27.0 kGy	3.78 ± 0.030

The data show that after irradiation, the pH of the irradiated aqueous solution decreases, becomes acidic to a pH value beyond the permissible norm set by Regulation No. 9 [11] which allows the pH in drinking water to be from 6.5 to 9.5.

The increase in the acidity of the water solution after radiation exposure is a well-known effect, which is explained by the formation of organic and mineral acids, together with the other end products CO₂ and H₂O obtained as a result of the complete mineralization of the organic pollutants [17].

CONCLUSIONS

Experiments conducted with water contaminated with seven highly volatile chlorinated hydrocarbons at concentrations between 75 and 750 ppb showed that gamma irradiation with absorbed dose of 5.8 kGy was sufficient to destroy trichloromethane, bromodichloromethane, tribromomethane, dibromo chloromethane, trichloroethene, and tetrachloroethene to safe low concentrations. Absorbed dose of 17.8 kGy was found to be required to destroy 1,2-dichloroethane to the permitted concentration levels in drinking water, when 1.01 kGy/h dose rate is used. The increased acidity of the water as a result of the gamma irradiation showed the need for further treatment of the irradiated water to reach a pH that fits within the permissible norms.

The results of the present study may be useful in planning the application of gamma irradiation for the removal of chlorinated hydrocarbons from drinking water.

REFERENCES

1. N. Getoff, *Radiat. Phys. Chem.*, **35** (1-3), 432 (1990).
2. J. J. Rook, *Water Treat. Exam.*, **23** (2), 234 (1974).
3. D.T. Boyles, in: Hydrocarbons and halogenated hydrocarbons in the aquatic environment, D. MacKay, B. K. Afghan (eds.), Environmental Science Research, vol. 16. Springer, Boston, MA, 1980, p. 545.
4. N. Getoff, *Appl. Radiat. Isotopes*, **37**, 1103 (1986).
5. N. Getoff, *Appl. Radiat. Isotopes*, **40**, 585 (1989).
6. N. Getoff, *Radiat. Phys. Chem.*, **47**, 581 (1996).
7. IAEA-TECDOC-1598, Radiation treatment of polluted water and wastewater, IAEA, Vienna, 2008.
8. X. Wu, T. Yamamoto, M. Hatashita, *Bull. Chem. Soc. Jpn.*, **75**, 2527 (2002).
9. R. W. Hummel, A. B. Van Cleave, J. W. Spinks, *Can. J. Chem.*, **32**, 522 (1954).
10. A. A. Basfar, H. M. Khan, A. A. Al-Shahrani, *Radiat. Phys. Chem.*, **72**, 555 (2005).
11. Regulation No. 9 on the quality of water intended for drinking and household purposes. LEX-FAOC033621, State Gazette No. 30, 28 March 2001.
12. N. Getoff, *Radiat. Phys. Chem.*, **65**, 437 (2002).
13. G. R. Choppin, J. Liljenzin, J. Rydberg, Radiochemistry and nuclear chemistry, Third edition, Butterworth-Heinemann, Woburn, 2002.
14. J. W. Schulte, J. F. Suttle, R. Wilhelm, *R. J. Am. Chem. Soc.*, **75**, 2222 (1953).
15. M. Ghalei, P. M. Khoshouei, J. Vandenborre, F. Guerard, G. Blain, M. Zarei, F. Haddad, M. Fattahi, *Radiat. Phys. Chem.*, **198**, 110224 (2022).
16. A. G. Plant, B. Kos, A. Jazbec, L. Snoj, M. J. Joyce, V. Najdanovic-Visak, *Ind. Eng. Chem. Res.*, **62** (49), 21152 (2023).
17. M. Torun, D. Solpan, O. Güven, *Hacet J. Biol. Chem.*, **42** (1) 115 (2014).