Application of Radiation Technology in Removing Endocrine Micropollutants from Waters and Wastewaters—A Review

Anna Bojanowska-Czajka

Laboratory of Nuclear Analytical Methods, Institute of Nuclear Chemistry and Technology, 03-195 Warsaw, Poland; a.bojanowska@ichtj.waw.pl

Abstract: Advanced Oxidation Processes (AOPs) are increasingly being adopted as a post-treatment after conventional wastewater treatment, mainly due to the efficient removal of biodegradable organic micropollutants. Endocrine disruptors are a specific group of such micropollutants. Many scientific studies demonstrate their extremely harmful effects on living organisms, even at low concentrations in water and wastewater. AOPs based on the generation of reactive species using radiation technologies, these being gamma radiation and electron beam, are still not being used to their full potential. This publication presents the application possibilities of using ionizing radiation for the degradation of selected endocrine micropollutants in water and wastewater.

Keywords: endocrine micropollutants; AOPs; radiation technology; gamma radiation; electron beam; degradation mechanism; toxicity monitoring

1. Introduction

A current challenge is ensuring access to water, both for drinking and for industrial purposes. According to the latest report by the WHO and UNICEF, around 2.1 billion people around the world do not have access to drinking water where they live [1]. Lack of access to safe drinking water is causing, among other things, the worsening of the health of local communities. The decrease in available resources as well as in their quality is mainly caused by constantly developing urbanization and industrialization. Pollutants entering the environment can generally be divided into inorganic and organic pollutants. Conventional inorganic water pollutants include $F^-$ or $NO_3^-$ alongside trace amounts of heavy metals (Pb, Cd, Cr, Ni, Zn, As, Hg, etc.). The effects of these contaminants on human health and the environment are relatively well described, and effective methods and technologies for treating water containing these types of contaminants have been developed. Organic pollutants pose a much greater challenge because they are usually very difficult to biodegrade, among which, endocrine disrupting compounds (EDCs) merit special attention.

In most cases, these contaminants are not present in the water alone but in mixtures. Such situations are dangerous because there is still very little knowledge about undesirable synergistic effects. Many of these chemicals are not required to be monitored as they have no regulatory status. Increasingly, these compounds are detected in natural and drinking waters and wastewaters at relatively low concentration levels (ng dm$^{-3}$ and µg dm$^{-3}$, respectively) [2,3], however, long-term exposure of living organisms to these contaminants is still under investigation. No effective technologies have yet been developed to remove all these contaminants simultaneously, even though some contaminants have been shown to decompose by a certain degree in selected processes. The subject of this work is a review of the application possibilities of both gamma radiation and electron beams for the decomposition of endocrine micropollutants in waters and wastewaters.
2. Radiation Technologies

The idea of using ionizing radiation to degrade contaminants in the aqueous phase is based on the assumption that any emitted radiation is characterized by the ability to deposit its energy in the surrounding medium. This energy excites the atoms of the medium, removing electrons from them or breaking the chemical bonds between their molecules [4]. The application of ionizing radiation in water and wastewater treatment is possible due to the fact that radiation, in giving up a part of its energy to the medium, which is water, causes radiolysis of its molecules.

2.1. Type of Radiation Sources

Various types of ionizing radiation, both electromagnetic and corpuscular, can be used in radiation methods for environmental protection. Electromagnetic radiation involves gamma radiation and X-rays, while corpuscular radiation primarily involves accelerated electrons with energies ranging from 0.5 to 13 MeV. The isotopes $^{60}$Co and $^{137}$Cs are most commonly used as sources of gamma radiation, with $^{60}$Co being favored by the higher energy of emitted radiation (1.173 MeV) compared to $^{137}$Cs. The advantage of using $^{60}$Co and $^{137}$Cs sources is the ability to deeply penetrate gamma radiation, which has primarily found application in the sterilization of medical materials, the treatment of cancer, and food irradiation. The disadvantages of gamma radiation include the long irradiation time necessary to obtain higher doses, the need for periodic replacement of the radionuclide, and the continuous potential risk of radiation contamination. Different to electron accelerators, isotope radiation sources are also less accepted by the public because of a fear of induced radioactivity.

The advantage of using a beam of accelerated electrons is the relatively simple way of producing them and the simple mechanism of transferring energy to the medium. The principal components of an electron beam accelerator are source, accelerating structure, and delivery system. The main difference between EB accelerator models is the method of generating the electric field. There are three main classes: high-voltage direct current (DC), radio frequency (RF), and microwave linear accelerators (LINAC). Present technical evolutions and trends in electron beam accelerators are favorable to more widely investigated direct current systems based on the well-proven ELV and Dynamitron technology. Modern accelerators make it possible to provide electrons with energy favorable for research, they also allow for adjusting the intensity of the beam and changing the cross-section and direction of the stream. The beam of high-energy electrons is characterized by a smaller, deep penetration in the medium than gamma radiation however, the possibility of obtaining a beam with a strictly defined energy makes this type of radiation applicable in many industries as well as in environmental protection [5]. An additional advantage of using accelerators is that they can be turned off, which cannot be performed with a gamma radiation source. The most important limitations of an electron beam installation for wastewater treatment are the restrictions of beam penetration and the appropriate distribution of the material Electron beam installations have a higher dose rate compared to gamma sources, ensuring that more energy is delivered to the system in a much shorter time. However, there are literature reports that clearly show that the dose rate has a significant effect on the degradation efficiency of selected organic pollutants [6].

2.2. Water Radiolysis

The main idea of using ionizing radiation for water and wastewater treatment is based on the simultaneous generation of oxidizing and reducing species during water radiolysis. The same radicals are formed in the reaction environment by the action of gamma radiation and electron beams. Electron accelerators are primarily used in applications due to their safe operation and their high power. The electron beam, in a very short time period (of the order of s), causes the simultaneous ionization of a huge number of water molecules, as according to Equation (1) [7]:

\[
2H_2O \rightarrow H_2O_2 + 2e^- + 2H^+ \quad (1)
\]
\[ H_2O \rightarrow \cdot OH \quad (2.7) + e_{aq}^- \quad (2.6) + \begin{array}{c} \text{H}^\star \quad (0.55) + \text{H}_2 \quad (0.45) + \text{H}_2\text{O}_2 \quad (0.71) + \text{H}_3\text{O}^+ \quad (2.6) \end{array} \] (1)

The efficiency of the irradiation process is evaluated by calculating the chemical yield of the radiation (G-value, \( \mu \text{MJ}^{-1} \)), which determines the number of individuals of a given type that is formed or decomposed as a result of 100 eV absorption and is represented by Equation (2).

\[ G = \frac{6.023 \times 10^{23} \times \text{C}}{D \times 6.24 \times 10^{16}} \] (2)

where \( \text{C} \) is the concentration of formed individuals (M) and \( D \) is the absorbed dose (Gy).

The radiation efficiencies have the same values for high-energy electron and photon X-rays as well as gamma rays. It is assumed that the temperature does not practically affect the efficiency of water radiolysis products, while the pH value has a significant influence. In acidic solutions, the \( G (e_{aq}^-) \) values are lower while the \( G (\cdot \text{H}) \) values are higher, and this is related to Reaction (3):

\[ e_{aq}^- + \text{H}_2\text{O} \leftrightarrow \text{H}_{aq}^- + \text{OH}_{aq}^- \quad pK_a = 6.3 \] (3)

Among the reactive species formed during the radiolysis of water, the most reactive is the hydroxyl \( \cdot \text{OH} \) radical, for which the oxidizing potential is in the range of 2.8 V (pH 0) and 1.95 (pH 14) relative to the saturated calomel electrode [8]. The hydroxyl radical is a very nonselective species, it reacts very quickly with most of the organic impurities and the reaction rates are diffusion-controlled \( 10^{8}-10^{10} \, \text{M}^{-1}\text{s}^{-1} \). The decomposition of an organic substance by reaction with a hydroxyl radical can be as follows:

- Radical addition;
- Hydrogen abstraction;
- Electron transfer;
- Combination/recombination of radicals.

The primary products of water radiolysis, mainly hydroxyl radicals, undergo numerous reactions with organic impurities present in the solution. These transformations successively lead to the formation of carbonyl radicals (\( R^\star \_ \) or \( R^\star \cdot \text{OH} \)) and then, in reactions with \( \text{O}_2 \), to the formation of peroxyl radicals (ROO\( \star \)). The end products of these transformations are \( \text{H}_2\text{O}_2 \) and peroxide, which, as highly reactive individuals, are responsible for the degradation and even mineralization of these pollutants [9].

Hydroxyl radicals have a very short lifetime; they are only generated in situ, in this case, by the action of gamma rays or electron beams on water molecules. The advantage of ionizing radiation-based processes over other AOPs is that, simultaneously alongside the hydroxyl radical, strongly reducing species \( e_{aq}^- \) and the hydrogen atom \( \cdot \text{H} \) are generated with the highest efficiency compared to other AOPs. From a basic research point of view, it is important to carry out the process in such conditions where only one selected product of water radiolysis predominates and not their mixture. It is then possible to determine the contribution of individual radicals to the radiation decomposition of the selected impurity, as well as to determine the mechanism of decomposition. A commonly used method of ensuring the predominance of \( \cdot \text{OH} \) radicals in irradiated solutions is their saturation with \( \text{N}_2\text{O} \), which, as a result of the following Reaction (4):

\[ e_{aq}^- + \text{N}_2\text{O} + \text{H}_2\text{O} \rightarrow \text{N}_2 + \text{OH}^- + \cdot \text{OH} \quad k = 9.1 \times 10^9 \text{M}^{-1}\text{s}^{-1} \] (4)

causes the conversion of \( e_{aq}^- \) into an additional amount of \( \cdot \text{OH} \) radicals, under such conditions only \( \cdot \text{OH} \) and \( \cdot \text{H} \) remain in the solution in a percentage ratio of 90/10 [10]. Moreover, when \( \text{H}_2\text{O}_2 \) is present in the irradiated solution, hydroxyl radicals dominate as a result of Reaction (5) [11]:

\[ e_{aq}^- + \text{H}_2\text{O}_2 \rightarrow \cdot \text{OH} + \text{OH}^- \quad k = 1.2 \times 10^{10} \text{M}^{-1}\text{s}^{-1} \] (5)
In research practice, N₂O is much more commonly used due to the fact that N₂O itself and the nitrogen formed during the process are practically inert towards the compounds present in the solution. In the case of hydrogen peroxide, it is difficult to estimate the exact amount needed to achieve the intended effect. When H₂O₂ is present in the solution in excess of the substance being decomposed, it can also react with the •OH radical as well as other radicals, as according to Reaction (6) [7]:

\[
•OH + H₂O₂ → H₂O + O₂⁻ \quad k = 2.7 \times 10^7 M^{-1}s^{-1}
\]  

(6)

On the other hand, in order to eliminate hydroxyl radicals from the reaction environment, solutions before irradiation should be deaerated and an appropriate amount of tert-butyl alcohol (0.2–1 M) should be added [12], which acts as a scavenger of hydroxyl radicals, as according to Reaction (7):

\[
•OH + (CH₃)₃COH → H₂O + •CH₂(CH₃)₂COH \quad k = 6 \times 10^8 M^{-1}s^{-1}
\]  

(7)

Other classic hydroxyl radical scavengers include thiourea, dimethylurea, or several alcohols such as methanol and ethanol.

The pH of the irradiated solution also plays an important role (Figure 1). When the experiment is carried out in an acidic environment, it is practically only the hydrogen atom present, while in neutral and alkaline solutions the equilibrium shifts towards the formation of eaq⁻ (Reactions (8) and (9)).

\[
e_{aq}^- + H^+ → H^* \quad (8)
\]

\[
H^* + OH^- → e_{aq} \quad (9)
\]

Figure 1. Effect of pH on G-values of primary products of water radiolysis [13].

Water and wastewater subjected to purification and treatment processes are very complex matrices. There is a whole spectrum of chemical compounds that significantly affect the efficiency of the purification process. As mentioned earlier, the reactive individuals formed by radiolysis of water are non-selective to the substances present in the solution. In real wastewater, there is competition between the pollutants to be degraded and the anions present in the solution, i.e., Cl⁻, CO₃²⁻, HCO₃⁻, NO₃⁻, or SO₄²⁻, as well as the humic compounds for reaction with primary radiolysis products of the water. This competition can affect the efficiency of the purification process [14], these substances are called •OH radical scavengers as they usually cause a decrease in the degradation efficiency [15,16]. Wojnarovits and Takacs [17] showed that the pH value of a radiation-treated solution has a significant effect on the progress of competitive reactions with hydroxyl radicals. The reaction with chloride ions is predominant at pH < 5, while the reaction with carbonate and bicarbonate ions is predominant at a neutral or slightly alkaline pH. Very often, in order to reduce the amount of the dose necessary to achieve a satisfactory degree of decomposition of organic pollutants, chemical support is used by adding, for
example, ozone [18] or hydrogen peroxide [19,20]. One of the most effective methods is to combine radiation technologies with biological treatment [21,22]. Taking into account all the limitations of the use of radiation technologies, primarily electron accelerators, and compared to other AOPs, ionizing radiation technology provides economical, reliable, and safer operations leading to a reduction in the production of secondary toxic intermediates. The world’s largest wastewater treatment plant (capacity 30,000 m$^3$/day) using electron beam technology started up in China in 2020 [23]. Treatment in this installation is provided to water contaminated with residues of non-biodegradable industrial dyes built on the technology provided by the IAEA since 2010; the purification process will save 4.5 billion liters of fresh water per year, which will then be subjected to the treatment process.

3. Endocrine-Disrupting Compounds EDCs

A special type of micropollutant occurring in waters and sewages is the compounds causing disorders of the proper functioning of the endocrine system, the so-called endocrine-disrupting compounds (EDCs). These compounds act directly on the endocrine system, being able to block or mimic the natural hormones responsible for the functioning of certain organs of the human or animal body [2,24]. Additionally, these compounds may cause the growth of certain metabolic disorders, including obesity and diabetes, as well as endometriosis [2]. EDCs are very often defined as exogenous substances or mixtures of substances that can interfere with every aspect of the endocrine system. These compounds may exhibit low acute toxicity but, at the same time, may affect reproduction in fish, even at very low exposure levels <1 ng dm$^{-3}$ [25]. In addition, the effects of such exposure may not cause any symptoms for an extended period of time.

These compounds are continuously released into the environment, knowingly or unknowingly, mainly due to weak regulatory standards, especially in developing countries. It should be noted that only substances that are commonly found in the environment in significant concentrations and simultaneously posing a threat to the environment and/or human health are covered by legal standards. In accordance with Article 16 of the Water Framework Directive [26], a list of priority substances is being developed that pose a threat to the aquatic environment and, consequently, to humans. This list includes diclofenac, 17 alpha-ethinylestradiol EE2, 17 beta-estradiol E2, and perfluoroacetate sulfonic acid. This risk is assessed according to a procedure based on scientific principles, i.e., in order to include a substance in the list of priority substances in the field of water policy, reliable scientific evidence must be presented regarding the risk of the substance, in particular its aquatic ecotoxicity and human toxicity. Complicated procedures cause only a small number of compounds to be regulated. In addition, the degradation and transformation products of these substances in the environment remain beyond any control, which may pose a greater risk to the environment and living organisms than the parent compounds [27].

Contaminants that cause endocrine disruption include:

1. Natural and artificial estrogens;
2. Bisphenol A;
3. Parabens;
4. Perfluorinated compounds PFOA and PFOS;
5. Pesticides (e.g., atrazine);
6. Psychotropic drugs (carbamazepine and fluoxetine);
7. NSAIDs (DCF and IBU);
8. Antibiotics (see Table 1).

All these micropollutants are a big problem for conventional wastewater treatment plants. A number of literature reports show that they enter into natural waters in unchanged form after the wastewater treatment process [28]. As mentioned earlier, due to the low concentrations of these types of contaminants in wastewater (ppb or ppt) and their complex chemical structure, technologies commonly used in wastewater and drinking water treatment plants may not be efficient enough to remove them completely. Many
applications of irradiation processes to remove various types of endocrine-disrupting micropollutants have been described in the literature, some of which will be discussed below.

### Table 1. Selected antibiotic degradation using radiation technologies.

| Compound          | Initial Concentration/Additives | Dose/Kind of Radiation | Yield of Degradation/Mineralization | Refs. |
|-------------------|---------------------------------|------------------------|-------------------------------------|-------|
| Sulfamethoxazole (SMX) | 0.1 mM                          | 5 kGy/γ                | Decomposition—100%                 | [29]  |
| SMX               | 0.1 mM                          | 4 kGy/γ                | Improvement in biodegradability     | [30]  |
| Lincomycin (LMC)  | 17 mg dm⁻³                      | 2 kGy/γ                | Improvement in biodegradability of about 18.9% | [22]  |
| SMX               | 17 mg dm⁻³                      | 2 kGy/γ                | Improvement in biodegradability of about 28.33% | [22]  |
| Tetracycline (TCN) | 17 mg dm⁻³                      | 2 kGy/γ                | Improvement in biodegradability     | [22]  |
| SMX               | 1 mg dm⁻³                       | 300 Gy/γ               | Degradation—100%                   | [31]  |
| SMX               | 2 mg dm⁻³                       | 300 Gy/γ               | Degradation—96.2%                  | [31]  |
| SMX               | 5 mg dm⁻³                       | 300 Gy/γ               | Degradation—91.3%                  | [31]  |
| SMX               | 5 mg dm⁻³ +2 mM NO₂⁻            | 100 Gy/γ               | Degradation—44.84%                 | [31]  |
| Sulfadiazine (SD) | 25 mg dm⁻³ +18.5 mM H₂O₂ +0.3 mmol dm⁻³ Fe²⁺ pH 2.6 | 1 kGy/γ                | Degradation—100% Mineralization—74% | [32]  |
| Sulfametiazol (SMT) | 20 mg dm⁻³ pH 6.5              | 5 kGy/γ                | Degradation—95.5% Mineralization—6.8% | [33]  |
| Amoxicillin, Cefradine, LMC, TCN | 30 mg dm⁻³                  | 2 kGy/γ                | Degradation—100%                   | [34]  |
| Amoxicillin, Ofloxacin, Cefradine | 50 mg dm⁻³, pH 9               | 30 kGy EB              | Degradation—97%                    | [35]  |
| TCN               | 300 mg kg⁻¹ (Livestock samples) | 1 kGy EB               | Degradation—42.77%                 | [36]  |
| Norfloxacin, Ciprofloxacin | 0.1 mM                       | 2 kGy/γ                | Degradation—100% TOC reduction—25% | [37]  |
| Ornidazole        | 50 mg dm⁻³                      | 3 kGy/γ                | Degradation—100%                   | [38]  |

#### 3.1. Estrogen Degradation

Natural estrogens are estrone (E1), 17β-estradiol (E2), and estriol (E3). If they enter living organisms from the outside, they are regarded as endocrine-disrupting compounds. E2 is the most common and causes the most endocrine disruption, although several E2 metabolites also have estrogenic endocrine activity. Chemically, E2 is a steroid that is a derivative of estrone. Estrogens play an important role in human health; however, when released into the environment, they become a problem. Synthetic estrogens are used as an ingredient in some oral contraceptives and in hormone replacement therapy [39]. In recent years, with the development of sensitive analytical techniques, it has become possible to determine estrogens at low concentration levels.

It has been shown that conventional wastewater treatment plants are not able to completely degrade this type of pollutant, and their removal requires the search for more advanced technologies. Recently, natural estrogens have been reported in both drinking water and surface water [39]. So far, all knowledge about the adverse effects of estrogens on living organisms has meant that estrogens and their degradation products have been the first, next to diclofenac, to be included in the watch list in accordance with Directive 2013/39/EU of the European Parliament and of the Council adopted on 12 August 2013.
Based on the available data, it is assumed that adverse effects due to the presence of E2 in water occur for concentrations above 0.03 nM [40].

In one of the first studies concerning the use of γ radiation to decompose trace amounts of 17 β-estradiol (E2) in water, it was shown that the dose of 10 kGy is sufficient for the complete degradation of 1.8 nM, while the estrogenic activity decreased to an acceptable level only after the application of the dose of 30 kGy [41]. By mineralization we mean the chemical decomposition of organic matter into simple inorganic substances including water, carbon dioxide, nitrogen, chlorine, phosphorus, sulfur, etc. However, decomposition and degradation are very often used as synonyms. If an attempt is made to determine the difference, decomposition can be regarded as a process that leads to other, new organic compounds while degradation leads to the formation of similar structures with smaller masses (degradation of perfluorinated acids also leads to the formation of acids, but with shorter chains [6]). The rate constant for the reaction of E2 with the •OH radical was also estimated to be $1.6 \times 10^{10} \text{M}^{-1} \text{s}^{-1}$. Removal of estrogenic activity has also been tested for various effluents containing 17β-estradiol (E2), estrone (E1), and 17α-ethynylestradiol (EE2) [42]. The greatest activity was shown by livestock effluents due to higher concentrations of E2, E1, and EE2, which did not decompose completely after the application of the 10 kGy dose, so that estrogenic activity remained at a higher level compared to domestic and industrial wastewater. The degradation of 17β-estradiol (E2) in aqueous solutions was also studied using electron beam (EB) [43].

Experiments carried out using acetonitrile/water and ethanol/water solutions showed that the role of •OH is dominant in the degradation of E2, and the reducing individuals have a minor participation in its degradation. Acidic or alkaline conditions are more favorable for E2 removal than neutral conditions. At pH values 9.1 and 4.9, the E2 degradation efficiency at a dose of 10 kGy was 88.3% and 79.4%, respectively, whereas only a 53.4% reduction was obtained at the same dose at pH 6.8. The addition of an appropriate amount of H$_2$O$_2$ also promoted the degradation of E2.

Synthetic estrogens such as dienestrol (DS), norethindrone (NET), and quinestrol (QS) are separate groups of compounds. These estrogens are used on a large scale, mainly in hormone replacement therapy and in the treatment of breast cancer, osteoporosis, and prostate cancer. They are designed to be resistant to structural changes to increase their persistence in the body, which simultaneously makes them more stable than natural estrogens in the environment [44,45]. For DS, NET, and QS with initial concentrations of 2 mg dm$^{-3}$, it was observed that estrogen concentrations decreased when increasing the absorbed dose; at a dose of 6 kGy, the degradation efficiency was 100%. The highest efficiency of TOC reduction was obtained for oxygenated solutions; above 3 kGy, there was a rapid reduction in TOC, and in parallel with the decrease in the TOC value, a decrease in toxicity to rotifers was observed [46].

3.2. Bisphenol A Degradation

One of the most commonly used compounds from the bisphenol group is bisphenol A. It is mainly used as a monomer for the production of polycarbonate, epoxy, and unsaturated polyester–styrene resins, and also as flame retardants, fungicides, antioxidants, and rubber chemicals. Moreover, BPA has been used as a component of resin in dental fillings, as internal coatings on cans, as an ingredient in powder coatings, and as an additive in thermal paper [47,48]. BPA has been shown in many studies to act through several different receptor-mediated mechanisms to disrupt the endocrine system and in many ways has become a model micropollutant that is classified as an EDC [49]. The annual output of BPA worldwide is evaluated to be around 3 million tons, and this amount continues to increase due to high demand and consumption in developing countries [48]. BPA is well soluble in water (approximately 300 mg dm$^{-3}$); this is why wastewater containing BPA easily releases BPA into the aqueous environment.

Gamma radiation [15,50–53] has been used much more frequently than EB [54] for the radiolytic decomposition of BPA. Rate constants with the major products of water
radiolysis were experimentally determined for the •OH radical in the range $6.9 \times 10^9$ to $1.85 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$ [50,53], for $e_{\text{aq}}^-$ in the range $1.8 \times 10^9$–$7.0 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ [53,54], and for •H $7.7 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$ [54]. These data suggest that, under oxidative conditions, a better degradation efficiency of BPA is achieved in aqueous solutions. In our previous study on BPA degradation using gamma radiation it was found that, in the primary reaction of •OH radicals with BPA, two isomers of hydroxycyclohexadienyl radicals (1,2) and phenoxyl-type radical (3) (Figure 2) are formed. These radicals are the first step in the formation of all identified products.

![Figure 2. The first step of the % •OH-induced degradation of BPA [15].](image)

Based on the identification of BPA decomposition products, bond cleavage between rings in the BPA molecule was excluded. The authors suggest other processes involving the cleavage of a single benzene ring.

For small initial concentrations of 1 µg dm$^{-3}$, no significant differences in degradation efficiency were observed under the dominance of one selected water radiolysis product [15]. This is satisfactory from a technological point of view. Strong matrix effects were also found for BPA with initial concentrations of both 1 µg dm$^{-3}$ and 10 mg dm$^{-3}$. In the case of BPA 10 mg dm$^{-3}$, a dose of 0.3 kGy is needed to achieve 100% degradation (distilled water), for river waters this increases to 0.7 kGy, while for more complex wastewater matrices, the doses range from 5 to 10 kGy or more. The obtained data indicate that the matrix effect on the required absorbed dose should be investigated in each case.

3.3. Paraben Degradation

Parabens are an example of very popular preservatives used in both personal care and pharmaceutical products. Parabens are alkyl esters of ε-hydroxybenzoic acid; their widespread use is mainly due to their broad spectrum of antibacterial, antimicrobial, and antifungal activities, as well as their stability over the pH range and good water solubility [55–57]. Parabens began to be used on a large scale in the cosmetics industry in the 1930s and 1940s. Today, the presence of parabens in cosmetic ingredients is a very controversial topic. In 2007, parabens were added to the list of compounds that have a negative effect on the endocrine system, however, the literature reports on this topic appeared much earlier [58].

Gamma radiation was first used to determine the radiation resistance of methylparaben used in pharmaceutical products undergoing radiation sterilization [39]. It was found that for a dose of 5 kGy, used in sterilization, methylparaben does not undergo any transformation either in solid form or in aqueous solution with an initial concentration of 10 µM. Only for high doses above 50 kGy was a slight decomposition in aqueous solution observed. A much higher degradation efficiency for MP was obtained for aqueous aerated solutions with an initial concentration of 3.29 µM where all of the MP was degraded after the 50 Gy dose was applied [60]. In the case of an aqueous solution of butylparaben with an initial concentration of 1 mM, a dose as high as 90 kGy was needed to achieve 90% mineralization [61]. The use of radiation pre-treatment significantly increased the biodegradability of an aqueous solution of methyl 3,5-dichloro-4-hydroxybenzoate (MDHB) [62]. The obtained data indicate that the effectiveness of MDHB and total organic carbon (TOC)
removal in the irradiation process increased with the absorbed dose, regardless of the initial concentration of MDHB (in the range 1–10 mg dm$^{-3}$) at the absorbed dose of 800 Gy. However, the maximum TOC removal efficiency was only 15.3%.

Based on the identified by-products, a suggested degradation pathway was presented using the combined irradiation and biological treatment process (Figure 3). Furthermore, the maximum TOC elimination efficiency was 70.1% within 240 h, which suggested that some by-products may have stability, and more research is needed to determine the fate of by-products generated during the combined irradiation and biological treatment process. It has been shown that 4-hydroxybenzoate (4-HBA) shows much less radiation resistance than its ethyl ester 4-hydroxybenzoic ethyl ester (4-HBAEE) [63]. A dose of 1.4 kGy is needed to achieve 50% decomposition for 4-HBA, while for the same amount of 4-HBAEE this increases to 3.2 kGy due to the protective effect of the ester bond prior to decarboxylation.

![Figure 3](image-url)

**Figure 3.** The possible degradation pathway of MDHB during the combined irradiation and biological treatment process. The brackets represent the biodegradation products. The dashed line represents presumable further transformation [62].

### 3.4. Perfluorinated Compound Degradation

Perfluorinated compounds are a relatively recently investigated group of micropollutants responsible for endocrine disruption of living organisms. They were synthesized for the first time in the 1950s and have found numerous applications in industry, including for firefighting agents, personal care products, and herbicides. The many industrial uses of perfluoroalkyl substances (PFAS), combined with their extremely long half-life in the human body and extreme persistence in the environment, have led to widespread and chronic exposure to them. The adverse endocrine effects of perfluorinated compounds still require much research, but it is known that they depend on the concentration, chain length, and type of functional group alongside the age, sex, and species of exposed organisms [64].

The first work on the application of ionizing radiation to perfluorinated surfactants concerned the use of an electron beam from an accelerator with an energy of 6 MeV to determine the rate constants of perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) reactions with $^\cdot$OH radicals and a hydrated electron [65]. The investigations were carried out in a nanosecond pulse radiolysis system with spectrophotometric detection using aqueous solutions of ammonium perfluorooctanoate and tetraethylammonium perfluorooctanesulfonate. The obtained constants had values for $^\cdot$OH radicals: $-3.0 \times 10^7$ M$^{-1}$s$^{-1}$ for e$_{aq}^-$, $1.3-5.1 \times 10^7$ M$^{-1}$s$^{-1}$ for PFOA, and $-3.0 \times 10^7$ M$^{-1}$s$^{-1}$ and $7.3 \times 10^7$, respectively, for PFOS. The obtained values indicate that the reactions of PFOA and PFOS with $^\cdot$OH or e$_{aq}^-$ radicals are 2-3 orders of magnitude lower than the reactions of many other organic molecules, which are also micropollutants. On the other hand, similar values of the reaction constants with both $^\cdot$OH and e$_{aq}^-$ indicate that both
PFOS and PFOA can potentially react with all major products of water radiolysis, and the application of the radiation method requires careful optimization.

In recent years, several papers have been published on the use of gamma ionizing radiation [6,66,67] and the electron beam [6,68–70] to degrade PFOA and PFOS in aqueous solutions. When gamma radiation was used to degrade PFOA with an initial concentration of 20 mg dm$^{-3}$, the authors showed that both a hydrogen atom and an electron are necessary for the process. On the other hand, as the concentration of hydroxyl radicals decreased, a lower degree of defluorination was observed, which means that the C–F bond cannot be effectively broken in the absence of $^*$OH radicals. The first use of the electron beam for the decomposition of PFOA concerned a solution prepared in 0.1 mM phosphate buffer with an initial concentration of 0.5 mg dm$^{-3}$ [69]. The addition of 20 mg dm$^{-3}$ NO$_3^-$ was shown to significantly increase the defluorination efficiency from 34.6% to 93.3% at a dose of 10 kGy. This is attributed to the formation of highly reducing NO$_3^\bullet^2^-$ radicals. A high 95% degradation efficiency for PFOA and an 85% efficiency for PFOS was obtained for an EB irradiated solution at pH 13 [70]. The lower degradation efficiency of PFOS as compared to PFOA is due to the more difficult oxidation of sulfonate to sulfate.

The decomposition of PFOA occurred with the highest efficiency in strongly alkaline solutions; in addition, the effect of the dose rate on the decomposition efficiency of PFOA was observed for the first time. For an aqueous, deaerated PFOA solution with an initial concentration of 10 µg dm$^{-3}$ when $\gamma$-rays were applied for a dose of 10 kGy, a degradation efficiency of 55% was obtained. However, for the electron beam, even for the 50 kGy dose, no PFOA decomposition was observed.

In the case of $\gamma$ irradiation of PFOS, the efficiency of the decomposition of linear PFOS isomers is lower than for all branched isomers. The most energy-efficient process is gamma irradiation where, in a neutral, deaerated solution, 90% efficiency of PFOS decomposition can be obtained at an absorbed dose of 10 kGy for an initial PFOS concentration of 0.1 mg L$^{-1}$ [6]. Figure 4 shows the main pathways of the postulated mechanisms of radiolytic PFOS decomposition under different conditions of treatment using ionizing irradiation. As for the mechanism of the decomposition process, the primary and the fastest process is the reaction of PFOS with hydrated electrons, resulting in the formation of C$_8$F$_{17}$SO$_3^\bullet^2^-$ radicals. In the presence of either a formate or 2-propanol in irradiated solutions, C$_8$F$_{17}$SO$_3^\bullet^2^-$ radicals are formed in the reactions of PFOS with CO$_2^\bullet$ or (CH$_3$)$_2^\bullet$C-OH radicals [6].

Figure 4. Schematic diagram of the suggested mechanism of radiolytic decomposition of perfluorooctanesulfonate (PFOS) under different conditions [6].
In the case of environmental samples, i.e., contaminated water or sand, the application of the electron beam allows for obtaining a high degree of degradation for PFOA > 90% and a much lower degree for PFOS (only about 40%) [70].

3.5. Atrazine Degradation

Atrazine is an example of a pesticide compound whose residues in the environment cause changes in the endocrine system of living organisms [71–73]. Atrazine belongs to the s-triazine derivatives. Compounds from this group have a ring structure and are characterized by strong aromaticity and high chemical stability in biodegradation-based decomposition processes. Although the use of atrazine has been banned, it can still be detected in all types of natural waters due to its previous large-scale use.

It was found that γ irradiation in the presence of humic substances (HS) (200 mg dm$^{-3}$) combined with sodium bicarbonate (1 g dm$^{-3}$) allowed for removing atrazine and its degradation products from contaminated water at a level ≤ 20 times the maximum allowable concentration of atrazine and its metabolites (IMAC) in drinking water [74]. The reaction of e$_{aq}^{-}$ ($k = 4.8 \times 10^9$ M$^{-1}$s$^{-1}$) with atrazine is faster than the reaction of *OH radicals ($3.0 \times 10^9$ M$^{-1}$s$^{-1}$) with atrazine (about 50% higher), and this supports the assumption that reduction reactions dominate the radiolysis of atrazine, leading to a higher degradation yield. Reducing conditions can be achieved by the addition of a HS/carbonate mixture, which acts as a scavenger of hydroxyl free radical *OH. In addition, the formation of active radicals from the oxidation of humic acid may also play an important role in atrazine degradation. As is shown in Figure 5, the dominant atrazine metabolic reactions are dechlorination, dealkylation, and deamination. The synergistic effect of humic acid was also confirmed by Khan et al. [75]. As a result of the reaction with e$_{aq}^{-}$ and the *OH radical, a high degree of organic chlorine and nitrogen mineralization to chloride, nitrate, and ammonium ions can be achieved. The formation of acetate ions from carbon atoms of the side chains was also observed. It was found that the electron beam can be extremely effective in removing atrazine; 90% efficiency for the initial concentration of 6 mg dm$^{-3}$ was already obtained at the dose of 0.77 kGy [76].

![Figure 5. Chemical structure and potential degradation pathways of the main atrazine by-products by ionizing radiation][74].

3.6. Psychotropic Drug Degradation

3.6.1. Carbamazepine

Carbamazepine (CBZ) is a first-generation anticonvulsant drug widely used in the clinical treatment of epilepsy, trigeminal neuralgia, and some psychiatric diseases. The
negative effects of carbamazepine on aquatic microorganisms and human health have been observed [77,78]. Due to its stable chemical structure, CBZ is resistant to both conventional and advanced wastewater treatment processes, and thus is one of the most persistent pharmaceutical micropollutants in the aquatic environment [79].

The use of an electron beam has brought satisfactory results in the decomposition of an aqueous solution of carbamazepine with an initial concentration of 50 mg dm$^{-3}$ [80]. The obtained results suggest that low pH promotes the degradation process as does the presence of HSO$_4^-$ and SO$_4^{2-}$ in solution. Naturally occurring CO$_3^{2-}$, NO$_2^-$, NO$_3^-$, NH$_4^+$, and Cl$^-$ in water negatively affected the degradation efficiency of carbamazepine.

The use of an electron beam for acidic aerated carbamazepine solutions containing 2.5 mM of H$_2$O$_2$ allowed for both 100% degradation and mineralization [81]. Compared to the UV/H$_2$O$_2$ process, the use of an electron beam made it possible to obtain a greater degree of decomposition with less energy [82]. Anions naturally occurring in surface waters had a much greater impact on reducing the effectiveness of the UV/H$_2$O$_2$ process than in the case of the electron beam. A high degree of mineralization, about 40%, was obtained by adding 50 mM hydrogen peroxide at an absorbed dose of 2.63 kGy [20]. Moreover, it was found that supporting electron beam irradiation with the addition of H$_2$O$_2$ also allows it to permanently remove some mutagenic and carcinogenic decomposition products from the solution, such as acridine.

As with diclofenac (DCF), studies have also been carried out on the degradation efficiency of carbamazepine at relatively low concentration levels of 10 $\mu$g dm$^{-3}$ in real samples such as surface water and hospital wastewater [83]. Compared to the results presented earlier for DCF and ibuprofen (IBU), carbamazepine did not achieve such high yields, with only 37% for hospital effluent after a 25 Gy dose. To improve the degradation efficiency and to increase the degree of mineralization, the addition of persulfate was used [84,85]. It was shown that for an initial carbamazepine concentration of 0.04 mM, irradiation in the presence of PMS (peroxymonosulfate) increased the degradation and mineralization, which increased to 45% after applying a dose of 300 Gy. Importantly, the molar ratio of PMS to carbamazepine was not significant [84]. Furthermore, Zhang et al. [85] found that the biodegradability of carbamazepine was enhanced by the combination of gamma irradiation and PS (persulfate) addition. As presented in Figure 6, hydroxyl radical OH provided a powerful impact on CBZ degradation.

![Proposed mechanism of gamma radiolysis of CBZ](image)

Figure 6. Proposed mechanism of gamma radiolysis of CBZ [85].
3.6.2. Fluoxetine

Fluoxetine (FLX) is another example of a psychotropic drug whose use has steadily increased in recent years. This increased consumption is mainly due to the increasing prevalence of mental disorders in modern societies. This causes an increase in pharmaceutical residues, initially in the wastewater discharged to the treatment plant and, finally, in the environment. Fluoxetine causes endocrine disruption in some aquatic species [86].

One of the first applications of ionizing radiation to FLX degradation was the degradation in an aqueous solution with an initial concentration of 19.4 ± 0.2 mg dm\(^{-3}\) by electron beam [87]. Degradation of more than 90% was obtained at the dose of 0.5 kGy; however, 80% of the total concentration of organic carbon remained in the solution even after the dose of 7.5 kGy.

Based on the identified products of fluoxetine decomposition in the first step, the electrophilic addition of OH radicals to aromatic rings is postulated. In the next steps, further hydroxylation of fluoxetine molecules and accompanying defluorination are observed. A 30% efficiency of F\(^-\) ion removal was observed for doses above 1 kGy. Based on the determination of the concentration of the formed NO\(_3^-\) and NH\(_4^+\) ions, it can be estimated that, after the application of 7.5 kGy, the nitrogen-bonded carbon atoms are mineralized by 8.5%.

The decomposition of FLX primarily by a reaction with the OH radical was also confirmed by Jl et al. [88]. In the reaction with the radical OH, FLX formed a hydroxylated adduct of the aromatic ring, while in the reaction of FLX with the anion of the sulfate radical (SO\(_4^\cdot^-\)), a cation of the benzene radical was formed; in reaction with H\(_2\)O, this then provided the adduct OH. The rate constants for the reaction of FLX with hydroxyl radical OH, hydrated electron (e\(_{aq}\)\(^-\)), and sulfate radical SO\(_4^\cdot^-\) were also determined and were 7.8 × 10\(^{-9}\); 2.3 × 10\(^9\) and 1.1 × 10\(^9\) M\(^{-1}\)s\(^{-1}\), respectively. In addition, it has been shown that an acidic solution is more favorable for FLX degradation and the presence of inorganic anions has little or no effect on the electron beam degradation efficiency of FLX [89]. The proposed mechanism of degradation of FLX in such conditions is presented in Figure 7.

![Proposed degradation pathway of FLX degradation using EB](image)

**Figure 7.** Proposed degradation pathway of FLX degradation using EB [89].

The application of an electron beam to an aqueous solution of FLX and to a mixture of FLX and propranolol, a popular hypertension drug, caused a significant decrease in
toxicity in both cases [90]. The application of a 5 kGy dose allowed for an 80% reduction in toxicity for both single pharmaceuticals and the binary mixture towards *Daphnia similis*, and a 20% reduction towards *Vibrio fischeri*. It is interesting to note that the use of higher doses of 7.5 and 10 kGy enhanced the toxic effects compared to non-irradiated samples. Moreover, Jl et al. [88] observed a significant decrease in toxicity of electron beam-treated FLX solutions towards *Daphnia similis* by about 87%, and slightly less towards *Vibrio fischeri*, by about 10%.

3.7. Non-Steroidal Anti-Inflammatory Drug Degradation

Non-steroidal anti-inflammatory drugs (NSAIDs), including analgesics, are among one of the most common groups of pharmaceutical contaminants, especially diclofenac (DCF) and ibuprofen (IBU). Consumption of these drugs is increasing every year [91]; the levels of DCF concentrations identified in surface waters have reached 15 µg dm⁻³ while in the waters discharged by wastewater treatment plants it can reach 5.5 µg dm⁻³ [92]. Both DCF and its metabolites, 5-hydroxy diclofenac and N, 5-dihydroxydiclofenac, can cause liver damage in humans [93]. Significant population declines in Asian Gyps vultures have also been associated with the contamination of their natural habitat with diclofenac [94]. The relatively low removal of DCF from wastewater in conventional treatment plants (20–35%) has been repeatedly indicated, thus suggesting that this drug is resistant to biodegradation [95,96].

One of the first tests for DCF removal concerned the use of gamma radiation to decompose 0.1 M DCF in an aqueous solution [97]. It has been shown that both the hydroxyl radical •OH and the hydrated electron e⁻aq participate in the reaction of DCF decomposition and reduction in toxicity. It has been shown that in the γ/N₂O system, the dose needed to decompose 480 µM was reduced from 7.4 to 1.47 kGy as compared to free O₂ [98]. It was also noted that the addition of H₂O₂, S₂O₈²⁻, or the saturation of the solution before irradiation with N₂O significantly increases the degree of mineralization. The radiolytic degradation of diclofenac mainly occurs via hydroxyl radical reactions, and the quantitative participation of reactive radicals can be represented as follows: •OH > e⁻aq > •H [99]. The determined rate constants for the reaction with the hydroxyl radical •OH and electron e⁻aq are (1.24 ± 0.02) × 10¹⁰ M⁻¹ s⁻¹ and (3.1 ± 0.2) × 10⁷ M⁻¹ s⁻¹, respectively [83], which is in agreement with data presented previously for •OH 9.0 × 10⁸ M⁻¹ s⁻¹ [100] and for •OH (9.29 ± 0.11) × 10⁹ M⁻¹ s⁻¹ and (1.53 ± 0.03) × 10⁶ M⁻¹ s⁻¹ [101].

The presence of various natural waters, i.e., nitrate, nitrite, carbonate, or bicarbonate, have reduced the efficiency of DCF degradation process. It has been shown that the DCF degradation efficiency is definitely higher in acidic aqueous solutions than in alkaline or neutral ones [102]. The presence of humic acid had a negative effect on the degradation of diclofenac. At 0.8 kGy, when the humic acid concentration was 30 mg dm⁻³, the degradation efficiency of diclofenac decreased from 80.8% to 62.9% [16]. Regarding DCF decomposition in natural aqueous matrices, the DCF content of these samples was at levels previously determined for this type of natural samples [83]. To achieve 100% degradation efficiency of DCF 10 µg dm⁻³ in river water the required dose was 100 Gy, while in hospital wastewater it was 250 Gy. An electron beam was also used to degrade DCF in aqueous solutions, similar to gamma radiation a 100% degradation efficiency was obtained at relatively low doses while mineralization occurred much slower even for higher doses [103].

The proposed degradation pathway presented in Figure 8 includes the electrophilic addition of hydroxyl radicals generated from water radiolysis to the two aromatic rings in the DCF molecule followed by the oxidation of hydroxide groups attached to the CH₂COOH bearing ring; dehalogenation through dissociative solvated electron attachment to the aromatic ring bearing the chlorine atoms and/or fast HCl elimination following •OH radical attack on the carbon atoms at the chlorine substituent; C–N bond cleavage, preserving the nitrogen-containing group on one aromatic moiety.
Figure 8. Proposed DCF degradation pathway by EB [103].

At the same time, the toxicity to V. fischeri after a dose of 5 kGy decreased from (19.6 ± 1.6) TU to (6.2 ± 2.3) TU and from (6.8 ± 0.9) TU to (3.1 ± 0.2) TU in the absence and presence of FLX, respectively, added to the irradiated solution. Pre-irradiation of DCF solutions with an electron beam significantly improves biodegradation [104]. A significant improvement in the decomposition efficiency of 15 mg dm$^{-3}$ of DCF treated with an electron beam was observed in the presence of the addition of 20 mg of commercial titanium oxide TiO$_2$ as a catalyst [105]. The application of the co-metabolism (co-oxidation) route of irradiation in the presence of ethylene glycol to DCF caused a threefold increase in the biodegradability of DCF [106].

Moreover, in the case of IBU, the effect of the solution’s pH on the degradation efficiency was observed; it was higher in acidic medium than in neutral or basic medium. Further, the presence of CO$_3^{2-}$, NO$_3^-$, CH$_3$OH, and thiourea in the solution reduced the degradation process of IBU [107]. The degradation of ibuprofen is more efficient under oxidative than reductive conditions [108]. The reaction with the *OH radical led to the formation of mainly hydroxy-cyclohexadienyl-type radical intermediates. It has also been shown that irradiation in the presence of K$_2$S$_2$O$_8$ decreased TOC values by approximately 80% [109].

3.8. Antibiotic Degradation

Among the numerous categories of antibiotics, sulfonamides are the most commonly used substances worldwide in both developed and developing countries. Some researchers do not classify sulfonamides as antibiotics. They consider that, as fully synthetic pharmaceuticals, they are not antibiotics in the strict sense of the word, despite their antibacterial activity. Sulfonamides such as sulfathiazole (STZ), sulfamethazine (SMZ), and sulfamethoxazole (SMX) are commonly detected in surface waters [110,111] because they are polar and highly soluble in water [112,113]. It has been shown that gamma radiation can be effective in removing sulfamethoxazole (SMX) residues from aqueous solutions [29].

The degradation process was mainly caused by the reaction with the *OH radical. The COD and TOC values obtained indicated complete mineralization. The observed initial increase in phytotoxicity was predominately due to H$_2$O$_2$ formed during irradiation. An increase in the BOD$_3$ value after irradiation was also observed, which indicated the conversion of the non-biodegradable compound to biologically degraded substances [30]. This is in agreement with results previously obtained [22] where the application of pre-irradiation with a dose of 2 kGy for aqueous solutions containing SMX, lincomycin (LMC), NO$_3^-$ concentration increases, the efficiency decreases. The anions present in natural waters also indicate the conversion of the non-biodegradable compound to biologically degraded...
and tetracycline (TCN) with an initial concentration of 17 mg dm\(^{-3}\) improved the biological degradation of these compounds.

As expected, the initial concentration of SMX has a significant effect on its removal efficiency [31]. The efficiency of the process depends on the initial concentration; as the concentration increases, the efficiency decreases. The anions present in natural waters also affect the efficiency of the process, with a greater effect observed for NO\(_3^-\) than NO\(_2^-\). Furthermore, it was observed that after a dose of 400 Gy, the removal efficiency of 5 mg dm\(^{-3}\) SMX is independent of the presence of inorganic anions. The effect of the presence of Cr (VI) in the form of K\(_2\)Cr\(_2\)O\(_7\) with an initial concentration of 0.01 mmol dm\(^{-3}\) on the removal efficiency of 5 mg L\(^{-1}\) SMX from aqueous solutions was also determined. The observed effect was in opposition to that of anion addition; the radiolytic removal efficiency of both SMX and Cr (VI) in the mixture was higher than that of single impurities. Other authors [116] showed that the presence of 0.1 g dm\(^{-3}\) Fe\(_3\)O\(_4\) increased SMX degradation for different initial concentrations ranging from 5 to 30 mg dm\(^{-3}\) compared to the control group that did not contain Fe\(_3\)O\(_4\). Furthermore, it was shown that SMX could be degraded over a wide range of pH values (3.01–10.96), and the degradation efficiency was over 98%. SMX mineralization in the presence of Fe\(_3\)O\(_4\) increased by about 200%.

Similar results were obtained for the degradation of aqueous sulfadiazine SD solution under gamma irradiation [117]. Although the addition of Fe ions can significantly increase SD degradation, the TOC removal in this case increased slightly, which may suggest that SD mineralization does not occur as easily as SMX mineralization. It was also found that pre-irradiation can improve biodegradability; a 14.5% increase in biodegradability was observed after a dose of 1 kGy [33]. The effect of the matrix on the EB beam decomposition efficiency was also observed, which decreased to 75% in surface water for STZ compared to 90% efficiency in distilled water after a dose of 0.5 kGy was delivered to the system [118].

Degradation mechanism for SMX using EB is presented in Figure 9.

![Figure 9. Potential degradation pathways of SMX within EB irradiation process [118].](image)

Initially, the S–C bond of SMX was attacked by free radicals, leading to products 1 and 2. Benzene on SMX could be directly hydroxylated to form product 3, and the double bond on the isoxazole ring was added by hydroxylation to form product 4. EB-induced cleavage of the S–N bond may have led to the formation of intermediates 5, 6, and 7; meanwhile, further hydroxylation of product 5 may have produced product 9, and hydrogen-substituted hydroxyl on the aniline of product 7 may have produced product 8. When the amino group in benzene and the methyl group in isoxazole are oxidized to
nitro and carboxyl groups, respectively, substances 10 and 11 may be formed. In particular, substance 12 is the result of further hydroxylation of sub-substance 11.

Toxicity measurements carried out with the use of luminescent bacteria showed that the use of an electron beam will significantly reduce the toxicity of sulfonamides in relation to aquatic ecosystems. Similar observations were reported by Kim et al. [119]; for an aqueous solution of sulfamethazine with an initial concentration of 30 mg dm$^{-3}$ after a dose of 2 kGy, the toxicity to green algae decreased sevenfold. The results indicate that the $^{•}$OH radical plays a dominant role in the degradation of sulfonamide group antibiotics. Much better results were obtained for tetracycline and lincomycin, for which a 53- and 37-fold decrease in toxicity, respectively, were observed under the same conditions.

Radiation technologies have also been successfully used to remove residues of other types of antibiotics including $\beta$-lactams (amoxicillin, cefradine) [34,35], as well as other antibiotics (lincomycin and tetracycline) [22,34,36,119,120]. It has also been shown that by using an electron beam to utilize medical intravenous infusion bottles, satisfactory results can be obtained for the degradation of amoxicillin, ofloxacin, and cefradine [35] (see Table 1). The use of an electron beam for tetracycline degradation in artificially contaminated pig manure also provided satisfactory results [36].

The degradation efficiency under gamma irradiation for the group of antibiotics tetracycline (TC), chlortetracycline (CTC), and oxytetracycline (OTC) was investigated in different matrices [120]. It has been shown that degradation is lowest in an acidic environment, pH = 2, slightly increases from pH 4 to 8, and decreases at pH = 10. The addition of H$_2$O$_2$ (1–5 $\mu$mol) to the irradiation increased the degradation efficiency. The presence of free radical scavengers Cl$^-$, CO$_3^{2-}$, NO$_3^-$, NO$_2^-$, and humic acid had an effect on TC degradation, which was higher at low concentrations of Cl$^-$, CO$_3^{2-}$, and humic acid and significantly decreased at low concentrations of NO$_3^-$ and NO$_2^-$. The significantly reduced process efficiency in the presence of electron scavengers (NO$_3^-$ and NO$_2^-$) indicates that TC degradation occurs by both oxidation and reduction, with reduction predominating. In the range of applied doses, it was not possible to achieve complete mineralization, but the formed degradation products were characterized by lower toxicity than the initial substances.

In the case of fluoroquinolone antibiotics, i.e., norfloxacin and ciprofloxacin, gamma radiation also provided satisfactory results (Table 1) [37]. To achieve 40% mineralization, a dose of 6 kGy must be applied to the system. Acute toxicity determined with Vibrio fischeri bacteria showed increased toxicity at low doses, indicating that the early degradation products are more toxic than the starting molecules. The results of biodegradation experiments carried out in activated sludge showed that the degradation products became available for the metabolic processes of microorganisms.

One of the widely used antibiotics is ornidazole (ORZ), a synthetic nitroimidazole used to treat infections caused by both anaerobic bacteria and protozoa. In the case of aqueous solutions containing ornidazole, the satisfactory results were obtained both with the use of $\gamma$ radiation [38] and electron beam [121] (see Table 1). ORN degradation occurs more effectively under acidic conditions than under alkaline or neutral conditions. A greater degree of ORN degradation is observed in the presence of CO$_3^{2-}$ and t-BuOH, indicating that oxidation by the $^{•}$OH radical oxidation reaction is the main route of ORZ degradation. It is notable that an increase in the degree of mineralization after electron beam irradiation was achieved by the addition of H$_2$O$_2$; 10 mM achieved a TOC reduction of 46.8% [121].

4. Conclusions

Every year, endocrine disrupting micropollutants are causing more and more problems for institutions responsible for wastewater treatment and supply of drinking water. In particular, influent is characterized by high BOD, COD, solid auxiliary chemicals, and low BOD/COD. Methods such as chemical coagulation/flocculation, adsorption by activated carbon, and membrane filtration do not provide high removal efficiency. In fact, the purification process is based on the transfer of contaminants from one phase to another and not on
their decomposition. In addition, e-beam radiation with high ionization energy (4.5 MeV) is not easily interfered or scattered by insoluble solids, while the widely described UV radiation technology with low energy can be attenuated. Basic research and development work is being carried out all over the world to develop new, more efficient technologies for the treatment of wastewaters and waters with this type of pollution. The results concerning the application of radiation technologies presented in this paper suggest that both gamma radiation and the electron beam allow for obtaining satisfactory decomposition and mineralization efficiency and reduce toxicity for many EDCs. Gamma installations have been implemented on an industrial scale, e.g., for the production of fertilizers from sewage sludge. There are also many facilities in operation that use ionizing radiation from gamma sources for wastewater treatment [122]. For practical and safety reasons, the installations used for water, wastewater, and sludge treatment are mostly based on the electron beam. The absence of secondary radioactivity and the ability to switch off power quickly, which results in the absence of radiation, is particularly safe for staff and the local community. A particularly important property of radiation technologies, compared to other AOPs, is that they are non-selective processes that can be used to degrade compounds with different structures and properties. A unique advantage in relation to other AOPs is the possibility of the simultaneous degradation of pollutants by oxidation and reduction. Practically, radiation technologies do not require the use of additional reactants; in some cases, such addition significantly increases the effectiveness of the process. The most important advantage of radiation technologies, especially those using electron beams, is the relatively short time period required compared to other AOPs, which allows for obtaining satisfactory results. The major barrier to radiation technologies are economic factors, especially those related to the large investment costs necessary at the plant construction stage. There have been many attempts at economic analyses concerning both the investment costs and the cost of treating 1 m$^3$ of water/wastewater. Depending on the adopted initial conditions, the costs of treatment of 1 m$^3$ ranged from USD 0.075 to 3.17 [123]. Particularly promising are the results indicating an increase in biodegradability after the application of small doses of 1–2 kGy of ionizing radiation. It should be expected that the practical application of radiation technologies in the treatment of water and wastewater can be really helpful for making progress in this field.

Funding: The paper’s preparation and publication have been supported by the funds of the Polish Ministry of Education and Science, INCT statutory and co-financed by International Cooperation, EU Grant Agreement No 730871, IFAST Innovation Fostering Accelerators Science and Technology.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Conflicts of Interest: The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References
1. Report Genewa/Nowy Jork, 13 lipca 2017 r.—(WHO) i UNICEF. Progress on Drinking Water, Sanitation and Hygiene: 2017 Update and Sustainable Development Goal Baselines. Available online: https://www.who.int/mediacentre/news/releases/2017/launch-version-report-jmp-water-sanitation-hygiene.pdf (accessed on 28 October 2021).
2. Giulivo, M.; de Alda, M.L.; Capri, E.; Barcelo, D. Human exposure to endocrine disrupting compounds: Their role in reproductive systems, metabolic syndrome and breast cancer. A review. Environ. Res. 2016, 151, 251–264. [CrossRef]
3. Rogowska, J.; Cieszynska-Semenowicz, M.; Ratajczyk, W.; Wolska, L. Micropolllutants in treated wastewater. Ambio 2020, 49, 487–503. [CrossRef] [PubMed]
4. Abdel Rahman, R.O.; Kozak, M.W.; Hung, Y.T. Radioactive pollution and control. In Handbook of Environment and Waste Management; Hung, Y.T., Wang, L.K., Shammas, N.K., Eds.; World Scientific Publishing Co.: Singapore, 2014; pp. 949–1027.
5. Chmielewski, A.G. Electron Accelerators for environmental protection. Rev. Accel. Sci. Technol. 2011, 4, 147–159. [CrossRef]
6. Trojanowicz, M.; Bartosiewicz, I.; Bojanowska-Czajka, A.; Szreder, T.; Bobrowski, K.; Nałecz-Jawecki, G.; Męczyńska-Wielgosza, S.; Nichipore, H. Application of ionizing radiation in decomposition of perfluorooctane sulfonate (PFOS) in aqueous solutions. Chem. Eng. J. 2020, 379, 122303. [CrossRef]
19. Buxton, G.V.; Greenstock, C.L.; Helman, W.P.; Ross, A.B. Critical review of rate constants for reaction of hydrated electrons, hydrogen atoms and hydroxyl radical (•OH/•HO) in aqueous solution. J. Phys. Ref. Data 1988, 17, 513–531. [CrossRef]

20. Wojnarovits, L.; Takacs, E.; Djakka, K.; Emmi, S.S.; Russo, M.; D’Angelantonio, M. Re-evaluation of the rate constant for the H atom reaction with tert-butanol in aqueous solution. Radiat. Phys. Chem. 2004, 69, 217–219. [CrossRef]

21. Ponomarev, A.V.; Ershov, B.G. The green method in water management: Electron beam treatment. Environ. Sci. Pollut. Res. 2014, 21, 1028–1034. [CrossRef] [PubMed]

22. Kim, H.Y.; Lee, M.M.; Kim, T.H.; Yu, S. Enhanced biodegradability of pharmaceuticals and personal care products by ionizing radiation. Water Environ. Res. 2015, 87, 321. [CrossRef] [PubMed]

23. Available online: https://www.iaea.org/newscenter/news/started-with-iaea-support-chinas-electron-beam-industry-opens-worlds-largest-wastewater-treatment-facility (accessed on 28 October 2021).

24. Viera, W.T.; Barbosa de Farias, M.; Spaolonzi, M.P.; Carlos de Silva, M.G.; Viera, A.M.G. Removal of endocrine disruptors in wastewater by adsorption, membrane filtration and biodegradation. A review. Environ. Sci. Technol. 2012, 46, 6205–6217. [CrossRef] [PubMed]

25. Galuke, L.S.; Strand, S.E.; Kalhorn, T.F.; Stensel, H.D. Estrogen biodegradation kinetics and estrogenic activity reduction for two bioavailable, endocrine disruptors treated with indirect aerobic biodegradation processes. Environ. Sci. Technol. 2017, 51, 1245–1254. [CrossRef] [PubMed]

26. Garnaga, G. Integrated assessment of pollution in the Baltic Sea. Ekologija 2012, 58, 331–335. [CrossRef]

27. Giebułtowicz, J.; Nałęcz-Jawecki, G. Occurrence of antidepressant residues in the sewage-impacted Vistula and Utrata rivers and tap water in Warsav (Poland). Ecotoxicol. Environ. Saf. 2014, 104, 103–109. [CrossRef] [PubMed]

28. Galu, G.; Casay, T.; Patzay, G.; Csonka, E.; Wojnarovits, L.; Takacs, E. Oxidative and reductive degradation of sulfamethoxazole in aqueous solutions: Decomposition efficiency and toxicity assessment. J. Radioanal. Nucl. Chem. 2014, 301, 475–482. [CrossRef]

29. Li, N.; Lei, Z.D.; Wang, T.; Wang, J.J.; Zhang, X.D.; Xu, G.; Tang, L. Radiolysis of carbamazepine aqueous solution using electron beam irradiation combined with hydrogen peroxide: Efficiency and mechanism. Chem. Eng. J. 2016, 295, 484–493. [CrossRef]

30. Ponomarev, A.V.; Ershov, B.G. The green method in water management: Electron beam treatment. Environ. Sci. Technol. 2020, 54, 5331–5344. [CrossRef] [PubMed]

31. Kim, H.Y.; Lee, M.M.; Kim, T.H.; Yu, S. Enhanced biodegradability of pharmaceuticals and personal care products by ionizing radiation. Water Environ. Res. 2015, 87, 321. [CrossRef] [PubMed]

32. Available online: https://www.iaea.org/newscenter/news/started-with-iaea-support-chinas-electron-beam-industry-opens-worlds-largest-wastewater-treatment-facility (accessed on 28 October 2021).

33. Viera, W.T.; Barbosa de Farias, M.; Spaolonzi, M.P.; Carlos de Silva, M.G.; Viera, A.M.G. Removal of endocrine disruptors in wastewater by adsorption, membrane filtration and biodegradation. A review. Environ. Sci. Technol. 2012, 46, 6205–6217. [CrossRef] [PubMed]

34. Giebułtowicz, J.; Nałęcz-Jawecki, G. Occurrence of antidepressant residues in the sewage-impacted Vistula and Utrata rivers and tap water in Warsav (Poland). Ecotoxicol. Environ. Saf. 2014, 104, 103–109. [CrossRef] [PubMed]

35. Sag, G.; Csány, T.; Patzay, G.; Csonka, E.; Wojnarovits, L.; Takacs, E. Oxidative and reductive degradation of sulfamethoxazole in aqueous solutions: Decomposition efficiency and toxicity assessment. J. Radioanal. Nucl. Chem. 2014, 301, 475–482. [CrossRef]

36. Galu, G.; Casay, T.; Patzay, G.; Csonka, E.; Wojnarovits, L.; Takacs, E. Oxidative and reductive degradation of sulfamethoxazole in aqueous solutions: Decomposition efficiency and toxicity assessment. J. Radioanal. Nucl. Chem. 2014, 301, 475–482. [CrossRef]
37. Tezge, A.; Sagi, G.; Kovacs, K.; Homlok, R.; Toth, T.; Mohacsi-Farkas, C.; Wojnarovits, L.; Takacs, E. Degradation of fluoroquinolone antibiotics during ionizing radiation treatment and assessment of antibacterial activity, toxicity and biodegradability of the products. Radiat. Phys. Chem. 2018, 147, 101–105.

38. Changorta, R.; Guin, J.P.; Dhir, A.; Varshney, L. Decomposition of antibiotic ornidazole by gamma irradiation in aqueous solution: Kinetic and its removal mechanism. Environ. Sci. Pollut. Res. 2018, 25, 32591–32602.

39. Nazari, E.; Suja, F. Effects of 17β-estradiol (E2) on aqueous organisms and its treatment problem: A review. Rev. Environ. Health 2016, 31, 465–491. [CrossRef] [PubMed]

40. Harries, J.E.; Runnalls, T.; Hill, E.; Harris, C.A.; Maddix, S.; Sumpter, J.P.; Tyler, C.R. Development of a reproductive performance test for endocrine disrupting chemicals using pair-breeding fathead minnows (Pimephales promelas). Environ. Sci. Technol. 2000, 34, 3003–3011. [CrossRef]

41. Kimura, A.; Taguchi, M.; Arai, H.; Hiratsuka, H.; Namba, H.; Kojima, T. Radiation induced decomposition of trace amounts of 17β-estradiol in water. Radiat. Phys. Chem. 2004, 69, 295–301. [CrossRef]

42. Ahn, B.Y.; Kang, S.W.; Yoo, J.; Kim, W.K.; Bae, P.H.; Jung, J. Identification of estrogenic activity change in sewage, industrial and livestock effluents by gamma-irradiation. Radiat. Phys. Chem. 2012, 81, 1757–1762. [CrossRef]

43. Ren, L.; Wu, M.; Xu, G.; Liu, N.; Bu, T.; Tang, L.; Wang, L.; Zhou, J. Electron Beam Radiolysis of 17beta-Estradiol in Aqueous Solutions. In Proceedings of the 2011 5th International Conference on Bioinformatics and Biomedical Engineering, Wuhan, China, 10–12 May 2011. [CrossRef]

44. Scherr, F.F.; Sarmah, A.K.; Di, H.J.; Cameron, K.C. Degradation and metabolite formation of 17beta-estradiol-3-sulphate in New Zealand pasture soils. Environ. Int. 2009, 35, 291–297. [CrossRef] [PubMed]

45. Fent, K.; Escher, C.; Caminada, D. Estrogenic activity of pharmaceuticals and pharmaceutical mixtures in a yeast reporter gene system. Reprod. Toxicol. 2006, 22, 175–185. [CrossRef] [PubMed]

46. Wu, M.H.; Li, J.L.; He, X.X.; Xu, G.; Ding, G.J.; Shi, W.Y. Radiation removal of synthetic estrogens in aqueous solution: Influence of reduction or oxidation system and toxicity test. Nucl. Sci. Tech. 2016, 27, 22. [CrossRef]

47. Fromme, H.; Kuchler, T.; Otto, T.; Pilz, K.; Muller, J.; Wenzel, A. Occurrence of phthalates and bisphenol A and F in the environment. Water Res. 2002, 36, 1429–1438. [CrossRef]

48. Staples, C.A.; Dorn, P.B.; Klecka, G.M.; O’Block, S.T.; Harris, L.R. A review of the environmental fate, effects, and exposures of bisphenol A. Environ. Sci. Technol. 2011, 45, 101–105. [CrossRef] [PubMed]

49. Nagel, S.C.; Bromfiesl, J.J. Bisphenol A: A Model Endocrine Disrupting Chemical with a New Potential Mechanism of Action. Endocrinology 2013, 154, 1962–1964. [CrossRef] [PubMed]

50. Peller, J.R.; Mezyk, S.P.; Cooper, W.J. Bisphenol A reactions with hydroxyl radicals: Diverse pathways determined between deionized water and tertiary treated wastewater samples. Res. Chem. Intermed. 2009, 35, 21–34. [CrossRef]

51. Peller, J.R.; Cooper, W.J.; Ishida, K.P.; Mezyk, S.P. Evaluation of parameters influencing removal efficiencies for organic contaminants in advanced oxidation processes. J. Water Supply Res. Technol.—AQUA 2011, 60, 69–78. [CrossRef]

52. Guo, Z.; Dong, Q.; Zhang, C. Gamma radiation for treatment of bisphenol A solution in the presence of different additives. Chem. Eng. J. 2012, 183, 10–14. [CrossRef]

53. Rivera-Utrilla, J.; Abdel Daim, M.M.; Sánchez-Polo, M.; Ocampo-Pérez, R.; López-Péñalver, J.J.; Velo-Gala, I.; Mota, A.J. Removal of compounds as plasticizers and herbicides from water by means of gamma irradiation. Sci. Total Environ. 2016, 569–570, 518–526. [CrossRef]

54. Xu, G.; Ren, H.; Wu, M.H.; Liu, N.; Yuan, Q.; Tang, L.; Wang, L. Electron-beam induced degradation of bisphenol A. Nucl. Sci. Tech. 2011, 22, 277–281.

55. Alcudia-Leon, M.C.; Lucena, S.; Cardenas, M.; Valcarcel, M. Determination of parabens in waters by magnetically confined hydrophobic nanoparticle microextraction coupled to gas chromatography/mass spectrometry. Microchem. J. 2013, 110, 643–648. [CrossRef]

56. Haman, C.; Dauchy, X.; Rosin, C.; Munoz, J.F. Occurrence, fate and behaviour of parabens in aquatic environments: A review. Water Res. 2015, 68, 1–11. [CrossRef]

57. Soni, M.G.; Carabin, I.G.; Burdock, G.A. Safety assessment of esters of p-hydroxybenzoic acid (parabens). Food Chem. Toxicol. 2005, 43, 985–1015. [CrossRef] [PubMed]

58. Routledge, E.J.; Parker, J.; Oдум, J.; Ashby, J.; Sumpter, J.P. Some alkyl hydroxyl benzoate preservatives (parabens) are estrogenc. Toxicol. Appl. Pharmacol. 1998, 153, 12–19. [CrossRef]

59. Angelini, G.; Bucci, R.; Colosimo, M.; Margonelli, A. Stability of methyl p-hydroxybenzoate (methylparaben) to gamma radiolysis. Radiat. Phys. Chem. 1998, 51, 77–83. [CrossRef]

60. Barrosiewicz, I.; Bojanowska-Czajka, A.; Trojanowicz, M. Application of ionizing radiation for radiolytic decomposition of methylparaben. INCT Annu. Rep. 2020, 62–68. Available online: www.ichtj.waw.pl/ichtj/publ/annual/anrep20.pdf (accessed on 28 October 2021).

61. Guin, J.P.; Bhardwaj, Y.K.; Varshney, L. Efficient degradation of butylparaben by gamma radiolysis. Appl. Radiat. Isot. 2017, 122, 21–27. [CrossRef]

62. Wang, S.; Wang, J.; Sun, Y. Degradation of chlorinated paraben by integrated irradiation and biological treatment process. J. Environ. Manag. 2017, 189, 29–35. [CrossRef]
90. Boiani, N.F.; Silva, V.H.O.; Garcia, V.S.G.; Del-Sole, S.V.; Borrely, S.I. Electron beam irradiation of pharmaceuticals aiming at toxicity reduction: A binary mixture of fluoxetine and propranolol. *Ecotoxicol. Environ. Contam.* 2019, 14, 53–58.

91. Acuna, V.; Ginebreda, A.; Mor, J.R.; Petrovic, M.; Sabater, S.; Sumpter, J.; Barceló, D. Balancing the health benefits and environmental risks of pharmaceuticals: Diclofenac as an example. *Environ. Int.* 2015, 85, 327–333. [CrossRef] [PubMed]

92. Capodaglio, A.G.; Bojanowska-Czajka, A.; Trojanowicz, M. Comparison of different advanced degradation processes for the removal of the pharmaceutical compounds diclofenac and carbamazepine from liquid solutions. *Environ. Sci. Pollut. Res.* 2018, 25, 27704–27723. [CrossRef]

93. O’Connor, N.; Dargan, P.I.; Jones, A.L. Hepatocellular damage from non-steroidal anti-inflammatory drugs. *Q. J. Med.* 2003, 96, 787–791. [CrossRef]

94. Gilbert, M.; Watson, R.T.; Virani, M.Z.; Oaks, J.L.; Ahmed, A.; Chaudhry, M.J.I.; Arshad, M.; Mahmood, S.; Ali, A.; Khan, A.A. Rapid population declines and mortality clusters in three Oriental white-backed vulture Gyps bengalensis colonies in Pakistan due to diclofenac poisoning. *Oryx* 2006, 40, 388–399. [CrossRef]

95. Vergili, I.; Kaya, Y.; Gönder, Z.B.; Boergers, A.; Tuerk, J. Occurrence and Prioritization of Pharmaceutical Active Compounds in Domestic/Municipal Wastewater Treatment Plants. *Bull. Environ. Contam. Toxicol.* 2019, 102, 252–258. [CrossRef] [PubMed]

96. Luo, Y.; Guo, W.; Ngo, H.H.; Nghiem, L.D.; Hai, F.I.; Zhang, J.; Liang, J.; Wang, X.C. A review on the occurrence of micropollutants in the aquatic environment and their fate and removal during wastewater treatment. *Sci. Total Environ.* 2014, 473, 619–641. [CrossRef] [PubMed]

97. Homlok, R.; Takacs, E.; Wojnarovits, L. Elimination of diclofenac from water using irradiation technology. *Chemosphere* 2011, 85, 603–608. [CrossRef]

98. Alkhuraiji, T.S. Advanced oxidation process based on water radiolysis to degrade and mineralize diclofenac in aqueous solution. *Sci. Total Environ.* 2019, 688, 708–717. [CrossRef] [PubMed]

99. Nisar, J.; Sayed, M.; Kgan, F.U.; Khan, H.M.; Iqbal, M.; Khan, R.A.; Anas, M. Gamma-irradiation induced degradation of diclofenac in aqueous solution: Kinetics, role of reactive species and influence of natural water parameters. *J. Environ. Chem. Eng.* 2016, 4, 2573–2584. [CrossRef]

100. Kimura, A.; Osawa, A.M.; Taguchi, M. Decomposition of persistent pharmaceuticals in waste water by ionizing radiation. *Radiat. Phys. Chem.* 2012, 81, 1508–1512. [CrossRef]

101. Yu, H.; Nie, E.; Xu, J.; Yan, S.; Cooper, W.J.; Song, W. Degradation of diclofenac by advanced oxidation and reduction process: Kinetic studies, degradation pathways and toxicity assessments. *Water Res.* 2013, 47, 1909–1918. [CrossRef] [PubMed]

102. Liu, G.; Luo, X.; Zheng, Z.; Zheng, B.; Zhang, J.; Zhao, Y.; Yang, X.; Wang, J.; Wang, L. Factors that have an effect on degradation of diclofenac in aqueous solution by gamma ray irradiation. *Environ. Sci. Pollut. Res.* 2011, 18, 1243–1252. [CrossRef] [PubMed]

103. Alkhuraiji, T.S. Advanced oxidation process based on water radiolysis to degrade and mineralize diclofenac in aqueous solution. *Sci. Total Environ.* 2019, 688, 708–717. [CrossRef] [PubMed]

104. Nisar, J.; Sayed, M.; Kgan, F.U.; Khan, H.M.; Iqbal, M.; Khan, R.A.; Anas, M. Gamma-irradiation induced degradation of diclofenac in aqueous solution: Kinetics, role of reactive species and influence of natural water parameters. *J. Environ. Chem. Eng.* 2016, 4, 2573–2584. [CrossRef]

105. Illes, E.; Takacs, E.; Dombi, A.; Gajda-Schrantz, K.; Racz, G.; Conter, K.; Wojnarovits, L. Hydroxyl radical induced degradation of ibuprofen. *Sci. Total Environ.* 2013, 447, 286–292. [CrossRef]

106. Guin, J.P.; Naik, D.B.; Bhardwaj, Y.K.; Varshney, L. Studies on oxidative radiolysis of ibuprofen in presence of potassium persulfate. *Radiat. Phys. Chem.* 2014, 100, 38–44. [CrossRef]

107. Deng, W.; Li, N.; Zheng, H.; Lin, H. Occurrence and risk assessment of antibiotics in river water in Hong Kong. *Ecotoxicol. Environ. Saf.* 2016, 125, 121–127. [CrossRef]

108. Tong, L.; Huang, S.; Wang, Y.; Liu, H.; Li, M. Occurrence of antibiotics in the aquatic environment of Jianghan Plain, central China. *Sci. Total Environ.* 2014, 497, 180–187. [CrossRef] [PubMed]

109. Ou, D.; Chen, B.; Bai, R.; Song, P.; Lin, H. Contamination of sulfonamide antibiotics and sulfamethazine-resistant bacteria in the downstream and estuarine areas of Jialing River in Southeast China. *Environ. Sci. Pollut. Res.* 2015, 22, 12104–12113. [CrossRef]

110. Zhang, R.; Tang, J.; Li, J.; Zheng, Q.; Liu, D.; Chen, Y.; Zou, Y.; Chen, X.; Luo, C.; Zhang, G. Antibiotics in the offshore waters of the Bohai Sea and the Yellow Sea in China: Occurrence, distribution and ecological risks. *Environ. Pollut.* 2013, 174, 71–77. [CrossRef] [PubMed]

111. Baran, W.; Adamek, E.; Sobczak, A.; Makowski, A. Photocatalytic degradation of sulfa drugs with TiO$_2$ Fe salts and TiO$_2$/FeCl$_3$ in aquatic environment-Kinetics and degradation pathway. *Appl. Catal. B* 2009, 90, 516–525. [CrossRef]

112. Kim, K.S.; Kam, S.K.; Sun, M.Y. Elucidation of the degradation pathways of sulfonamide antibiotics in a dielectric barrier discharge plasma system. *Chem. Eng. J.* 2015, 271, 31–42. [CrossRef]
116. Zhuan, R.; Wang, J. Enhanced mineralization of sulfamethoxazole by gamma radiation in the presence of Fe\textsubscript{3}O\textsubscript{4} as Fenton catalyst. Environ. Sci. Pollut. Res. 2019, 26, 27712–27725. [CrossRef]
117. Wan, Z.; Wang, J.L. Removal of sulfonamide antibiotics from wastewater by gamma irradiation in presence of iron ions. Nucl. Sci. Tech. 2016, 27, 104. [CrossRef]
118. Liu, N.; Huang, W.; Li, Z.; Shao, H.; Wu, M.; Lei, J. Radiolytic decomposition of sulfonamide antibiotics: Implications to the kinetics, mechanisms and toxicity. Sep. Purif. Technol. 2018, 202, 259–265. [CrossRef]
119. Kim, Y.Y.; Yu, S.; Lee, M.J.; Kim, T.H.; Kim, S.D. Radiolysis of selected antibiotics and their toxic effects on various aquatic organisms. Radiat. Phys. Chem. 2009, 78, 267–272. [CrossRef]
120. Lopez-Penalver, J.J.; Gomez-Pacheco, C.V.; Sanchez Polo, M.; Rivera Utrilla, J. Degradation of tetracycline in different water matrices by advanced oxidation/reduction processes based on gamma radiation. J. Chem. Technol. Biotechnol. 2013, 88, 1096–1108. [CrossRef]
121. Changotra, R.; Duin, J.P.; Khader, A.A.; Dhir, A. Radiolytic degradation of ornidazole in aqueous solution by electron beam irradiation: Implications to parameters, kinetics, toxicity and cost evaluation. J. Environ. Chem. Eng. 2020, 8, 104423. [CrossRef]
122. Siwek, M.; Edgock, T. Application of electron beam water radiolysis for sewage sludge treatment—a review. Environ. Sci. Pollut. Res. 2020, 27, 42424–42448. [CrossRef]
123. Trojanowicz, M.; Bobrowski, K.; Szreder, T.; Bojanowska-Czajka, A. Gamma-ray, X-ray and electron beam based processes. In Advanced Oxidation Processes for Wastewater Treatment; Academic Press: Cambridge, MA, USA, 2018; pp. 257–331. [CrossRef]