

Decomposition of Contaminants of Emerging Concern in Advanced Oxidation Processes [†]

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[†] Presented at the 2nd International Electronic Conference on Water Sciences, 16–30 November 2017;

Available online: <http://sciforum.net/conference/ecws-2>.

Published: 16 November 2017

Abstract: This paper compared the removal degrees of selected contaminants of emerging concern, such as H₂O₂, O₃, UV and UV/TiO₂, in water solutions during advanced oxidation processes (AOPs). The tested micropollutants belong to the following groups: pharmaceuticals, dyes, UV filters, hormones, pesticides and food additives. The highest removal rate of pharmaceutical compounds was observed during the UV/TiO₂ process. The decomposition of hormones in this process exceeded 96% and the concentration of the UV filter dioxybenzone was reduced by 75%. Toxicological analysis conducted in post-processed water samples indicated the generation of several oxidation by-products with a high toxic potential.

Keywords: AOPs; organic micropollutants; toxicological analysis

1. Introduction

Water is a very valuable resource, and has a high impact on the whole ecosystem including human beings. The water environment is particularly vulnerable to pollution by several contaminants of emerging concern. The occurrence of those compounds was reported by many authors [1–4]. The negative impact was also investigated in several articles in the last decade [5,6].

Advanced oxidation processes provide a good opportunity for the decomposition of different kinds of micropollutants, especially hardly biodegradable or non-biodegradable compounds [7]. The main assumption of those processes is the complete mineralization of organic compounds to H₂O and CO₂. However, under actual process conditions, micropollutants degraded to different biologically active transformation products [8]. The decomposition of pollutants occurs as a result of the reaction between high reactive oxidation species such as O₃, H₂O₂ and free radicals [9]. Organic compounds show varying susceptibility to chemical or photochemical decomposition. Therefore, it is necessary to select an optimal process for the degradation of each individual group of compounds.

This paper presents a comparison of removal degrees of organic micropollutants, such as H₂O₂, O₃, UV and UV/TiO₂, in water solutions during selected advanced oxidation processes (AOPs). To determine the susceptibility of particular types of micropollutants to oxidation processes, different groups of contaminants of emerging concern were tested, i.e., pharmaceuticals, dyes, UV blockers, pesticides, hormones and food additives. The oxidation processes were also evaluated according to the potential toxic effect of post-treated water solutions using the Microtox[®] bioassay.

2. Material and Methods

2.1. Material and Reagents

The analytical standards of pharmaceutical compounds, i.e., carbamazepine, benzocaine, diclofenac sodium salt and Ibuprofen sodium salt; dye—acridine; UV blocker—dioxibenzene; pesticides—triallat, triclosan and oxadiazon; hormones— β -estradiol, 17 α -ethinylestradiol, mestranol and progesterone; food additives—butylated hydroxytoluene and caffeine of purity grade >97% were supplied by Sigma-Aldrich (Poznań, Poland) (Table 1). Hydrogen peroxide (H₂O₂) as a 30% solution in water was supplied by the same company. Titanium dioxide with the acronym P25 was purchased from Evonik Degussa GmbH (Hanau, Germany). Disposable SPE cartridges Supelclean™ ENVI-8 and Supelclean™ ENVI-18 for the extraction of the analytes from water solutions were supplied by Sigma-Aldrich (Poznań, Poland). In the study methanol, acetonitrile, acetone and dichloromethane of purity grade >99.8%, obtained from Avantor Performance Materials Poland S.A. (Gliwice, Poland), were also used.

Table 1. Characteristics of the tested organic compounds.

Group	Name	Molecular Formula	Molecular Weight, g/mol	Solubility in Water, mg/L	pK _a
Pharmaceuticals	Carbamazepine, CBZ	C ₁₆ H ₁₂ N ₂ O	236.30	17	2.30
	Benzocaine, BE	C ₉ H ₁₁ NO ₂	165.19	1310	2.51
	Diclofenac sodium salt, DCF	C ₁₄ H ₁₀ Cl ₂ NNaO ₂	318.13	50	4.15
	Ibuprofen sodium salt, IBU	C ₁₃ H ₁₇ NaO ₂	228.26	100	4.91
Dyes	Acridine, ACR	C ₁₃ H ₉ N	179.22	38.4	5.6
UV blockers	Dioxibenzene, BZ8	C ₁₄ H ₁₂ O ₄	244.24	Insoluble	6.99
Pesticides	Triallat, TRI	C ₁₀ H ₁₆ Cl ₃ NOS	304.66	4.1	- ¹
	Triclosan, TCS	C ₁₂ H ₇ Cl ₃ O ₂	289.54	0.1	7.9
	Oxadiazon, ODZ	C ₁₅ H ₁₈ Cl ₂ N ₂ O ₃	345.22	0.7	- ²
Hormones	β -Estradiol, E2	C ₁₈ H ₂₄ O ₂	272.38	3.6	10.33
	17 α -Ethinylestradiol, EE2	C ₂₀ H ₂₄ O ₂	296.40	11.3	10.33
	Mestranol, EEME	C ₂₁ H ₂₆ O ₂	310.43	1.13	17.59
	Progesterone, P4	C ₂₁ H ₃₀ O ₂	314.46	8.81	18.92
Food additives	Butylated Hydroxytoluene, BHT	C ₁₅ H ₂₄ O	220.35	0.6	12.23
Other	Caffeine, CAF	C ₈ H ₁₀ N ₄ O ₂	194.19	21600	14.0

¹ no data; ² non-ionizable.

2.2. Water Samples

Deionized water solutions with the addition of patterns of the tested organic micropollutants, at the concentration of 500 μ g/L, constituted the subject of the study. The compound standard solutions were prepared by dissolving 10 mg of each analyte in 10 mL of methanol. Compound patterns were used due to the weak solubility of some micropollutants in water solutions, especially in deionized water. The pH of the prepared water solutions was adjusted to 7 using 0.1 mol/L HCl or 0.1 mol/L NaOH. Preliminary studies indicated no influence of the used acid and alkali on the decomposition of the tested micropollutants before the implementation of oxidation processes. The experiments for all tested compounds were carried out separately.

2.3. Advanced Oxidation Processes

A laboratory glass batch reactor with a volume of 0.7 L, obtained from Heraeus (Hanau, Germany), was used for the implementation of the oxidation processes (Figure 1). To eliminate the influence of UV light on the reaction mixtures during the H₂O₂ and O₃ processes, the reactor was placed in a dark chamber. The dose of H₂O₂ was equal to 3, 6, 9 and 12 mg/L. The oxidizing reagent was introduced to the reaction mixture in the form of a 30% solution. The O₃ system consisted of an ozone generator Ozoner FM500 by WRC Multiozon (Sopot, Poland) and a ceramic diffuser (Figure

1a). The O_3 dose was set to 1, 3, 5 and 10 mg/L. The contact time between the oxidizing reagents and the prepared water solutions was 30 min.

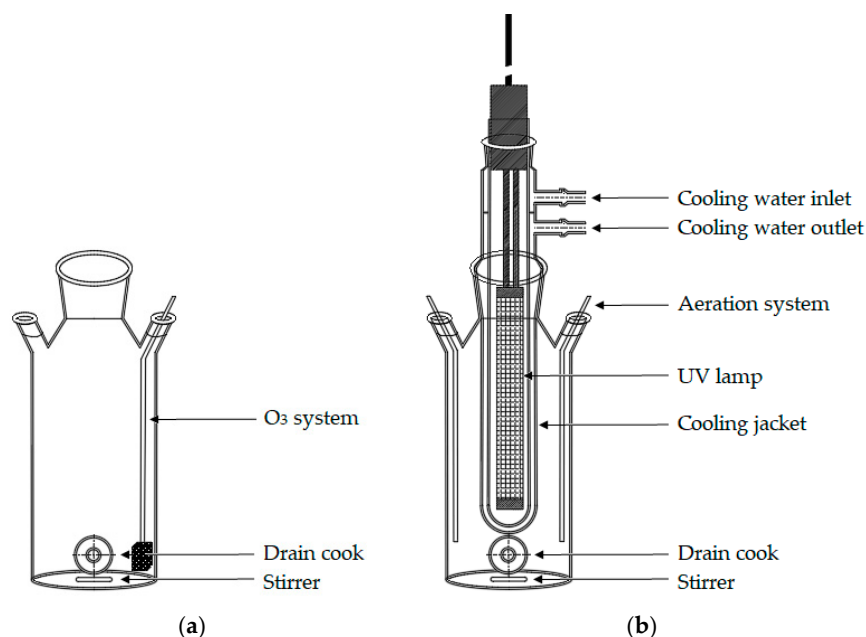


Figure 1. Reactor for the (a) H_2O_2 , O_3 and (b) UV, UV/ TiO_2 [10] process.

In order to carry out the UV and UV/ TiO_2 processes, the reactor was equipped with a medium-pressure mercury vapour UV lamp with the power of 150 W (Figure 1b). The lamp was placed into the reactor 90 s after lighting it up. This ensured a stable intensity of irradiation from the first second of the process. Additionally, the UV lamp was placed in a glass cooling jacket cooled by tap water of 15 ± 1 °C. Therefore, the temperature of the reaction mixtures was kept constant at 20 ± 1 °C. The radiation that emanated from the UV lamp, according to the data given by the producer Heraeus (Hanau, Germany), had a wavelength λ_{exc} equal to 313, 365, 405, 436, 546 and 578 nm. The reactor was also aerated by an aeration pump with the capacity of 4 L air per minute.

The dose of the catalyst in the UV/ TiO_2 process was 50 mg TiO_2 /L. To ensure the adsorption of micropollutants on the surface of the catalyst, the contact time of TiO_2 with the mixtures before the implementation of the UV irradiation process was set to 15 min. This step was also carried out in a dark chamber. The separation of catalyst particles from the post-processed suspensions was conducted through a microfiltration set equipped with membrane filters of 0.45 µm pore sizes by Merck Milipore (Darmstadt, Germany).

Both UV-based oxidation processes were carried out at 10, 30 and 60 min. To ensure proper mixing of the reaction water solutions, the reactor was placed on a magnetic stirrer during all oxidation processes.

2.4. Analytical Procedure and Toxicity Assessment

The analytical procedure of tested compounds was performed using GC-MS chromatography with electron ionization preceded by solid phase extraction (SPE). The volume of analyzed water samples was equal to 20 mL. The pH of each sample after the oxidation process was adjusted to 7. Details of the used SPE cartridges and the organic solvents for the extraction of different compound groups are listed in Table 2.

The 7890B GC-MS(EI) chromatograph by Perlan Technologies (Warszawa, Poland) was incorporated for micropollutant determination. An SLB™—5 ms 30 m × 0.25 mm capillary column of 0.25 µm film thickness, obtained from Sigma-Aldrich (Poznań, Poland), was used for the micropollutants analysis. The oven temperature programme was as follows: 80 °C (6 min), 5 °C/min up to 260 °C, 20 °C/min up to 300 °C (2 min). A helium flow rate of 1.1 mL/min was used as the carrier gas. The temperature of the ion trap was equal to 150 °C, the temperature of the ion source

was set at 230 °C and the injector temperature was set at 250 °C. The mass detector operated in the ion recording mode in the range of 50 to 400 *m/z*.

Table 2. Solid Phase Extraction details for different compound groups.

Compound Group	Pharmaceuticals; Food Additive	Dyes; UV Blocker; Pesticides; Other	Hormones
Cartridge type	Supelclean™ ENVI-8	Supelclean™ ENVI-18	Supelclean™ ENVI-18
Cartridge bed	Octylsilane (C ₈)	Octadecylsilane (C ₁₈)	Octadecylsilane (C ₁₈)
Conditioning	5.0 mL of methanol	5.0 mL of acetonitrile; 5.0 mL of methanol	3.0 mL of dichloromethane; 3.0 mL of acetonitrile; 3.0 mL of methanol
Washing	5.0 mL of deionized water		
Sample flow (mL/min)	1.0		
Vacuum drying time (min)	5.0		
Extract elution	3.0 mL of methanol	1.5 mL of methanol; 1.5 mL of acetonitrile	2.0 mL of dichloromethane; 1.5 mL of acetonitrile; 1.5 mL of methanol

The Microtox® test was used to determine the toxic potential of the micropollutant water solutions before and after the tested oxidation processes. The bioassay was based on the measurement of the intensity of light emission by selected strains of luminescent bacteria *Aliivibrio fischeri*. These bacteria are considered to be highly sensitive to a broad range of toxic substances including organic micropollutants [11]. The test procedure assumes that the estimation of the toxic effect of the tested sample is comparative to a reference nontoxic sample (2% NaCl solution). Based on the obtained results, the micropollutant water solutions were classified to particular toxicity classes according to guidelines given by Mahugo Santana et al. [12] and Werle and Dudziak [13].

3. Results and Discussion

3.1. Degradation of Micropollutants in AOP

Figure 2 presents the rates of concentration decrease of selected organic micropollutants in water solutions in the presence of such oxidizing agents as H₂O₂ and O₃. It was observed that the concentration of micropollutants decreased with the increase of the dose of oxidation agent. The oxidation supported by H₂O₂ was most favorable for butylated hydroxytoluene (Figure 2a). The concentration of this micropollutant decreased by over 42% in the reaction mixture that contained 3 mg H₂O₂/L and reached 62% in the presence of 12 mg H₂O₂/L. The highest removal degree, which exceeded 81%, was observed for the hormone mestranol in the presence of 12 mg H₂O₂/L. The decrease of progesterone also reached 60%. H₂O₂ had the least effect on the decomposition of caffeine. The decomposition of this compound did not exceed 3%.

O₃, at doses of 1 and 3 mg/L, does not have a significant impact on the decomposition of tested micropollutants. Only the concentration of triclosan decreased by over 25% at the concentration of 3 mg O₃/L. The dose of 5 mg O₃/L had the most beneficial impact on the decomposition of carbamazepine. However, the highest removal degree in the reaction mixture containing 10 mg O₃/L, which reached 52%, was noted for Triclosan. In the presence of those dose of O₃, ibuprofen was oxidized by over 40%.

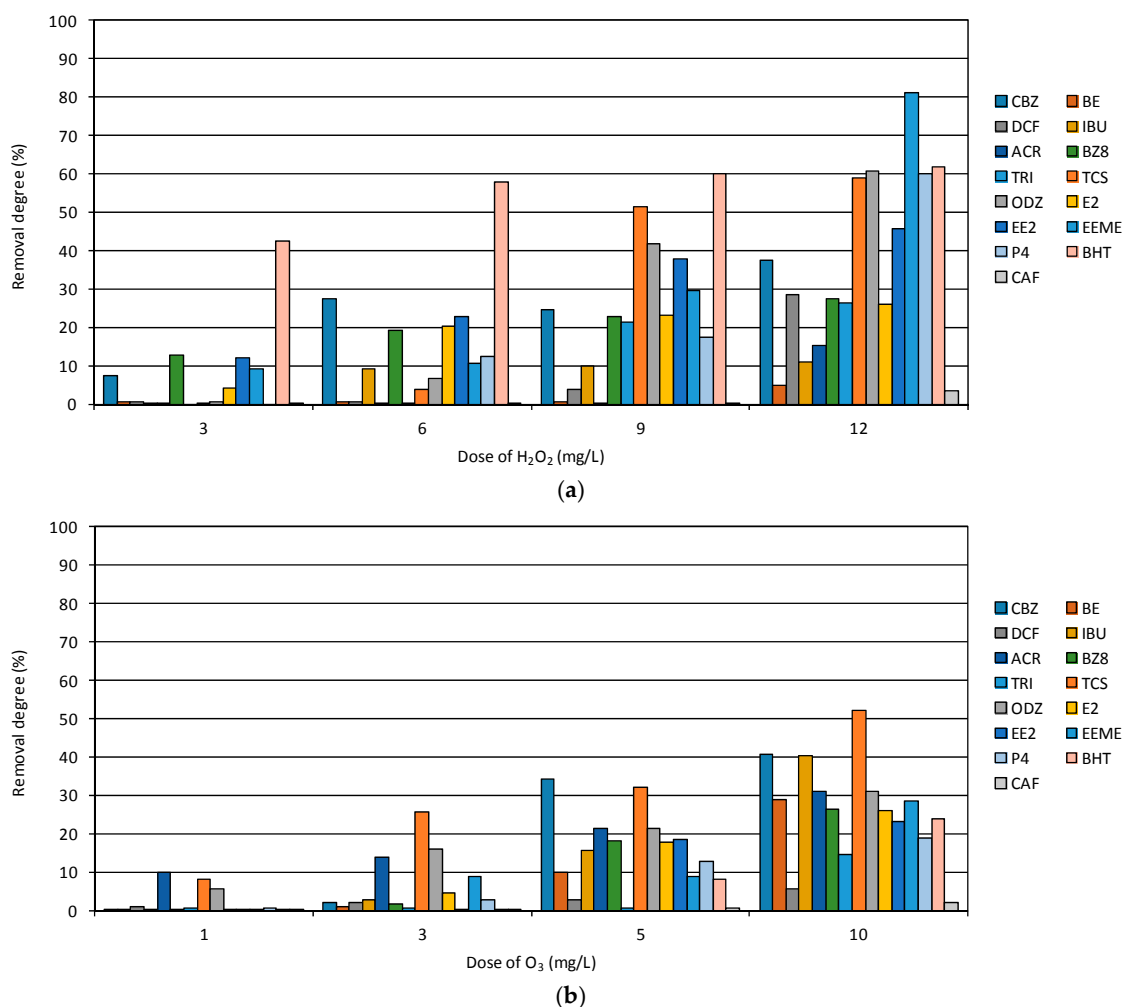


Figure 2. Degradation of micropollutants in the (a) H_2O_2 and (b) O_3 process.

The literature indicated that UV-based processes are among the most effective advanced oxidation processes for the removal of different kinds of organic micropollutants [14]. Additionally, the presence of inorganic catalysts supported the generation of high reactive radicals, which are able to decompose organic micropollutants. Therefore, the next part of the study was focused on the evaluation of the oxidation of tested contaminants of emerging concern in the presence of UV light. The impact of the presence of TiO_2 catalyst on the decrease of micropollutants was also examined. The obtained results are presented in Figure 3. The implementation of UV light significantly increases the decomposition of tested organic micropollutants. Only after 10 min of UV irradiation did the concentration of all tested pesticides—triallat, triclosan and oxadiazon—decrease significantly 85% (Figure 3a). The same removal degree was also observed for butylated hydroxytoluene. With the increase of the irradiation time, a constant decrease of micropollutant was reported. Only caffeine and dioxybenzone, which belong to the group of compounds perceived as UV blockers, did not show any susceptibility to the photochemical decomposition. The removal rate of pharmaceutical compounds after 60 minutes of UV irradiation ranged from 12% for acridine to 35% for ibuprofen. On the other hand, the concentration of hormones decreased 73% for β -estradiol to above 96% for mestranol. High removal degrees of environmental hormones after single UV irradiation, especially progesterone, were also reported by AlAani et al. [15].

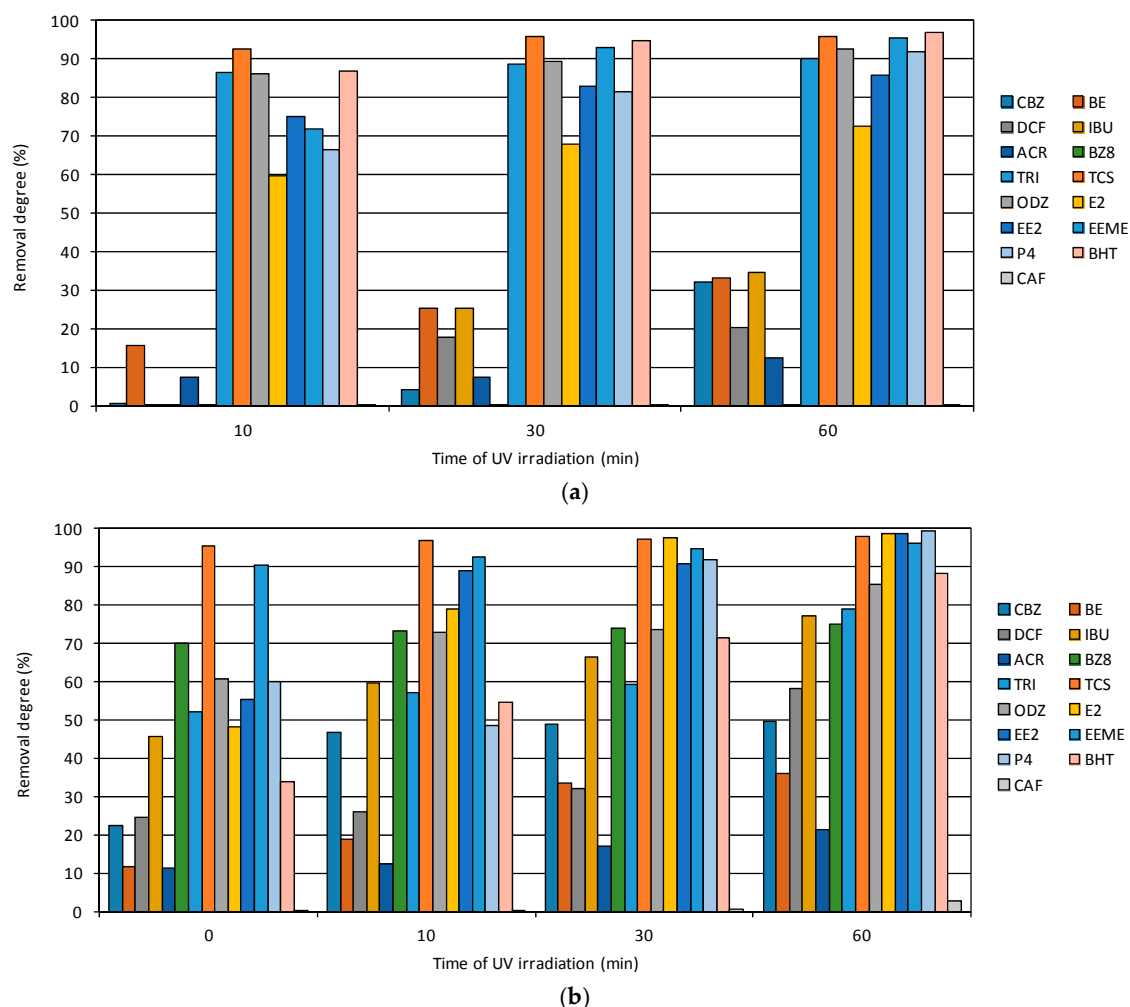


Figure 3. Degradation of micropollutants in the (a) UV and (b) UV/TiO₂ process.

The presence of the TiO₂ catalyst contributed to the increase of the micropollutant removal (Figure 3b). Firstly, the adsorption efficiency of the investigated compounds on the catalyst surface was checked. The contact of the catalyst with the reaction mixture is necessary for the distribution of the catalyst in the total volume of micropollutant water suspensions and to initiate the adsorption in active centres of TiO₂. The oxidation of micropollutants by highly reactive OH• formed in this process occurs mainly on those micropollutants which are adsorbed on the catalyst surface or are in direct proximity to the active centers [16]. The adsorption process allowed high removal rates of dioxybenzone (removal degree of 70%), triclosan (removal degree of 95%) and mestranol (removal degree of over 90%) to be obtained. The start of UV irradiation initiated a rapid decomposition of hormones and some pharmaceutical compounds. In general, the UV/TiO₂ process resulted in a much more efficient removal of different contaminants than the UV process. After 60 min of UV irradiation, the removal degree of hormones exceeded 96% and the removal of pharmaceuticals from different therapeutic groups ranged from 21% for acridine and 36% for benzocaine to 77% for the ibuprofen sodium salt.

3.2. Toxicological Assessment of Post-Processed Water Solution

The toxicological analysis of water solutions leads to an indirect assessment of the formation of oxidation by-products of the tested parent compounds. Firstly, the influence of the micropollutant water solutions, before their treatment in several oxidation processes, on the indicator organisms was tested. Figure 4 presents the obtained results of the toxicological assessment and classification of water samples to toxicological classes. Mahugo Santana et al. [12] proposed four classes of solution toxicity. Water solutions which incur an inhibition of bacterial bioluminescence of over 75% are

classified as highly toxic. The triclosan water solution was characterized by such a toxicity effect. Solutions that cause a toxic effect from 50 to 75% are considered as toxic and solutions that cause a toxic effect from 25 to 50% are considered low toxic. Such properties were observed for the acridine, dioxybenzone and 17 α -ethinylestradiol water solutions. The toxic effect of the remaining solutions was under 25% and they were classified as non-toxic.

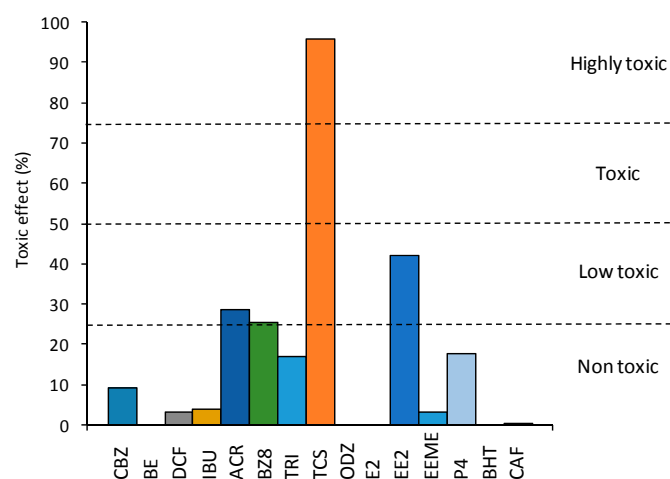


Figure 4. Toxicity of micropollutant water solutions.

The treatment of micropollutant water solutions in chosen oxidation processes resulted in an increase in their toxicity. Figure 5 summarizes the toxic effect of the treated water solutions after the H₂O₂ process (dose of the oxidizing agent was equal to 12 mg/L), O₃ (10 mg/L), UV and UV/TiO₂ (60 min of irradiation). The highest toxicity effect increase was observed for the carbamazepine and acridine solution after all oxidation processes. In addition, after the O₃ process, the triclosan solution incurred an inhibition of bacterial bioluminescence of over 99%. On the other hand, the UV/TiO₂ process led to a decrease of triclosan post-process solution and it was classified as toxic. The highest toxicity effect of pharmaceutical post-process solutions, excluding the diclofenac and ibuprofen sodium salt solutions, was observed after the UV/TiO₂ process. In previous research on the decomposition of pharmaceutical compounds during the UV/TiO₂ process, the formation of toxic transformation products was indicated [14]. Some authors also proposed degradation paths of different compounds during the oxidation processes [10,17]. In general, the oxidation of micropollutants does not lead to a complete mineralization and the formed transformation products are still biologically active compounds.

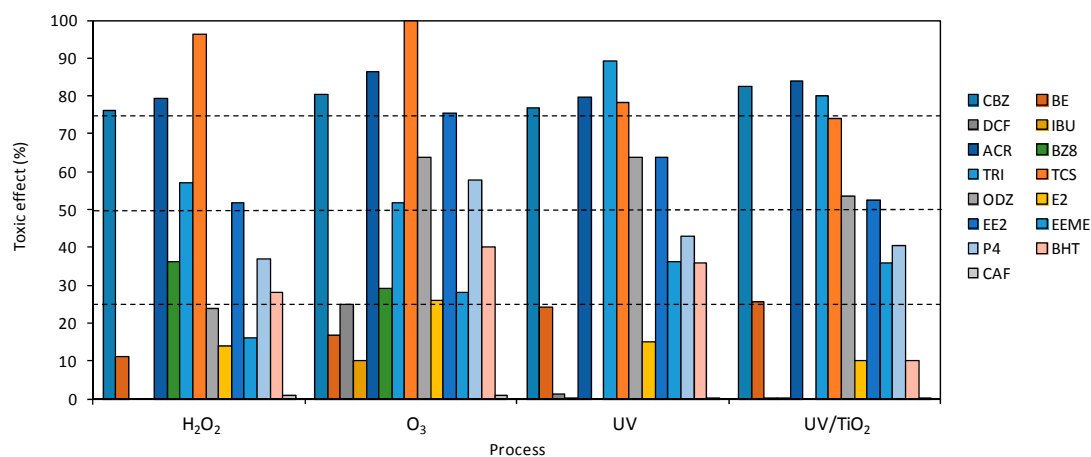


Figure 5. Change in the toxicity of the micropollutant water solution after selected oxidation processes.

4. Conclusions

On the basis of the assessments conducted on the decomposition of different groups of organic micropollutants in selected oxidation processes, the following general conclusions can be drawn:

- UV-based oxidation processes are more effective for the micropollutant decomposition than the H₂O₂ and O₃ processes.
- The highest removal rate of pharmaceutical compounds was observed during the UV/TiO₂ process. Only acridine was more effectively oxidized by the O₃ process. The TiO₂-supported process also allows for a 96% removal of hormones.
- Pesticides and the food additive BHT were most effectively oxidized by the UV process and their removal degrees exceeded 90%.
- Dioxybenzone was mainly reduced by the process of adsorption on the surface of the TiO₂ catalyst—70% removal was achieved.
- The lowest removal degree in all examined processes was observed in the case of caffeine. The removal of this compound requires the implementation of different types of treatment processes such as membrane technologies.
- The toxicological analysis of post-processed water samples indicated the generation of several oxidation by-products with a high toxic potential.

Acknowledgments: The studies were performed within the framework of the project founded by the Polish Ministry of Science and Higher Education.

Conflicts of Interest: The authors declare no conflict of interest.

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