Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2018.22233

117 (2018) 181–187
June

Decomposition of micropollutants and changes in the toxicity of water matrices subjected to various oxidation processes

Mariusz Dudziak*, Edyta Kudlek, Edyta Burdzik-Niemiec

Institute of Water and Wastewater Engineering, Silesian University of Technology, Konarskiego 18, 44-100 Gliwice, Poland, Tel./Fax: +48 32 237 10 47; email: mariusz.dudziak@polsl.pl

Received 9 December 2017; Accepted 21 March 2018

ABSTRACT

The generation of toxic by-products is an adverse effect that accompanies the processes of chemical oxidation, which is increasingly being used to eliminate organic micropollutants from wastewater. This paper concentrates on assessing the elimination of selected organic micropollutants (bisphenol A, 17α-ethinylestradiol and 17β-estradiol) and evaluating the changes in the toxicity of wastewater after various oxidation processes (UV, UV/O_3, UV/TiO_2) that were conducted for 30 min for comparative purposes. The toxicity of wastewater was assessed with the help of selected indicator organisms (bacteria, crustacea, a water plant) from different taxonomic groups. Regardless of the type of researched oxidation process, the effectiveness of micropollutant elimination increased with time, and oestrogens (17α-ethinylestradiol, 17β-estradiol) were more susceptible to degradation than bisphenol A. Nevertheless, after every oxidation process, the wastewater was toxic to one or more groups of indicator organisms. Among the researched oxidation processes, the most efficient process for degrading micropollutants was the UV/O_3 process. The wastewater treated by this process was toxic only to bacteria, which was the most sensitive group among the indicator organisms. This paper also presents an interesting phenomenon regarding the influence of an environmental matrix on observed toxicity.

Keywords: Micropollutants; Wastewater; Oxidation processes, Toxicity

1. Introduction

Currently, there is a demand for new technological solutions that would allow a reduction in both the amount and load of micropollutants that enter surface waters from discharges of urban sewage treatment plants. This is because the conventional treatment systems that are most commonly used are ineffective in eliminating low molecular organic substances found at low concentration levels (i.e., micropollutants) [1,2].

In the area of wastewater treatment, oxidation constitutes a key element in the technology of industrial wastewater treatment [3] and in the post-treatment of municipal wastewater that contains various organic pollutants, including micropollutants [1,2,4–7].

Among the oxidation processes used in the treatment of wastewater, the so-called advanced processes using hydroxyl radicals or other peroxyl radicals are gaining popularity. The processes of advanced oxidation also utilise the synergy of various oxidants (ozone, hydrogen peroxide, etc.) and UV irradiation to boost the effectiveness and reduce the amount of time needed to degrade organic compounds [3,4,7,8–10].

Chemical oxidants are also the source of various unfavourable phenomena [3,11–14]. All strong oxidants, to a greater or lesser degree, lead to the formation of oxidation by-products, which often have unknown biological activities. The formation of oxidation by-products may have a dramatic impact on the toxicity of the treated solution. This problem also occurs during advanced oxidation processes [3,11,12]. However, the literature on this topic is still scant.

* Corresponding author.

Presented at the 13th Conference on Microcontaminants in Human Environment, 4–6 December 2017, Czestochowa, Poland.

Based on this information, this paper concentrates on assessing the degree of degradation of selected micropollutants and changes in the toxicity of wastewater after subjection to various oxidation processes.

2. Materials and methods

2.1. Research subject

The tests focused on three different organic micropollutants, that is, bisphenol (a compound of the phenol group, used in the production of plastics), 17α-ethinylestradiol (synthetic oestrogen found in the majority of modern combined contraceptives) and 17β-estradiol (natural oestrogen). Bisphenol A, 17α-ethinylestradiol and 17β-estradiol were provided by Sigma-Aldrich (Poland). In this work, model tests were carried out. The applied concentrations of micropollutants were higher than observed in the water environment (surface waters, wastewater). The adopted order of magnitude facilitates the analytical procedure, and thus increases the accuracy of the measurements. Samples consisted of micropollutants solutions (concentrations ranging from 0.1 to 5.0 mg/L) in both deionised water with nutrient salts and wastewater effluent.

2.2. Physicochemical analyses

The general parameters (i.e., pH and temperature) were measured using a laboratory multi-parameter metre inoLab® 740, which is manufactured by WTW (Poland). Absorbance was measured at a wavelength of 254 nm using a UV/VIS Cecil 1000 of Analytik Jena AG (Poland), and the concentration of total organic carbon was determined using a HiPerTOC analyser of Thermo Electron (Poland). Micropollutants were extracted by solid phase extraction (SPE) and further analysed by high-performance liquid chromatography (HPLC). SPE was performed with Supelclean™ ENVI-18 cartridges (6 mL, 1.0 g, Supelco) which were conditioned with both methanol (5 mL) and acetonitrile (5 mL). Then they were washed with deionised water (5 mL) and eluated with 1 mL of a mixture of acetonitrile:methanol (60:40, v/v). The extracts were evaporated under a nitrogen stream. The analysis of the extracted micropollutants was performed by HPLC with UV detection (λ = 220 nm) (Varian Inc., USA). Separation was performed with an analytical column Microsorb 100 C18 (250 × 4.6 mm, 5 μm) from Thermo Scientific (USA). The mixture of acetonitrile and water in the volume ratio of 85:15 (v/v) was the mobile phase. All of the used solvents were of analytical grade of the company Avantor Performance Materials Poland S.A. (Poland).

Deionised water was the basis for the preparation of research solutions. Micropollutants were dissolved in deionised water and then diluted with the relevant nutrient salt solutions required for the indicator organisms used in accordance with the recommended procedures (section 2.3).

The treated wastewater was collected from the drain of a mechanical and biological wastewater treatment plant located in southeast Poland, which initially did not contain the tested compounds. The physicochemical characteristics of the tested model solutions are presented in Table 1. Sample pH was adjusted to 7.0 with the addition of 0.1 mol/L HCl or 0.2 mol/L NaOH.

2.3. Toxicological tests and toxicity

The tested solutions were assessed with regard to their toxicity. For this purpose, three different types of biotests were used, that is, a Microtox® enzymatic test, a Daphtoxkit F® survival test and a *Lemna minor* growth test, to assess the toxicity towards bacteria, crustacea and vascular plants.

The Microtox biotest® of the MicroBioTests Inc. (Belgium), which uses *Aliivibrio fischeri* bioluminescence bacteria as indicator organisms, was performed in accordance with the screening test procedure of MicrotoxOmni in the Microtox Model 500 analyser of the company Modern Water Inc. (USA). The bacteria that were used are highly sensitive to a wide range of both organic and inorganic toxicants [15]. The test provides a percentage of bioluminescence inhibition, which represents the value of the inhibited metabolic processes of the indicator organisms that have been exposed to the tested sample for 5 min against the value from the control sample (i.e., 2% solution of NaCl).

The Daphtoxkit F® biotest of the MicroBioTests Inc. (Belgium) uses freshly hatched freshwater crustaceans (*Daphnia magna*) as indicator organisms. The test was performed according to Standard Operational Procedure in accordance with ISO 6341 [16]. The number of dead organisms was read after 24 h.

The *Lemna minor* biotest was conducted on vascular plants in accordance with OECD Guideline 221 (2001) [17]. The plants used in the tests came from on-site farming. The test consisted of observing changes in the plants' morphology. The test was performed at a temperature of 25°C ± 2°C and at a continuous light exposure of 6,000 lux. The toxicity was assessed after 7 d, and the result was the percentage of growth inhibition experience by the plant fronds.

The effect of the toxicity (%) was determined according to the equation:

$$E = \frac{100 \cdot \left(E_K - E_T\right)}{E_K}, \% \quad (1)$$

Table 1
Physicochemical characteristics of the tested solution

	Deionised water	Deionised water with salts	Wastewater effluent
pH (original)	5.8	6.7	7.2
Conductivity (μS/cm)	5.18	33,400.00 mS	9,850.00
Absorbance (UV_{254}) (1/cm)	0.000	0.00	0.218
Total organic carbon (TOC) (mg/L)	0.00	0.00	33.01

where E_K is the effect observed in a blank sample, E_T is the effect observed in a test sample.

Depending on the given test, the effect was measured by the decrease in bioluminescence (i.e., the enzymatic Microtox® test) or organism viability (i.e., the *Daphnia magna* test) and leaf growth (i.e., the *Lemna minor* test).

To eliminate the influence of the oxidant presence on the ecotoxicological analysis, solid sodium sulphate of Sigma-Aldrich (Poland) was added to the sample.

The toxicity of samples was classified using a common system, which is used by many researchers [15,18–21] and is based on the extent of the toxicity observed in the indicator organisms (Table 2).

2.4. Oxidation processes

The photodegradation experiments included photolysis (UV), photolysis–ozonisation (UV/O_3) and photocatalysis (UV/TiO_2). They were performed in a laboratory glass batch reactor with a capacity of 0.7 L of Heraeus (Germany) for 30 min. The reactor was equipped with an immersion medium pressure UV lamp of 150 W located in a cooling jacket made of Duran 50 glass, which emanated radiation with a wavelength λ_{exc} range from 313 to 578 nm. The lamp was placed in a cooling jacket, which enabled to keep a constant temperature of the conducted process that did not exceed 20°C ± 1°C. The reactor was placed on a magnetic stirrer and connected to an aeration pump of capacity of 4 L air per minute to oxidate the system. In the case of a combined process, UV/O_3 ozone was produced from the air by an Ozone FM 500 generator with a capacity of 0.14 mg/s (WRC Multiozon, Poland) and directed to the reactor through a ceramic diffuser. The dose of ozone was kept at a constant level of 3 mg/L, and the contact time between the oxidant and water was 1 min. On the other hand, in the UV/TiO_2 process, the catalyst, that is, titanium dioxide, was added into the solution and stirred for 15 min to ensure homogeneity before light exposure. The catalyst was commercial titanium dioxide P25 of Degussa (Germany) at a dose of 100 mgTiO_2/L. Titanium dioxide P25 contains a mixture of anatase and rutile (70:30, w/w).

The above conditions were selected for the oxidation processes based on previous research in this area [22–24].

The effectiveness of micropollutant elimination was assessed by monitoring for changes in concentrations (C/C_0), where C and C_0 are the concentrations of a compound in wastewater after and before the oxidation process, respectively.

The presented results are the arithmetic average of the four repeats of each experiment. For all cases, the assigned error (estimated based on the standard deviation) did not exceed 5% so the results are presented without marking of the ranges of error.

Table 2
Samples toxicity classification system [15,18–21]

Effect (%)	Toxicity class
<25	Non toxic
25–50	Low toxic
50.1–75	Toxic
75.1–100	Highly toxic

3. Results and discussion

3.1. Relationship between toxicity and concentration of selected micropollutants for deionised water solution

As part of the preliminary research, in the prepared solutions of deionised water with salts, the influence of the concentration of bisphenol A, 17α-ethinylestradiol and 17β-estradiol on bacterial bioluminescence inhibition was assessed (Fig. 1). The micropollutants were tested separately. It was determined that

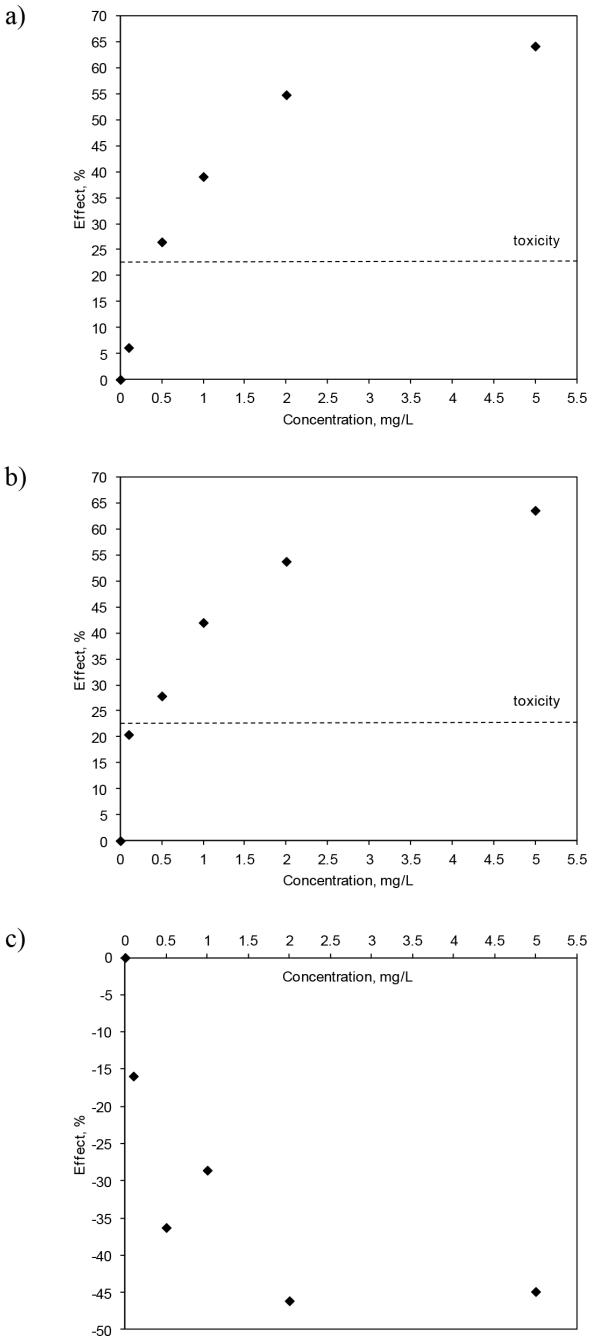

Fig. 1. Influence of the concentration of (a) bisphenol A, (b) 17α-ethinylestradiol and (c) 17β-estradiol on *Aliivibrio fischeri* bacteria (enzymatic test).

as the concentration of bisphenol A and 17α-ethinylestradiol in the deionised water with salts increased, bioluminescence became increasingly inhibited. As presented in Table 2, the solutions containing bisphenol A or 17α-ethinylestradiol at concentrations above 0.5 mg/L were toxic. In the solutions containing 17β-estradiol, regardless of its concentration, no toxicity was observed. It was, however, reported that 17β-estradiol stimulated the bioluminescence of bacteria. In the work by Schultis and Metzger [25], the oestrogenic activity of this micropollutant has been documented.

Table 3 shows the results of the remaining toxicological tests (i.e., the survival test with crustacea and the growth test with a water plant). Despite the fact that during the investigation of toxicity, the concentration of micropollutants was the same as that in the enzymatic test, and the results of the analyses were presented in a table due to the lack of a clear linear dependence of the tested variables.

Toxicity to both the crustacea and the water plant was reported in solutions whose concentrations of bisphenol A were above 1.0 mg/L. The results indicate that these organisms are not as sensitive to bisphenol A as bacteria. In the case of 17α-ethinylestradiol, the compound was found to be toxic to crustacea and bacteria in solutions with concentrations of the compound exceeding 0.5 mg/L. In the case of the water plant, however, no toxicity was observed, regardless of the concentration of 17α-ethinylestradiol. Additionally, no toxicity was detected for solutions containing 17β-estradiol.

Based on the obtained results, the following research hypothesis may be formulated: the effective elimination of toxic micropollutants from an aqueous solution occurred with the help of oxidation processes and resulted in lowered toxicity. An exception to this rule suggests the existence of other dangerous phenomena occurring during the execution of these processes. Nevertheless, a complex biological evaluation of the impact on micropollutants should be based on tests using various indicator organisms due to their varying sensitivity to micropollutants.

3.2. Toxicity tests for various matrices

Subsequently, the toxicity of wastewater with and without the addition of the tested micropollutant models was examined (Fig. 2). The results were compared with the results of the analyses that used deionised water with salts that also contained a mixture of micropollutants. In the case of deionised water with salts containing bisphenol A and 17α-ethinylestradiol, toxicity was reported for all three tested indicator organisms (i.e., bacteria, crustacea, the water plant), with bacteria being the most sensitive organisms. Wastewater without the addition of micropollutants was toxic only to bacteria. Once the tested micropollutant models were added, toxicity was observed, but only to the water plant.

The source of the toxicity of wastewater without the addition of micropollutants was not identified. What was

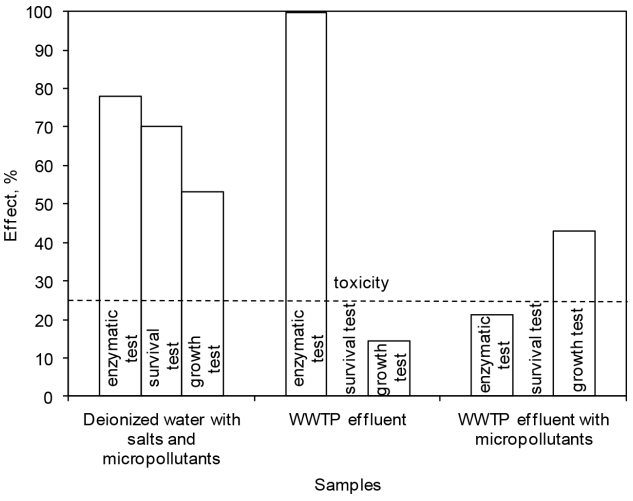

Fig. 2. Toxicity of deionised water containing salts and wastewater with and without micropollutants (concentration of particular compounds was 1 mg/L).

Table 3
Influence of micropollutants concentrations on crustacea and a water plant

Test	Bisphenol A concentration (mg/L)					
	0	0.1	0.5	1.0	2.0	5.0
	Effect (%) (toxicity class[a])					
Survival with *Daphnia magna*	0 (–)	0 (–)	10 (–)	35 (+)	45 (+)	50 (+)
Growth with *Lemna minor*	0 (–)	8 (–)	17 (–)	58 (++)	58 (++)	92 (+++)
Test	17α-ethinylestradiol concentration (mg/L)					
	0	0.1	0.5	1.0	2.0	5.0
	Effect (%) (toxicity class[a])					
Survival with *Daphnia magna*	0 (–)	5 (–)	25 (+)	45 (+)	50 (+)	55 (++)
Growth with *Lemna minor*	0 (–)	0 (–)	0 (–)	0 (–)	0 (–)	8 (–)
Test	17β-estradiol concentration (mg/L)					
	0	0.1	0.5	1.0	2.0	5.0
	Effect (%) (toxicity class[a])					
Survival with *Daphnia magna*	0 (–)	0 (–)	0 (–)	0 (–)	10 (–)	5 (–)
Growth with *Lemna minor*	0 (–)	0 (–)	0 (–)	0 (–)	0 (–)	0 (–)

[a](–) non toxic; (+) low toxicity; (++) toxic; (+++) high toxicity.

surprising, however, was the difference in toxicity between deionised water and wastewater, given the fact that both of these substances contained the same concentration of micropollutants. This phenomenon was further investigated.

Wastewater is a complex mixture of various organic and inorganic compounds. The presence of microorganisms means that there are various biochemical processes occurring in the water matrix that have an effect on the concentration levels of organic micropollutants. Micropollutants present in wastewater may be adsorbed onto the organic or inorganic matter particles present in this mixture. They may also be desorbed. Micropollutants may also form complex compounds with other wastewater ingredients. Complex compounds that are formed may be less toxic than a single compound. That is why it cannot be inferred that the observed toxicity of real wastewater would result only from the concentration of toxic micropollutants.

The research by López-Peñalver et al. [26] also demonstrates that dissolving the same weighed amount of tetracycline into two different environmental matrices, that is, surface water and wastewater, resulted in wastewater showing less bacterial bioluminescence inhibition than that specified for surface water. Therefore, in the area of environmental research, it is essential to conduct tests using real environmental matrices.

3.3. Evaluation of different oxidation processes with regard to micropollutant elimination and changes in wastewater toxicity

The last stage of research consisted of assessing the elimination of the tested micropollutants and the changes in wastewater toxicity caused by the use of various oxidation processes over different periods of time (Fig. 3). The concentration of each micropollutant in wastewater was 1 mg/L.

Regardless of the type of researched oxidation process (i.e., UV, UV/O_3, UV/TiO_2), the effectiveness of micropollutant elimination increased with time, with oestrogens (17α-ethinylestradiol, 17β-estradiol) being more susceptible to degradation than bisphenol A. Nevertheless, after every oxidation process, the wastewater was toxic to one or more groups of indicator organisms (i.e., bacteria, crustacea, the water plant). This phenomenon was also influenced by oxidation time. To compare the obtained correlations, the oxidation time was set to 30 min, the time at which the greatest degradation of the tested micropollutants was achieved.

Among the researched oxidation processes, the best efficiency in terms of micropollutant degradation was demonstrated by the UV/O_3 process. After 30 min of the process that eliminated bisphenol A, 17α-ethinylestradiol and 17β-estradiol, the detected changes in concentrations (C/C_0) were 0.009, 0.007 and 0.002, respectively. The reduction in the concentrations of specific compounds was very large, exceeding 99%. During UV/O_3, the selected indicators of wastewater quality, that is, absorbance and total organic carbon, were also significantly reduced. The reduction in absorbance and total organic carbon amounted to 61.2% and 48.1%, respectively. Additionally, the treated wastewater was toxic only to bacteria, which was the most sensitive among the groups of indicator organisms. According to the toxicity classes presented in Table 2, the toxicity of the treated wastewater was low.

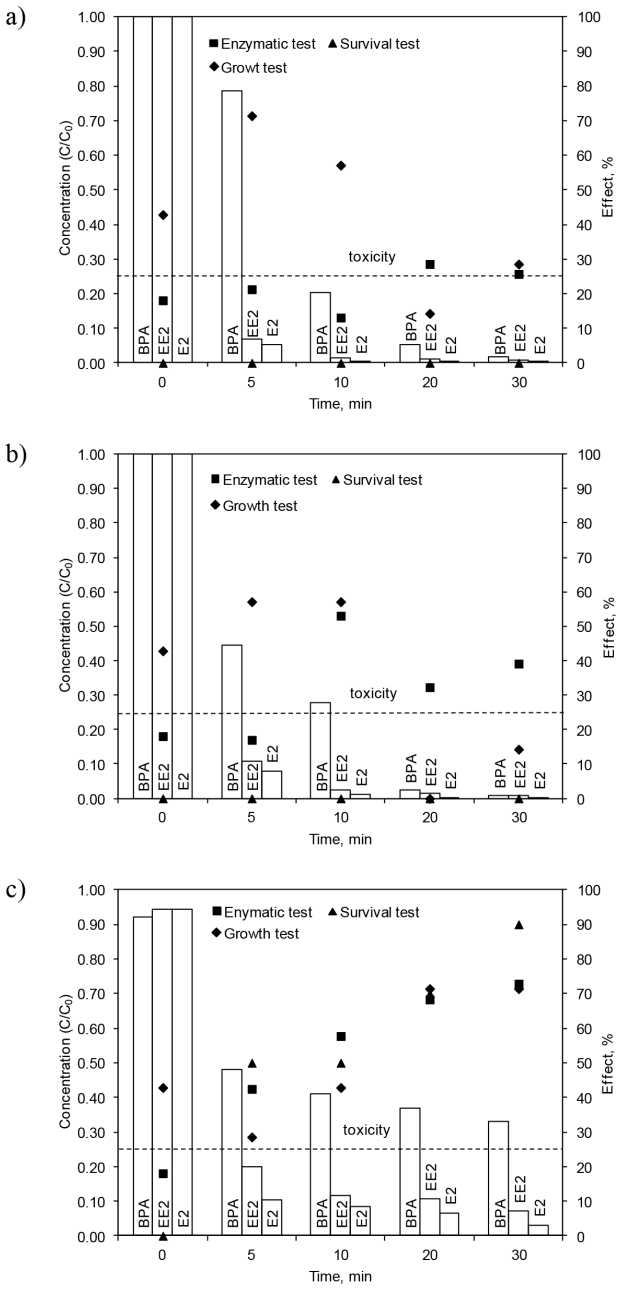

Fig. 3. Elimination of tested micropollutants and changes in the toxicity of wastewater subjected to various oxidation processes (concentration of particular compounds was 1 mg/L): (a) UV, (b) UV/O_3, (c) UV/TiO_2.

After 30 min, the effectiveness of the UV process, in terms of the elimination of bisphenol A, 17α-ethinylestradiol and 17β-estradiol (C/C_0), was also high and amounted to 0.017, 0.008 and 0.003, respectively. Of particular concern is the fact that the treated wastewater was toxic to both bacteria and the water plant. The toxicity of the treated wastewater was low (Table 2).

After UV/TiO_2, the observed elimination of bisphenol A, 17α-ethinylestradiol and 17β-estradiol (C/C_0) was 0.330, 0.071 and 0.031, respectively, and the treated wastewater was toxic to bacteria, crustacea and the water plant.

Comparing these results against Table 2 allowed us to determine that the treated wastewater was toxic or highly toxic to bacteria, plants and crustacea. In the UV/TiO_2 process, the decomposition of micropollutants was smaller than in UV process, and post-process solutions were more toxic. The used catalyst contains a mixture of anatase and rutile. During photocatalytic oxidation, some of the hydroxyl radicals react with rutile that may limit the distribution of low-molecular micropollutants. It does not happen in the case of the UV process. The difference in the toxicity of post-process solutions is related to the toxicity of the produced by-products [27,28]. In the UV/TiO_2 process, the formed by-products are more toxic than in UV process. Based on previous results [23], the toxicity of the catalyst particles can be excluded. Adsorption of micropollutants on the catalyst particles was insignificant and did not exceed a 8% level.

Summarizing this part of the research, it can be inferred that an ecotoxicological analysis is a good and fast indirect tool for evaluating new technologies of wastewater treatment with regard to the occurrence of dangerous phenomena, such as the formation of toxic by-products during the degradation of pollutants, including micropollutants. This is particularly important in the case of oxidation processes. It needs to be emphasised that the traditional identification of oxidation by-products requires the use of time-consuming chromatographic analytic procedures. Degradation by-products of the tested micropollutants were not identified in this research. However, the wastewater used in this study was collected from an actual wastewater treatment plant discharge site, so the added micropollutants may not have been the only source of toxicity. The investigated oxidation processes were evaluated alongside one another, so the obtained results provide insight into the impacts of particular processes on the formation of toxic by-products during the degradation of pollutants. One attempt has been made to answer the question about why the toxicological effects obtained as a result of the performed oxidation processes were so different. The different results may be caused by various toxic by-products that formed during the degradation of pollutants; these by-products would be dependent on the type of the oxidation process that was used. Equally important in this regard is the durability of the toxic by-products produced during the degradation of pollutants. This was confirmed by the correlation that was explained earlier in this paper. Wastewater treated with comparable oxidation processes was toxic to one or more groups of indicator organisms (i.e., bacteria, crustacea, the water plant).

4. Conclusions

- The evaluation of new technologies of wastewater treatment, with regard to the occurrence of dangerous phenomena, should be supported by ecotoxicological analyses that use indicator organisms from different taxonomic groups. This is of particular importance in the case of oxidation processes. An ecotoxicological analysis allows researchers to determine, in an indirect way, whether toxic by-products are being generated by oxidation processes.
- Among the tested oxidation processes (i.e., UV, UV/O_3, UV/TiO_2), the most effective one, with regard to micropollutant (i.e., bisphenol A, 17α-ethinylestradiol and 17β-estradiol) degradation, was UV/O_3, as the treated wastewater was toxic only to bacteria, which are the most sensitive of the chosen indicator organisms (i.e., bacteria, crustacea, water plants). The effectiveness of the UV process was also high, but the treated wastewater was still toxic to both bacteria and the water plant. The least effective treatment was the UV/TiO_2 process, as the treated wastewater was still toxic to all three groups of indicator organisms.

Acknowledgement

This work was supported by Ministry of Science and Higher Education Republic of Poland within statutory funds.

References

[1] M. Włodarczyk-Makuła, Application of UV rays to removal of polycyclic aromatic hydrocarbons from treated wastewater, J. Environ. Sci. Health A, 46 (2011) 248–257.
[2] M. Włodarczyk-Makuła, Changes of PAHs content in wastewater during oxidation process [Zmiany ilościowe WWA w ściekach oczyszczonych podczas utleniania], Annu. Set Environ. Prot. [Rocznik Ochrona Środowiska], 13 (2011) 1093–1104 (in Polish).
[3] L. Bilińska, M. Gmurek, S. Ledakowicz, Comparison between industrial and simulated textile wastewater treatment by AOPs – biodegradability, toxicity and cost assessment, Chem. Eng. J., 306 (2016) 550–559.
[4] R. Rosal, A. Rodríguez, J.A. Perdigón-Melón, M. Mezcua, M.D. Hernando, P. Letón, E. García-Calvo, A. Agüera, A.R. Fernández-Alba, Removal of pharmaceuticals and kinetics of mineralization by O_3/H_2O_2 in a biotreated municipal wastewater, Water Res., 42 (2008) 3719–3728.
[5] S. Carbonaro, M.N. Sugihara, T.J. Strathmann, Continuous-flow photocatalytic treatment of pharmaceutical micropollutants: activity, inhibition, and deactivation of TiO_2 photocatalysts in wastewater effluent, Appl. Catal., B, 129 (2013) 1–12.
[6] J. Choi, H. Lee, Y. Choi, S. Kim, S. Lee, W. Choi, J. Lee, Heterogeneous photocatalytic treatment of pharmaceutical micropollutants: effects of wastewater effluent matrix and catalyst modifications, Appl. Catal., B, 147 (2014) 8–16.
[7] L. Prieto-Rodríguez, I. Oller, N. Klamerth, A. Agüera, E.M. Rodríguez, S. Malato, Application of solar AOPs and ozonation for elimination of micropollutants in municipal wastewater treatment plant effluents, Water Resour., 47 (2013) 1521–1528.
[8] L. Pengxiao, Z. Hanmin, F. Yujie, Y. Fenglin, Z. Jianpeng, Removal of trace antibiotics from wastewater: a systematic study of nanofiltration combined with ozone-based advanced oxidation processes, Chem. Eng. J., 240 (2014) 211–220.
[9] J. Richard, A. Boergers, C. vom Eyser, K. Bester, J. Tuerk, Toxicity of the micropollutants bisphenol A, ciprofloxacin, metoprolol and sulfamethoxazole in water samples before and after the oxidative treatment, Int. J. Hyg. Environ. Health, 217 (2014) 506–514.
[10] S. Miralles-Cuevas, I. Oller, A. Agüera, J.A. Sánchez Pérez, R. Sánchez-Moreno, S. Malato, Is the combination of nanofiltration membranes and AOPs for removing microcontaminants cost effective in real municipal wastewater effluents?, Environ. Sci. Water Res. Technol., 2 (2016) 511–520.
[11] M. Bourgin, E. Borowska, J. Helbing, J. Hollender, H.P. Kaiser, C. Kienle. C.S. McArdell, E. Simon, U. von Gunten, Effect of operational and water quality parameters on conventional ozonation and the advanced oxidation process O_3/H_2O_2: kinetics of micropollutant abatement, transformation product and bromate formation in a surface water, Water Res., 122 (2017) 234–245.
[12] B. Cédat, C. de Brauer, H. Métivier, N. Dumont, R. Tutundjan, Are UV photolysis and UV/H_2O_2 process efficient to treat

estrogens in waters? Chemical and biological assessment at pilot scale, Water Res., 100 (2016) 357–366.
[13] R.O. Pereira, C. Postigo, M.L. de Alda, L.A. Daniel, D. Barceló, Removal of estrogens through water disinfection processes and formation of by-products, Chemosphere, 82 (2011) 789–799.
[14] Y. Souissi, S. Kinani, S. Bouchonnet, S. Bourcier, C. Malosse, M. Sablier, N. Creusot, E. Mombelli, S. Aït-Aïssa, Photolysis of estrone generates estrogenic photoproducts with higher activity than the parent compound, Environ. Sci. Pollut. Res., 21 (2014) 7818–7827.
[15] G. Ricco, M.C. Tomei, R. Ramadori, G. Laera, Toxicity assessment of common xenobiotic compounds on municipal activated sludge: comparison between respirometry and Microtox, Water Res., 38 (2004) 2103–2110.
[16] ISO 6341, Water Quality – Determination of the Inhibition of the Mobility of *Daphnia magna* Straus (Cladocera, Crustacea) – Acute Toxicity Test, 2012.
[17] Organisation for economic cooperation and development (OECD) guidelines 221 for the testing of chemicals, *Lemna sp.*, Growth Inhibition Test, 2006.
[18] C. Mahugo Santana, Z. Sosa Ferrera, M.E. Torres Padrón, J.J. Santana Rodríguez, Methodologies for the extraction of phenolic compounds from environmental samples: new approaches, Molecules, 14 (2009) 298–320.
[19] L. Põllumaa, A. Kahru, L. Manusadzianas, Biotest and chemistry-based hazard assessment of soils, sediments and solid wastes, J. Soil. Sediments, 4 (2004) 267–275.
[20] M. Miles, R. Dutton, Testing the effects of spinosad to predatory mites in laboratory, extended laboratory, semi-field and field studies, IOBC/WPRS Bull., 26 (2003) 9–20.
[21] S. Werle, M. Dudziak, Ocena toksyczności osadów ściekowych oraz produktów ubocznych powstających podczas ich zgazowania (Evaluation of toxicity of sewage sludge and gasification waste-products), Przem. Chem., 92 (2013) 1350–1353.
[22] M. Dudziak, E. Burdzik, Oxidation of bisphenol A from simulated and real urban wastewater effluents by UV, O_3 and UV/O_3, Desal. Wat. Treat., 57 (2016) 1075–1083.
[23] J. Bohdziewicz, E. Kudlek, M. Dudziak, Influence of the catalyst type (TiO_2 and ZnO) on the photocatalytic oxidation of pharmaceuticals in the aquatic environment, Desal. Wat. Treat., 57 (2016) 1552–1563.
[24] E. Kudlek, M. Dudziak, J. Bohdziewicz, Influence of inorganic ions and organic substances on the degradation of pharmaceutical compound in water matrix, Water, 8 (2016) 1–18.
[25] T. Schultis, J.W. Metzger, Determination of estrogenic activity by LYES-assay (yeast estrogen screen-assay assisted by enzymatic digestion with lyticase). Chemosphere, 57 (2004) 1649–1655.
[26] J.J. López-Peñalver, M. Sánchez-Polo, C.V. Gómez-Pacheco, J. Rivera-Utrilla, Photodegradation of tetracyclines in aqueous solution by using UV and UV/H_2O_2 oxidation processes, J. Chem. Technol. Biotechnol., 85 (2010) 1325–1333.
[27] I.K. Konstantinou, T.A. Albanis, TiO_2-assisted photocatalytic degradation of azo dyes in aqueous solution: kinetic and mechanistic investigations: a review, Appl. Catal., B, 49 (2004) 1–14.
[28] M. Dudziak, Microtox as a tool to evaluate unfavourable phenomenon occurrences during micropollutants decompositions in AOPs, Archit. Civ. Eng. Environ., 8 (2015) 85–90.