Abstract: Every compound that potentially can be harmful to the environment is called a Contaminant of Emerging Concern (CEC). Compounds classified as CECs may undergo different transformations, especially in the water environment. The intermediates formed in this way are considered to be toxic against living organisms even in trace concentrations. We attempted to identify the intermediates formed during single chlorination and UV-catalyzed processes supported by the action of chlorine and hydrogen peroxide or ozone of selected contaminants of emerging concern. The analysis of post-processing water samples containing benzocaine indicated the formation of seven compound intermediates, while ibuprofen, acridine and β-estradiol samples contained 5, 5, and 3 compound decomposition by-products, respectively. The number and also the concentration of the intermediates decreased with the time of UV irradiation. The toxicity assessment indicated that the UV-catalyzed processes lead to decreased toxicity nature of post-processed water solutions.

Keywords: contaminants of emerging concern; UV; advanced oxidation processes; by-products

1. Introduction

Contaminants of emerging concern (CECs) have been discovered in every type of natural water worldwide [1–3]. Christen et al. [4] and Kim et al. [5] reported that the exposure to CECs from the group of pharmaceuticals and pesticides causes a deterioration of human health, including the appearance of cancer diseases and cognitive effects. This proves that these compounds are harmful to aquatic organisms and the entire ecosystem fed by waters containing CECs [6].

The literature indicates that many CECs are hardly degradable or completely resistant to conventional water and wastewater treatment methods such as coagulation, sedimentation, filtration, and biological-based processes [7,8]. Even adsorption on activated carbon cannot cope with the removal of compounds with low hydrophobicity from different water matrices [9]. Compounds with phenolic and amine groups or other electron-donating functional groups can be decomposed by selective oxidants such as ozone (O₃), hydrogen peroxide (H₂O₂), or chlorine and chlorine dioxide [10,11].

Water treatment plans still use the chlorination process as one of the most effective methods for water disinfection. Chlorine (Cl₂), chlorine dioxide (ClO₂), or sodium hypochlorite (NaOCl) reagents are used as disinfectants. However, the oxidizing effect can also be used as an effective and simple method for decomposing organic compounds.

The main oxidizing agent is hypochlorous acid (HOCI), which is formed by the aqueous transformation of Cl₂ according to Equation (1) [12]. HOCI in water solution can dissociate to hypochlorite anions (ClO⁻) (Equation (2)). In neutral water conditions, ClO⁻ are less effective oxidants than HOCI [13].

\[ \text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{HOCl} + \text{Cl}^- + \text{H}^+ \] (1)
The addition of another oxidant or precursor of reactive radicals to the reaction matrix, such as H$_2$O$_2$ or O$_3$, can improve the decomposition of organic compounds in two ways: (1) by the direct action with the compound’s molecule or (2) by the initiation of the generation process of other high reactive species [14]. Moreover, implementing the chlorination process together with UV light, can improve the decomposition of contaminant. During UV-catalyzed processes, decomposition of compounds is also caused by their direct photodecomposition and the generation of several radicals (Equations (3) and (4)), like HO•, O•− and reactive chlorine species such as chlorine atoms (Cl•) and (Cl$_2$•−) [15–17]. The oxidation potential of Cl• is 2.47 V and 2.00 V, respectively [18]. Compared to the oxidation potential of HO•, which is equal to 2.80 V, they can also be called strong oxidants. Fang et al. [15] pointed out that Cl• can react more effectively with acetic acid, benzoic acid, and phenol than HO•.

\[
\text{HOCl} / \text{OCl}^- + \text{hv} \rightarrow \text{HO}^\cdot / \text{O}^\cdot + \text{Cl}^\cdot
\]  

(3)

\[
\text{Cl}^\cdot + \text{Cl}^- \leftrightarrow \text{Cl}_2^\cdot
\]  

(4)

The coexistence of different types of oxidants not always has a positive effect on the decomposition of contaminants. HOCl and ClO$$^\cdot$$, which did not come into reaction with contaminates or decompose to reactive radicals, can act as a scavenger for HO• and Cl• according to Equations (5)–(8) [15].

\[
\text{HO}^\cdot + \text{HOCl} \rightarrow \text{ClO}^\cdot + \text{H}_2\text{O}
\]  

(5)

\[
\text{Cl}^\cdot + \text{HOCl} \rightarrow +\text{H}^\cdot
\]  

(6)

\[
\text{HO}^\cdot + \text{OCl}^- \rightarrow \text{ClO}^\cdot + \text{OH}^-
\]  

(7)

\[
\text{Cl}^\cdot + \text{OCl}^- \rightarrow \text{ClO}^\cdot + \text{Cl}^-
\]  

(8)

The exact transformation mechanisms of different CECs during reactive chlorine species coexisting with other oxidants and UV radiation are still unclear. Oxidants and radicals’ action removes CECs or deactivates pathogenic microorganisms and reacts with other compounds present in the disinfected water matrix, leading to several harmful chlorination by-products. The most known chlorination intermediates are trihalomethanes (THMs), and haloacetic acids (HAAs) [19,20], but also chlorination by-products of several CECs are detected in chlorinated water.

The paper presents an attempt to identify the intermediates of selected CECs formed during UV-catalyzed oxidation processes conducted in the presence of chlorine supported by the action of hydrogen peroxide and ozone. Identification of transformation products arising in real water matrices and the determination of their toxicity will give an accurate picture of their potentially dangerous impact on aquatic ecosystems. The comprehension of the CECs decomposition pathways caused by specific physicochemical factors will allow for the development of effective hybrid methods for eliminating the aquatic environment. A single chlorination process was carried out to estimate the decomposition ability of chlorine. The action of chlorine was supported by UV irradiation compared with O$_3$ and H$_2$O$_2$. CECs from the group of pharmaceutical compounds, dye additives, and synthetic hormones were introduced into water solutions based on deionized and surface water and subjected to oxidation agents. The generated by-products were extracted from the post-processed water solutions by the use of Solid Phase Extraction and then chromatographically analyzed and identified based on their mass spectra compared to the National Institute of Standards and Technology NIST v17 database. Bacterial-based toxicological tests confirmed the potentially toxic nature of the intermediates.

2. Results and Discussion

Experiments based on the single chlorination and UV-catalyzed chlorination processes assisted by the action of O$_3$ and H$_2$O$_2$ of CECs water solutions were performed. These processes were assessed...
both in terms of removing individual compounds and the formation of decomposition by-products and their toxicity to living water organisms.

2.1. Chlorination of CECs

The first stage of the study was devoted to assessing the effectiveness of the CECs’ decomposition during dark chamber chlorination, where chlorine was introduced into the water in the form of NaOCl. The influence of chlorine dose on the decomposition of tested CECs in deionized water solutions and surface water solutions is presented in Figures 1 and 2, respectively. The decomposition of compounds occurs during action with HOCl and ClO$^-$ according to Equation (9) [13], leading to the formation of new products, which also should be decomposed.

$$\text{HOCl/OCI}^- + \text{organic contaminant} \rightarrow \text{product} \quad (9)$$

Sivey and Roberts [21] demonstrated that Cl$_2$ under low pH values and Cl$_2$O could act as active chlorination agents during the chlorination process and interact with compounds in the treated water solutions. All tested CECs have an aromatic ring in their structure. Therefore, their decomposition should occur due to specific reactions on certain moieties bound to the aromatic ring and the electrophilic substitution of chlorine in the ortho or para position [22].

Figure 1. Change of (a) IBU, (b) BE, (c) ACR, and (d) E2 concentration during single chlorination of deionized water solutions.
As expected, the removal degree of all tested compounds increased with the increase of the chlorine concentration. IBU and BE were the least susceptible to the action of chlorine. No increase of IBU concentration was observed after 2 min reaction time for chlorine doses equal to 0.5 and 1.0 mg L\(^{-1}\) in deionized and surface water solutions. The BE removal noted after a 2 min reaction time for the chlorine dose equal to 0.5, 1.0, 2.0, and 3.0 mg L\(^{-1}\) was only 0.2, 0.7, 1.1, and 1.6%, respectively, in deionized water solutions. An extension of the reaction time to 20 min by the chlorine dose equal to 0.5 mg L\(^{-1}\) allowed for a 3.1% removal of these CECs and an 8% removal for the chlorine content equal to 3.0 mg L\(^{-1}\). Meanwhile, the IBU concentration decreased only by 9% after 30 min of process elongation by the 3.0 mg L\(^{-1}\) chlorine dose. Similar low IBU decomposition ability under chlorine action was noted by Xiang et al. [23]. The removal degree of this compound did not exceed 3.1% after 20 min of dark chlorination. The obtained results reconfirmed the recalcitrance of IBP to chlorination.

Higher decomposition rates were noted for ACR. This compound’s concentration in the presence of 3.0 mg L\(^{-1}\) of chlorine decreased by over 20% after 10 min of single dark chlorination and over 26% after 30 min of process duration. It can be concluded that single NaOCl as a source of HOCl and ClO\(^-\) is not sufficient for the decomposition of IBU, BE, and ACR.

A reverse observation was noted in the case of the hormone E2 chlorination. The addition of only 0.5 mg L\(^{-1}\) of chlorine to the compound solution based on deionized water led to over 75% and 98% decomposition after 10 and 30 min, respectively. Meanwhile, a complete removal of E2 was observed after 30 min of reaction with the chlorine dose equal to 2 mg L\(^{-1}\). Li et al. [24] also observed a complete removal of this hormone during the chlorination process carried out in neutral conditions.
Similar test results to those obtained for deionized water were noted for a test carried out on surface water (Figure 2). Only the removal degrees of ACR increased for all tested chlorine doses at about 5% and reached, for example, for the free chlorine dose equal to 3.0 mg L\(^{-1}\) 30%. Therefore, it can be assumed that organic and inorganic matter in surface water promotes the decomposition of this compound under the influence of chlorine. However, further research in this area is required to determine which component of the natural water matrix is responsible for increasing the removal degree of ACR.

Special attention should be paid to inorganic compounds occurring in real water solutions, i.e., NO\(_3^−\) and NH\(_4^+\), whose presence was confirmed in the tested water matrixes. Those compounds can influence the decomposition of compounds and can react with reactive forms of chlorine. However, Qiang and Adams [25] indicated a negligible chlorine reactivity with NH\(_4^+\), although NO\(_3^−\) and N\(_2\) can be formed during reaction of HOCl with NH\(_3\). This leads to the formation of mono-, di- and trichloramine.

2.2. Decomposition of CECs in UV-Catalyzed Chlorination Processes

The unsatisfactory low removal degree of IBU, BE, and ACR noted during single chlorination forces another treatment process. Therefore, processes integrated the action of chlorination with UV irradiation, additionally supported by the presence of H\(_2\)O\(_2\) or O\(_3\) were implemented. Figures 3 and 4 compared the removal degrees of tested CECs noted in deionized and surface water solution exposed to UV irradiation in the presence of NaOCl and H\(_2\)O\(_2\) (UV/NaOCl/H\(_2\)O\(_2\) process) or O\(_3\) (UV/NaOCl/O\(_3\)) respectively.

![Figure 3](image-url)  
**Figure 3.** Change of CECs concentration during the UV/NaOCl/H\(_2\)O\(_2\) conducted on (a) deionized and (b) surface water solutions.

![Figure 4](image-url)  
**Figure 4.** Change of CECs concentration during the UV/NaOCl/O\(_3\) conducted on (a) deionized and (b) surface water solutions.
The applied UV light source, during the reactions with HOCl, ClO$^-$ (Equations (3) and (4)) and O$_3$ as well as H$_2$O$_2$, induced the formation of several reactive radicals which are responsible for a non-selective decomposition of compounds. It should also be emphasized that UV light as an electromagnetic wave carries energy in the form of photons. The interaction of one or more photons with a given compound leads to the chemical transformation of the bonds between atoms that make up the compound molecule [26]. This process results in the photodecomposition of the compound molecule. The maximum absorbance of IBU, BE, and E2 were below the wavelengths, which can get into the irradiated solution. However, those compounds and others occurring, especially in surface water matrixes, can still absorb UV radiation energy and undergo the photo-decomposition process. The energy needed for the dissociation of an H–OH bound, and the formation of HO$^*$ exceeds 5 eV [27]. Therefore, the simultaneous application of UV irradiation with different wavelengths and the effect of chlorine and O$_3$ or H$_2$O$_2$ allows for obtaining a required number of free radicals for the decomposition of CECs and their intermediates.

In both UV/NaOCl/H$_2$O$_2$ and UV/NaOCl/O$_3$ processes, preferable removal degrees of BE, ACR, and E2 were observed for compounds occurring in deionized water solutions. This difference in process effectiveness was especially notable during the UV/Cl$_2$/H$_2$O$_2$ process. For example, 2 min of process implementation led to a 60% removal of E2 in the surface water solution, while removing this compound noted in the deionized water matrix exceeded 93%. After 20 min of process duration, complete removal of E2 in deionized water was noted. The concentration of this contaminant in surface water was reduced by 80% (20 min of process duration). The final removal of BE and ACR noted in deionized water samples was equal to 27 and 53%, whereas removing these compounds observed in surface water reached only 22 and 43%, respectively. Only in the case of IBU were higher removal degrees were noted in surface water solutions. For example, after 20 min of UV/NaOCl/H$_2$O$_2$ process, the concentration of IBU decreased by 35% in deionized water solutions and over 41% in surface water solutions. Previous studies [28] on the influence of organic and inorganic compounds on the decomposition of IBU in UV-catalyzed processes indicated that the presence of Ca$^{2+}$, Mg$^{2+}$, NH$_4^+$, Cl$^-$, CO$_3^{2-}$, HCO$_3^-$, HPO$_4^{2-}$ as well as SO$_4^{2−}$ ions increased the decomposition process of this pharmaceutical compound.

Higher compound removal degrees were noted during the UV/NaOCl/O$_3$ process. E2 occurring in deionized water was completely removed after 5 min of UV irradiation, and after 20 min of process implementation, complete removal of this compound was also noted in the surface water matrix. BE and ACR concentration was reduced in deionized water by over 63% and in the surface water only by 55%. Meanwhile, the removal degree of IBU in surface water reached a value of 65%.

It can be concluded that the higher effectiveness of the UV/Cl$_2$/O$_3$ against the UV/Cl$_2$/H$_2$O$_2$ process was the result of the formation of a larger number of radicals during the O$_3$ self-decomposition in water. Among these radicals, HO$^*$, HO$_2^*$, HO$_3^*$, HO$_4^*$, O$_2^{•−}$ and O$_3^{•−}$ can be mentioned [29]. Whereas the irradiation of H$_2$O$_2$ with UV light leads to the formation of OH$^*$ radicals [30]. However, HO$^*$ radicals are endowed with the strongest oxidation potential, and they can abate compounds that are resistant to O$_3$ or H$_2$O$_2$ decomposition [31]. It should also be mentioned that UV irradiation leads to an increase of the quantum yields and the molar absorption coefficients of OCI, OCI, leading to a higher and faster production of radicals during the decomposition processes [15,32,33].

### 2.3. Identification of Decomposition By-Products

The implementation of the tested CECs decomposition processes allows for a decrease of the contaminant’s concentrations and leads to the generation of several by-products. Those intermediates were formed during reactions between the parent compounds and chlorine and/or other reactive species. The intermediates were identified based on their mass spectra using the NIST v17 database (Table 1). The identified by-products decomposed more slowly than the parent micropollutants and were detected even after 20 min of UV-catalyzed process implementation. The single chlorination process led to four BE intermediates: Ethyl 4-chlorobenzoate, 4-Chloroaniline, Chlorohydroquinone, and 2,5-Dichlorohydroquinone, while the chlorination of ACR solutions resulted in the formation
of 9-Chloroacridine and Salicylic acid. The subjection of IBU water solutions to single dark chlorination resulted in three intermediates: 1-(4-Isobutylphenyl)ethanol, 4-Acetylbenzoic acid, and 4-Ethylbenzaldehyde. Intermediates detected in each process are summarized in Table 2. The chlorination process led to small modifications in the structures of the compounds and the formation of more oxidized or chlorinated molecules. This is connected because HOCl can react with organic compounds in three types of reactions: oxidation reactions, addition reactions to unsaturated bonds, and electrophilic substitution reactions at nucleophilic sites [34]. Electrophilic substitution reactions are considered the most common mechanisms during chlorination; therefore, chlorine substitution sites will most likely be on the tested compounds’ aromatic ring [35].

### Table 1. Identified CECs by-products during the performed experiments.

| Parent Compound | Identified Compound | Structural Formula | CAS-RN | Similarity, % | Molecular Weight |
|-----------------|---------------------|--------------------|--------|---------------|-----------------|
| IBU             | 1-Hydroxyibuprofen   | C_{13}H_{18}O_{3}  | 53949-53-4 | 96            | 222.28          |
|                 | 1-(4-Isobutylphenyl)ethanol | C_{13}H_{18}O | 40150-92-3 | 84            | 178.27          |
|                 | 4'-Isobutylacetophenone | C_{13}H_{18}O | 38861-78-8 | 98            | 176.25          |
|                 | 4-Acetylbenzoic acid  | C_{13}H_{18}O | 586-89-0 | 85            | 164.16          |
|                 | 4-Ethylbenzaldehyde   | C_{13}H_{18}O | 4748-78-1 | 92            | 134.17          |
|                 | Ethyl 4-hydroxybenzoate | C_{12}H_{16}O | 120-47-8 | 74            | 166.17          |
|                 | Ethyl 4-chlorobenzoate | C_{12}H_{16}ClO | 7335-27-5 | 84            | 184.62          |
|                 | 4-Chloroaniline        | C_{12}H_{16}ClO | 106-47-8 | 86            | 127.57          |
|                 | 4-Chlorophenol         | C_{12}H_{16}ClO | 106-48-9 | 99            | 128.55          |
|                 | 3,4-Dichlorophenol     | C_{12}H_{16}ClO | 95-77-2 | 98            | 163.00          |
|                 | 1-Hydroxyibuprofen     | C_{13}H_{18}O | 824-69-1 | 80            | 179.00          |
|                 | 1-(4-Isobutylphenyl)ethanol | C_{13}H_{18}O | 578-95-0 | 70            | 195.22          |
|                 | Ethyl 4-hydroxybenzoate | C_{13}H_{18}O | 10399-73-2 | 75            | 195.22          |
|                 | Ethyl 4-chlorobenzoate | C_{13}H_{18}O | 22817-17-0 | 90            | 195.22          |
|                 | 4-Chloroaniline        | C_{13}H_{18}O | 1207-69-8 | 72            | 213.66          |
|                 | 4-Chlorophenol         | C_{13}H_{18}O | 69-72-7 | 80            | 138.12          |
|                 | 3,4-Dichlorophenol     | C_{13}H_{18}O | 362-05-0 | 92            | 288.40          |
|                 | 2-Hydroxyestradiol     | C_{13}H_{18}O | 144082-88-2 | 78            | 286.40          |
|                 | Estradiol-3,4-quinone  | C_{13}H_{18}O | 2380-91-8 | 80            | 138.16          |
|                 | 4-(1-Hydroxyethyl)phenol | C_{13}H_{18}O | 578-95-0 | 70            | 195.22          |
|                 | Acridone               | C_{13}H_{18}O | 10399-73-2 | 75            | 195.22          |
|                 | Acridine-10-oxide      | C_{13}H_{18}O | 22817-17-0 | 90            | 195.22          |
|                 | 4-Chloroanidine        | C_{13}H_{18}O | 1207-69-8 | 72            | 213.66          |
|                 | 4-Chlorophenol         | C_{13}H_{18}O | 69-72-7 | 80            | 138.12          |
|                 | 3,4-Dichlorophenol     | C_{13}H_{18}O | 362-05-0 | 92            | 288.40          |
|                 | 2-Hydroxyestradiol     | C_{13}H_{18}O | 144082-88-2 | 78            | 286.40          |
|                 | Estradiol-3,4-quinone  | C_{13}H_{18}O | 2380-91-8 | 80            | 138.16          |
| E2              | 2-Hydroxyestradiol     | C_{13}H_{18}O | 362-05-0 | 92            | 288.40          |
|                 | Estradiol-3,4-quinone  | C_{13}H_{18}O | 144082-88-2 | 78            | 286.40          |
|                 | 4-(1-Hydroxyethyl)phenol | C_{13}H_{18}O | 2380-91-8 | 80            | 138.16          |

### Table 2. CECs by-products identified in selected processes during the performed experiments.

| Process | Cl<sub>2</sub> | UV/Cl<sub>2</sub>/H<sub>2</sub>O<sub>2</sub> | UV/Cl<sub>2</sub>/O<sub>3</sub> |
|---------|----------------|--------------------------------|-------------------------------|
| 2 min   | 10 min | 20 min | 2 min | 10 min | 20 min | 2 min | 10 min | 20 min |
| IBU     | Ethyl 4-hydroxybenzoate | - | - | - | - | - | - | + | + |
|         | Ethyl 4-chlorobenzoate | - | - | - | + | + | + | + | + |
|         | 4-Chloroaniline | + | + | + | + | + | + | + | + |
|         | 4-Chlorophenol | + | + | + | + | + | + | + | + |
|         | Chlorohydroquinone | + | + | + | + | + | + | + | + |
|         | 2,5-Dichlorohydroquinone | + | + | + | + | + | + | + | + |
| ACR     | Lucindone | - | - | - | + | + | + | + | + |
|         | Acridine-10-oxide | - | - | - | + | + | + | + | + |
|         | 2-Hydroxyestradiol | - | - | - | + | + | + | + | + |
|         | Estradiol-3,4-quinone | - | - | - | + | + | + | + | + |
|         | 4-(1-Hydroxyethyl)phenol | + | + | + | + | + | + | + | + |

* - not detected; + — detected.

During the implemented decomposition processes, the IBU intermediates were mainly formed at the first stage by hydroxylation and chlorine substitution. However, the implemented GC-MS analysis
does not allow for detecting IBU by-products with chlorine atoms in their structure. Such compounds were identified by Li et al. [36] and Xiang et al. [23]. The possible decomposition pathway of IBU with the identified intermediates is shown in Figure 5.

![Figure 5. Possible decomposition of (1) IBU with the identified intermediates (2) 1-Hydroxyibuprofen, (3) 1-(4-Isobutylphenyl)ethanol, (4) 4'-Isobutylacetophenone, (5) 4-Acetylbenzoic acid, and (6) 4-Ethylbenzaldehyde.](image)

Ethyl 4-hydroxybenzoate and Ethyl 4-chlorobenzoate were formed by the denitration of the BE molecule and the substitution of the nitric group by the hydroxyl group and chlorine, respectively. Other BE intermediates were possibly generated by the attack of \( \text{OH}^- \) and chlorine on the compound’s phenolic ring. The possible decomposition pathway of BE is summarized in Figure 6.

![Figure 6. Possible decomposition of (1) BE with the identified intermediates (2) Ethyl 4-hydroxybenzoate, (3) Ethyl 4-chlorobenzoate, (4) 4-Chloroaniline, (5) 4-Chlorophenol, (6) 3,4-Dichlorophenol, (7) Chlorohydroquinone, and (8) 2,5-Dichlorohydroquinone.](image)
The ACR decomposition by-products Acridone, Acridine-10-oxide, and 2-Hydroxyacridine were mainly formed by the attack of reactive oxygen species of the compound molecule. Meanwhile, 9-Chloroacridine results from the substitution of chlorine to the phenolic ring (Figure 7). Further hydroxylation and the deamination of the formed intermediates led to carbon atom ring-opening and Salicylic acid formation, which was subject to further decomposition.

![Figure 7](image_url)

**Figure 7.** Possible decomposition of (1) ACR with the identified intermediates, (2) Acridone, (3) Acridine-10-oxide, (4) 2-Hydroxyacridine, (5) 9-Chloroacridine, and (6) Salicylic acid.

The applied analytical method based on gas chromatography allows only for the detection of three E2 intermediates, resulting from reactive oxygen species action (Figure 8). Steroid hormones are typically composed of four carbon atoms rings—three cyclohexane rings and one cyclopentane ring. The reactive species, in general, firstly attacks the first cyclohexane ring, which leads to the formation of hydroxylated compounds like 2-Hydroxyestradiol. Li et al. [24] pointed out that the decomposition of E2 occurs by the halogenation of the aromatic ring followed by the cleavage of the benzene moiety and chlorine substitution formation generation of THMs and HAAs from phenolic intermediates.

### 2.4. Toxicological Assessment

A toxicological assessment is necessary to determine whether the proposed decomposition processes of pollutants do not deteriorate the quality of treated water solutions. It has already been proved that the initial contaminants occurring in non-treated water were sometimes less toxic than the intermediates detected in post-processed water solutions [37]. The preformation of fast toxicological tests like the bacterial-based Microtox® gives a quick response about the impact of the post-processed water on living organisms. Studies indicated a good interspecies correlation between saltwater bacteria like the used *Aliivibrio fischeri* and other freshwater bacteria or fishes [38]. The *Aliivibrio fischeri* are also considered extremely sensitive to a wide range of pollutants and reagents occurring in water [39].
It should be noted that chlorine is used in water treatment processes to protect water before secondary contamination [40]. Therefore, it should be toxic to pathogens and small test organisms. Before the proper toxicological test, the adopted sample preparation methodology allowed for the exclusion of chlorine influence on test bacteria. Chlorinated water samples without the addition of tested CECs were characterized by a toxicological effect lower than 9% (Figure 9), which classified them, according to the guidelines given by Mahugo Santana et al. [41], as non-toxic. Therefore, the results presented in Figures 10–12 resulted from generated parent compound intermediates.

Figure 8. Possible decomposition of (1) IBU with the identified intermediates, (2) 2-Hydroxyestradiol, (3) Estradiol-3,4-quinone, and (4) 4-(1-Hydroxyethyl)phenol.

![Chemical structure](image)

Figure 9. Change in the toxicity of chlorinated (a) deionized and (b) surface water samples without the addition of CECs.
ACR-containing surface water samples before the addition of NaOCl had a toxic effect which exceeded 28%, and according to the toxicity classification, it should be assigned as low toxic (25.0% < toxic effect ≤ 50.0%) against the test bacteria. Whereas IBU, BE, and E2 in the tested concentration of 500 μg L\(^{-1}\) were non-toxic (totoxic effect ≤ 25.0%).

The presence of chlorine during the implementation of a single chlorination process initiated the compounds’ decomposition, leading to an increase in toxicity. It was noted that the toxic effect
increased with the increase of the chlorine dose in both deionized and surface water solutions (Figure 10). For example, BE and E2 solutions treated by 0.5 and 1.0 mg L\(^{-1}\) of chlorine were still non-toxic, while the dose of 3.0 mg L\(^{-1}\) resulted in the increase of the BE solution toxicity to a toxic level (50.0% \(<\) toxic effect \(\leq 75.0\%\)) and the E2 solution toxicity to a low toxic level. The chlorination process’s implementation did not significantly affect the toxicity of the IBU-containing solution, which remained non-toxic for each tested dose of chlorine. The highest toxicity during single chlorination was observed for ACR post-processed solution. The addition of 0.5 or 1.0 mg/L of chlorine to the ACR water solution led to the formation of several toxic intermediates in deionized and surface water solutions, which increased the toxicity to a toxic level. The addition of 2.0 and 3.0 mg/L of chlorine resulted in the generation of highly toxic solutions (toxic effect \(>\) 75.0%). The toxicity noted for deionized water solutions containing BE, ACR, and E2 (Figure 10a) was 5%, 8%, and 2%, respectively, higher than the toxicity noted for surface water solutions (Figure 10b).

The post-processed samples obtained during the UV-catalyzed treatment methods were also subjected to toxicological tests (Figures 11 and 12). It was noted that the implementation of UV irradiation supported by the action of 1.0 mg L\(^{-1}\) chlorine and H\(_2\)O\(_2\) or O\(_3\) resulted in an increase of the toxicity of all tested compound solutions in the first 5 min of the treatment process compared to the single chlorination process. This phenomenon confirms the generation of toxic by-products identified during the chromatographic analysis. In general, the toxicity of samples collected after the process carried out with the presence of O\(_3\) (UV/NaOCl/O\(_3\)) was higher than the toxicity of samples subjected to the simultaneous action of UV light, chlorine, and H\(_2\)O\(_2\) (UV/NaOCl/H\(_2\)O\(_2\)).

For example, E2 solutions irradiated for 2, 10, and 20 min in the presence of H\(_2\)O\(_2\) were characterized by non-toxicity. Only the sample after 5 min of UV/NaOCl/H\(_2\)O\(_2\) was low toxic. Samples of the same contaminant subjected to the UV/NaOCl/O\(_3\) process were classified after 5 min as near medium toxic, but after 20 min, their toxicity was reduced to a non-toxic level. The chromatographic analysis indicated that the signals caused by the formed intermediates after 10 min of UV irradiation become weaker than those after 5 min. This means that after this time of the process, the concentration of by-products decreased. This was also reflected in the toxicity results. All tested compounds’ toxicity increased in the first 5 min of UV-catalyzed process implementation and then decreased after 10 and 20 min of process duration. For example, the toxicity of the ACR-containing surface water solution treated by UV/NaOCl/H\(_2\)O\(_2\) decreases from a high toxic level to a medium toxic level. Donner et al. [42] noted an increase in the toxicity during the irradiation of carbamazepine solutions with UV light in the first 30 min. ACR is a toxic decomposition by-product of carbamazepine. The occurrence of this compound and other carbamazepine intermediates increased toxicity. Further irradiation of the pharmaceutical solution leads to the decomposition of acridine and decreased solution toxicity.

The BE and E2-containing solutions’ toxicity decreased during both UV/NaOCl/H\(_2\)O\(_2\) and UV/NaOCl/O\(_3\) processes from a low toxic to a non-toxic level. Only IBU solutions subjected to the UV/NaOCl/O\(_3\) were characterized by increasing toxicity during the first 2, 5, and 10 min. Moreover, the surface water IBU solution after a 10 min exposure to the UV/NaOCl/O\(_3\) process was characterized by a toxic level. It can be summarized that the decomposition of compounds does not always have a beneficial impact on the treated water quality. The generated compound oxidation by-products can radically influence water toxicity and force the necessity to implement further and more complex treatment processes.

3. Materials and Methods

3.1. Water Samples

The research subject constituted water solutions prepared on deionized water with a conductivity of 18 M\(\Omega\) cm\(^{-1}\) and surface water matrices (conductivity of 0.152 mS cm\(^{-1}\), TOC of 1.546 mg L\(^{-1}\), COD of 89 mg O\(_2\) L\(^{-1}\), N-NH\(_4\) of 0.9 mg L\(^{-1}\), N-NO\(_3\) of 2.1 mg L\(^{-1}\)) spiked with CECs standards. Ibuprofen sodium salt (IBU), benzocaine (BE), acridine (ACR), and \(\beta\)-estradiol (E2) were chosen as
representative compounds from the group of pharmaceutical compounds, dye additives, and synthetic hormones. The concentration of the compounds in the prepared water solutions was set on 500 \( \mu g \) L\(^{-1}\). Each compound standard solution was prepared by dissolving 10 mg of each analyte in 10 mL of methanol. The use of compound standard solutions allows for the complete dissolution of the analytes and obtains precisely defined CECs concentrations. Standards of the tested CECs with a purity of over 99%, 97%, and 98% were purchased from Sigma-Aldrich (Poznan, Poland). The characteristic of the compound is presented in Table 3. The selected compound concentrations, which exceeded the usual environmental concentrations, allowed for an increase in the accuracy of the analytical measurements. Absorption spectra of all tested compounds were measured using the Spectroquant Pharo 300 UV/Vis spectrophotometer by Merck (Darmstadt, Germany) and compared in Figure 13. The maximum absorbance \( \lambda_{\text{max}} \) for IBU, BE, ACR, and E2 was estimated for both deionized and surface water matrixes and were set on 274 nm, 286 nm, 340 nm 280 nm, respectively.

Table 3. Characteristics of the tested organic compounds [43].

| Compound | Structural Formula | Molecular Formula | Molecular Weight, g mol\(^{-1}\) | Solubility in Water, mg L\(^{-1}\) |
|----------|--------------------|-------------------|---------------------------------|----------------------------------|
| IBU      | ![IBU structure](https://example.com/ibu_structure.png) | C\(_{13}\)H\(_{17}\)NaO\(_2\) | 228.26                          | 100                              |
| BE       | ![BE structure](https://example.com/be_structure.png)  | C\(_4\)H\(_{11}\)NO\(_2\) | 165.19                          | 1310                             |
| ACR      | ![ACR structure](https://example.com/acr_structure.png) | C\(_{13}\)H\(_9\)N | 179.22                          | 38.4                             |
| E2       | ![E2 structure](https://example.com/e2_structure.png) | C\(_{18}\)H\(_{24}\)O\(_2\) | 272.38                          | 3.6                              |

Figure 13. UV-VIS spectrum of (a) IBU, (b) BE, (c) ACR, and (d) E2 in deionized and surface water samples.
The experiments for all CECs were performed separately in neutral conditions. The pH of each tested water solution was adjusted to 7.0 using 0.1 mol L\(^{-1}\) NaOH or 0.1 mol L\(^{-1}\) HCl. Preliminary studies indicated that the very low volumes of the added alkali or acid did not influence the decomposition of the tested micropollutants.

3.2. Decomposition Processes

All prepared water solutions were subjected to the action of the chlorination process. It was carried out using sodium hypochlorite (NaOCl) with a nominal free chlorine content of 6% (w/v) purchased from Chemoform (Sosnowiec, Poland). The experiment was conducted on four different chlorine doses equal to 0.5, 1.0, 2.0, and 3.0 mg L\(^{-1}\) and measured as a total chlorine concentration by the use of the HI-93414-02 EPA Compliant Turbidity and Free & Total Chlorine Meter by HANNA Instruments Inc. The chlorine doses were selected as part of preliminary studies considering doses used for the chlorination of tap water under normal and special (emergency water pollution) operating conditions. Therefore, these are doses that can be introduced into the water by any water treatment station that uses chlorination as a water disinfection method.

The single chlorination process was carried out in a dark chamber to omit the influence of any light source on the chlorine caused decomposition of tested compounds. The water samples were also exposed to chlorine’s action in the presence of UV irradiation supported by hydrogen peroxide (H\(_2\)O\(_2\)) or ozone (O\(_3\)). The H\(_2\)O\(_2\) and O\(_3\) doses used in this study was estimated in preliminary tests and set on 3.0 mg L\(^{-1}\). The single chlorination process was carried out 2, 10, 20, and 30 min and stopped by sodium thiosulphate (Na\(_2\)S\(_2\)O\(_3\)) at a dose of 100 mg L\(^{-1}\), which acts as an excess chlorine removing agent. Na\(_2\)S\(_2\)O\(_3\) with a purity of 98% was purchased from Merck KGaA (Darmstadt, Germany). O\(_3\) was generated by an ozonation machine Ozoner FM500 from WRC Multiozon (Gdańsk, Poland) and introduced in the tested water samples using a ceramic diffuser with a height of 25 mm, and a diameter of 12 mm. The O\(_3\) concentration in the water solutions was measured using a photometric method on the Spectroquant® by Merc Sp. z o.o. (Warszawa, Poland). The ozonation reaction was stopped after the UV irradiation time by sodium sulfite Na\(_2\)SO\(_3\) at a concentration of 24 mmol L\(^{-1}\). A 150 Watt medium-pressure mercury lamp placed in a glass cooling sleeve by Heraeus (Hanau, Germany) was used as the UV light source during all UV-catalyzed decomposition methods. The irradiation time was set as 2, 5, 10, and 20 min, and the radiation flux emitted by the lamp is summarized in Table 4.

Figure 14 shows the characteristic of radiation wavelengths emitted by the used UV lamp, and Table 5 shows the energy of light, which reached the water matrix. The energy of light was calculated based on the multiplication of the Planck’s constant with the frequency of light.

Experiments for all tested compounds were carried out separately and repeated three times.

| Radiation Flux ψ, W | Wavelength λ, nm |
|-------------------|------------------|
| Direct lamp radiation | 238/40 254 265 280 297 302 313 334 366 390 405/08 436 492 546 578 |
| Radiation passing through the sleeve | 1.0 4.0 14.0 0.7 1.0 1.8 4.3 0.5 6.4 0.1 3.2 4.2 0.1 5.1 4.7 |

| Energy of light reaching the water matrix, eV | 297 302 313 334 366 390 405 406 407 408 436 492 546 578 |
|-----------------------------------------------|------------------|
| Energy of light reaching the water matrix, eV | 4.17 4.11 3.96 3.71 3.39 3.18 3.06 3.05 3.04 2.84 2.52 2.27 2.15 |
3.3. Analytical Procedure and Toxicity Assessment

The analytical procedure of the tested CECs was adopted from previous studies [11] and based on the extraction of analytes from water matrixes by solid-phase extraction (SPE) and their chromatographic analysis. The SPE was performed by the use of Supelclean™ ENVI-8 and Supelclean™ ENVI-18 cartridges obtained from Sigma-Aldrich (Poznań, Poland) with a silica gel base material with C8 (octyl) and silica gel base material with C18 (octadecyl) bonding bed type, respectively. The used SPE procedure allowed for obtaining a recovery of the tested CECs, which exceeded 95%.

The chromatographic analysis was conducted using the GC-MS (EI) chromatograph model 7890B by Perlan Technologies (Warszawa, Poland). The chromatograph was equipped with an SLB™—5 ms 30 m x 0.25 mm capillary column of 0.25 µm film thickness from Sigma-Aldrich (Poznań, Poland). The applied column oven temperature program was: 80 °C (6 min), 5 °C/min up to 260 °C, 20 °C/min up to 300 °C (2 min). Helium 5.0 was used as a carrier gas during the analyses. The temperatures of the ion trap, ion source, and column injector were equal to 150 °C, 230 °C, and 250 °C, respectively. All SPE extract were analyzed twice, in the selected ion monitoring (SIM) mode to monitor CECs decomposition by-products. The TIC mode was performed in the range from 50 to 400 m/z.

The percentage of removal of each CECs after the implementation of decomposition processes was calculated according to Equation (10), where \( C_i \) and \( C_p \) are the initial and post-processed compound concentrations in mg L\(^{-1}\), respectively [44]:

\[
\text{Removal} (\%) = \frac{C_i - C_p}{C_i} \times 100
\]

The post-processed samples were also subjected to a spectroscopic analysis performed on the Spectroquant Pharo 300 UV/Vis spectrophotometer by Merck (Darmstadt, Germany), which can measure the UV-VIS spectrum of samples in the range from 200 to 600 nm. The spectroscopic measurement indicated only the decrease of the initial compound concentration (it was discussed in Sections 2.1 and 2.2, based on the percentage of removal calculated from the data obtained by the GC-MS analysis). The UV-VIS spectrum did not indicate the formation of intermediates, which was related to their low concentrations. Therefore, the results were not presented in the paper.

The toxicological evaluation, which gives an answer about the potentially toxic nature of the newly generated decomposition by-products, was carried out using the Microtox® test. The test procedure...
is based on the measurement of the changes in the behavior of saltwater bioluminescent bacteria *Aliivibrio fischeri* according to the Screening Test procedure of MicrotoxOmni system, which controls the work of the Microtox analyzer Model 500 by Modern Water (London, United Kingdom). The test results were expressed as a percentage of bacterial bioluminescence inhibition caused by changes in the bioindicators’ metabolic processes exposed to a toxicant for 15 min. The results were compared to a reference nontoxic sample (2% NaCl solution). The collected samples were subjected to toxicological test after 24 h incubation in a cooled dark chamber to exclude the possible chlorine impact, which was left in the post-processed water solutions.

Assignment errors marked on figures presented in this paper were estimated based on the standard deviation for three repetitions of each test. The error values for all tested samples did not exceed 2.0%.

4. Conclusions

Based on the conducted compound decomposition assessments in the selected oxidation processes, it can be concluded that the lowest compound removal degrees were observed during single dark chlorination. Moreover, the decomposition rates of all tested compounds obtained in this process conducted in deionized water matrices were very similar to those noted in surface water matrices. The difference in the compound’s removal degrees in both matrices did not exceed 2% and was within the measurement error. Further, the occurrence of chlorine in the reaction matrices leads to the generation of intermediates with chlorine atoms in their structure. It was also noted that the compound concentration decreases with the increase of the chlorine concentration. Higher chlorine concentrations also lead to an increase of the by-products forming. The conduction of UV-catalyzed oxidation processes shows that the combination of the UV radiation with the action of chlorine and O₃ was more effective for compound decomposition than the UV chlorination process supported by the presence of H₂O₂. The implementation of the UV radiation in oxidants’ presence results in the decrease of the number and concentration of formed by-products after 20 min of process elongation. However, it should be noted that during the first 10 min of both UV/NaOCl/H₂O₂ and UV/NaOCl/O₃ processes, several oxidized intermediates were formed. The UV-catalyzed processes also lead to the decrease of the toxicity of the post-processed water solutions, which still depend on the type of decomposed compounds and the UV irradiation time.

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