proceedings

Proceeding

Decomposition of Contaminants of Emerging Concern in Advanced Oxidation Processes †

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† Presented at the 2nd International Electronic Conference on Water Science, 16–30 November 2017.

Academic Editor: name
Received: date; Accepted: date; Published: date

Abstract: The paper compared the removal degrees of selected contaminants of emerging concern in water solutions during advanced oxidation processes AOPs such as H_2O_2, O_3, UV and UV/TiO_2. The tested micropollutants belong to the group of pharmaceuticals, dyes, UV filters, hormones, pesticides and food additives. The highest removal rate of pharmaceutical compounds was observed during the UV/TiO_2 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

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1. Introduction

Water is a very valuable resource, and have a high impact on the whole ecosystem including human being. 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 of the last decade [5,6]

Advanced oxidation processes give an good opportunity for the decomposition of different kinds of micropollutants especially hardly or non-biodegradable compounds [7]. The main assumption of those processes is the complete mineralization of organic compounds to H_2O and CO_2. However, under actual process conditions micropollutants degraded to different biological active transformation products [8]. The decomposition of pollutants occurs as a result of reaction between high reactive oxidation species such as O_3, H_2O_2 and free radicals [9].Organic compounds show varying susceptibility for the chemical or photochemical decomposition. Therefore, it is necessary to select an optimal process for the degradation of each individual group of compound.

The paper presents the comparison of removal degrees of organic micropollutants in water solutions during selected AOPs such as H_2O_2, O_3, UV and UV/TiO_2. 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 – dioxybenzone; pesticides – triallat, triclosan and oxadiazon; hormones - β-estradiol, 17α-ethinylestradiol, mestranol and progesterone; food additive - butylated hydroxytoluene and caffeine of purity grade >97% were supplied by Sigma-Aldrich (Poznań, Poland) (Table 1). Hydrogen peroxide (H_2O_2) 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 form water solutions were supplied by Sigma-Aldrich (Poznań, Poland). In the study methanol and acetonitrile, acetone and dichloromethane of purity grade >99.8% by Avantor Performance Materials Poland S.A. (Gliwice, Poland) were also used.

Table 1. Characteristic of the tested organic compounds.

Group	Name	Molecular formula	Molecular weight, g/mol	Solubility in water, mg/L	pK_a
Pharmaceuticals	Carbamazepine, CBZ	$C_{16}H_{12}N_2O$	236.30	17	2.30
	Benzocaine, BE	$C_9H_{11}NO_2$	165.19	1310	2.51
	Diclofenac sodium salt, DCF	$C_{14}H_{10}Cl_2NNaO_2$	318.13	50	4.15
	Ibuprofen sodium salt, IBU	$C_{13}H_{17}NaO_2$	228.26	100	4.91
Dyes	Acridine, ACR	$C_{13}H_9N$	179.22	38.4	5.6
UV blockers	Dioxybenzone, BZ8	$C_{14}H_{12}O_4$	244.24	Insoluble	6.99
Pesticides	Triallat, TRI	$C_{10}H_{16}Cl_3NOS$	304.66	4.1	-[1]
	Triclosan, TCS	$C_{12}H_7Cl_3O_2$	289.54	0.1	7.9
	Oxadiazon, ODZ	$C_{15}H_{18}Cl_2N_2O_3$	345.22	0.7	-[2]
Hormones	β-Estradiol, E2	$C_{18}H_{24}O_2$	272.38	3.6	10.33
	17α-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	$C_8H_{10}N_4O_2$	194.19	21600	14.0

[1] no data

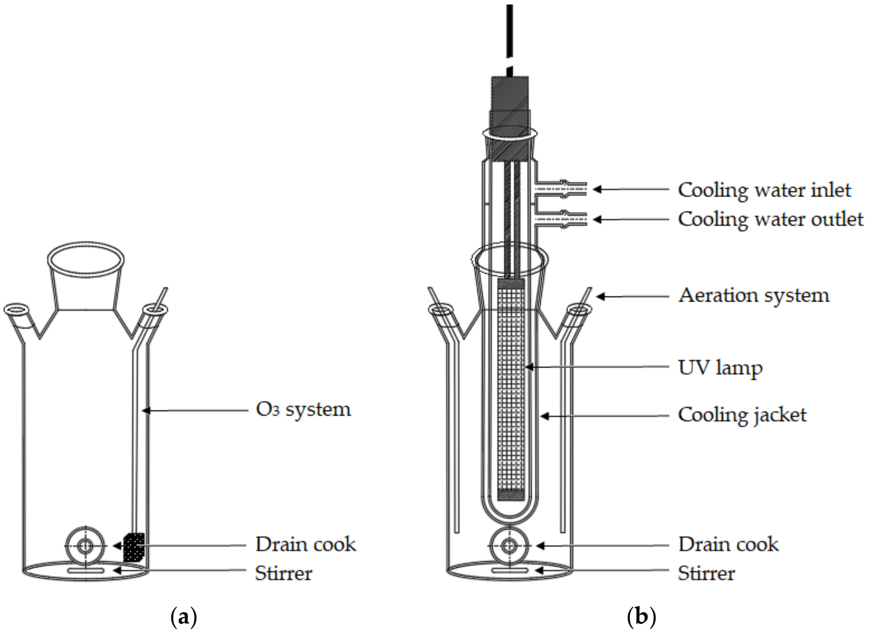
[2] non-ionizable

2.1. Water Samples

Deionized water solutions with the addition of patterns of the tested organic micropollutants of the concentration of 500 μg/L constituted the subject of the study. The compound standard solutions were prepared by dissolving of 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.

2.1. Advanced Oxidation Processes

A laboratory glass batch reactor with a volume of 0.7 L by 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 H_2O_2 and O_3 processes the reactor was placed in a dark chamber. The dose of H_2O_2 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 O_3 system was consisted of an ozone generator Ozoner FM500 by WRC Multiozon (Sopot, Poland) and a ceramic diffuser (Figure 1 **(a)**). 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 minutes.



(**a**) (**b**)

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 1 **(b)**). 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 were keep constant at 20 ± 1°C. The radiation emanated by the UV lamp according to the data given by the producer Heraeus (Hanau, Germany) had wavelength λ_{exc} equal to 313, 365, 405, 436, 546 and 578 nm. The reactor was also aerated by an aeration pump of 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 time of contact of TiO_2 with the mixtures before the implementation of 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 membrane 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 during all oxidation processes on a magnetic stirrer.

2.1. Analytical Procedure and Toxicity Assessment

The analytical procedure of tested compounds was performed by the use of the 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 were listed in Table 2.

The 7890B GC-MS(EI) chromatograph by Perlan Technologies (Warszawa, Poland) was incorporated for micropollutant determination. SLB™ - 5 ms 30 m × 0.25 mm capillary column of 0.25 μm film thickness by 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 to300°C (2 min). Helium a 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 on 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.

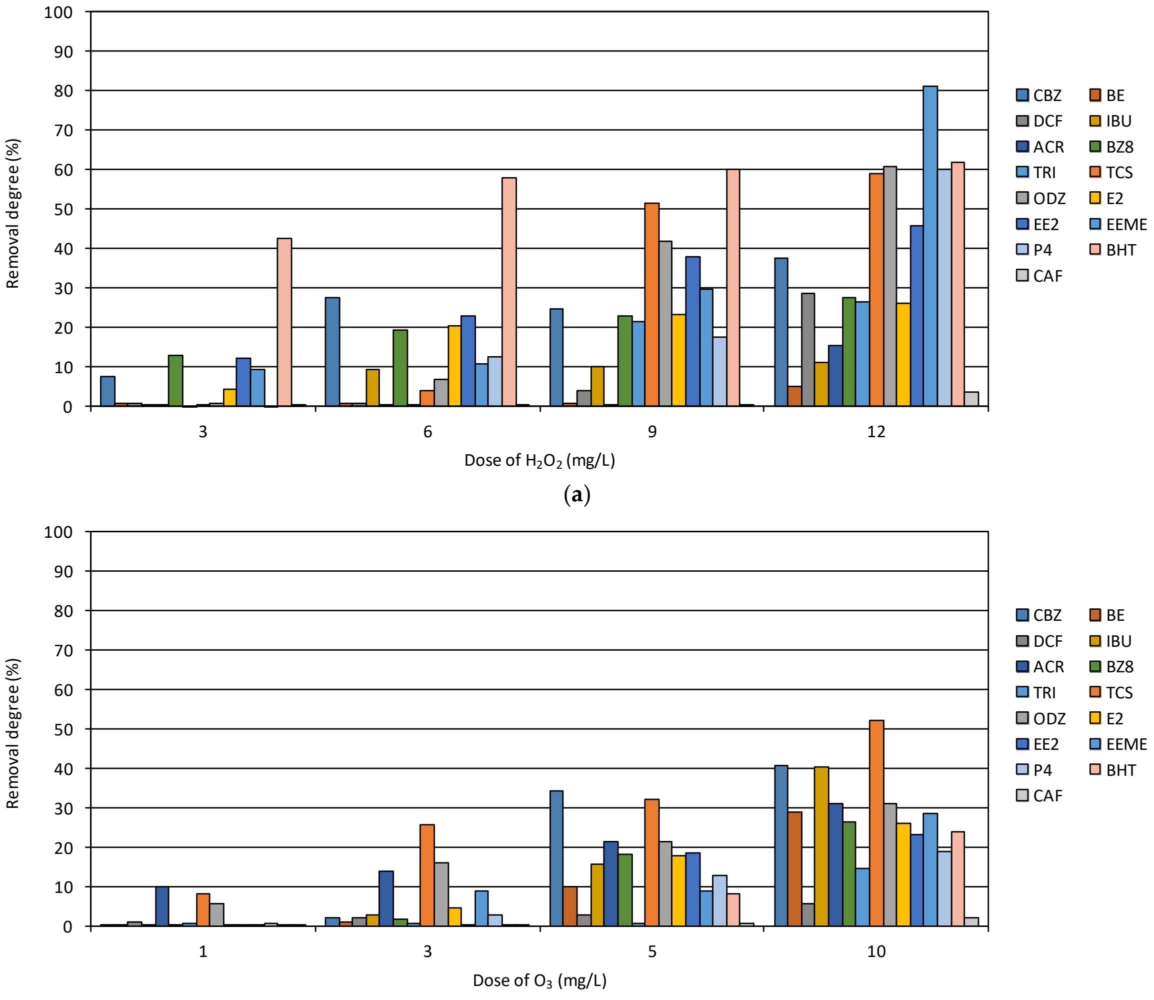
Compound group	**Pharmaceuticals** **Food additive**	**Dyes** **UV blocker** **Pesticides** **Other**	**Hormones**
Cartridge type	Supelclean™ ENVI-8	Supelclean™ ENVI-18	Supelclean™ ENVI-18
Cartridge bed	Octylsilane (C_8)	Octadecylsilane (C_{18})	Octadecylsilane (C_{18})
Conditioning	5.0 mL of methanol	5.0 mL of acetonitrile 5.0 mL of methanol	3.0 mL of dichloromethane 3.0 mL of acetonitrile 3.0mL 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 use to determine the toxic potential of the micropollutant water solutions before and after the tested oxidation processes. The bioassay is based on the measurement of the intensity of light emission by selected strains of luminescent bacteria *Aliivibrio fischeri*. This bacteria are considered to be high sensitive for a broad range of toxic substances including organic micropollutants [11]. The test procedure assumes the estimation of the toxic effect of the tested sample 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 H_2O_2 and O_3. In was observed that the concentration of micropollutants decreased with the increase of the dose of oxidation agent. The oxidation supported by H_2O_2 was most favorable for butylatedhydroxytoluene (Figure 2 **(a)**). The concentration of this micropollutant decreased by over 42% in the reaction mixture contained 3 mg H_2O_2/L and reached 62% in the presence of 12 mg H_2O_2/L. The highest removal degree exceeded 81% was observed for the hormone mestranol in the presence of 12 mg H_2O_2/L. The decrease of progesterone also reached 60%. H_2O_2 has the least effect on the decomposition of caffeine. The decomposition of this compound does not exceeded 3%.



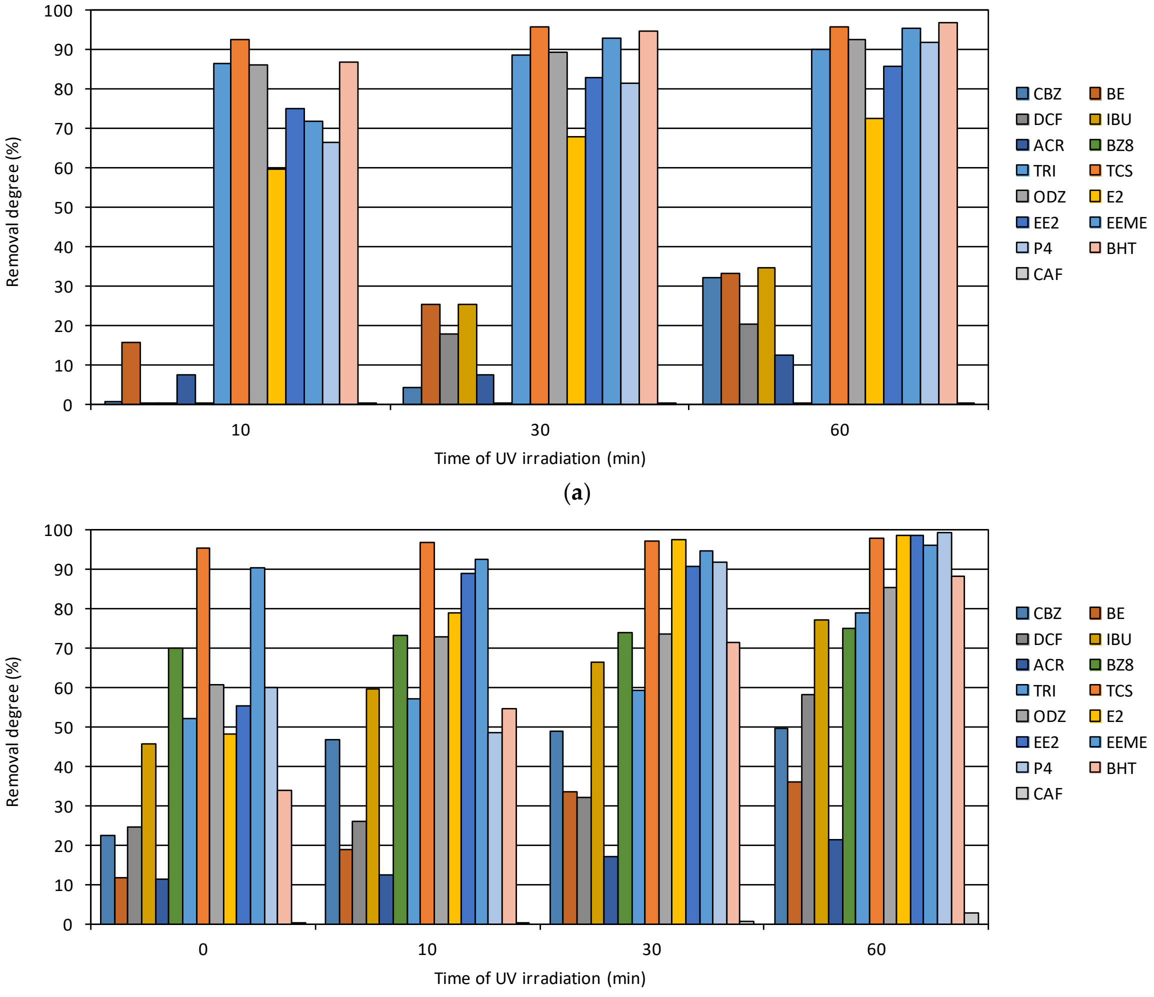
(**a**)

(**b**)

Figure 2. Degradation of micropollutants in the (**a**) H_2O_2 and (**b**) O_3process

O_3 in the dose of 1 and 3 mg/L does not have a significant impact on the decomposition of tested micropollutant. Only the concentration of triclosan decreased by over 25% for the concentration of 3 mg O_3/L. The dose of 5 mg O_3/L had the most beneficial impact on the decomposition of carbamazepine. However the highest removal degree in the reaction mixture containing 10 mg O_3/L, which reached 52%, was noted for Triclosan. Also ibuprofen oxidize in the presence of those dose of O_3 by over 40%.

The literature indicated that UV-based processed are one of 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. Also the impact of the presence of TiO_2 catalyst on the decrease of micropollutants was examined. The obtained results were presented on Figure 3. The implementation of UV light significant increases the decomposition of tested organic micropollutants. Only after 10 min of UV irradiation the concentration of all tested pesticides: triallat, triclosan and oxadiazon decreased significantly 85% (Figure 3 **(a)**). 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 belongs 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 decreases 73% for β-estradiol to above 96% for mestranol. High removal degrees of environmental hormones, especially progesterone, after single UV irradiation were also reported by AlAani at al. [15].



(**a**)

(**b**)

Figure 3. Degradation of micropollutants in the (**a**) UV and (**b**) UV/TiO_2 process

The presence of the TiO_2 catalyst contributed to the increase of the micropollutant removal (Figure 3 **(b)**). Firstly, efficiency of adsorption of 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 TiO_2. The oxidation of micropollutants by high reactive $OH^\bullet$ formed in this process occurs mainly on those, which are adsorbed on the catalyst surface or occurred in the direct proximity of the active centers [16]. The performation of adsorption process allowed to obtain high removal rates of dioxybenzone (removal degree of 70%), triclosan (removal degree of 95%) and mestranol (removal degree over 90%). The start of UV irradiation initiated a rapid decomposition of hormones and some pharmaceutical compound. In general the UV/TiO_2 process resulted in much more efficient removal of different contaminates 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 solution 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 obtain 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 affect an over 75% inhibition of bacterial bioluminescence are classified as highly toxic. The triclosan water solution was characterized by such toxicity effect. Solutions causing a toxic effect from over 50 to 75% are considered as toxic and solutions of a toxic effect from over 25 to 50% are low toxic. Such properties were observed for the acridine, dioxybenzone and 17α-ethinylestradiol water solutions. The toxic effect of the remaining solutions were under 25% and classified them as non toxic.

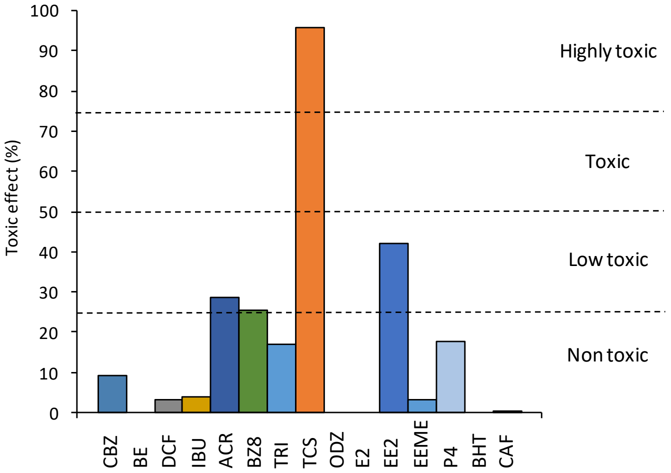


Figure 4. Toxicity of micropollutant water solutions

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 process of H_2O_2 (dose of the oxidizing agent was equal to 12 mg/L), O_3 (10 mg/L), UV and UV/TiO_2 (60 minutes of irradiation). The highest toxicity effect increase was observed for the carbamazepine and acridine solution after all oxidation processes. In addition the triclosan solution after the process of O_3 affected an over 99% inhibition of bacterial bioluminescence. On the other hand the UV/TiO_2 lead to an decrease of triclosan post-process solution and classified it as toxic. The highest toxicity effect of pharmaceutical post-process solutions, excluding the diclofenac and ibuprofen sodium salt solutions, was observed after the UV/TiO_2. In previous research on the decomposition of pharmaceutical compound during the UV/TiO_2 the formation of toxic transformation products were indicated [14]. Some authors also proposed degradation paths of different compounds during oxidation processes [10,17]. In general the oxidation of micropollutants does not lead to a complete mineralization and the formed transformation products are still biological active compound.

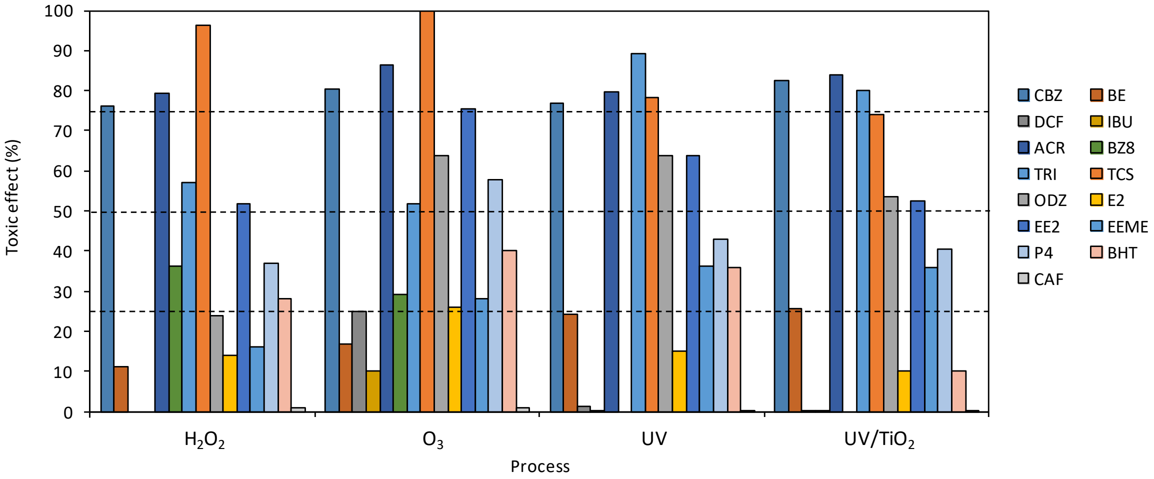


Figure 5. Change in toxicity o micropollutant water solution after selected oxidation processes

4. Conclusions

On the basis of the conducted investigations on the assessment of the decomposition of different groups of organic micropollutants in selected oxidation processes following general conclusions can be formed:

- UV-based oxidation processes are more effective for the micropollutant decomposition than the H_2O_2 and O_3 process.
- The highest removal rate of pharmaceutical compounds was observed during the UV/TiO_2 process. Only acridine was more effective oxidize by the O_3 process. The TiO_2 supported process allows also for a 96% removal of hormones.
- Pesticides and the food additive BHT were mostly effective 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 TiO_2 catalyst 75%.
- The lowest removal degree in all examined processes was observed in 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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