

MAŁGORZATA WOLSKA<sup>1</sup>

## EFFECTS OF UV IRRADIATION ON BIODEGRADABILITY OF NATURAL ORGANIC MATTER

Changes in concentration of total organic carbon in natural organic matter during UV irradiation have been examined, and especially its biodegradable fraction. The studies have shown better effectiveness of elimination of organic substances for highly contaminated water than that obtained for pre-treated water. UV irradiation assured the decrease of all fractions of total organic carbon, which indicates the domination of mineralization over the transformation of multi-molecular substances into simpler ones. This means that organic substances were mineralised during UV irradiation. The effective elimination of non-biodegradable dissolved organic substances absorbing UV radiation ensures a very large decrease in potential of disinfection of by-products.

### 1. INTRODUCTION

The necessity of removal of effective organic substance from water for human consumption stems from the hazards that these substances may present to human health [1]. Some constituents of natural organic matter are toxic [2], while others may pose a hazard due to transformations they undergo during the water treatment [3, 4]. The greatest amount of hazardous organic substances are formed during chemical oxidation with the use of chlorine-based oxidants. The commonness of the use of chlorine as a disinfectant makes the removal of organics substances, especially disinfection of by-products, the object of attention [5, 6]. Fewer studies concern the effective elimination of the biodegradable fraction of organic substances, which determines development of microorganism, including pathogen development [7–9]. The presence of BDOC in water introduced into the distribution system intensifies biofilm development and is considered the main cause of lack of water biostability. This is in fact the main cause of secondary water

---

<sup>1</sup>Wrocław University of Science and Technology, Chair of Water and Sewage Treatment Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, e-mail address: malgorzata.wolska@pwr.edu.pl

contamination in the distribution system. Therefore, it is significant to maximally limit the amount of BDOC in water for human consumption.

## 2. EXPERIMENTAL

Evaluations of changes in biodegradability levels of organic substances caused by UV irradiation were performed for raw surface (RW) water and water after pre-treatment in technical conditions (TW). Studies were conducted in laboratory conditions with the use of a low pressure UV lamp (type UVL0121SP), which was capable of radiation dosages sufficient for disinfection [10]. The UV irradiation times used were 10, 20, 30, 40, 50 and 60 min.

For this study, raw surface water taken in a water treatment plant was used, along with this same water after treatment in real-life conditions. This treatment consisted of coagulation/sedimentation, filtration through a sand bed, indirect oxidation (ozonation) and absorption with granulated activated carbon. The water samples were taken before chemical disinfection with chlorine and chlorine dioxide.

The treated water samples were taken some time after taking raw water samples, which was due to the time it takes water to flow through the water treatment system. The use of the UV irradiation process on waters with varying contamination levels and different organic substance structure would allow determining the susceptibility of organic matter to transformation and degradation, in particular changes in their biodegradability levels. In samples before and after UV exposure, color intensity ( $C$ ),  $UV_{254}$  absorbance ( $A$ ), dissolved organic carbon (DOC) content, and biodegradable dissolved organic carbon (BDOC) content were determined. Non-biodegradable dissolved organic carbon content was calculated as the difference between concentrations of DOC and BDOC.

Color intensities and UV absorbance were determined with a Shimadzu spectrophotometer using samples filtered through membrane pads with 0.45  $\mu\text{m}$  pores. DOC concentrations were determined with a Hach-Lange TOC analyzer. BDOC concentrations were determined as the difference in DOC concentration before and after incubation with microorganisms in accordance with standard methods. The samples were fertilized with bacteria characteristic of the aquatic environment, and were incubated for five days at thermostatic conditions. Details of this procedure have been described by Servais [11]; the method is recommended by *Standard Methods for the Examination of Water and Wastewater*, 20th Edition, Washington, DC, 1998.

## 3. RESULTS AND DISCUSSION

Raw water (RW) contained more than twice as much dissolved organic carbon than treated water (TW) (Table 1). The biodegradable fraction percentage in raw water was in the range of 5.5–7.1% while in treated water it amounted to 3.6–10.5%. A significant

increase in the contents of biodegradable substance in water after water treatment may be explained by the transformation of organic substance during chemical oxidation [12, 13], leading to formation of organic substances of a low molecular weight, more readily absorbed by microorganisms. However, despite a higher participation of the biodegradable fraction in pre-treated water, the concentration was lower than that found for raw water.

Table 1

Ranges of water quality indicators for raw and treated water before and after photolysis

Indicator	Raw water		Treated water	
	Before	After	Before	After
C, g Pt/m <sup>3</sup>	7.80–11.10	3.70–9.50	2.30–4.40	1.50–3.80
A, m <sup>-1</sup>	9.00–20.50	2.20–15.36	2.92–3.52	1.72–3.30
DOC, g C/m <sup>3</sup>	6.68–14.30	2.74–11.78	2.77–4.10	1.54–3.64
BDOC, g C/m <sup>3</sup>	0.39–0.89	0.07–0.64	0.12–0.42	0.02–0.35
NBDOC, g C/m <sup>3</sup>	6.29–13.51	2.53–11.24	2.48–3.68	1.52–3.29

Elevated DOC levels in water were accompanied by higher color intensities which was due to the presence of humic acids [14]. On the other hand, aromatic compounds dominated among non-biodegradable substances, causing larger UV absorbance values [15, 16] which was confirmed by the linear correlation that was found. UV radiation caused an improvement in all analyzed water quality indicators, and the degree of improvement depended on the irradiation time and the water contamination level (Fig. 1).

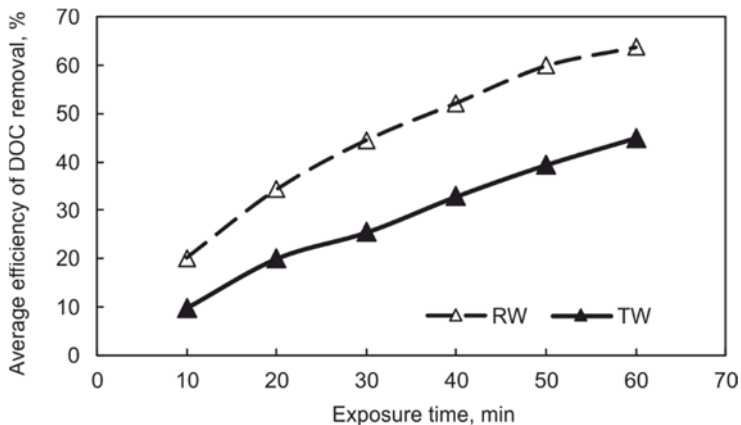


Fig. 1. Effect of UV exposure time on organic substance elimination

Along with an increase in UV exposure time, there was an increase in organic substance removal effectiveness. Irrespective of initial water contamination, the largest increase in process effectiveness was observed in the first 30 min, while a further increase

in exposure time improved process effectiveness only insignificantly. The effectiveness in removing dissolved organic carbon from raw water was much greater than that for the less contaminated treated water. A similar relationship was found by Imoberdof and Mohseni [17] in their studies. A significant influence of water contamination levels on effectiveness of UV irradiation is confirmed by the following linear correlation found at a confidence level of  $\alpha = 0.05$ :

$$\Delta\text{DOC} = 0.6078\text{DOC}_0 - 0.4194$$

Among the removed organic substances, the biodegradable fraction made up only 6.5–10.4% and 8.9–18.7% of removed DOC for raw and treated water respectively (Fig. 2).

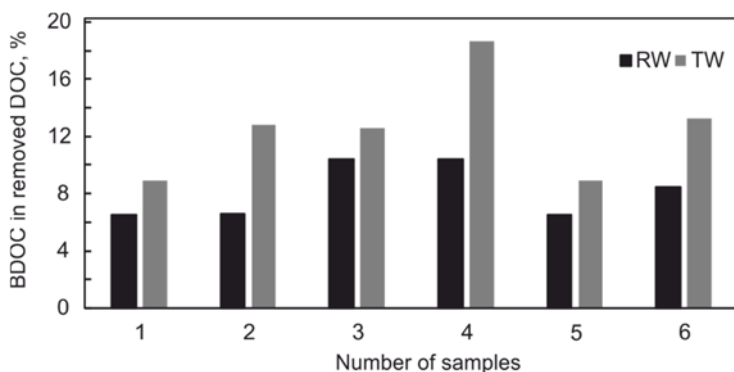


Fig. 2. The percentage of biodegradable organic substances in DOC

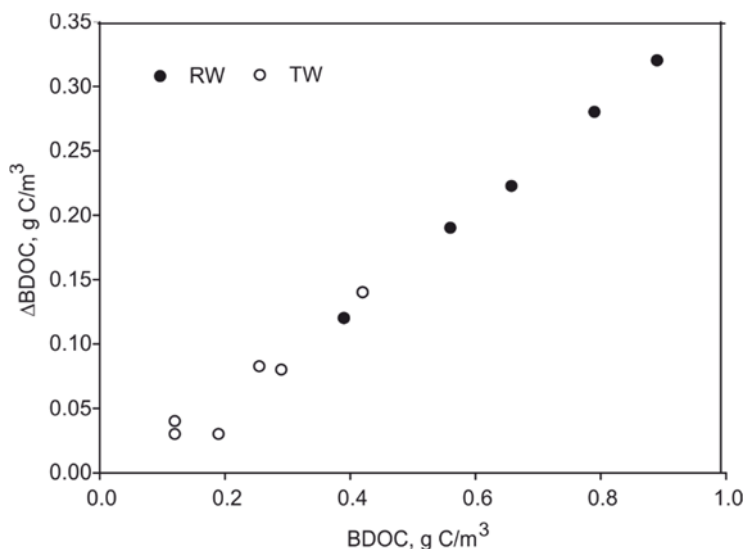


Fig. 3. The effect of initial BDOC concentration on the degree of its reduction

Such a small percentage of BDOC in removed DOC is caused by the fact that final concentration is a result of the mineralization of organic substance [18] and NBDOC transformation into biodegradable carbon, which takes place during UV irradiation [19]. The reduction of BDOC concentration found for both water sources indicates a domination of mineralization of organic substance when compared to transformation which could occur simultaneously. An inverse relationship was found by Paul et al. [20], which was caused by a higher simple organic compound content in water used for that study. Despite a small percentage of the biodegradable fraction in removed DOC, a reduction of BDOC was significant, and for both water sources was directly proportional to BDOC content in illuminated water (Fig. 3). Consequently, on average 3 times as much biodegradable substance was removed from raw water than from pre-treated water (Table 2).

Table 2

Ranges of effectiveness and reductions in values  
of water quality indicators (for 30 min UV exposure)

Indicator	Raw water		Treated water	
	Reduction	Effectiveness	Reduction	Effectiveness
C, g Pt/m <sup>3</sup>	2.70–6.40	34.62–57.66	0.80–2.30	32.50–52.27
A, m <sup>-1</sup>	6.84–17.10	54.98–83.41	0.90–1.62	25.71–46.02
DOC, g C/m <sup>3</sup>	4.53–8.79	50.08–70.32	0.90–2.22	27.11–54.15
BDOC, g C/m <sup>3</sup>	0.32–0.65	57.14–83.93	0.08–0.28	58.62–84.21
NBDOC, g C/m <sup>3</sup>	4.06–8.22	48.32–70.80	0.74–1.94	25.63–52.72

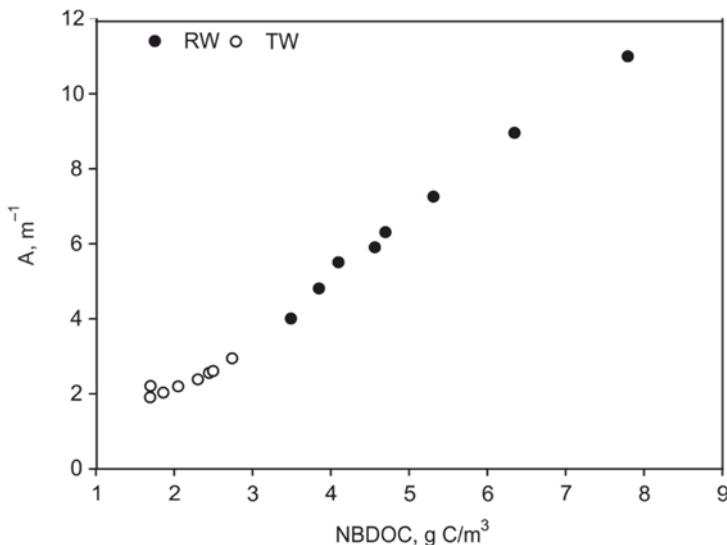


Fig. 4. Dependence of UV absorbance  $A$   
on the NBDOC concentration in water after UV irradiation

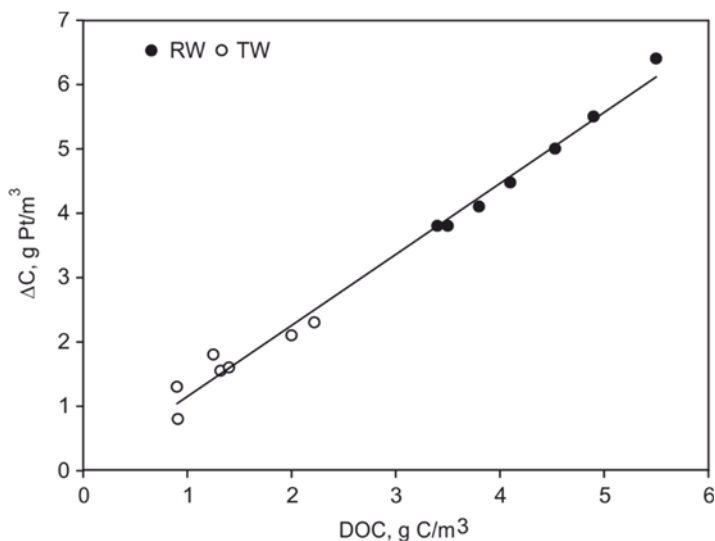


Fig. 5. Relationship between color intensity and DOC concentration

The effectiveness of removing biodegradable organic substances was similar under UV irradiation for both water types, despite a very large difference in the reduction of this fraction. This may be caused by a more intense transformation process in the more contaminated raw water, which resulted in a larger increase in BDOC and in the removal of organic substances susceptible to transformation in subsequent treatment stages. The biggest difference between initial and final irradiation was found for UV absorbance, whose value was larger in waters before irradiation. The larger effectiveness in eliminating aromatic substances in raw waters confirms that the effectiveness of the process is larger when substance concentration is higher. Refractive compounds dominated among the removed non-biodegradable organic substances, which is shown by relationship that was found between the NBDOD values and UV absorbance in water after UV irradiation (Fig. 4). On the other hand, the effective elimination of humic substances among dissolved organic carbon is shown by the almost proportional decrease in color intensity and DOC (Fig. 5).

A consequence of the effective elimination of organic substances of high molecular weight during initial and final irradiation was an increase of the percentage of BDOC in DOC amounting to 2.8% for raw water and 7.2% for the pre-treated one on average.

#### 4. CONCLUSIONS

- The factors determining the effectiveness of mineralization of organic substance were irradiation time and the input water contamination level.

- Irrespective of water contamination level, this process ensured an effective elimination of DOC and its biodegradable and non-biodegradable fractions.
- Content of organic substance in waters before the process influenced the elimination of organic substance, and had no effect on the types of substances removed.
- Due to the domination of the non-biodegradable fraction, significantly higher amounts of these substance were removed during UV irradiation.
- A large effectiveness in reducing UV absorption and NBDIOC indicates effective disinfection by-product elimination if UV irradiation is use before chlorination process.
- A reduction in biodegradable substance content during the UV irradiation allows one to limit development of secondary microorganism potential. This is particularly significant with respect to pre-treated water when UV irradiation is the last treatment process prior to disinfection.

## REFERENCES

- [1] CHOWDHURY S., *Heterotrophic bacteria in drinking water distribution system. A review*, Environ. Monit. Assess., 2012, 184 (10), 6087.
- [2] MARSCHNER B., KALBITZ K., *Controls of bioavailability and biodegradability of dissolved organic matter in soils*, Geoderma, 2003, 113 (3), 211.
- [3] LIN Y.L., CHIANG P.C., CHANG E.E., *Removal of small trihalomethane precursors from aqueous solution by nanofiltration*, J. Hazard. Mater., 2007, 146 (1), 20.
- [4] KALAJDŽIĆ B., HABUDA-STANIĆ M., ROMIĆ Ž., KULEŠ M., *Removal of natural organic matter from groundwater using Fenton's process*, Global Nest. J., 2013, 15, 13.
- [5] CHEN B., WESTERHOFF P., *Predicting disinfection by-product formation potential in water*, Water Res., 2010, 44 (13), 3755.
- [6] LIN Y.L., CHIANG P.C., CHANG E.E., *Reduction of disinfection by-products precursors by nanofiltration process*, J. Hazard. Mater., 2006, 137 (1), 324.
- [7] CHANDY J.P., ANGELS M.J., *Determination of nutrients limiting biofilm formation and the subsequent impacts on disinfectant decay*, Water Res., 2001, 35 (11), 2677.
- [8] HALLAM N.B., WEST J.R., FORESTER C.F., SIMMS J., *The potential for biofilm growth in water distribution systems*, Water Res., 2001, 35 (17), 4063.
- [9] CHIEN C.C., KAO C.M., DONG C.D., CHEN T.Y., CHEN J.Y., *Effectiveness of AOC removal by advanced water treatment systems. A case study*, Desalination, 2007, 202 (1), 318.
- [10] LYON B.A., DOTSON A.D., LINDEN K.G., WEINBERG H.S., *The effect of inorganic precursors on disinfection byproduct formation during UV-chlorine/chloramine drinking water treatment*, Water Res., 2012, 46 (15), 4653.
- [11] SERVAIS P., ANZIL A., VENTRESQUE C., *Simple method for determination of biodegradable dissolved organic carbon in water*, Appl. Environ. Microb., 1998, 55 (10), 2732.
- [12] YANG X., SHEN Q.Q., GUO W.H., PENG J.F., LIANG Y.M., *Precursors and nitrogen origins of trichloronitromethane and dichloroacetonitrile during chlorination/chloramination*, Chemosphere, 2012, 88 (1), 25.
- [13] MATILAINEN A., YEPSÄLAINEN M., SILLANPÄÄ M., *Natural organic matter removal by coagulation during drinking water treatment. A review*, Adv. Coll. Interfac., 2010, 159 (2), 189.
- [14] CORIN N., BACKLUND P., KULOVAARA M., *Degradation products formed during UV-irradiation of humic waters*, Chemosphere, 1996, 33 (2), 245.

- 
- [15] ANDO N., MATSUI Y., KUROTOBI R., NAKANO Y., MATSUSHITA T., OHNO K., *Comparison of natural organic matter adsorption capacities of super-powdered activated carbon and powdered activated carbon*, Water Res., 2010, 44 (14), 4127.
- [16] LEE S., CHO J., SHIN H., SON B., CHAE S., *Investigation of NOM size, structure and functionality (SSF): impact on water treatment process with respect to disinfection by-products formation*, J. Water Supp. Res. T, 2003, 52 (8), 555.
- [17] IMOBERDORF G., MOHSENI M., *Degradation of natural organic matter in surface water using vacuum-UV irradiation*, J. Hazard Mater., 2011, 186 (1), 240.
- [18] WANG W., WANG W., FAN Q., WANG Y., QIAO Z., WANG X., *Effects of UV radiation on humic acid coagulation characteristics in drinking water treatment processes*, Chem. Eng. J., 2014, 256, 137.
- [19] KULOVAARA M., *Light-induced degradation of aquatic humic substances by simulated sunlight*, Int. J. Environ. Anal. Chem., 1996, 62 (2), 85.
- [20] PAUL A., DZIALLAS K., ZWIRNMANN E., GJESSING E.T., GROSSART H.P., *UV irradiation of natural organic matter (NOM). Impact on organic carbon and bacteria*, Aquat. Sci., 2012, 74 (3), 443.