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Decomposition of Contaminants of Emerging Concern in Advanced Oxidation Processes

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Abstract: This paper compares 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, UV/TiO_2, UV/H_2O_2, and UV/O_3. 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/TiO_2 process. The decomposition of hormones in this process exceeded 96% and the concentration of the UV filter dioxybenzone was reduced by 75%. The pesticide triallat and the food additive butylated hydroxytoluene were most effectively oxidized by the UV process and their removal degrees exceeded 90%. The lowest removal degree in all examined processes was observed in the case of caffeine. Toxicological analysis conducted in post-processed water samples indicated the generation of several oxidation by-products with a high toxic potential. The presence of those compounds was confirmed by the GC-MS analysis. The performance of the UV/O_3 process leads to the increase of the toxicity of post-processed water solutions, especially solutions containing degradation by-products of carbamazepine, diclofenac sodium salt, acridine, trialatte, triclosan, and β-estradiol were characterized by high toxicity.

Keywords: AOPs; organic micropollutants; toxicological analysis

1. Introduction

Water is a very valuable resource, and has a high impact on the whole ecosystem, including on human beings. The water environment is particularly vulnerable to pollution by several contaminants of emerging concern. The occurrence of those compounds has been reported by many authors [1,2]. Particular attention should be paid to compounds which are considered to be hardly biodegradable and are most commonly identified in water streams, such as pharmaceuticals (carbamazepine, benzocaine, diclofenac, ibuprofen), dyes (acridine), UV blockers (dioxybenzone), pesticides (triallat, triclosan, oxadiazon), hormones (β-estradiol, 17α-ethinylestradiol, mestranol, progesterone), and food additives (butylated hydroxytoluene). Their negative impact on the environment was also investigated in several articles in the last decade [3,4].

Advanced oxidation processes (AOPs) provide a good opportunity for the decomposition of different kinds of micropollutants, especially hardly biodegradable or non-biodegradable compounds [5]. 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 biologically active transformation products [6]. The decomposition of pollutants occurs as a result of the reaction between high reactive oxidation species, such as O_3, H_2O_2, and free radicals [7]. 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.

One of the most commonly used AOP methods is heterogeneous photocatalysis, which uses various types of semiconductors to catalyze the formation of highly reactive hydroxyl radicals ($OH^{\bullet}$) and the decomposition of compounds [8–10]. The major photocatalysts used to remove organic contaminants are TiO_2, ZnO, SnO_2, CeO_2, Fe_2O_3, WO_3, and ZnS [11,12]. However, some metal oxides may have a negative effect on living organisms [13]. UV-based AOPs supported by oxidation compounds also give very interesting results in terms of the decomposition of a large number of micropollutants [14].

Due to the high costs of running AOPs and the ability to generate many decomposition by-products, chemical or photochemical decomposition of contaminants should be the last option for water treatment. Micropollutants should be recovered or recycled during the process in which they are used in order to minimize the environmental impact. The implementation of membrane processes, nanofiltration, or reverse osmosis gives such possibilities. Fodi et al. proposed the coupling of a nanofiltration module to a continuous-flow rector for in situ solvent and reagent recycling in the pharmaceutical sector [15]. This system allows recycling 90% of solvents and reagents during manufacturing processes. Moreover, the integration of diafiltration processes allows obtaining a high purity product and leads to a reduction in the general production costs [16]. It should be mentioned that the so-called green technology membrane process is quite far from green. Membrane production generates large streams of toxic solvent-water mixtures [17] which become a major problem for conventional wastewater treatment plants based on activated sludge. During membrane filtration, two streams are always produced: permeate and retentate, one of which is a waste product and requires further processing. Nevertheless, the application of such technologies is not always possible.

Sustainable wastewater treatment methods are also a promising solution for the removal of hazardous organic contaminants. The concept of these methods is based on the natural-energy operation, balanced investment and economic output and stable high-quality treatment performance without a negative impact on the environment [18,19]. AOPs with some operation modifications can also be an opportunity during the sustainable wastewater treatment method development. Hence, there is the need to study and describe the effects of the implementation of advanced methods for the elimination of micropollutants from environmental streams.

This paper presents a comparison of removal degrees of organic micropollutants in water solutions during selected AOPs, such as H_2O_2, O_3, UV, UV/TiO_2, UV/H_2O_2, and UV/O_3. 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 experiments were carried out on micropollutant solutions in deionized water to identify decomposition by-products, which are the result of only oxidizing agents' action. GC-MS (EI) analysis was used to identify potential oxidation by-products formed during the implemented treatment processes. The oxidation processes were also evaluated according to the potential toxic effect of post-treated water solutions using the Microtox® bioassay.

2. Materials 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 additives—butylated hydroxytoluene and caffeine of purity grade >97.0% were supplied by Sigma-Aldrich (Poznań, Poland) (Table 1). Hydrogen peroxide (H_2O_2) as a 30% solution in water (purity grade >99.8%) was supplied by the same company. Titanium dioxide with the acronym P25 was purchased from Evonik Degussa GmbH (Hanau, Germany). The particle size of the applied catalyst (mixture of anatase and rutile 75:25 v/v) according to the producer is about 21 nm. 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 (MeOH), acetonitrile (ACN), and dichloromethane (DCM) 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 [20].

Group	Name	Molecular Formula	Molecular Weight, g mol^{-1}	Solubility in Water, mg L^{-1}	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.

2.2. Water Samples

Deionized water (conductivity of 18 MΩ cm^{-1}) solutions with the addition of the tested organic micropollutants standards, at the concentration of 500 µg L^{-1}, 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 standard solutions were used due to the weak solubility of some micropollutants in water solutions, especially in deionized water. High concentrations of micropollutants that exceeded the usual environmental concentrations were applied in order to increase the accuracy of the analytical measurements. The pH of the prepared water solutions were adjusted to 7 using 0.1 mol L^{-1} HCl (purity grade >99.8%) or 0.1 mol L^{-1} NaOH (purity grade >99.6%). 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 were carried out on micropollutant solutions in deionized water to identify decomposition by-products, which are the result of only oxidizing agents' action. Therefore, the experiments for all tested compounds were carried out separately and repeated three times.

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 all 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^{-1}. The oxidizing reagent was introduced to the reaction mixture in the form of a 30% solution. The O_3 system consisted of an Ozoner FM500 ozone generator 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^{-1}. The O_3 concentrations were measured photometrically using the Spectroquant® Ozone Test by Merck KGaA (Darmstadt, Germany). The contact time between the oxidizing reagents and the prepared water solutions was 30 min.

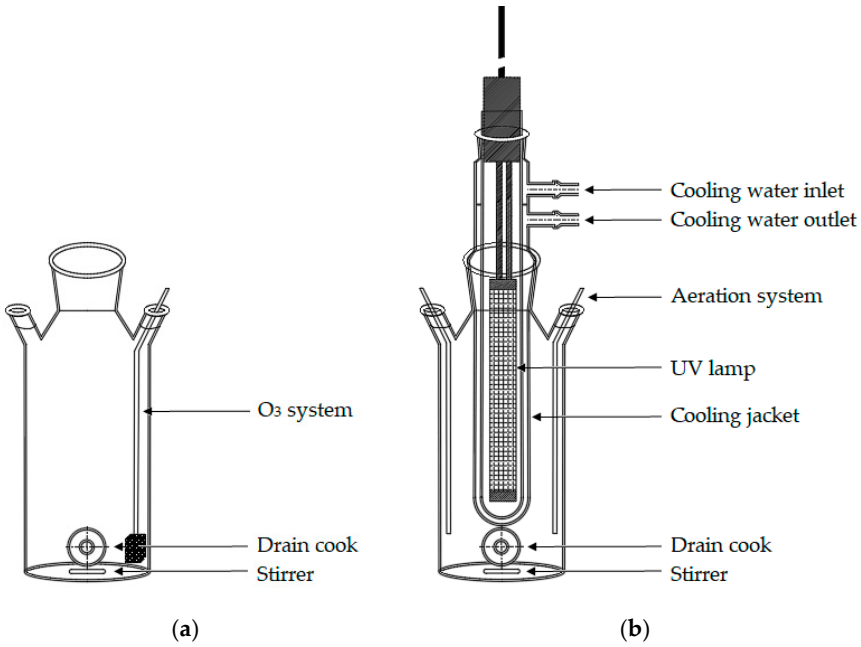


Figure 1. Reactor for the (**a**) H_2O_2, O_3, and (**b**) UV, UV/TiO_2 [21] processes.

In order to carry out the UV, UV/TiO_2, UV/H_2O_2, and UV/O_3 processes, the reactor was equipped with a medium-pressure mercury vapor UV lamp with a 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. Thus, the oxygen flow rate applied to the reactor was 0.84 L min^{-1}. The oxygen concentration measured in the aerated water solution was equal to 6.32 mg L^{-1}.

The dose of the TiO_2 catalyst in the UV/TiO_2 process was 50 mg L^{-1}. 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 with a 0.45 membrane pore size from Merck Millipore (Darmstadt, Germany).

The dose of H_2O_2 during the implementation of the UV/H_2O_2 process was equal to 12 mg L^{-1}, while the dose of O_3 was set to 10 mg L^{-1}.

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 Assestment

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. The pH of some samples (especially after the UV/TiO_2 and UV/O_3 processes) ranged from 7.10 to 8.25. Details of the used SPE cartridges and the organic solvents for the extraction of different compound groups are listed in Table 2. Recovery of the tested compounds using the SPE procedure exceeded 95%.

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	
Cartridge bed	silica gel base material with C_8 (octyl) bonding, polymerically bonded	silica gel base material with C_{18} (octadecyl) bonding, polymerically bonded	
Bed weight (mg)	1000		
Bed pore size (Å)	60		
Bed surface area (m^2 g^{-1})	475		
Material of cartridge filter	PE frit (20 µm porosity)		
Conditioning	5.0 mL of MeOH	5.0 mL of ACN; 5.0 mL of MeOH	3.0 mL of DCM; 3.0 mL of ACN; 3.0 mL of MeOH
Washing	5.0 mL of deionized water		
Sample flow (mL min^{-1})	1.0		
Vacuum drying time (min)	5.0		
Extract elution	3.0 mL of MeOH	1.5 mL of MeOH; 1.5 mL of ACN	2.0 mL of DCM; 1.5 mL of ACN; 1.5 mL of MeOH

The 7890B GC-MS(EI) chromatograph by Perlan Technologies (Warszawa, Poland) was incorporated for micropollutant determination. An SLB^{TM}—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 program 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. All post-processed water samples after the SPE extraction were analyzed twice, in the SIM mode (monitoring of the compound concentration) and in the TIC mode (identification of generated by-products). The analysis in the SIM mode allowed obtaining lower detection limits of the analyzed compounds.

The percentage of removal of each micropollutant after AOP application was calculated according to Equation (1), where C_i and C_p are the initial and post-processed compound concentrations (mg L^{-1}), respectively [22]:

$$Removal\ (\%) = \frac{C_i - C_p}{C_i} \cdot 100 \quad (1)$$

Assignment errors were estimated on the basis of the standard deviation for three repetitions of each test.

2.5. Toxicity Assestment

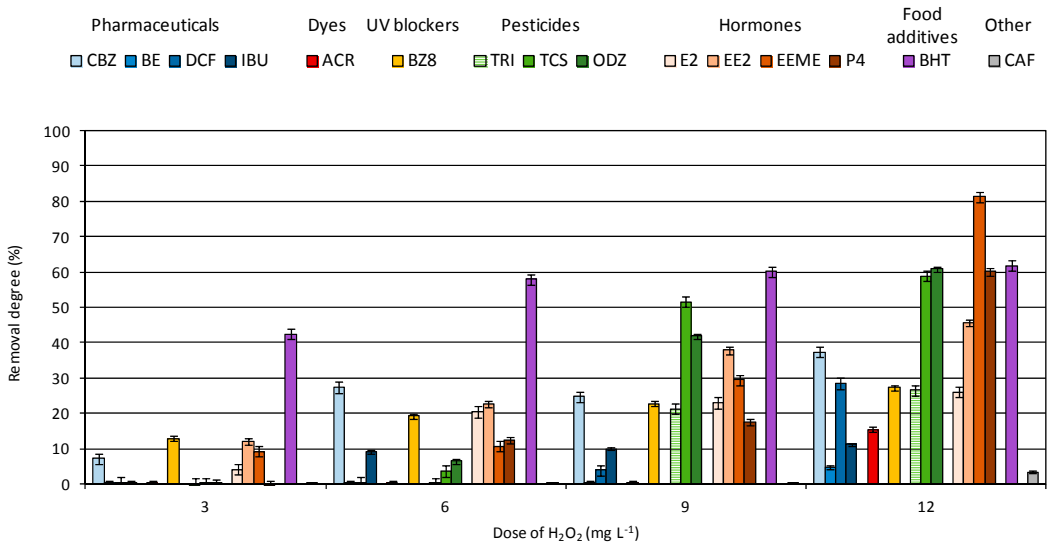
The Microtox® test was used to determine the toxic potential of the micropollutant water solutions before and after the tested oxidation processes. The bioassay was based on the measurement of the intensity of light emission by selected strains of luminescent bacteria *Aliivibrio fischeri*. These bacteria are considered to be highly sensitive to a broad range of toxic substances, including organic micropollutants [23]. 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. [24] and Werle and Dudziak [25].

3. Results and Discussion

3.1. Degradation of Micropollutants in Single AOP

Figure 2a,b 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. It 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 butylated hydroxytoluene (Figure 2a). The concentration of this micropollutant decreased by over 42% in the reaction mixture that contained 3 mg L^{-1} of H_2O_2 and reached 62% in the presence of 12 mg L^{-1} of H_2O_2. The highest removal degree, which exceeded 81%, was observed for the hormone mestranol in the presence of 12 mg L^{-1} of H_2O_2. The decrease of progesterone also reached 60%. H_2O_2 had the least effect on the decomposition of caffeine. The decomposition of this compound did not exceed 3%.

O_3, at doses of 1 and 3 mg L^{-1}, 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 L^{-1} of O_3. The dose of 5 mg L^{-1} of O_3 had the most beneficial impact on the decomposition of carbamazepine. However, the highest removal degree in the reaction mixture containing 10 mg L^{-1} of O_3, which reached 52%, was noted for triclosan. In the presence of those doses of O_3, ibuprofen was oxidized by over 40%.



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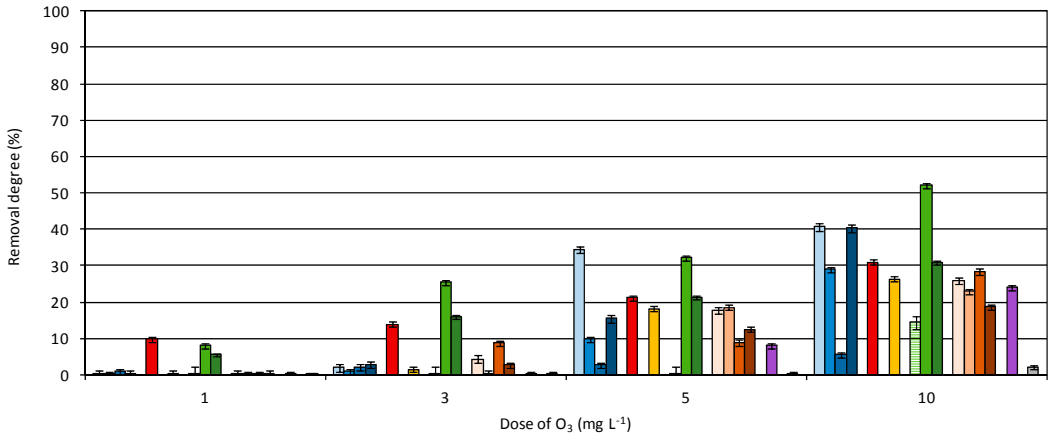
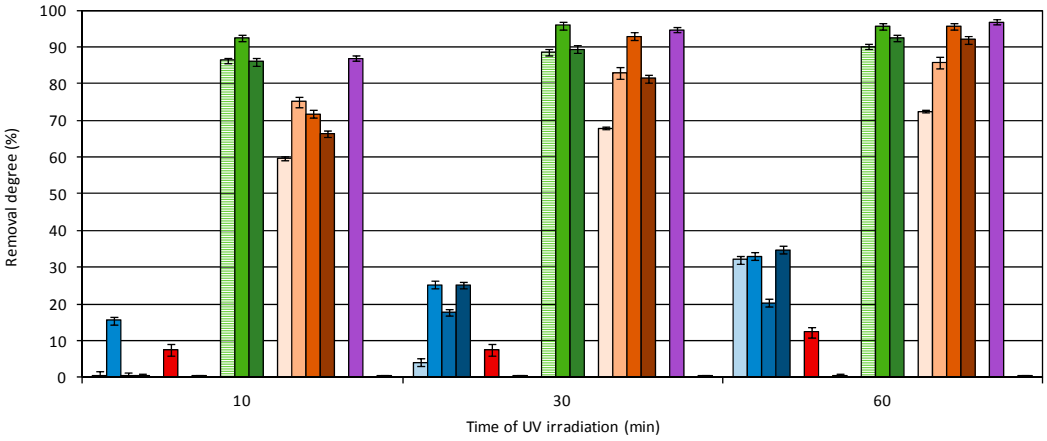


(**b**)

Figure 2. *Cont.*



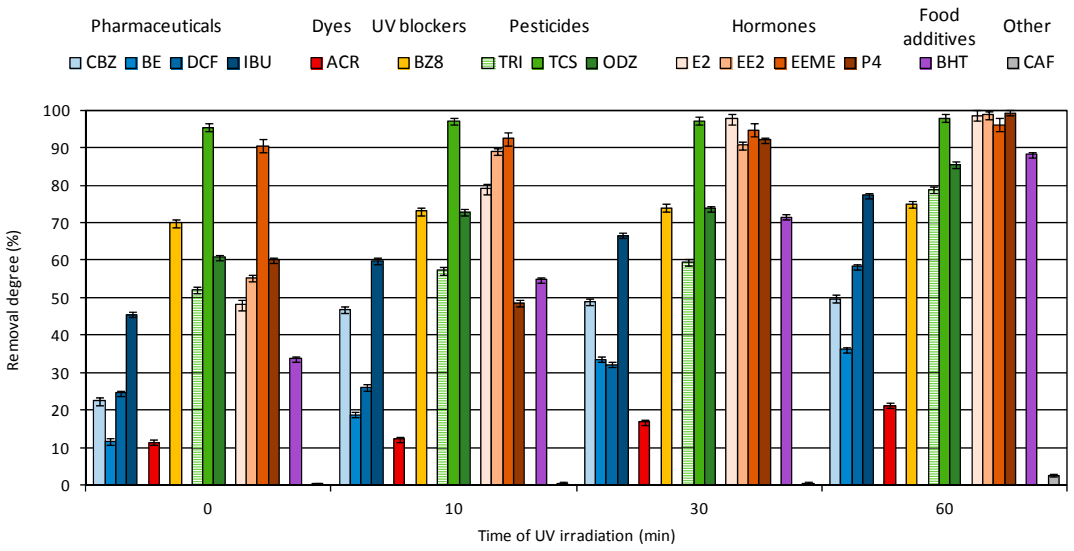
(**c**)

Figure 2. Degradation of micropollutants in the (**a**) H_2O_2, (**b**) O_3 and (**c**) UV processes.

The literature indicated that UV-based processes are among the most effective advanced oxidation processes to remove various types of organic micropollutants [13]. Additionally, the presence of inorganic catalysts or other oxidation agents supports the generation of highly-reactive radicals, which are able to degrade organic micropollutants. Therefore, the next part of the study is focused on the evaluation of the oxidation of tested contaminants of emerging concern in the presence of UV light. The obtained results are presented in Figure 2c. 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 by 85% (Figure 3). The same removal degree was also observed for butylated hydroxytoluene. With the increase of the irradiation time, a constant decrease of micropollutants 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 min 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. [26].

3.2. Degradation of Micropollutants in UV-Based AOP

The impact of the addition of TiO_2 catalyst, H_2O_2, or O_3 to the reaction mixture on the decrease of micropollutants was also examined (Figure 3). The presence of the TiO_2 catalyst contributed to the increase of the micropollutant removal (Figure 3a). 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 the micropollutant water suspensions and to initiate the adsorption in active centers of TiO_2. The oxidation of micropollutants by highly-reactive $OH^{\bullet}$ 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 [27]. The adsorption process allowed obtaining high removal rates of dioxybenzone (removal degree of 70%), triclosan (removal degree of 95%), and mestranol (removal degree of over 90%). The start of UV irradiation initiated a rapid decomposition of hormones and some pharmaceutical compounds. In general, the UV/TiO_2 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.



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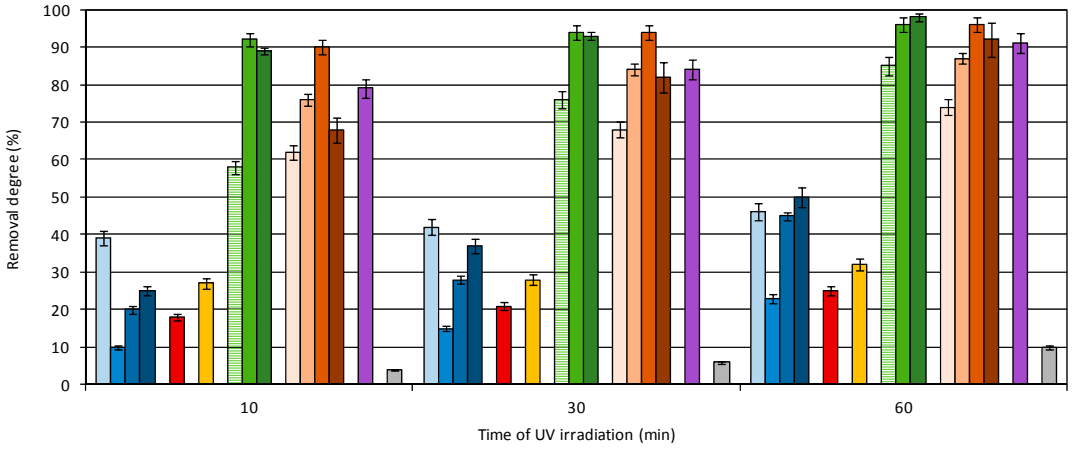

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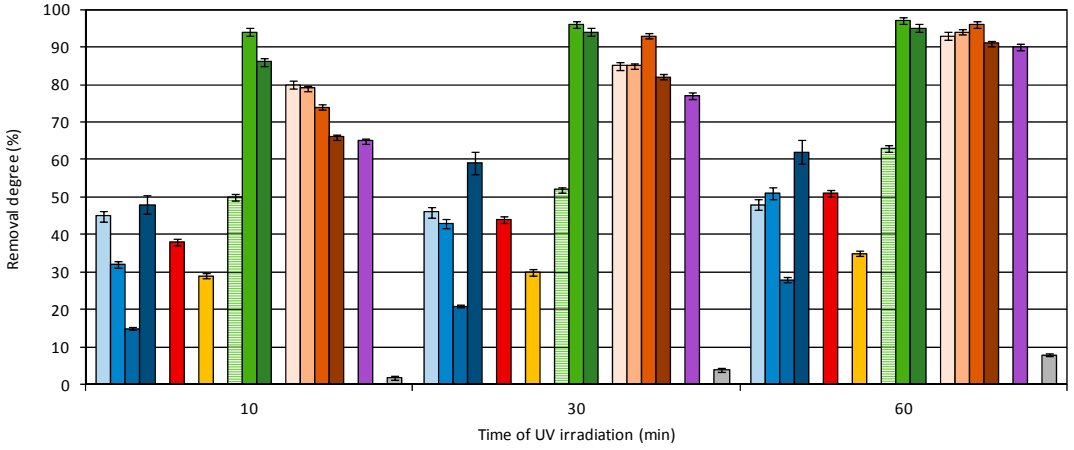


(**c**)

Figure 3. Degradation of micropollutants in the (**a**) UV/TiO_2, (**b**) UV/H_2O_2, and (**c**) UV/O_3 processes (the doses of TiO_2, H_2O_2 and O_3 were equal to 50, 12 and 10 mg L^{-1} respectively).

For all UV-based oxidation processes, it was observed that the concentration of micropollutants decreased with the increase of the irradiation time. The UV-irradiation time, which corresponds to the radiation dose, therefore, plays a significant role in the decomposition of micropollutants. This dependency is particularly evident in the reduction of pharmaceutical compounds and hormones.

The highest removal rate of BE, which reached 51%, was observed in the water solution after 60 min of the UV/O_3 process (Figure 3c). Other pharmaceuticals, such as carbamazepine, diclofenac, and ibuprofen sodium salt, were more effectively removed during the UV/TiO_2 process. The process of UV decomposition supported by the presence of O_3 also allows for more than a 51% reduction of acridine concentration. In addition, the UV process in the presence of other oxidizing agents also promoted the decomposition of oxadiazone, butylated hydroxytoluene, and caffeine. The removal degree of those compounds reaches 98%, 91%, and 10%, respectively, for 60 min of the UV/H_2O_2 process (Figure 3b), whereas, for the 60 min of the UV/O_3 process the concentration of oxadiazone was reduced by more than 95%, butylated hydroxytoluene by over 90%, and caffeine by 8%. Therefore, it can be concluded that the highest removal degree of caffeine was obtained by UV/H_2O_2 treatment.

Differences in the removal rates of the examined compounds, which were observed in all conducted AOPs, results mainly from the different chemical structures of the decomposed compounds. Suzuki et al. [28] reported that aromatic compounds were slower to degrade than the open-chain compounds. Additionally, the number of carbon atoms and the presence of functional groups determine the ability of a compound to decompose [28]. The type of chemical bonds between the atoms of the compound molecule and their energy also determines the emerging decomposition by-products and their future mineralization.

3.3. Decomposition By-Product Identification

The AOPs are based on the attack of compound bonds with the weakest dissociation energy, which easily loses electrons, by high-reactive species [29]. This happens in accordance with the bond dissociation energies theory and leads to the formation of several decomposition by-products of parent compounds. The conducted chromatographic analysis of the post-processed water solutions indicated the formation of such intermediates. Based on the mass spectra of the newly-formed compounds and the NIST 17 database software, an attempt has been made to identify the by-products. Figures 4–17 present the possible degradation pathways of selected contaminants of emerging concern. All by-products shown in the figures were detected in both H_2O_2, O_3, UV, UV/TiO_2, UV/H_2O_2, and UV/O_3 processes. Therefore, the identified compounds do not clearly indicate the exact degradation mechanism of the tested compounds. They were formed as a direct reaction of primary oxidants on the compounds or as a result of reactions between compounds and the generated high-reactive species, like the hydroxyl radical $OH^{\bullet}$.

The benzocaine decomposition is a good example of the correctness of the bond dissociation energies theory. The C–N bond has the weakest bond energy of 305 kJ·mol^{-1} [30] and this was the first to be dissociated. This reaction allows the formation of ethyl 4-hydroxybenzoate (Figure 5). During the AOPs conducted on the last tested pharmaceutical compound, ibuprofen sodium salt water solution, three by-products were identified, i.e., 1-hydroxyibuprofen, 4-acetylbenzoic acid, and 4-oxohexanoate (Figure 7). It can be assumed that the cyclic intermediate 4-oxohexanoate was generated by successive hydroxylation of 4-acetylbenzoic acid. da Silva et al. [31] drew the same conclusions.

The decomposition of acridine resulted in the formation of two intermediates: acridine-N-oxide and 2-hydroxyacridine (Figure 8), whereas during the oxidation of dioxybenzone 2,2′,4-trihydroxybenzophenone was detected (Figure 9).

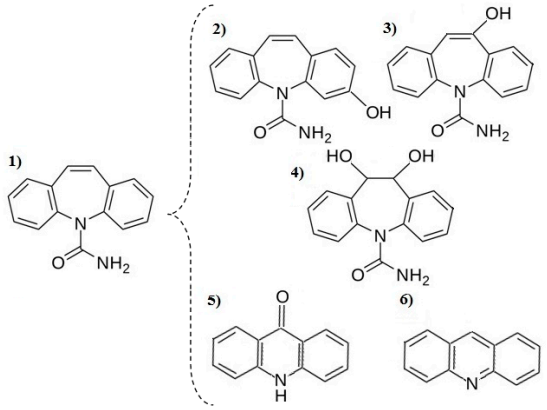


Figure 4. Identified **1** carbamazepine by-products, where **2** is 3-hydroxycarbamazepine, **3** is 10,11-dihydro-10-hydroxycarbamazepine, **4** is dihydrocarbamazepine-10,11-trans-diol, **5** is 9-acridone, and **6** is acridine.

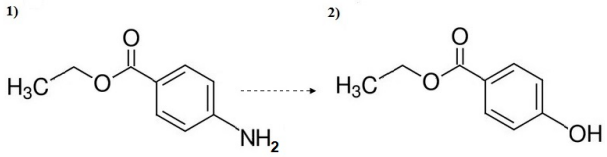


Figure 5. Identified **1** benzocaine by-product, where **2** is ethyl 4-hydroxybenzoate.

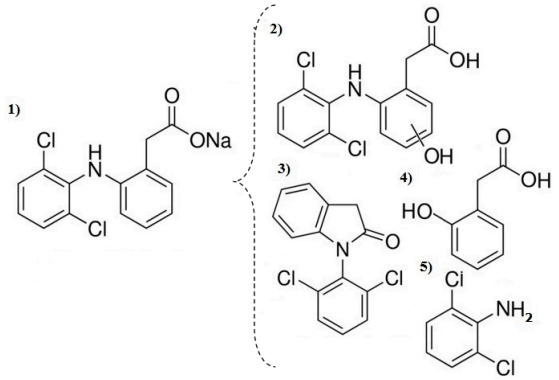


Figure 6. Identified **1** diclofenac sodium salt by-products, where **2** is 4′-hydroxydiclofenac, **3** is 1-(2,6-dichlorophenyl)-2-indolinone, **4** is 2-hydroxyphenylacetic acid, and **5** is 2,6-dichloroaniline.

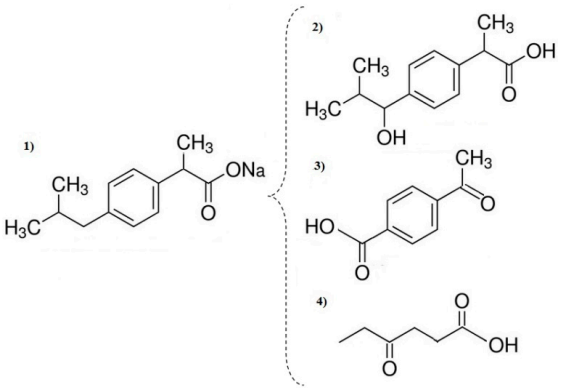


Figure 7. Identified **1** ibuprofen sodium salt by-products, where **2** is 1-hydroxyibuprofen, **3** is 4-acetylbenzoic acid and **4** 4-oxohexanoate.

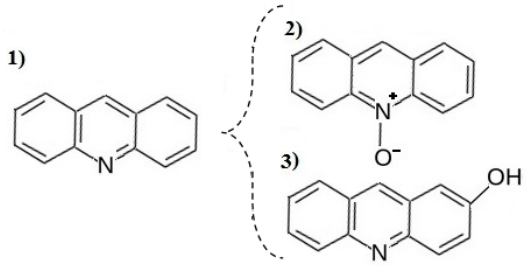


Figure 8. Identified **1** acridine by-products, where **2** is acridine-N-oxide and **3** is 2-hydroxyacridine.

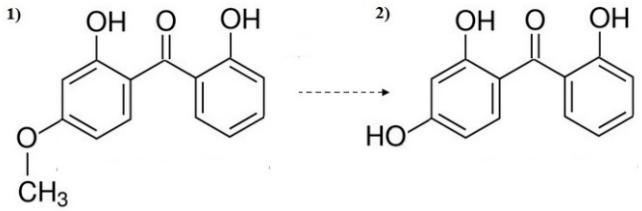


Figure 9. Identified **1** dioxybenzone by-product, where **2** is 2,2′,4-trihydroxybenzophenone.

The oxidation of triallate leads to the disconnecting of one atom of chlorine from the molecule and the formation of diallate (Figure 10). During the decomposition of triclosan (Figure 11) and oxadiazon (Figure 12) no detachment of chlorine atoms from the molecule has been observed. The attack of $OH^{\bullet}$ radicals caused, in the case of triclosan water solutions, the decomposition of the molecule to 2,3-dichlorophenol and chlorophenol. Son et al. [32] reported during the process of UV irradiation and the UV/TiO_2 process, the formation of similar triclosan intermediates.

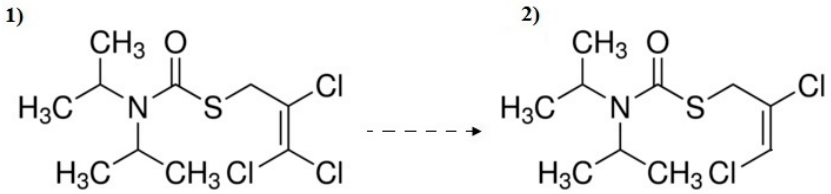


Figure 10. Identified **1** triallate by-product, where **2** is diallate.

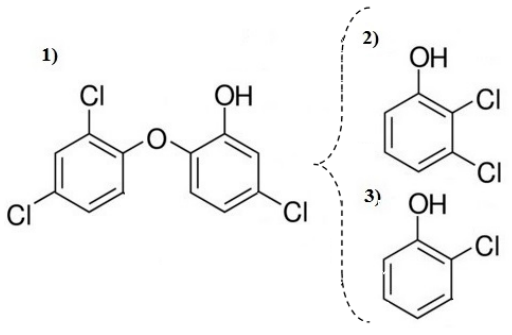


Figure 11. Identified **1** triclosan by-products, where **2** is 2,3-dichlorophenol and **3** is chlorophenol.

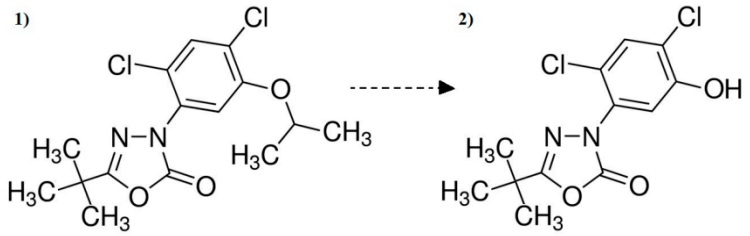


Figure 12. Identified **1** oxadiazon by-product where **2** is 5-tert-Butyl-3-(2,4-dichloro-5-hydroxyphenyl)-1,3,4-oxadiazol-2(3H)-one.

The analysis of post-processed hormone water solution pointed that all newly-formed intermediates still remain endocrine disrupting compounds (Figures 13–16). For example, the decomposition of progesterone resulted in the generation of corticosterone, aldosterone, and cortisone. Barron et al. [33] reported during the O_3 of progesterone two non-named major by-products, which are the result of successive progesterone ozonide formation, hydration of the compound and, finally, the loss of the hydrogen peroxide molecule or Baeyer–Villiger rearrangement.

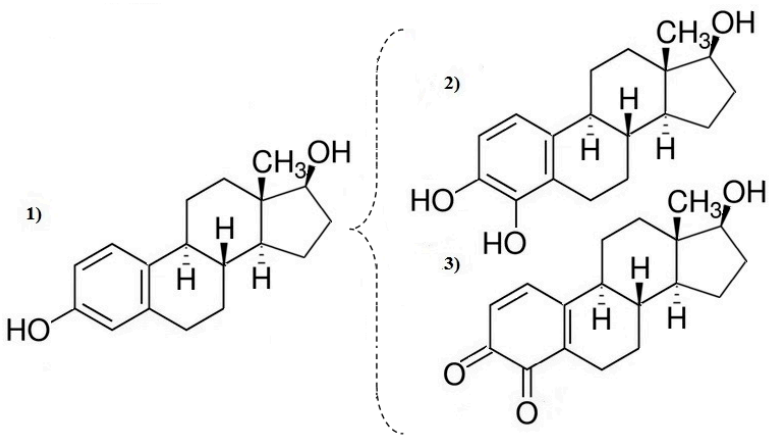


Figure 13. Identified **1** β-estradiol by-products, where **2** is 2-hydroxyestradiol and **3** is (17β)-17-Hydroxyestra-1,5(10)-diene-3,4-dione.

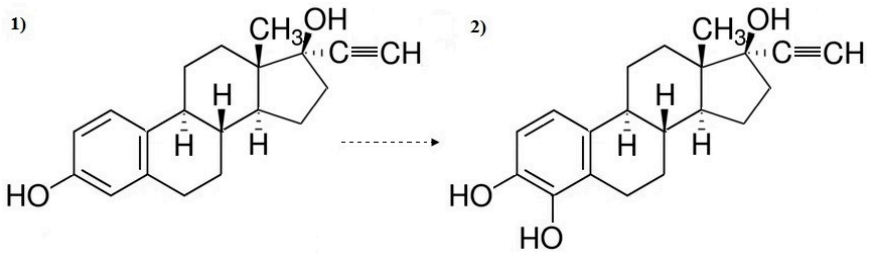


Figure 14. Identified **1** 17α-ethinylestradiol by-product, where **2** is 2-hydroxy-17α-ethinylestradiol.

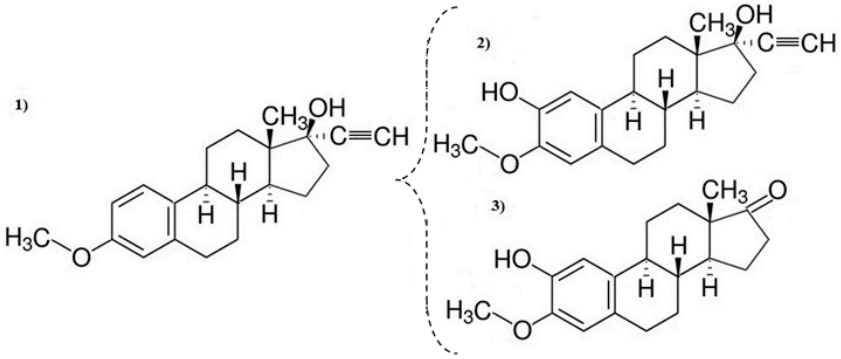


Figure 15. Identified **1** mestranol by-products, where **2** is 2,6-di-tert-butylhydroquinone and **3** is 2-hydroxy-3-methoxy-estrone.

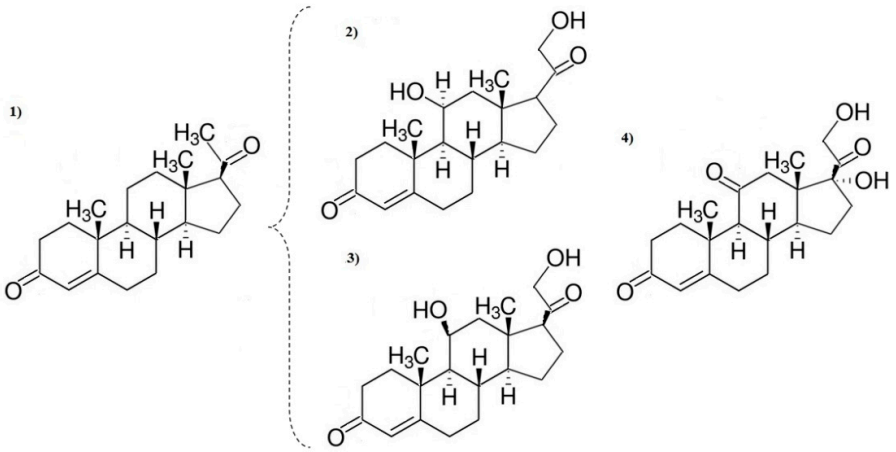


Figure 16. Identified **1** progesterone by-products: **2**, corticosterone; **3**, aldosterone; and **4**, cortisone.

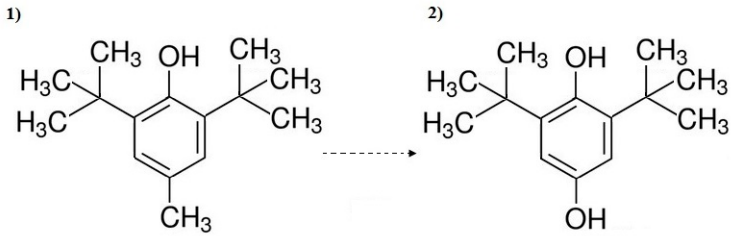


Figure 17. Identification of **1**, butylated hydroxytoluene by-product, where **2** is 2,6-di-tert-butylhydroquinone.

The largest number of by-products were detected in solutions containing carbamazepine (Figure 4). The decomposition process of this pharmaceutical compound leads to the formation of five intermediates: 3-hydroxycarbamazepine, 10,11-dihydro-10-hydroxycarbamazepine, dihydrocarbamazepine-10,11-trans-diol, 9-acridone, and acridine. Four by-products were identified during the decomposition of diclofenac sodium salt (Figure 6). Previous studies on the identification of oxidation by-products formed during the UV/TiO_2 process of water solution containing carbamazepine and diclofenac sodium salt at a higher concentration of 1 mg L^{-1}, indicating the formation of more by-products [21].

Only during the decomposition of caffeine no by-products were identified. The presence of newly-formed biologically-active compounds suggests that the toxicity of post-process solutions increased significantly. The toxicological assessment of all water solutions was undertaken in the next stage of this study.

3.4. Toxicological Assessment of Post-Processed Water Solution

Toxicological analysis of water solutions is not only a method of assessing the biological effect of the tested samples, but also 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 18 presents the obtained results of the toxicological assessment and classification of water samples to toxicological classes. Mahugo Santana et al. [24] 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 to have low toxicity. Such properties were observed for the acridine, dioxybenzone, and 17α-ethinylestradiol water solutions. The toxic effect of the remaining solutions was under 25% and they were classified as non-toxic.

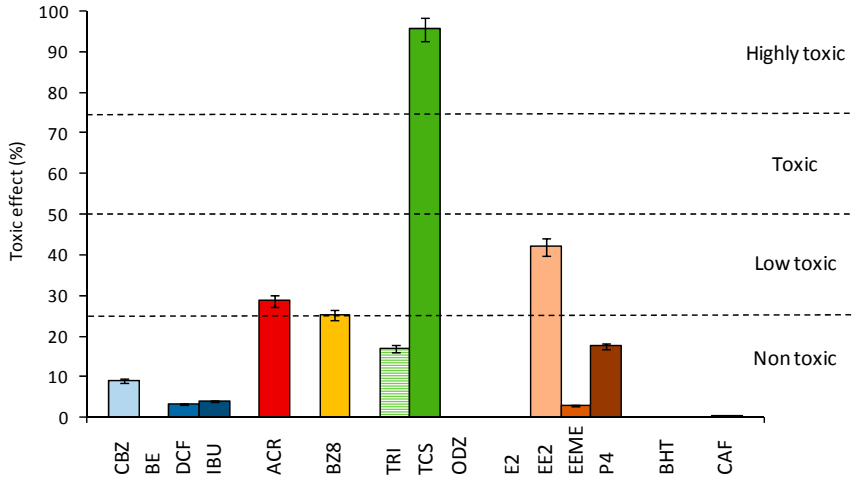


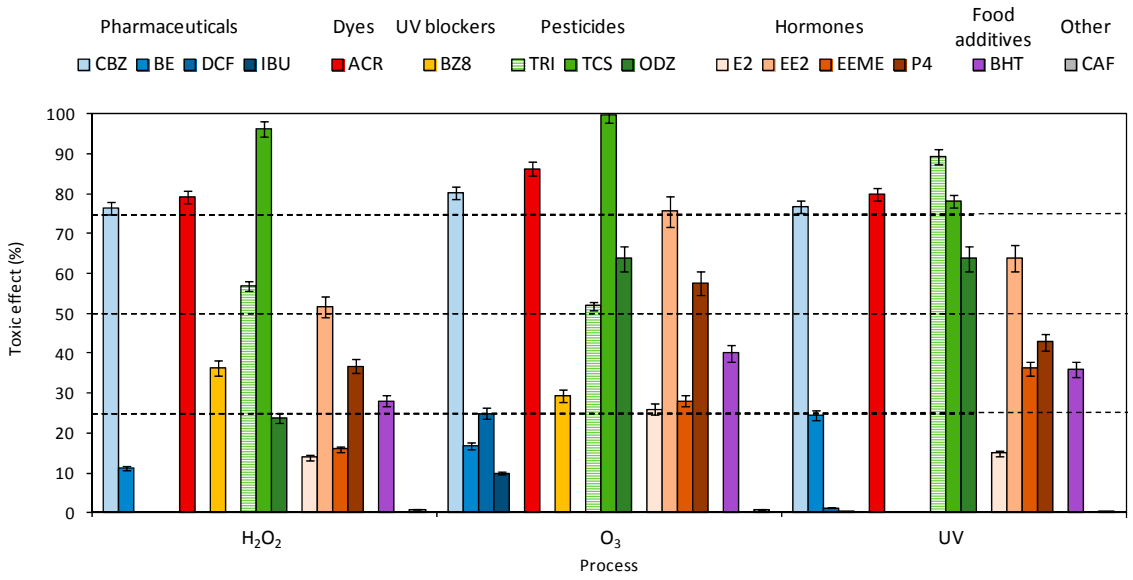
Figure 18. Toxicity of micropollutant water solutions.

The treatment of micropollutant water solutions in chosen oxidation processes resulted in an increase in their toxicity. Figure 19 summarizes the toxic effect of the treated water solutions after the H_2O_2 process (the dose of the oxidizing agent was equal to 12 mg L^{-1}), O_3 (10 mg L^{-1}), UV, UV/TiO_2 (60 min of irradiation), UV/H_2O_2 (60 min), and UV/O_3 (60 min). The highest toxicity effect increase was observed for the carbamazepine and acridine solution after all oxidation processes. In addition, after the O_3 process, the triclosan solution incurred an inhibition of bacterial bioluminescence of over 99%. On the other hand, the UV/TiO_2 process led to a decrease of the triclosan post-process solution and it was classified as toxic. In previous research on the decomposition of pharmaceutical compounds (diclofenac and ibuprofen sodium salt solutions) during the UV/TiO_2 process, the formation of toxic transformation products was indicated [21]. The highest toxicity effect of pharmaceutical post-process solutions was observed after the UV/O_3 process.

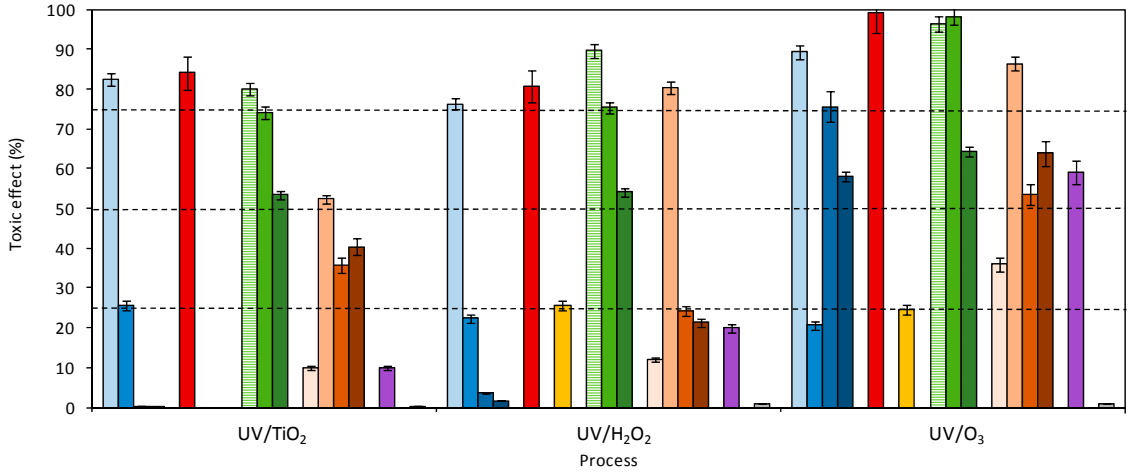
The significant increase in the toxicity of the diclofenac sodium salt water solution after UV/O_3 treatment may by the result of the formation of several by-products, such as 2-(2-chloro-phenylamino)-benzaldehyde [34]. Schulze et al. [35] reported that this intermediate is 10 times more toxic than diclofenac. 2-(2-chloro-phenylamino)-benzaldehyde was not detected by the applied analytical methodology, but it can still occur in the post-processed diclofenac sodium salt water solution. For example, Kovacic et al. [36] reported by the use of high-performance liquid chromatography–electrospray ionization-tandem mass spectrometry (HPLC–ESI-MS/MS) the formation of (8-hydroxy-9H-carbazol-1-yl) acetic acid and (8-chloro-9H-carbazol-1-yl) acetic acid during UV-based diclofenac sodium salt degradation. Subjecting water solutions of hormonal

compounds to the UV/O_3 process also led to a significant increase of their toxicity. For example, β-estradiol water solution after the 60 min of UV/O_3 process were classified as low toxic, whereas mestranol and progesterone post-processed solutions became toxic. The highest toxicity among hormones, was noted for 17α-ethinylestradiol. The intermediates of this compound inhibited the metabolic processes of the test indicator organisms by over 86%. Therefore, this solution must be considered as highly toxic. A similar high toxicity for the 17α-ethinylestradiol post-processed water solution was observed after the UV/H_2O_2 treatment.

Calza et al. [37] and Juretic et al. [38] reported that dihydroxy-derivatives of some organic compounds with their corresponding quinone structures are more toxic than their monohydroxy-precursors. Moreover, open-ring by-products are generally less toxic than aromatic compounds [39]. In general, the oxidation of micropollutants does not lead to a complete mineralization and the formed transformation products are still biologically active compounds.



(**a**)



(**b**)

Figure 19. Change in the toxicity of the micropollutant water solution after (**a**) single oxidation processes (dose of H_2O_2 = 12 mg L^{-1}; dose of O_3 = 10 mg L^{-1}; 60 min of UV irradiation) and (**b**) selected combinations of AOPs (60 min of UV irradiation).

4. Conclusions

Based on the decomposition assessments of different groups of organic micropollutants in selected oxidation processes, it can be concluded that UV-based oxidation processes are more effective for the micropollutants decomposition than H_2O_2 and O_3 processes. The tested compounds have different oxidation capacities in the examined processes:

- The highest removal rate of pharmaceutical compounds was observed during the UV/TiO_2 process. Only acridine and benzocaine were more effectively oxidized by the UV/O_3 process.
- The TiO_2-supported process also allows 96% removal of hormones. Triallat and the food additive BHT were most effectively oxidized by the UV process and their removal degrees exceeded 90%. Triclosan was reduced by 98% during the UV/TiO_2 process and oxadiazon reached the highest removal degree during the UV/H_2O_2 process.
- Dioxybenzone was mainly reduced by the process of adsorption on the surface of the TiO_2 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. Especially the performance of the UV/O_3 process leads to the increase of the toxicity of post-processed water solution. The conducted GC-MS analysis allowed for the identification of several formed intermediates and the estimation of possible compound degradation pathways.

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

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