

Review

# Selected Micropollutant Removal from Municipal Wastewater

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**Abstract:** Micropollutants belong to various groups of chemicals. One of the most diverse and large group of them are pharmaceuticals. The presence of pharmaceutical residues in wastewater poses a significant challenge to water quality and environmental health. This paper provides an overview of recent advancements in the removal of pharmaceuticals from water, focusing on various treatment processes and their effectiveness in eliminating micropollutants. Through a review of the literature, including studies on ozonation, UV irradiation, sulfate radical-based technologies, and photocatalytic processes, insights into degradation mechanisms and optimal conditions for their removal are synthesized. Additionally, with new legislation mandating the monitoring of selected micropollutants and the implementation of quaternary treatment in wastewater treatment plants, the paper discusses prospects for future research and recommendations for effective pharmaceutical removal. Key actions include conducting comprehensive laboratory and pilot trials, implementing quaternary treatment of wastewater, continuously monitoring water quality, investing in research and development, and promoting collaboration and knowledge sharing among stakeholders. By embracing these strategies, we can work towards safeguarding water resources and protecting public health from the adverse effects of pharmaceutical contamination.

**Keywords:** micropollutants; municipal wastewater; pharmaceuticals; quaternary treatment; removal of pollutants



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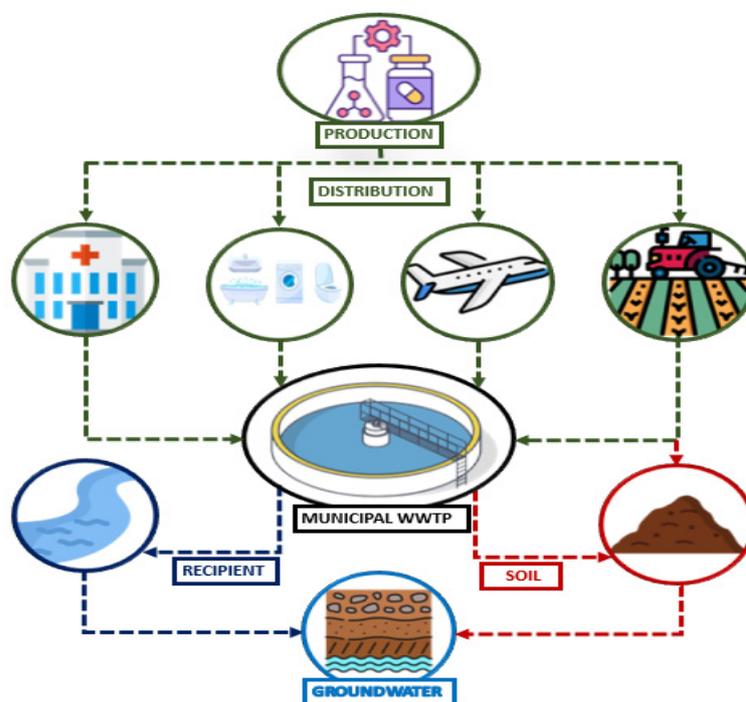
## 1. Introduction

The European Commission proposal [1,2] for the revision of the Council Directive of 21 May 1991, on the treatment of municipal wastewater “Urban Wastewater Treatment Directive—UWWTD” [3] accentuates not only the protection of the environment but also the protection of people’s health.

Serious problems include the widespread occurrence and presence of micropollutants (MPs) and new emerging substances, the so-called “emerging pollutants” (EPs) in the aquatic environment [4]. Micropollutants are characterized by adverse effects on aquatic ecosystems and human health, even when present at low concentrations ( $\mu\text{g/L}$  to  $\text{ng/L}$ ). These effects may include acute and chronic toxicity, bioaccumulation and bioconcentration in food chains, genotoxicity, or endocrine effects [5].

Micropollutants enter the water environment mainly from wastewater treatment plants (WWTPs), as current treatment technologies are not efficient enough to remove them (Figure 1). Micropollutants enter municipal wastewater from a variety of sources, including activities such as bathing, cleaning, washing, toilets, and medication use, which include both parent compounds and their by-products of metabolic transformation. Due to the complex chemical composition of these substances, it is necessary to use technologies

aimed at their removal from wastewater. In addition, research is important to know the potential consequences of the presence of micropollutants in aquatic ecosystems and their penetration into groundwater [6].



**Figure 1.** Pathways of the distribution of selected micropollutants (MPs) in the environment.

Emerging pollutants can be synthetic or naturally occurring chemicals that are not routinely monitored in the environment but have the potential to enter the environment in the ways mentioned above and cause adverse ecological and health effects [7]. In some cases, it is possible that the release of new pollutants into the environment has been going on for a long time, but their identification was only possible with the development of new detection methods. New sources of emerging pollutants can be created by the synthesis of new chemical compounds or changes in the use and disposal of existing chemicals [8].

Decision [9] contains a list (“watch list”) of selected substances for monitoring throughout the European Union. In addition to the substances previously recommended for inclusion in Directive 39/2013/EU (diclofenac and the synthetic hormone 17- $\alpha$ -ethinylestradiol (EE2) and the natural hormone 17- $\beta$ -estradiol (E2)), the first list of 10 substances/groups of substances also refers to three macrolide antibiotics (azithromycin, clarithromycin, and erythromycin), another natural hormone (estrone (E1)), some pesticides (methiocarb, oxadiazon, imidacloprid, thiacloprid, thiamethoxam, clothianidin, acetamiprid, and trialate), a UV filter (2-ethylhexyl-4-methoxycinnamate), and an antioxidant (2,6-di-*tert*-butyl-4-methylphenol) commonly used as a food additive. The proposal [1] for the revision of the Council Directive of 21 May 1991, on the treatment of municipal wastewater “Urban Wastewater Treatment Directive—UWWTD” includes explicitly 12 micropollutants (10 pharmaceuticals and 2 anti-corrosives) that will be discussed in this review paper.

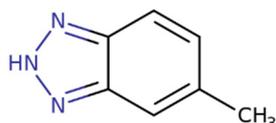
The rapid growth of pharmaceutical consumption in recent years has led to an increase in the presence of these compounds in wastewater. However, their widespread use has inadvertently led to the introduction of pharmaceuticals into recipients through the discharge of treated or untreated wastewater. As a result, trace amounts of these compounds can be found anywhere in water bodies, and they can disrupt the balance of aquatic ecosystems and pose potential risks to organisms. In addition, the persistence of certain pharmaceutical products amplifies concerns about long-term environmental consequences [10]. They could at even very small concentrations promote the development of resistance genes in the envi-

ronment [11]. Among the more important sources of these genes are the effluents of treated water and waste sludge from municipal sewage treatment plants or plants for the treatment of wastewater from animal farms. When antibiotics enter the environment, they also have a direct bactericidal and bacteriostatic effect, which can also mean the disappearance of a certain population of microorganisms and thus their role in the ecosystem.

The presence of pharmaceuticals in wastewater is mainly attributed to their incomplete metabolism and excretion by humans and animals. Traditional wastewater treatment plants, designed to deal with organics, nitrogen, and phosphorus pollutants in municipal WWTP, may not be equipped to effectively remove these complex compounds. Pharmaceutical compounds can be transformed during the wastewater treatment process, which creates new transformation products. These products exhibit higher persistence and biological activity compared to the parent compounds.

The proposal of the European Commission [1,2] for the revision of the Council Directive of 21 May 1991 on the treatment of municipal wastewater “Urban Wastewater Treatment Directive—UWWTD also includes requirements for the implementation of the quaternary treatment of 12 selected MPs in municipal wastewater treatment plants (MWWTP). The main goal of the paper was to provide information about these MPs, their basic characteristics, sources, and impacts on human health and the environment, as well as a brief overview of the know-how on treatment methods.

In the proposal of the revised directive [1] in Appendix No. 1 on p. 8 under Category (b) paragraph (iv) a mixture of 4-methylbenzotriazole (CAS number 29878-31-7) and 6-methylbenzotriazole (CAS number 136-85-6) is mentioned. Only 5-methylbenzotriazole can be traced under the registration CAS number 136-85-6. No reliable literature is available for the compound 6-methylbenzotriazole, while for the compound 5-methylbenzotriazole, a lot of literature is available. During a more detailed search, it was found out that in the directives of the European Parliament and the Council, there are chemical substances listed according to the European Chemicals Agency (ECHA) [12], where 6-methylbenzotriazole (CAS number 136-85-6) can be found. Based on the structural formula presented ([13], Figure 2), the formula belongs to 5-methylbenzotriazole.



**Figure 2.** 5-methylbenzotriazole—5MeBZT [13].

In the literature [14] other names according to IUPAC are also given. Likewise, on the ECHA website ([12], for example, in the “Particle size distribution” section, it is named as 5-methylbenzotriazole. Similarly, in the section “Biodegradation in water: screening tests: in the section “Remarks” there is information about 5-methylbenzotriazole. From this one could conclude that it could be the same compound that has several synonyms/synonymous names but has one CAS registration number. Based on the above, we also included 5-methylbenzotriazole, or a mixture of 4-methylbenzotriazole (CAS 29878-31-7) and 5-methylbenzotriazole (CAS No 136-85-6) in the evaluated micropollutants.

The proposed directive [1] lists two groups of pollutants depending on their degradability (very easy and easy to decompose). In Table 1, there are also given information on the types (pharmaceutical and anti-corrosion substances), the specification of their functions, and CAS numbers.

The proposal of the revised directive [1] requires individual EU member states to define areas in which the concentration or accumulation of micropollutants in question poses a risk to human life or the environment. The removal of these 12 micropollutants will be carried out in quaternary treatment in the following time horizons:

- By 2035, all WWTPs > 100,000 PE must be equipped with a quaternary level of treatment, and at least 50% of the WWTPs > 10,000 PE must also have quaternary treatment.

- By 2040, all WWTPs > 10,000 PE in the areas where micropollutants pose a risk to human health or the environment should be equipped with a quaternary treatment stage. For quaternary treatment, 80% removal efficiency of at least 6 of the 12 micropollutant compounds listed above is required.

**Table 1.** Two groups of pollutants according to directive proposal [1].

Group	Compound	Label	Function	CAS No.
I—Very easily decomposed	Amisulpride	AMI	Anti-psychotic	71675-85-9
	Carbamazepine	CAR	Anti-epileptic drug	298-46-4
	Citalopram	CIT	Antidepressant	59729-33-8
	Clarithromycin	CLA	Antibiotic	81103-11-9
	Diclofenac	DIC	Anti-rheumatic, analgesic	15307-86-5
	Hydrochlorothiazide	HCH	Diuretic	58-93-5
	Metoprolol	MET	Beta-blocker (heart)	37350-58-6
	Venlafaxine	VEN	Antidepressant	93413-69-5
II—Easily removable	Benzotriazole	BZT	Anti-corrosive	95-14-7
	Candesartan	CAN	Anti-hypertension	139481-59-7
	Irbesartan	IRB	Anti-hypertension	138402-11-6
	4-methylbenzotriazole	4MeBZT		29878-31-7
	6-methylbenzotriazole	6MeBZT	Anti-corrosive	136-85-6
	5-methylbenzotriazole	5MeBZT		136-85-6

In recent years, different approaches have been investigated for the effective removal of these pharmaceutical compounds from wastewater. With the ongoing amendment of the EU legislation on urban wastewater treatment [1], stricter requirements for pollutant removal are expected to drive the need for innovative environmental technologies. Diverse pollutants in urban wastewater, including micropollutants, require advanced treatment technologies that integrate biological, physical, and chemical processes [15]. Various advanced treatment processes have been developed to address the challenges associated with the removal of pharmaceuticals and other micropollutants from wastewater. These methods, including ozonation, UV/O<sub>3</sub> systems, UV/H<sub>2</sub>O<sub>2</sub> systems, UV/chlorine systems, photocatalysis, Fenton and Fenton-like processes, and persulfate (PS)-based AOP processes, represent innovative approaches that go beyond the conventional wastewater treatment. This review article is focused on the processes of the removal of the selected micropollutants, their sources, and their impacts on human health and the environment. Removal processes, reactors, and technologies are described, and new challenges are emphasized in the context of the proposed directive [1].

## 2. Selected Micropollutants

### 2.1. Characterization of Selected Pharmaceuticals

Amisulpride is categorized as an atypical anti-psychotic and is used to treat psychosis associated with schizophrenia as well as manic episodes in individuals with bipolar disorder [16]. It is considered a contaminant capable of entering the aquatic environment and potentially leaching into groundwater. Furthermore, the confirmation of the formation of its distinct non-biodegradable N-oxide product during treatment with the current methods underscores the need for advanced treatment solutions [17].

Carbamazepine is a commonly prescribed anti-epileptic drug, whose frequent presence in the aquatic environment has raised concerns about its possible effect on aquatic organisms. Apart from being highly effective in treating psychomotor and grand mal seizures associated with epilepsy and bipolar disorders, this medication also demonstrates a prolonged half-life in the environment ( $82 \pm 11$  days), which places it among the most persistent drugs in the ecosystem. The persistence of carbamazepine in wastewater is attributed to the limited effectiveness of the current wastewater treatment processes in removing it [18]. The presence of carbamazepine has been shown to induce behavioral

changes in a variety of aquatic organisms. These changes include reduced stress responses, increased swimming speed, prolonged feeding, as well as modifications to physiological processes such as the reproductive system and hormone level [19].

Citalopram, an antidepressant, is classified as a selective serotonin reuptake inhibitor, which is commonly prescribed for mental disorders such as depression due to its minimal likelihood of interaction with other medications [20]. However, current WWTPs struggle to effectively remove more than 80% of this compound. As a result, citalopram is commonly found in surface waters worldwide, generally at concentrations ranging from ng/L to low µg/L. The accumulation of citalopram was evaluated in the liver, kidney, brain, and muscle tissues of various fish species. Citalopram exhibits neurotoxic effects on non-target aquatic animals, including fish [21].

Clarithromycin, an antibiotic, is used to treat chest infections, skin problems, and various infections. In addition, it is used to treat *Helicobacter pylori* infections, the bacterium responsible for causing ulcers [22]. The use of antibiotics leads to a decrease in the population of plankton and algae, thereby changing the composition of the aquatic community. In addition, antibiotics have the potential to accumulate in the food chain, posing a threat to human health. However, the primary problem associated with antibiotic pollution is the increased risk of the resistance of microorganisms to antibiotics [23].

Diclofenac is used for pain relief as a non-steroidal anti-inflammatory drug. Approximately 75% of the administered diclofenac reaches the water and soil environment, where its hydrophilic character and stability contribute to prolonged persistence. Increased exposure to diclofenac not only affects the health of aquatic organisms, higher plants, and mammals but also poses a significant threat, like clarithromycin. The presence of diclofenac and its metabolites in the environment may cause synergistic interactions with existing contaminants, increasing the risk of drug-resistant strains and the emergence of new contaminants [24].

Hydrochlorothiazide, a diuretic prescribed for hypertension and edema caused by fluid retention, undergoes minimal metabolism. At least 61% of the substance is excreted unchanged in the urine, with partial elimination in the feces, which eventually enters the water cycle [25]. Exposure to hydrochlorothiazide has the potential to disrupt the endocrine system of fish, affecting their reproductive processes and developmental patterns. In addition, the presence of hydrochlorothiazide in water sources may contribute to antimicrobial resistance, intensifying the challenges of treating infections in the future [26].

Categorized as a  $\beta$ -blocker within a class of drugs widely used to treat cardiovascular disorders such as abnormal heart rhythms, high blood pressure, and angina pectoris, metoprolol may have adverse effects on aquatic organisms. These effects may include disturbances in testosterone levels, reduced fertility and reproductive rate, and the induction of abnormal behavior [27].

Venlafaxine, a commonly prescribed antidepressant, is widely used to treat major depressive disorder, panic disorder, and anxiety. This antidepressant shows a high persistence in surface waters, with concentrations already detected in the range of mg/L. The presence of venlafaxine in municipal wastewater is associated with profound behavioral and physiological effects on aquatic organisms [28]. It affects the survival rate, reproduction rate, and behavior of aquatic vertebrates and invertebrates [29]. Fish exposed to the substance showed a remarkable increase in mortality, developmental delays, morphological abnormalities, and pathological changes in the brain, heart, cranial and caudal kidneys. In addition, changes in the activity of antioxidant enzymes and an increased lipid peroxidation were evident, even at the lowest concentrations examined [30].

Candesartan and irbesartan are categorized within a class of medications known as angiotensin-II receptor antagonists, commonly prescribed for the treatment of high blood pressure (hypertension) [31]. Short-term exposure to candesartan can induce acute toxicity in aquatic organisms, resulting in behavioral changes, reduced growth rate, and potential mortality. Long-term exposure to candesartan has the potential to interfere with

the endocrine systems of aquatic species, affecting reproduction, development, and overall ecosystem health [32].

## 2.2. Characterization of Selected Anti-Corrosives

H-benzotriazole (BZT) is a very dangerous and frequently used compound with carcinogenic and mutagenic effects on living organisms. It is used as an anti-corrosive in industrial operations, in the production of detergents, biocides, pharmaceuticals, rubber, tires, in cooling systems, and in the production of de-icing agents. Its derivatives are also used as UV stabilizers in paints, plastics, sunscreen preparations, and films. It is also used as an additive to petroleum products (hydraulic fluids and lubricants) [33]. BZT and its methylated analogs (tolyltriazole, TTri) are used as corrosion inhibitors. They are used in many industrial applications, in homes as part of dishwashing detergents, and as part of de-icing fluids used in airports and elsewhere. Its TTri-isomers (4-TTri) are typical polar trace pollutants and are poorly degradable [34].

Benzotriazoles exhibit significant solubility in water (28 g/L), and their stability, resistance to biodegradation, and limited sorption contribute to their presence in the environment in substantial quantities, including surface waters such as rivers and lakes, as well as soils where they may persist for extended periods of time [35–37]. Benzotriazole is categorized as harmful to aquatic organisms and can lead to adverse long-term effects in aquatic environments [35,36,38,39].

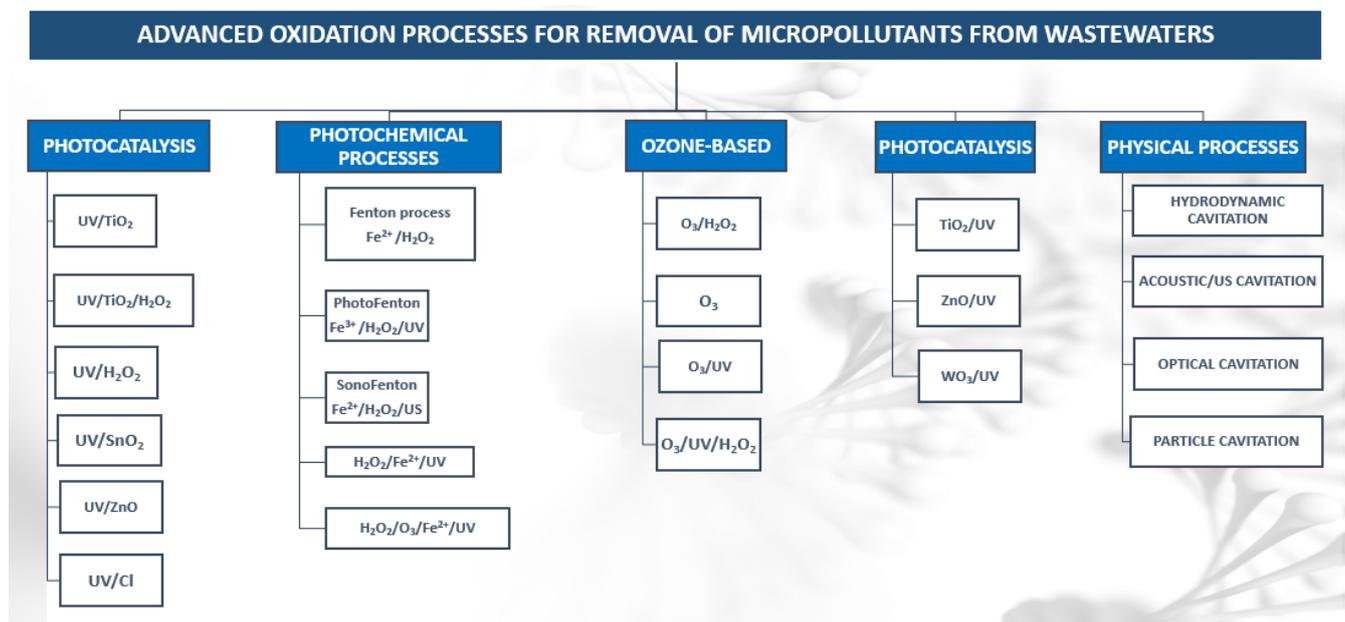
Methyl-substituted benzotriazoles are commonly used as substitutes for methyl-benzotriazoles (MeBZTs). Due to their high hydrophilicity and insufficient removal in wastewater treatment plants (WWTPs), these compounds have been widely detected in the aquatic environment, with concentrations typically ranging from tens of ng/L to tens of µg/L. Significant residual levels of these compounds have been found in plants, fish, air, tap water, and human urine, indicating potential risks to various organisms. Although the reported acute toxicity of these compounds is generally low, some observed sublethal effects, including endocrine disruption, hepatotoxicity, neurotoxicity, and the potential to promote the development of endometrial carcinoma, continue to be of increasing concern [40]. Recent research indicates that both BT and MeBZT exhibit toxicity to the luminescent bacteria used in the Microtox<sup>®</sup> assay [41].

## 3. Treatment Processes

Various advanced treatment methods have been developed to solve the problems associated with the removal of micropollutants. These methods go beyond the current wastewater treatment and include advanced oxidation processes (AOPs), photocatalysis, and other innovative technologies (Figure 3). Another modified method is the process of transforming sewage sludge into biochar to eliminate water contaminants. However, the understanding of sludge-derived biochar (SDB) for wastewater treatment remains restricted, lacking a comprehensive overview of how the modifications affect the mechanism of SDB adsorption or the catalytic removal of aqueous contaminants [42]. The pyrolysis of sewage sludge offers several beneficial outcomes, including the elimination of pathogens and gaseous emissions, as well as the recovery of energy- and nutrient-rich solid by-products suitable for soil improvement. The resulting biochar has potential for agricultural applications [43]. Understanding and implementing these advanced methods are essential steps towards achieving sustainable and comprehensive solutions for the removal of micropollutants from wastewater. Effective methods were developed for the removal of the above-mentioned pharmaceuticals and anti-corrosives.

Advanced oxidation processes (AOPs) have been proven to be effective techniques for the degradation and removal of contaminants from water systems. It is noteworthy that AOPs exceed the efficiency of individual oxidation processes. As a result, integrated systems, such as combining UV radiation with ozone, hydrogen peroxide and persulfate (PS), titanium dioxide (TiO<sub>2</sub>), and Fe(III), find application in the removal of micropollutants [44]. These systems show remarkable efficiency in treating drinking water containing organic

micropollutants while actively promoting their degradation. AOPs act as strong oxidizing agents through the formation of a hydroxyl group by combining free radicals [45].



**Figure 3.** Advanced oxidation processes for the removal of MPs.

AOPs offer several advantages for the treatment of organic contaminants in wastewater. First, they boast fast reaction rates for most organic pollutants, ensuring efficient degradation in a relatively short time frame. In addition, AOPs facilitate the degradation of pollutants rather than their concentration as is the case in membrane or adsorption systems, resulting in a more thorough removal from wastewater. These processes also do not generate solid residues, reducing the need for additional waste management measures. AOPs have a small footprint, making them suitable for implementation in a variety of wastewater treatment facilities. They can even completely mineralize most contaminants and ensure their transformation into harmless by-products. However, AOPs have some disadvantages. They may produce unknown products during the oxidation process, which may require further analysis to ensure the safety of the treated water. The water matrix can reduce their efficiency causing different interferences as well as the presence of residual oxidants can be a problem that requires careful monitoring and pretreatment measures to mitigate their effects on treatment efficiency [46].

Another important parameter is the consideration of the costs for individual processes. A recent study compared the energy costs of basic AOP processes using the electrical energy per order (EEO) parameter. Energy costs for O<sub>3</sub>/UV, H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub>/UV, and Cl<sub>2</sub>/O<sub>3</sub>/UV showed significantly lower costs than UV/H<sub>2</sub>O<sub>2</sub> and UV/Cl<sub>2</sub>, and ozonation appeared to be the most energy-efficient process [47].

From comparing the costs of six processes, the authors of [48] evaluated that the energy efficiency increased in the following order: O<sub>3</sub> < O<sub>3</sub>/UV ~ Cl<sub>2</sub>/O<sub>3</sub>/UV < H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub>/UV < UV/H<sub>2</sub>O<sub>2</sub>.

### 3.1. Ozonation Process

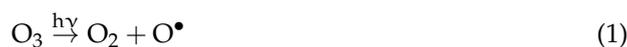
Ozone (O<sub>3</sub>) serves as a strong oxidizing agent to rapidly degrade MPs, especially those with available amino groups, double bonds, or aromatic groups [49]. Ozonation is strongly recommended for the removal of the organic MPs resistant to biological degradation. Dissolved ozone reacts with the most persistent MPs and its effectiveness depends on the content of the organic substances in wastewater [45].

The ozone reaction produces a secondary oxidant, the hydroxyl radical ( $\text{HO}^\bullet$ ), which enhances MP removal. The efficiency of ozonation is affected by the pH of the wastewater [50]. Low pH favors the direct ozone reaction, while high pH leads to the decomposition of ozone, producing  $\text{HO}^\bullet$  radicals. These radicals react non-selectively with trace organic compounds in wastewater. The transformation of MPs depends on their chemical structure, with ozone preferentially reacting with electron-rich groups such as phenols, amines, and carbon-carbon double bonds. The MPs with low ozone reactivity are removed by the hydroxyl radical mechanism, increasing biodegradability by converting them into simpler 3.1 molecules for subsequent biological treatment [45].

As stated above, ozone interacts with various MPs. However, due to the selective oxidation behavior between ozone and pollutants, the degradation of certain organic pollutants tends to be slow, leading to incomplete pollutant removal or the formation of toxic intermediates. Moreover, during the decomposition of certain organic pollutants by ozone, intermediates such as carboxylic acids and aldehydes may accumulate, which do not further react with ozone, reducing the efficiency of mineralization [51]. In addition, the limited solubility of ozone in water leads to inefficient use, which increases operating costs. The formation of disinfection by-products (DBPs) also represents a significant challenge that must be addressed when implementing ozone-based treatment processes [52]. Various AOPs have been modified to solve the problems of low ozone utilization efficiency and the ineffective mineralization of organic pollutants. These include methods such as the  $\text{O}_3/\text{UV}$  process, the  $\text{O}_3/\text{H}_2\text{O}_2$  process, and the combinations of ozone with biological treatment or other AOPs [53].

### 3.2. The UV/ $\text{O}_3$ System

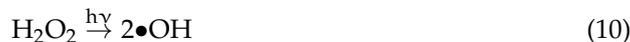
Ozonation, when used alone, offers several advantages over the current chemical oxidants such as chlorine or chlorine dioxide. However, it fails to create a sufficient concentration of hydroxyl radicals to achieve the complete mineralization of organic compounds. This limitation is attributed to the low kinetic constant of the direct ozone-pollutant reaction [54]. The reaction mechanism of the  $\text{O}_3/\text{UV}$  process to degrade organic pollutants in the environment can be primarily categorized into three phases: first, the direct oxidation and degradation of pollutants by  $\text{O}_3$  molecules; second, the UV-induced photodegradation of pollutants; and finally guiding  $\text{O}_3$  molecules by UV to generate  $\bullet\text{OH}$  for indirect pollutant oxidation. The generation of  $\bullet\text{OH}$  in the system can be described with the following reactions (1)–(9) [55]:



The process shows high oxidation capacity, no waste residues, and environmental friendliness. However, incompletely degraded MPs can produce toxic pollutants such as bromate able to induce kidney cancer in animals in lab tests [56]. If the concentration in the water exceeds  $50 \mu\text{g}/\text{L}$ , the question of bromate formation must be considered when applied to drinking water treatment [55].

### 3.3. The UV/H<sub>2</sub>O<sub>2</sub> System

The UV/H<sub>2</sub>O<sub>2</sub> processes use ultraviolet radiation to cleave the O–O bond in hydrogen peroxide and generate the hydroxyl radical (HO•) according to the reaction (10) [57].



Also, HO<sub>2</sub>, which is in an acid–base equilibrium with H<sub>2</sub>O<sub>2</sub> absorbs the UV radiation and produces HO• radicals (Equations (11) and (12)) [57].



Major design and operational factors include H<sub>2</sub>O<sub>2</sub> dosage, type and power of UV lamps, the reactor contact time, and control mechanisms such as pH and temperature. The elimination effectiveness of each pollutant relies on various factors, including the initial pollutant concentration, the pH of the system, and the quantity of H<sub>2</sub>O<sub>2</sub> applied [58]. Determining the optimum dose of H<sub>2</sub>O<sub>2</sub> for individual water sources is usually based on bench and pilot scale assessments, which are commonly estimated to be twice the TOC and not less than 1 to 2 mg/L [59]. The addition of a catalyst has the potential to increase the removal rate. The incorporation of bicarbonate or carbonate into the UV/peroxide system as a catalyst represents a promising approach to increase the removal time, efficiency, and the rate of the oxidation of organic compounds [58].

This process can generate larger amounts of OH radicals in comparison to the UV/O<sub>3</sub> process for the same amount of energy. However, due to interfering effects in water, the theoretical yield may be reduced below the value achievable by the H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub> process. Additionally, the presence of residual H<sub>2</sub>O<sub>2</sub> in the water may require removal downstream of the process. In summary, it is important to consider factors such as water composition, treatment goals, UV dosage, and cost [59].

### 3.4. The UV/Chlorine System

The UV/chlorine process serves as an alternative to the UV/H<sub>2</sub>O<sub>2</sub> process due to the higher UV absorbance and chlorine quantum yield compared to H<sub>2</sub>O<sub>2</sub>. In traditional AOPs, the primary radical is HO•, which plays a key role in the degradation of pollutants in water treatment. The UV/chlorine process introduces additional radicals due to the combination of UV light and chlorine such as HO• and reactive chlorine species (RCS), thus expanding the range of reactive species available for micropollutant degradation. The UV photolysis of HOCl and OCl<sup>−</sup> creates the primary radicals HO• and Cl•. These primary radicals then transform into secondary radicals (ClO• and Cl<sub>2</sub><sup>−</sup>•).



ClO• is generated through the interaction of HO•/Cl• and HOCl/OCl<sup>−</sup>, with second-order rate constants (k) ranging from (2.0–8.8) × 10<sup>9</sup> M<sup>−1</sup>s<sup>−1</sup>. Cl<sub>2</sub><sup>−</sup>• is produced when Cl• reacts with chloride ions (Cl<sup>−</sup>), with a rate constant of 6.5 × 10<sup>9</sup> M<sup>−1</sup>s<sup>−1</sup>, given that Cl<sup>−</sup> is consistently present in both free chlorine solutions and water environments. Notably, Cl• undergoes a rapid conversion to HO• through its reaction with H<sub>2</sub>O/OH<sup>−</sup> to initially form ClOH<sup>−</sup>• (Equation (14)). Subsequently, the equilibrium tends to favor the generation of HO• over Cl•.

In addition to RCS and HO•, atomic oxygen (O(3P)) is produced through the UV-induced breakdown of OCl<sup>−</sup>. It then rapidly combines with O<sub>2</sub> to form ozone (O<sub>3</sub>). The formation of O<sub>3</sub> is influenced by the wavelength of UV radiation, being minimal at 254 nm but gaining significance beyond 320 nm. Consequently, the involvement of O<sub>3</sub> becomes

more pronounced when employing UVA or polychromatic UV for the activation of free chlorine, contrasting with low-pressure UV systems. UV/chlorine offers several disinfection barriers in the treatment of drinking water and residual protection in water distribution systems. Importantly, it eliminates the need to cool residual oxidants as required in UV/H<sub>2</sub>O<sub>2</sub> AOPs [60–62].

### 3.5. Photo(cata)lysis

Photocatalysis refers to the process that occurs when a semiconductor material such as TiO<sub>2</sub>, ZnO<sub>2</sub>, SnO<sub>2</sub>, WO<sub>3</sub>, or Al<sub>2</sub>O<sub>3</sub> initiates a series of redox reactions in the presence of light. One of the main results of photocatalysis is the formation of highly toxic intermediates that further contribute to environmental contamination [63].

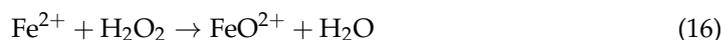
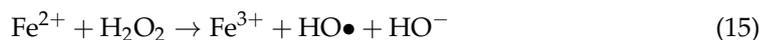
Titanium dioxide (TiO<sub>2</sub>) is a common and effective catalyst due to its stability, cost-effectiveness, and proven effectiveness [54]. The first reaction of the photocatalytic process is the absorption of UV light into the catalyst and the formation of electron–gap pairs. In environmental applications, photocatalytic processes are carried out in conditions where oxygen is present, and it is adsorbed onto the surface of the catalyst. Electrons reduce the oxygen adsorbed on the TiO<sub>2</sub> surface, thereby forming the superoxide radical ( $\bullet\text{O}_2^-$ ). This means that these sites become capable of oxidizing water into hydroxyl radicals, which ultimately oxidize organic matter. When organic matter is adsorbed on the catalyst surface, it can be directly oxidized due to electron transfer from the catalyst itself. The main advantage of these AOPs is that they can be operated under elevated pressure and at room temperature, with the option of using sunlight. The low price and the possibility of recycling the catalyst are also advantages. The special requirements and at the same time the shortcomings of this technique are that it is necessary to ensure uniform irradiation over the entire surface of the catalyst and to separate the catalyst from the suspension after the reaction is complete. TiO<sub>2</sub> is particularly effective as a photocatalyst in the field of pesticide oxidation due to its low price, non-toxicity, high oxidation capacity, and the possibility of immobilization on various surfaces. The latter avoids the separation of the catalyst from the suspension [64].

Stannic oxide nanoparticle functionalized with gallic acid has been shown to be a promising photocatalyst due to its high oxidation potential, photo absorption ability, surface reactivity, chemical inertness, relative nontoxicity, and long-term photochemical stability [65]. Disadvantages, however, include the difficulty in achieving uniform radiation over the entire catalyst surface on a larger scale and the need for a subsequent separation treatment to regenerate the catalyst, which increases the total cost of the process [54].

### 3.6. Fenton and Fenton-like Processes

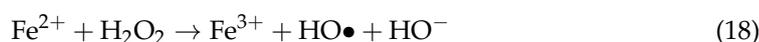
Fenton, Fenton-like processes, and Fenton's reagent are widely used to remove organic pollutants from industrial wastewater. The Fenton process is used to treat wastewater, municipal sludge, and contaminated soil with the aim of reducing toxicity, COD, and BOD and removing unpleasant odors. Fenton's reagent is most effective as a pretreatment method for COD values larger than 500 mg/L. As the concentration of pollutants in the wastewater decreases, so does the selectivity of the reaction [66].

The classic Fenton reaction represents the reaction of an iron salt with hydrogen peroxide, in which two different mechanisms are currently assumed, namely the formation of a hydroxyl radical (Equation (15)) or ferryl FeO<sup>2+</sup> (Equation (16)).



The reaction requires large amounts of dissolved iron salts, which makes the process more expensive. In addition, the EU water quality directive allows only small concentrations of dissolved iron in treated water, which means that the Fenton process must in some cases be followed by a process to remove iron from the water. This is usually

a physico-chemical process of coagulation and flocculation, which again produces large amounts of iron-containing sludge. These disadvantages of the process are the driving force behind the development of improved methods which, with a reduced iron concentration in the solution, still ensure sufficient oxidation efficiency. Among the improvements, the first concerns techniques that accelerate the formation of  $\text{Fe}^{2+}$  ions, which are crucial in the breakdown of hydrogen peroxide and thus the formation of hydroxyl radicals. Next is the combination of the Fenton process with UV light, which is called the photo-Fenton process, where the  $\text{Fe}^{3+}$  produced by the Fenton reaction is photoreduced to  $\text{Fe}^{2+}$  in the aqueous environment, which allows the continuation of the Fenton reaction and, in addition, the photoreduction of  $\text{Fe}^{3+}$  also generates the reactive  $\text{HO}\bullet$  radical. The reduction of  $\text{Fe}^{3+}$  back to  $\text{Fe}^{2+}$  can occur, albeit at a significantly slower rate compared to the production of  $\text{Fe}^{3+}$  from  $\text{Fe}^{2+}$  (Equations (17)–(19)). If the pH increases, the formed  $\text{Fe}^{3+}$  can also precipitate as oxyhydroxides [67].



The development of a heterogeneous process with a solid catalyst has made considerable progress in recent years. The use of a highly active, stable solid catalyst reduces the amount of  $\text{Fe}^{2+}$  ions in the solution and improves catalyst regeneration and reuse. This alternative process is labeled as the heterogeneous Fenton process. The last option under development is the combination of Fenton's reagent and electric current, which is called the electro-Fenton process, in which  $\text{H}_2\text{O}_2$  is produced in situ from oxygen and simultaneously  $\text{Fe}^{3+}$  is reduced to  $\text{Fe}^{2+}$  (Equations (20)–(22)) [68].



The iron salt-catalyzed production of hydroxyl radicals from hydrogen peroxide reaches its maximum in acidic conditions, at pH values between 3 and 5. Fenton's reagent has an oxidative effect on many organic substances, both aromatic (phenols, polyphenols, etc.) and aliphatic (alcohols, aldehydes, etc.). The mechanism of the oxidation of organic substances by Fenton's reagent is very complex and has not yet been studied in detail [69].

Without the presence of iron ions, hydroxyl radicals are not formed. As the concentration of iron ions increases, the rate of the oxidation of organic substances also increases, but only up to a certain limit. From then on, further increasing the iron ion concentration no longer increases the reaction rate. For most industrial applications, it does not matter whether  $\text{Fe}^{2+}$  or  $\text{Fe}^{3+}$  is used; the catalytic process continues as long as hydrogen peroxide and organic matter are present in the solution. However, if low doses of Fenton's reagent are added (<10–25 mg/L  $\text{H}_2\text{O}_2$ ), ferrous iron may be a more favorable option. High concentrations of peroxide can lead to the neutralization of hydroxyl radicals after reactions [54].

The rate of Fenton oxidation increases with temperature, and the treatment effect is most visible at temperatures around 20 °C. As the temperature increases between 40 and 50 °C, the effectiveness of the reagent decreases due to the accelerated decomposition of peroxide into oxygen and water. In the industrial applications, most processes take place between 20 and 40 °C [66].

### 3.7. Persulfate-Based AOP Processes

Persulfate (PS) in the context of advanced oxidation processes is usually referred to as peroxymonosulfate (PMS,  $\text{HSO}_5^-$ ) and peroxydisulfate (PDS,  $\text{S}_2\text{O}_8^{2-}$ ). While PMS alone can efficiently degrade certain electron-rich compounds, its effectiveness is greatly reduced

for other compounds without proper activation. Therefore, for the complex removal of contaminant mixtures, activation methods for the formation of highly reactive substances are necessary.

The activation approaches for PS can be broadly divided into two groups: catalyst-free and catalyst-based methods. Catalyst-free activation depends on external energy sources such as ultraviolet radiation, heat, ultrasound, and electricity, as well as certain chemicals such as alkaline solutions, quinones, and halides. However, this approach often requires high energy input, incurs significant equipment costs, and has a low lifetime. Alternatively, chemical activation processes, while avoiding the disadvantages of high energy requirements and equipment costs, are limited by chemical costs, reactor corrosion, and the formation of potentially hazardous by-products [70].

The authors of [71] proposed the Fe-based piezocatalysts (BFOs), which lead to a better catalytic activity for PS activation [71].

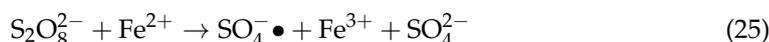
In recent years, catalyst-based activation approaches have gained ground in PS-AOP. Metal catalysts, such as  $\text{Fe}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Ag}^+$ ,  $\text{Fe}_3\text{O}_4$ ,  $\text{CuO}$ ,  $\text{MnO}$ ,  $\text{FeO}$ ,  $\text{Cu}^0$ ,  $\text{Co}/\text{TiO}_2$ ,  $\text{Au}/\text{TiO}_2$ , and  $\text{Fe}(\text{VI})$  have been increasingly employed. Metal ion speciation in homogeneous systems can be pH-dependent and lead to precipitates that are difficult to recycle. Another approach showed that the  $\text{Fe}(\text{VI})$ -based process can be cost-effective due to their reusability throughout the treatment process [72].

Some metal catalysts may exceed water quality standards in their residues, making them unsuitable for practical applications. Heterogeneous catalysts offer easy separation from treated water for reuse and show good stability under industrial conditions [70].

In terms of degradation kinetics, radical-based pathways typically show faster and more extensive mineralization compared to pathways involving non-radical oxidizing species such as singlet oxygen ( $^1\text{O}_2$ ). Radical-based approaches can achieve high removal efficiencies with relatively short contact times, although they are more susceptible to interference from compounds in the aqueous matrix. Conversely, non-radical systems offer advantages in minimizing water matrix interference and maintaining high contaminant degradation efficiency. Furthermore, radicals react indiscriminately with contaminants that have either electron-withdrawing groups (EWGs) or electron-donating groups (EDGs), while non-radical species preferentially react with EDG, thus optimizing degradation efficiency based on the functional groups present in the contaminants.

Temperature affects the rate of degradation, with a bell-shaped response observed due to the accelerated self-quenching of radicals or reactions with PS at high temperatures, leading to less reactive species that hinder efficacy. Radical pathways can also produce toxic halogenated by-products, making non-radical systems preferable in environments conducive to their formation. Overall, non-radical systems tend to have higher energy efficiency per oxidant (EE/O) values than radical systems due to slower degradation kinetics and lower energy requirements for catalyst production [70].

The use of sulfate radicals has a high redox potential of 2.5–3.1 V compared to the  $\text{OH}^\bullet$  radical (1.9–2.7 V) and is more selective than  $\text{OH}^\bullet$  in MP oxidation. The extended lifetime of  $\text{SO}_4^{\bullet-}$  (30–40  $\mu\text{s}$ ) in contrast to  $\text{OH}^\bullet$  (100 ns) increases its efficiency in the reaction with organic compounds through the electron transfer mechanism. As mentioned above, the formation of  $\text{SO}_4^{\bullet-}$  from peroxydisulfate can take place with the help of UV (Equation (23)), heat (Equation (24)), and also with the help of transition metals (Equation (25)) [73].



### 3.8. Overview of Processes for Removal of Pharmaceuticals

Various studies have investigated the efficiency of different treatment processes in removing MPs from wastewater, elucidating their degradation mechanisms and optimal conditions.

Deng [74] applied the ozonation process to investigate the ozonation performance of the reverse osmosis (RO) concentrate from municipal wastewater treatment using a semi-batch stirred reactor. In his work, the target micropollutant carbamazepine was added to municipal secondary waste as RO feed at a concentration of 10 mg/L. It is important to note solvents such as methanol or ethanol were not used to prepare the carbamazepine stock solution due to their effect on ozone consumption. Specifically, the presence of ethanol (0.05%, *v/v*) resulted in a significant inhibition of the ozonation efficiency of carbamazepine. The experiments were carried out in a stirred and thermostatic semi-batch reactor at a lab scale with a desired concentration of ozone of 10 mg/L, an ozone generator power of approximately 1.5, and a stable flow rate of 30 L/h. During the initial 60 min of the ozonation process, no dissolved ozone was detected, suggesting that all the transferred ozone was utilized at the interface or within the film layer. Ultimately, over 90% of the carbamazepine was removed at a low ozone dosage of 0.33 g of the consumed ozone per gram of the initial dissolved organic carbon (DOC). The RO concentrate contained an initial DOC of ~50.8 mg/L [74]. The degradation of carbamazepine by ozonation is associated with the carbon double bond attacked by molecular ozone [75].

In the research conducted by Lee et al. [76], more micropollutants (e.g., CAR, CLA, DIC, VEN, MET, and BZT) were investigated in ozonation batch reactors (180 mL) in a sample of wastewater effluent from a secondary sedimentation tank of the conventional activated sludge (CAS) treatment process and filtered through 0.45 µm pore size membrane filter. The findings indicated an almost-complete elimination of CAR, CLA, DIC, VEN, and MET and around 80% removal of BZT at a specific ozone dosage of 0.7 g O<sub>3</sub>/g DOC and an initial concentration of micropollutant of 475, 412, 348, 1472, 372, and 403 µg/L, respectively. Ozone decay in the wastewater samples was completed for 5 min. Ozone decay in the tested wastewater was completed within 5 min. In comparison, the addition of H<sub>2</sub>O<sub>2</sub> (5 mg/L) lowered the elimination level of VEN (±10%) and MET (±20%) [76].

However, in the work of Edefell et al. [77] the tertiary amines CLA and VEN underwent a transformation into their respective N-oxides during ozonation [77].

Jabbari et al. [78] found that the removal of DIC can be performed using ammonium persulfate to generate a sulfate radical as using UV alone is more likely to eliminate the chemical bond of micropollutants and lower efficiency in drug degradation. The findings showed 89% removal efficiency with a persulfate concentration of 200 mg/L, pH 6, an initial DIC concentration of 8 mg/L, and a reaction time of 30 min in the O<sub>3</sub>/UV/S<sub>2</sub>O<sub>8</sub> process. Humic acid was introduced as a scavenging compound, resulting in a reduction in the DIC removal rate from 89% to 76%. Thus, sulfate radical-based technologies show promising potential for the effective removal of these specific pharmaceuticals from wastewater treatment plants [76].

Lu et al. [73] reported an 85% decrease in DIC concentration after 60 min of UV light irradiation (254 nm and 75 W) combined with activated persulfate (UV/PS) with a degradation rate of  $5.0 \times 10^{-4} \text{ s}^{-1}$ . The findings indicate that the degradation of DIC decreases when exposed to UV radiation alone, resulting in a DIC removal of 13% within 60 min. This study was performed in a lab-scale (2 l) semi-continuous reactor. The increase in the pH value from 3 to 11 raised the degradation rate from  $4.7 \times 10^{-4} \text{ s}^{-1}$  to  $6.2 \times 10^{-4} \text{ s}^{-1}$ , indicating that the DIC degradation was more favorable under alkaline conditions. As the transformation products were evaluated as more toxic than the DIC itself, the authors suggested a longer degradation time [73].

Micropollutants including carbamazepine and diclofenac were reported to be removed by the UV/H<sub>2</sub>O<sub>2</sub> process. To achieve a 90% removal of DIC and CAR, the UV dose varies between compounds. Specifically, the necessary UV doses were 0.97 J/cm<sup>2</sup> for diclofenac and 2.25 J/cm<sup>2</sup> for carbamazepine, with a 25 mg/L H<sub>2</sub>O<sub>2</sub> dose. Experiments used solutions

prepared with MilliQ water, with the initial concentrations of DIC and CAR set at 0.14 mM and 0.006 mM, respectively [79].

Angosto et al. [80] observed that in the UV treatment, combined with hydrogen peroxide (5 mg/L), 99.2% of the initial diclofenac concentration (37.6 mg/L) was eliminated for an exposure time of 2 min of UV radiation. The process was carried out in aqueous effluents through biosorption with agrifood residues [80].

Fernández-Perales et al. [25] compared the efficiency of UV/H<sub>2</sub>O<sub>2</sub> and UV/K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> processes for the degradation of HCH. They found that the presence of radical promoters had a significant effect on the overall process of HCH degradation. Both photodegradation and mineralization rates varied depending on the system used in descending order: solar < UV < UV/K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> < UV/H<sub>2</sub>O<sub>2</sub>. Specifically, in the surface water, the degradation rates were 0.0006 per s (solar), 0.0013 per s (UV), 0.0009 per s (UV/K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>), 0.0025 per s (UV/H<sub>2</sub>O<sub>2</sub>) with the initial concentration of HCH 0.00005 M. In addition, the degradation rates increased with decreasing pH values. Conversely, the UV/H<sub>2</sub>O<sub>2</sub> system required more energy compared to UV/K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, which is a significant factor to consider when assessing its suitability for water treatment applications [25].

Jaén-Gil et al. [81] combined biological processes with UV/H<sub>2</sub>O<sub>2</sub> to remove metoprolol with an initial concentration of 2 µg/L. The experiments used 500 mL of wastewater, 15 mg/L H<sub>2</sub>O<sub>2</sub>, and a reaction time of 10 min, resulting in a UV dose or intensity of 29.4 J/cm<sup>2</sup>. The findings showed that the UV/H<sub>2</sub>O<sub>2</sub> treatment alone achieved 67.8% removal of the metoprolol, while a combined approach with CAS increased it to 85.6% [81].

Findings from a study by Keen et al. [82] suggest that the AOP products of carbamazepine can undergo mineralization through the activity of microorganisms present in AS processes. They performed the experiments using the synergy observed between advanced oxidation and biodegradation suggesting that a sequence involving UV/H<sub>2</sub>O<sub>2</sub> followed by some form of biological treatment has the potential to lead to carbamazepine mineralization [82].

In a study conducted by Zhu et al. [60] on the degradation of venlafaxine using the UV coupled with chlorine, it was observed that approximately 76% of venlafaxine (initial concentration of 2 mg/L) was degraded within 30 min of the UV/chlorine treatment and the rate constant reached 0.0467 per minute. Increasing a dose of chlorine from 2 to 6 mg/L, the rate constant enhanced to 0.0941 per minute [60].

Using C-TiO<sub>2</sub> as a photocatalyst, Spyrou et al. [83] demonstrated efficient heterogeneous photocatalysis without the formation of a harmful transformation product. During 120 min of irradiation, the degradation percentages for Amisulpride were 86.6% under UV-A and 58.1% under visible light (Vis) in ultrapure water [83]. The system, which operates under pressure and at room temperature, uses sunlight to irradiate the catalyst and contains low-cost and reusable catalysts, which can achieve the complete mineralization of various compounds [54]. TiO<sub>2</sub> significantly increased the rate of the degradation of citalopram and other pharmaceuticals [84,85].

In catalytic degradation using a solid catalyst, the process includes both an oxidation reaction and the adsorption of the contaminants on the surface of the catalyst [86].

Antopolou et al. [17] investigated the degradation of amisulpride via heterogeneous photocatalysis using g-C<sub>3</sub>N<sub>4</sub> as a catalyst with UV-A radiation. Remarkably high removal percentages were achieved in ultrapure water and wastewater, with a slower degradation rate observed in wastewater due to its complex composition [17]. The removal of venlafaxine exceeded 95% after 5 h of visible light irradiation using carbon nitride and polyvinylidene fluoride (PVDF) photocatalytic membranes designed for visible light applications [87].

Gros and Williams [16] investigated the photolytic degradation of amisulpride in a solar simulator system and revealed that even short exposure times to sunlight can lead to degradation in both clean water and wastewater from a lagoon treatment. It is important to note that these experiments were performed under simulated conditions and degradation is expected to be significantly slower under real environmental conditions, potentially at least

fivefold slower. The findings showed that the amisulpride exhibited a high susceptibility to direct photolysis, with a  $t_{1/2}$  of 2.79 h in ultrapure water, resulting in over 90% degradation within 9 h. This rapid degradation was anticipated due to the absorbance spectrum of amisulpride, which shows a maximum above 290 nm. However, in wastewater treatments, the degradation of the amisulpride was slightly reduced compared to ultrapure water ( $t_{1/2} = 4.2$  h), yet still significant [16]. Venlafaxine removal exceeded 95% after 5 h of visible light irradiation using carbon nitride–PVDF photocatalytic membranes designed for visible light applications [87].

With the simultaneous use of hydrogen peroxide in a photocatalytic reactor with flat cells, a significant increase in the rate of degradation was observed for all investigated substances. At the lowest tested dose of  $H_2O_2$ , amisulpride, candesartan, and diclofenac were not detected in the reactor effluent [88] (Table 2).

**Table 2.** Selected pharmaceutical removal processes.

Pharmaceuticals	Treatment Process	Efficiency	Notes	Reference
Amisulpride (AMI)	Photocatalysis	58.1%	C-TiO <sub>2</sub> /Vis	[83]
		86.6%	C-TiO <sub>2</sub> /UV-A	[83]
		80%	g-C <sub>3</sub> N <sub>4</sub> /UV-A	[17]
		<90%	direct photolysis	[16]
Carbamazepine (CAR)	Ozonation	<90%, ACR <sup>1</sup>	potential toxicity of TPs	[75] [76]
		Ozonation	80%	formation of TP
Citalopram (CIT)	Chlorination	40%	21 µg/L of ClO <sub>2</sub>	[89]
	UV	95%	131 µg/L of ClO <sub>2</sub>	
	Photo-Fenton	92–100% 90%	about 7 min–30 min, no TPs no TPs	
Clarithromycin (CLA)	Ozonation	ACR <sup>1</sup>	N-oxide TP	[76,77]
		76%	spiked STP at 0.1–0.3 mM O <sub>3</sub>	[90]
Diclofenac (DIC)	Ozonation	ACR <sup>1</sup>		[76]
	O <sub>3</sub> /UV/S <sub>2</sub> O <sub>8</sub>	89%		[78]
	UV/PS	85%		[73]
	UV/H <sub>2</sub> O <sub>2</sub>	99.2%		[80]
Hydrochlorothiazide (HCH)	Ozonation	99%	combined with Al <sub>2</sub> O <sub>3</sub> /GAC an amount of 7.5 mg/L of	[91]
	Photo-Fenton	71%	Fe <sup>2+</sup> , 50 mg/L of H <sub>2</sub> O <sub>2</sub>	[92]
Metoprolol (MET)	Ozonation	ACR <sup>1</sup>		[76]
	UV/H <sub>2</sub> O <sub>2</sub>	85.6%	combined with CAS	[91]
Venlafaxine (VEN)	Ozonation	ACR <sup>1</sup>	N-oxide TP	[76,77]
	UV/chlorine	76%		[60]
	Photocatalysis	95%	C <sub>3</sub> N <sub>4</sub> /PVDF/Vis	[87]
Candesartan (CAN)	Chlorination	35%	NaClO a total of 13% transformed into by-products	[93]
Irbesartan (IRB)	Moving bed biofilm reactor	90%	after 70 h	[94]
	Membrane biofilm reactor	100%	combined with forward osmosis, no TPs	

<sup>1</sup> ACR—almost-complete removal.

### 3.9. Anti-Corrosives Removal

Some of the studies investigated the adsorption process for removing selected anti-corrosives. The removal of these micropollutants by two biochars was studied by the authors of [95]. Studied adsorbents were synthesized from wild plum (WpOH) and apricot (AsPhA) kernels. The goal aim of this research was to optimize the adsorption of BZT and

various BZTs (i.e., 4-hydroxy-1H-benzotriazole (4-OHBZT), 4-methyl-1H-benzotriazole (4MeBT), 5methyl-1H-benzotriazole (5MeBT), 5-chloro-1H-benzotriazole (ClCBZT), and 5,6-dimethyl-1H-benzotriazole (DMBZT)). From the results of the batch adsorption assays resulted an equilibrium adsorption time of 240 min. The optimal process pH values varied between four and six for WpOH and AsPhA, respectively. The best description of the kinetics of the adsorption process was achieved by the Elovich model. The best correlation of the adsorption equilibrium data with the Freundlich isotherm indicates multilayer adsorption mechanisms. The values of the maximum adsorption capacity obtained for the mixture of the studied emerging micropollutants were 379 mg/g on WpOH and 526 mg/g on AsPhA. The concentrations of 4-OHBZT and BTZ decreased by >40% during conventional treatment. The concentrations of the other derivatives were below detection limits.

The results of the toxicity test carried out with *Vibrio fischeri* assays confirmed a significant decrease in raw and treated wastewater by adsorption on AsPhA. The authors of [96] investigated the adsorption and biodegradation of benzotriazole (BZT) and 5-methylbenzotriazole (5MeBZT) under anaerobic conditions. Experiments were conducted over 220 days in large laboratory columns to simulate a controlled aquifer recharge strategy. They worked with concentrations of micropollutants on the order of nanograms per liter. From the results of the sorption measurements followed the BZT and 5MeBZT retardation coefficients 2.0 and 2.2. After a biological lag time of approximately 30–60 days, the biodegradation of BZT and 5MeBZT was observed with first-order kinetics with half-lives of  $29 \pm 2$  and  $26 \pm 1$  days, respectively. No threshold effect on the biodegradation of BZT and 5MeBZT was observed at the concentrations of 200 ng/L.

Other studies were focused on applying biological processes as a potential method of BZT degradation. Struk-Sokołowska et al. [33] present the results of a study on the quantitative changes in BZT in a sequential batch reactor (SBR). The work cycle of the SBR consisted of the following six phases: filling (40 min), mixing (dephosphatation—20 min), the nitrification and oxidation of organic compounds (300 min), denitrification (30 or 60 min), settling, and decantation (40 min). During the research, 411 cycles of SBR were carried out, while the BZT concentration varied in the range of 50–1000 µg/L. The results show that when the BZT content does not exceed 200 µg/L in wastewater, this compound is removed with more than 80% efficiency. The highest efficiency (88.2%) was achieved at an initial concentration of 1000 µg/L. The lowest efficiency removal value (56.6%) was achieved at the BZT initial content of 1000 µg/L. In anaerobic conditions, BZT decomposition was 5.3 and 4.9 times slower compared to oxic conditions. Extending the denitrification phase from 30 to 60 min contributed to the release of phosphorous from the activated sludge to the WW in the SBR. BZT removal with an efficiency of more than 80% is possible with long HRT and SRT, if the BZT content in the WW does not exceed 200 µg/L.

The authors of [97] presented results of the removal of BZT and its derivatives 5MeBZT and 4MeBZT with *Lemna minor*. The experiments were carried out in a batch and continuous system. In the batch system, no inhibition of the specific growth rate of *Lemna minor* was observed at concentrations up to 200 µg/L. Except for 4MeBZT, the observed complete elimination of other 4MeBZT derivatives was achieved in these experiments. Half-life values were  $25 \pm 3.6$  d (4MeBZT). For all BZTs, the values of the plant uptake kinetic constants were much higher compared to the kinetic constants for hydrolysis and photodegradation mechanisms. The continuous flow *Lemna minor* system consisted of three mini ponds with a total hydraulic residence time of 8.3 d. Removal efficiency values of BZT and its derivatives were around 26% (4MeBZT). Using the model to describe the removal of micropollutants in this system, it was found that the main mechanism of BZT removal was uptake by plants [97].

The contents of benzotriazole (BZT) and tolyltriazole (TTZ) (a mixture of 4- and 5-methyl isomers of BZT) in the primary and secondary wastewater effluents ranged from 10 to 100 µg/L. The ranges of the concentrations in the Glatt River in ng/L varied from 636 to 3690 for BZT and from 122 to 628 for TTZ. The corresponding values of mass flows

varied from 93 to 1870 g/d for BZT and from 18 to 360 g/d for TTZ. The anti-corrosive agents BZT and TTZ occur in all municipal wastewater effluents and are only partly removed in mechanical–biological WWTP due to their high polarity, i.e., high solubility in water, and their bio resistance to biodegradation. Thus, residual amounts of BZT and TTZ are widely distributed in the receiving waters [35].

Kowalska et al. [98] investigated the possibilities of treating municipal WW, which contained environmentally relevant high concentrations of benzothiazole (BT) and benzotriazole (BZT). The experiments were carried out in aerated laboratory membrane bioreactors (MBR) with an internal microfiltration module and a model municipal WW. Both compounds are commonly used in industry and households and therefore occur in municipal WW and in the aquatic environment. Activated sludge was adapted to higher concentrations of BT and BZT, which was reflected in a multiple increase in the values of the kinetic parameters of their biological decomposition. After the adaptation period, BT and BZT removal efficiencies of 99.8% and 97.2% were measured. However, there were also recurring periods with unstable BZT removal. Overall removal efficiencies of 88% for BT and 84% for BZT were achieved. However, the share of activated sludge in the biotransformation of the BZT represented only less than 1% of the removed load. The remaining share of the biologically removed BT and BZT was attributed to the increased retention in the bioreactor because of membrane fouling. Due to the very low affinity of these compounds to the activated sludge, the process of adsorption to the activated sludge played a negligible role. The result shows that the BT and BZT were biodegraded by a catabolic rather than a co-metabolic mechanism. The results of this study show the feasibility of cleaning municipal WW with high BT and BOD content in MBR.

Mazioti et al. [99] studied the removal of five benzotriazoles and one benzothiazole in continuous laboratory aerobic bioreactors with activated sludge and attached growth biomass. The activated sludge bioreactor (ASBR) was operated with a low organic load. The moving bed biofilm reactor (MBBR) consisted of two reactors connected in a series, which were filled with K3-biocarriers. This system was operated while maintaining a low or high organic load. In the MBBR, higher loadings were observed to cause a significantly lower biological removal of four of the six compounds investigated. The comparison of the values of the specific removal rates revealed a higher degradation potential of the biofilm system for the target compounds compared to suspended biomass. Significant differences in the degradation ability were also observed for biomass cultivated in different MBBR systems. The results of the batch experiments showed that the co-metabolic biodegradation of the micropollutants took place at both lower and higher loads. Both the ASBR and MBBR systems showed the ability to biologically degrade the target compounds. The biodegradation efficiency varied for BZT from 43% to 76%. Greater MP removal capacity was observed for the biomass cultivated in MBBR especially when this system was operated at low organic load. The biodegradation of the MP in the batch tests was improved by the presence of easily degradable organic substances.

Several studies showed promising results of the Photo-Fenton process to remove BZTs.

Ahmadi et al. [100] report the results of research on the removal of benzotriazole (BZT) by the Photo-Fenton process in combination with nano zero-valent iron (NZVI). For the design and analysis, four operating parameters of the experiment with the initial concentrations of BZT (15–5 mg/L), NZVI (0.05–0.15 g/L), H<sub>2</sub>O<sub>2</sub> (0.5–1.5 mmol/L), and reaction time (30–90 min), and a response surface optimization methodology (RSM)-based on the Box–Behnken design was used. All experiments were carried out in the presence of UV radiation with a power source of 6 W. The results show a very good agreement (determination coefficient R<sup>2</sup> = 0.9500) between the experimental and predicted values of the BZT removal efficiency. The determined optimum values of the UV/NZVI/H<sub>2</sub>O process parameters (60 min reaction time, a BOD of 15 mg/L, 0.10 g/L of NZVI, and 1.5 mmol/L of H<sub>2</sub>O<sub>2</sub>) correspond to a total removal efficiency of 73.4% for BZT and 40% for COD.

To prevent the release of benzotriazoles into the environment, Weiss et al. [101] proposed the treatment of municipal wastewater using membrane bioreactors (MBRs) to improve the wastewater removal capabilities. However, this method did not completely prevent the release of benzotriazole into the wastewater from the plants. Complete removal was achieved only by the ozonation of water, which led to the almost-complete degradation of BZTs. Phyto transformation has also been proposed for the reduction of benzotriazole [21], but it is not feasible for the treatment of large volumes of municipal wastewater. The direct photochemical degradation of benzotriazoles was studied, with BZTs being significantly degraded by UV radiation but not mineralized, leading to the formation of aniline and phenazine as the major and more toxic intermediates [101].

Photogenerated species at the semiconductor/electrolyte interface facilitated the rapid conversion of the investigated benzotriazole substrates. Photocatalytic degradation resulted in the complete mineralization of the substrates (BZTs and TTZs), while no accumulation of persistent photostable intermediates was observed. A photocatalytic process using irradiated  $\text{TiO}_2$  and other advanced oxidation processes (AOPs) using HO as primary oxidants could be valuable in reducing these contaminants of emerging concern in both WWTP effluents and raw waters used for drinking water production. Further research is needed to assess the strengths and limitations and demonstrate the applicability of the photocatalytic technology for benzotriazole reduction in real-world scenarios [102].

Another study focused on the degradation of benzotriazole using the UV/chlorine system. It was performed in a bench-scale UV irradiation reactor where the degradation efficiency of benzotriazole reached 82.5% at 5  $\mu\text{M}$  chlorine within 30 min and with the pseudo-first-order rate constant of  $0.0605 \text{ min}^{-1}$ . The findings indicate that the higher dose of chlorine did not enhance the degradation efficiency, suggesting that the increased formation of  $\text{Cl}_2^{\bullet-}$  radicals had no effect on the degradation. However, the toxicity of the benzotriazoles was increased due to the formation of intermediates during the process [103].

The study by the authors of [104] deals with the removal of wastewater contaminants related to the production, use, and disposal of plastic materials. The related emerging contaminants were bisphenol A, phthalic acid esters, and benzotriazoles. Due to their low biological degradability in municipal wastewater treatment plants, advanced electrochemical oxidation processes have been developed. The authors of this work provide an overview of the use of electrochemical methods for the removal of these plastic-originated contaminants from wastewater and their mineralization. The transformation products were also identified, and their toxicity was evaluated as well as the energy requirements of the processes. The results of research on electrochemical methods for treating these contaminants over the last five years are presented and proven to be effective and useful in practice for removing selected contaminants from wastewater.

The work in [96] presents the results of research on the biodegradation of benzotriazole and 5-methylbenzotriazole (MeBZT). Long-term research (220 days) was carried out in large aerobic laboratory columns. The initial values of the concentrations of emerging pollutants were in the range of ng/L. The results showed that the biodegradation of BZT and 5MeBZT followed first-order kinetics. The half-life values for BZT  $29 \pm 2$  and for 5MeBT  $26 \pm 1$  days were measured after a 30–60-day lag phase. At the initial concentration of 200 ng/L, no threshold effect on the biological degradation process was observed. The results indicated that for the biodegradation of BZT and 5MeBZT, sufficient residence times in the aquifer are necessary, or sufficient distance between the injection of recycled water and the extraction of groundwater.

The authors of [105] investigated the possibility of reusing the water discharged from the cooling tower (CTW). The intention was to reduce the need for fresh water to be transported to the CTW and thereby alleviate the problems with its shortage. However, the reuse of cooling water requires desalination. To increase the efficiency of desalination, it is necessary to remove the chemicals that are used for water treatment. Such pre-treatment can be implemented in constructed wetlands (CWs). The authors studied the mechanisms underlying the removal of the conditioning benzotriazole (BZT) in CW. The results of the

batch experiments of biodegradation, adsorption, and photodegradation showed that BZT removal is the result of the processes of adsorption and aerobic biological decomposition. The BZT was resistant to photodegradation. The research was carried out using various semi-operational CWs in combination with the use of batch experiments with substrate from these CWs. The results of the research made it possible to determine the most important removal processes of BZT removal in CW.

#### 4. Micropollutant Removal in Municipal Wastewater Treatment Plants

Micropollutants enter the aquatic environment mainly from wastewater treatment plants, as commonly operated treatment technologies are not effective enough to remove them. Most of them are not removed or (bio)transformed in traditional wastewater treatment plants, and they can be persistent in aquatic ecosystems or form new chemicals reacting with natural humic substances in sunlight. They can be bioactive, pose endocrine effects, and they can bioaccumulate and biomagnify. Due to the serious negative effects on the environment, low concentrations, and in many cases the complex chemical structure, the issue of MP removal represents an urgent and current challenge to the research of treatment technologies, a study of their effects on the aquatic environment, and their penetration into groundwater [6].

They enter the environment from anthropogenic activities and belong mainly to the group of medicines (human or veterinary), pesticides and biocides, personal care products and synthetic fragrances, petroleum, as well as various industrial chemicals and additives. Degradation and combustion processes, which can produce polychlorinated dibenzodioxins (PCDDs) and some polyaromatic hydrocarbons (PAHs), are also important sources of micropollutants in the environment.

The published works show that the most important point sources of discharges of micropollutants into the environment are municipal wastewater treatment plants (WWTPs) due to low removal efficiencies [106,107]. In municipal WWTPs, only about half of the total amount of micropollutants contained in wastewater (WW) is removed, either by their degradation or by sorption into sludge. The fate of MPs in WWTPs related to their adsorption on suspended solids and primary and secondary sludge. Removal is a consequence of the coagulation and flocculation processes and usually less of biodegradation. The log  $K_{ow}$  ( $>2.5$ ) and  $pK_a$  are the important properties of the MPs when the potential for their removal from wastewater is considered. The concentration, presence of organic fraction, size, and surface charge of suspended solids define the extent of the adsorption of MPs. Most of the conventional WWTPs do not remove MPs by biodegradation or biotransformation and the removal rates vary significantly for different compounds, as well as for the same substance, due to operational conditions such as oxygen regime, food–microorganism's ratio, sludge retention time, hydraulic retention time, pH, redox potential, and temperature. Ozone- and UV-based AOPs and membrane filtration can be used for tertiary/quaternary purification due to their easy implementation and high speed. The values of partition coefficients and rate constants for various MPs are available for design and application purposes.

Luo et al. [6] summarize the occurrence of MP in the aquatic environment. The removal efficiency of selected MPs from OV in 14 countries/regions ranges from 12.5 to 100%. Biological treatment can remove polar persistent micropollutants. The efficiency of these processes can be increased by changing technological and operational parameters (sludge age, hydraulic residence time, temperature and redox conditions) and by applying of hybrid systems. Although advanced processes such as activated carbon adsorption, AOPs, nanofiltration, reverse osmosis, and membrane bioreactors can achieve a greater and more consistent removal of MP, they have high operating costs, and some generate by-products and concentrated wastes.

Deblonde et al. [108] monitored data on the concentrations and removal efficiencies of 50 pharmaceutical compounds, 6 phthalates, and bisphenol A at inflows and outflows in WWTPs. The phthalate removal efficiency is greater than 90% for most of the compounds studied. The rate of antibiotic removal is about 50% and for bisphenol A 71%. Analgesics,

anti-inflammatory drugs, and beta-blockers are the most resistant to removal (30–40% removal efficiency).

Singh et al. [109] published results from pilot plant ozonation after secondary municipal wastewater treatment in Canada for 41 target EPs at two doses of ozone (0.46 and 0.72 mg O<sub>3</sub>/mg DOC). At both doses of ozone, removal efficiencies of more than 80% were observed for seven EPs (bisphenol A, carbamazepine, diclofenac, indomethacin, lincomycin, sulfamethoxazole, and trimethoprim). At ozone doses of about 0.7 mg O<sub>3</sub>/g DOC after secondary treatment of municipal wastewater, the simultaneous disinfection and transformation of many EPs were achieved.

The first long-term ozonation in Switzerland was introduced at the Neugut WWTP with a capacity of 1,050,000 PE. In this operation, a specific ozone dose of 0.55 g O<sub>3</sub>/g DOC was determined to ensure an average reduction in the concentration of twelve selected indicator substances by 80%. After ozonation, additional biological treatment is required to eliminate possible ecotoxic effects caused by biodegradable transformation products and oxidation by-products [110].

The integration of chemical and biological processes, as well as the development of hybrid treatment methods, shows potential for improving removal efficiency while reducing costs. The accumulation and biosorption of hydrophobic organic substances by activated sludge eliminates them from wastewater. However, the disposal of contaminated sludge poses a new environmental problem, especially if the pollutants are reversibly bound. One of the current trends in sludge management is the research of integrated biological and chemical processes in order to minimize the production of excess sludge and to perform the simultaneous transformation/degradation of micropollutants sorbed on activated sludge [111].

The conclusions of the Ninth Implementation Report and the programs for the implementation of Council Directive 91/271/EEC on the treatment of municipal wastewater [112] show that 58% of sewage sludge has been reused, mostly in agriculture.

Ak et al. [113] showed that the anaerobic stabilization of excess sludge after ozonation practically doubled the volume of biogas produced compared to the conventional stabilization process, with no sludge to be produced for disposal. The removal rate of adsorbed endocrine disruptors on the sludge was increased by the ozonation of excess sludge.

The results of the authors Nie et al. [114] showed that ozonation led to a significant reduction in excess sludge produced in the system. Although ozonation caused a relatively lower specific rate of oxygen consumption by the microorganism-activated sludge, it had little effect on the performance of the system in removing COD and nitrogenous substances. The sludge reduction system was more favorable to the removal of target endocrine disruptors than the control system.

Burzio et al. [115] studied the removal of organic micropollutants (MPs) in a classic activated sludge system (CAS) and in an aerobic granular sludge (AGS) system at a WW treatment plant. A higher transformation efficiency for CAS was observed for most compounds. Compared to anoxic conditions, several micropollutants were transformed at comparable rates or faster than under aerobic conditions.

The fate of MPs in municipal wastewater treatment plants (WWTPs) is strongly dependent on adsorption to solid particles in primary and secondary sludge and dissolved organic carbon (DOC) [111].

Adsorption, coagulation–flocculation, and biodegradation are the basic removal processes. MP adsorption is significantly influenced by the concentration, organic fraction, and surface charge of undissolved substances. Most conventional WWTPs do not remove complex MPs efficiently through biodegradation or biotransformation. Their removal varies greatly due to operating conditions such as the biochemical environment (oxic, anoxic, and anaerobic), solid retention time (SRT), redox potential, pH, and temperature. The membrane bioreactor has a higher processing potential for moderately biodegradable compounds due to the greater adaptability of microorganisms at SRT and their diversity. Ozone- and UV-based AOPs and membrane filtration can be used for tertiary/quaternary purification

due to their easy implementation and high speed. The values of partition coefficients and rate constants for various MPs are available for design and application purposes.

Albergamo et al. [116] studied the effectiveness of reverse osmosis (RO) in pilot drinking water treatment for the removal of organic polar MPs. The experiments were carried out with the hypothetical intention of treating an anaerobic filtrate from the riverbank, which was enriched with thirty model compounds. A significant inverse correlation was observed between the size and transitivity of neutral hydrophilic species. In the case of moderately hydrophobic MPs, a weaker correlation was observed. Almost no permeability was observed for anionic MPs. However, it was possible to observe the penetration of small cationic MPs.

Boström [117] deals with the removal of seven active pharmaceutical ingredients (APIs) of different structures in two MWWTPs. All seven components were present in at least one influent sample. Only one component was significant in one MWWTP. All samples of WW at the exit from the secondary stage were subjected to tertiary treatment with activated carbon, biochar, or ozonation to further reduce concentrations in WW. The best performance was achieved with activated carbon. Acceptable results were also obtained by ozonation.

The combination of a fixed bed reactor (FBR) and a nanofiltration device (NF) for the removal of organic MPs was verified by Büning et al. [118]. The biological degradation of pollutants takes place in FBR and NF acts as a barrier for MP. It provides the simultaneous cleaning of the retentate by recirculating it into the FBR. The results of the experiments show that NF can remove on average more than 95% of the contained MPs. Retentate from NF was used in biodegradation testing in FBR. The results of the tests show that a significant biological degradation of various MPs was carried out in the FBR. The biological degradability of substances is confirmed by insignificant adsorption on the sludge and solid layers. Negligible biodegradation was observed for sulfamethoxazole and carbamazepine. Excluding these two MPs, the average degradation rate was 78%.

Hollender et al. [119] studied the removal efficiency of 220 micropollutants (MPs) in a municipal wastewater treatment plant (MWWTP) modernized with tertiary ozonation processes followed by sand filtration. Compounds containing aromatic/amine functions or double bonds (e.g., sulfamethoxazole, diclofenac, or carbamazepine) were eliminated below the detection limit with second-order rate constants at an ozone dose of  $0.47 \text{ gO}_3/\text{gDOC}$ . The removal efficiency of compounds more resistant to ozone oxidation (eg atenolol and benzotriazole) increased with an increasing ozone dose. At a moderate dose of ozone ( $\sim 0.6 \text{ gO}_3/\text{gDOC}$ ), a removal with an efficiency higher than 85% was achieved. Several micropollutants (e.g., triazine herbicides) with second-order rate constants  $<102 \text{ l/M 1/s}$  (slow reacting) persisted largely in WW. The ozonation process was accompanied by the formation of carcinogenic by-products and bromates. However, their concentrations were below or within the range of drinking water standards. The results show that biological sand filtration is an effective additional barrier for the elimination of biodegradable ozonation products. Additional post-ozonation requires about  $0.035 \text{ kWh/m}^3$ , which corresponds to 12% of the energy consumption in a medium-sized MWWTP providing nutrient removal. A promising technology for the expansion of MWWTP with nutrient removal for a significant reduction in MP content and ecotoxicity in the aquatic environment is the addition of powdered activated carbon (PAC) [120].

Boehler et al. [121] present the main results of pilot and operational applications of PAC addition in different technological schemes for MP removal in MWWTPs. The sorption efficiency of PAC for MP removal decreases significantly with increasing dissolved organic compounds (DOCs). Dosing  $5\text{--}10 \text{ gDOC/m}^3$  PAC to wastewater requires  $10\text{--}20 \text{ gPAC/m}^3$ . Countering the current use of waste PAC by recycling it from a contact tank improved overall MP removal compared to PAC application alone in WW by 10 to 50%. Similar removal of MP was observed with a dose of  $15 \text{ gPAC/m}^3$  to the flocculation sand filter and recycling of the washing water to the bioreactor. The application of PAC in MWWTP

appears to be a feasible technology for the elimination of MP (>80%) from WW comparable to post-ozonation.

Margot et al. [122] present the results of testing two large-scale pilot advanced methods at the MWWTP in Lausanne, Switzerland, over one year. A combined method of oxidation with O<sub>3</sub> followed by sand filtration (SF) and a combined method of adsorption process on powdered activated carbon (PAC) followed by either ultrafiltration (UF) or sand filtration were tested. During testing, more than 70 potentially problematic MPs (pharmaceuticals, endocrine disruptors, drug metabolites, pesticides, and other common chemicals) were analyzed and several ecotoxicological tests were performed. The results show that both methods significantly improved the quality of wastewater (WW). Compared to raw WW, MPs at an average dose of 5.7 mg<sub>O<sub>3</sub></sub>/L or a PAC dose between 10 and 20 mg/L were removed with an average efficiency of more than 80%. Both methods resulted in a significant reduction in WW toxicity, with better results obtained with PAC-UF. Despite the currently higher price, the PAC-UF method was the most suitable method for sensitive areas (drinking water sources or recreational waters). It enabled the good removal of most MP and other pollutants without creating problematic by-products, with the greatest decrease in toxicity and overall WW disinfection.

Since micropollutants are detected in surface waters in lower and lower concentrations, processes and technologies for their purification must be constantly improved. Both development and application trends are advanced methods at municipal wastewater treatment plants (MWWTPs) through the quaternary stage. In addition to assessing the required performance, the optimal fourth stage of cleaning should also be the result of a holistic assessment of sustainability, considering the adaptability of processes, and social, economic, and environmental parameters. Sturm et al. [123] investigated the potential of a tertiary stage MWWT to remove organic pollutants using an advanced oxidation process (AOP) (a combination of UV and H<sub>2</sub>O<sub>2</sub>) and with granular activated carbon (GAC). Average MP removal efficiency of 76.4 ± 6.2% and 90.0 ± 4.6% for GAC was achieved for AOP. After the saturation of GAC, there was a drop in performance from 97.6% in the first week to 80.7% in the thirteenth week. In the case of AOP, a higher removal efficiency was achieved after adjusting the doses of UV and H<sub>2</sub>O<sub>2</sub>. At the set parameters of 40 ppm H<sub>2</sub>O<sub>2</sub> and 10 kJ/m<sup>2</sup> UV bolus, removal reached 97.1%. AOP technology is more promising due to greater flexibility and adaptability to water quality in real-time, lower consumption of resources, as well as in terms of the disposal of produced waste and the sustainability of the compared methods.

In the overview article [124], Kumar et al. deal with technologies for removing pharmaceutical and personal care products (PPCPs) from wastewater. Modern and efficient AOPs require chemicals and energy, leading to high processing costs. The integration of chemical and biological processes has been proposed to reduce costs. The removal efficiency of PPCPs should be significantly increased by combining ozonation with activated carbon (AC). New technologies with lower operating costs include the photo-Fenton method, methods based on the use of solar radiation, as well as promising constructed wetlands. Other technologies include membrane processes, enhanced oxidation, and adsorption. Adsorption is preferred for its simplicity and low cost. However, its effectiveness and efficiency depend solely on the correct selection of suitable adsorbents. Further progress in technologies led to the development of efficient hybrid treatment methods (biodegradation together with physical adsorption and coupling photocatalysis). Recent progress in research on these hybrid systems has led to major breakthroughs such as modified adsorbents and nano-adsorbents that could be combined with other treatment methods. A potential approach to cleaning PPCP-containing WW can be to combine membrane bioreactors with RO or NF, as well as the use of biochar and zeolites as adsorbents. These recent advances have contributed to overcoming the limitations in the use of the adsorption process, which is becoming a promising technique for PPCP removal.

### *Prospects for the Implementation of Quaternary Wastewater Treatment*

As already mentioned in the introduction of this paper, the proposal of the revised directive [1] requires that individual EU member states define the areas in which the selected 12 MPs pose a risk to human life or the environment and define two time horizons for their removal from municipal wastewater during quaternary treatment:

- By 2035, all WWTPs > 100,000 PE and at least 50% of WWTPs > 10,000 PE must be equipped with a quaternary treatment stage.
- By 2040, all WWTPs > 10,000 PE must be equipped with a quaternary treatment stage.

At the same time, quaternary treatment requires 80% removal efficiency of at least 6 of the 12 considered MPs.

From the time horizons mentioned above, approximately 10 years remain until the first defined time horizon for the implementation of the quaternary stages. The very length of this period indicates that it will be a challenging period. The implementation of the directive will require the acquisition of a large set of data, the improvement of sampling and analytical techniques as well as investments in online and inline measuring equipment. All of this will presumably increase the price of treatment and affect residents and industry in the wastewater-catching area. At the same time, energy audits are scheduled every four years for water treatment plants and sewage systems, which will be targeted for potentially cost-effective use, and production of energy from renewable sources with an emphasis on exploiting the potential of biogas at the same time reducing methane emissions. The goal of the proposed directive is to achieve 100% energy neutrality for all MWWTP above 10,000 PE by 31 December 2040, which is an extremely optimistic goal, especially in terms of the size of the plants.

Obviously, data quality will increase with the amount of monitored data. On the other hand, when determining the length of monitoring campaigns, it is advisable to use statistical methods and modeling tools for processing the monitored data.

Aligning the concentrations of pollutants in discharged wastewater with the requirements of the revised directive on the treatment of municipal wastewater related to MP removal, which is being considered after its approval by the European Council, will be a matter of individual MWWTPs and will require several activities, analyses, and decisions [125]. The starting point will be an analysis of the specifics of the WWTP due to the presence of the MPs in question in the influent of MWWTP for the purpose of deciding which 6 of the 12 MPs will be removed. It will require longer-term qualitative and quantitative monitoring of the occurrence of the pollutants in question in WW at the inflow and outflow of the MWWTP.

The next step will be the acquisition of basic documents for the selection of processes/technologies to ensure the required removal of the selected MPs. An important part of this process is the synchronization of currently operated and anticipated/newly proposed processes and technologies to ensure the required removal of the selected MPs. Substantial information to support the final decision will be provided by analyses, mass balance calculations, and the evaluation of the results of longer-term monitoring of the occurrence and changes in the MPs. The processing of monitoring results and operational data should be sufficient for the selection of at least six MPs, which will be removed in the quaternary treatment at the MWWTP.

Such a database defines the framework for the period of the process-technological preparation of the quaternary MWWTP treatment. This stage will consist of an oriented literature search of published results, the selection of alternative processes/technology, laboratory/pilot research, the design of the industrial scale of the quarter stage, and its implementation at the MWWTP. It is obvious that the 10-year frame is quite ambitious, and it will require a lot of focused effort and investments to fulfill it. However, the objective of the renewal of the directive is to update the 30-year-old directive, improve the management of municipal wastewater, address the sources of pollution from the urban environment that were not yet adequately addressed in the old directive, and to achieve better alignment with the goals of the European Green Deal.

## 5. Conclusions

The rapid growth in pharmaceutical use has led to a significant increase in the presence of these compounds in wastewater systems. However, the widespread use of pharmaceuticals has inadvertently led to their introduction into various environments through the discharge of treated or untreated wastewater. Even trace amounts of these compounds in aquatic ecosystems can disrupt their balance and pose potential risks to organisms. In addition, the persistence of some pharmaceutical products exacerbates concerns about long-term environmental consequences.

The presence of pharmaceuticals in wastewater is mainly due to incomplete metabolism and excretion by humans and animals. Traditional wastewater treatment plants, designed primarily for common pollutants, may not be able to effectively eliminate these complex compounds. Pharmaceutical substances can undergo transformation during wastewater treatment, creating new transformation products that can show increased persistence and biological activity compared to the original compounds.

The proposed directive [1] on WW treatment requires the identification of areas where the concentrations or accumulation of micropollutants pose a risk to human health or the environment. It outlines the requirements for the removal of micropollutants, sets a minimum removal efficiency of 80%, and lists specific pharmaceuticals categorized based on their ease of degradation.

In conclusion, various treatment processes have been studied extensively for their efficacy in removing MPs from wastewater, shedding light on degradation mechanisms and optimal conditions. Key findings include the following:

- Ozonation has shown significant potential for removing MPs like carbamazepine, with over 90% removal achieved at low ozone dosages.
- UV irradiation enhances the degradation of MPs, particularly when combined with ozone or hydrogen peroxide, leading to accelerated transformation. Solar irradiation and visible light applications also contribute to the degradation of MPs, although degradation rates may vary depending on the water matrix and the specific compound.
- Sulfate radical-based technologies, such as UV/persulfate, exhibit promising results for removing pharmaceuticals like diclofenac, with removal efficiencies reaching up to 89%.
- Combined approaches, such as UV/H<sub>2</sub>O<sub>2</sub> followed by biological treatment, show promise in achieving mineralization of MPs like carbamazepine.
- Photocatalytic processes utilizing catalysts like TiO<sub>2</sub> and g-C<sub>3</sub>N<sub>4</sub> demonstrate high removal percentages for various MPs, especially when combined with hydrogen peroxide.
- The simultaneous use of hydrogen peroxide in photocatalytic reactors enhances degradation rates, leading to the effective removal of various types of MPs from wastewater.

Advanced oxidation processes take advantage of the high oxidation capacity of the hydroxyl radical for the oxidation of organic molecules under technically feasible conditions, i.e., at normal pressure and temperature. These techniques are thus useful for the removal of micropollutants, which are mostly non-biodegradable chemicals that (bio)accumulate in the environment due to their specific properties and have various, not yet well-known, even long-term harmful effects. These undesirable effects are a clear message to modern society that the spread of these substances into the environment must be better controlled and, above all, prevented, which is also what the development of legislation tends to do.

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### Abbreviations

4MeBZT	4-methylbenzotriazole
5MeBZT	5-methylbenzotriazole
6MeBZT	6-methylbenzotriazole
ACR	almost-complete removal
AMI	Amisulpride
AOP(s)	advanced oxidation process(es)
AS	activated sludge
AsPhA	apricot kernel
ASBR	activated sludge bioreactor
API(s)	active pharmaceutical ingredient(s)
BFO	piezocatalyst
BOD	biological oxygen demand
BT	benzothiazole
BZT(s)	Benzotriazole(s)
CAN	Candesartan
CAR	Carbamazepine
CAS	conventional activated sludge
CIT	Citalopram
CLA	Clarithromycin
CICBZT	5-chloro-1H-benzotriazole
CTW	cooling tower
CW	constructed wetlands
DBP(s)	disinfection by-product(s)
DIC	Diclofenac
DMBZT	5,6-dimethyl-1H-benzotriazole
DOC	dissolved organic carbon
EE2	17-alpha-ethinylestradiol
E1	estrone
E2	17-betaestradiol
ECHA	European Chemicals Agency
EDG	electron-donating group
EE/O	energy efficiency per oxidant
EP	emerging pollutants
EU	European Union
EWG	electron-withdrawing group
GAC	granulated activated carbon
HCH	Hydrochlorothiazide
IRB	Irbesartan
IUPAC	International Union of Pure and Applied Chemistry
MBBR	moving bed biofilm reactor
MET	Metoprolol
MP(s)	micropollutant(s)
MWW	municipal wastewater
MWWTP(s)	municipal wastewater treatment plants
NZVI	nano zero-valent iron
PAC	powdered activated carbon
PDS	peroxydisulfate
PE	Population Equivalent
PMS	peroxymonosulfate
PS	persulfate
PVDF	polyvinylidene fluoride
RCS	reactive chlorine species
RO	reverse osmosis

RSM	response surface methodology
TP(s)	transformation product(s)
TTZ	tolyltriazole
UF	ultrafiltration
UWWTD	Urban Wastewater Treatment Directive
VEN	Venlafaxine
WpOH	wild plum
WW	wastewater
WWTP(s)	wastewater treatment plant(s)

## References

1. Proposal for a Revised Urban Wastewater Treatment Directive—European Commission. Available online: [https://environment.ec.europa.eu/publications/proposal-revised-urban-wastewater-treatment-directive\\_en](https://environment.ec.europa.eu/publications/proposal-revised-urban-wastewater-treatment-directive_en) (accessed on 18 January 2024).
2. European Commission Proposal for a Directive of the European Parliament and of the Council on Setting Standards of Quality and Safety for the Donation, Procurement, Testing, Processing, Storage, and Distribution of Human Tissues and Cells; 2002. Available online: <https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:52002AE1361> (accessed on 28 January 2024).
3. EUR-Lex-01991L0271-20140101—EN—EUR-Lex. Available online: <http://data.europa.eu/eli/dir/1991/271/2014-01-01> (accessed on 30 March 2024).
4. Ribeiro, A.R.; Nunes, O.C.; Pereira, M.F.R.; Silva, A.M.T. An Overview on the Advanced Oxidation Processes Applied for the Treatment of Water Pollutants Defined in the Recently Launched Directive 2013/39/EU. *Environ. Int.* **2015**, *75*, 33–51. [CrossRef]
5. Baronti, C.; Curini, R.; D’Ascenzo, G.; Di Corcia, A.; Gentili, A.; Samperi, R. Monitoring Natural and Synthetic Estrogens at Activated Sludge Sewage Treatment Plants and in a Receiving River Water. *Environ. Sci. Technol.* **2000**, *34*, 5059–5066. [CrossRef]
6. Luo, Y.; Guo, W.; Ngo, H.H.; Nghiem, L.D.; Hai, F.I.; Zhang, J.; Liang, S.; 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**, *473–474*, 619–641. [CrossRef]
7. Mulkerrins, D.; Dobson, A.D.W.; Collieran, E. Parameters Affecting Biological Phosphate Removal from Wastewaters. *Environ. Int.* **2004**, *30*, 249–259. [CrossRef]
8. Welcome to the Norman Network | NORMAN. Available online: <http://www.norman-network.net> (accessed on 30 March 2024).
9. Commission Implementing Decision (EU) 2015/495 of 20 March 2015 Establishing a Watch List of Substances for Union-Wide Monitoring in the Field of Water Policy Pursuant to Directive 2008/105/EC of the European Parliament and of the Council. Off. J. Eur. Commun., L 78/40. Available online: [http://data.europa.eu/eli/dec\\_impl/2015/495/oj](http://data.europa.eu/eli/dec_impl/2015/495/oj) (accessed on 30 January 2024).
10. Eregowda, T.; Mohapatra, S. *Fate of Micropollutants in Engineered and Natural Environment. Resilience, Response, and Risk in Water Systems*; Springer Transactions in Civil and Environmental Engineering; Springer: Singapore, 2020; pp. 283–301.
11. Yu, D.; Yi, X.; Ma, Y.; Yin, B.; Zhuo, H.; Li, J.; Huang, Y. Effects of Administration Mode of Antibiotics on Antibiotic Resistance of *Enterococcus Faecalis* in Aquatic Ecosystems. *Chemosphere* **2009**, *76*, 915–920. [CrossRef]
12. Registration Dossier—ECHA. Available online: <https://echa.europa.eu/sk/registration-dossier/-/registered-dossier/23746/4/6> (accessed on 30 March 2024).
13. 6-Methyl-1H-Benzotriazole 3D-FM11772 | CymitQuimica. Available online: <https://cymitquimica.com/products/3D-FM11772/136-85-6/6-methyl-1h-benzotriazole/> (accessed on 30 March 2024).
14. Substance Information—ECHA. Available online: <https://echa.europa.eu/sk/substance-information/-/substanceinfo/100.004> (accessed on 30 March 2024).
15. Grandclément, C.; Seyssiecq, I.; Piram, A.; Wong-Wah-Chung, P.; Vanot, G.; Tiliacos, N.; Roche, N.; Doumenq, P. From the Conventional Biological Wastewater Treatment to Hybrid Processes, the Evaluation of Organic Micropollutant Removal: A Review. *Water Res.* **2017**, *111*, 297–317. [CrossRef]
16. Gros, M.; Williams, M.; Llorca, M.; Rodriguez-Mozaz, S.; Barceló, D.; Kookana, R.S. Photolysis of the Antidepressants Amisulpride and Desipramine in Wastewaters: Identification of Transformation Products Formed and Their Fate. *Sci. Total Environ.* **2015**, *530–531*, 434–444. [CrossRef]
17. Antonopoulou, M.; Papadaki, M.; Rapti, I.; Konstantinou, I. Photocatalytic Degradation of Pharmaceutical Amisulpride Using G-C3N4 Catalyst and UV-A Irradiation. *Catalysts* **2023**, *13*, 226. [CrossRef]
18. Qiang, L.; Cheng, J.; Yi, J.; Rotchell, J.M.; Zhu, X.; Zhou, J. Environmental Concentration of Carbamazepine Accelerates Fish Embryonic Development and Disturbs Larvae Behavior. *Ecotoxicology* **2016**, *25*, 1426–1437. [CrossRef] [PubMed]
19. Santariová, M.; Zadinová, K.; Vostrá-Vydrová, H.; Kolářová, M.F.; Kurhan, S.; Chaloupková, H. Effect of Environmental Concentration of Carbamazepine on the Behaviour and Gene Expression of Laboratory Rats. *Animals* **2023**, *13*, 2097. [CrossRef] [PubMed]
20. Osawa, R.A.; Carvalho, A.P.; Monteiro, O.C.; Oliveira, M.C.; Florêncio, M.H. Transformation Products of Citalopram: Identification, Wastewater Analysis and in Silico Toxicological Assessment. *Chemosphere* **2019**, *217*, 858–868. [CrossRef] [PubMed]

21. Hong, X.; Chen, R.; Zhang, L.; Yan, L.; Xin, J.; Li, J.; Zha, J. Long-Term Exposure to SSRI Citalopram Induces Neurotoxic Effects in Zebrafish. *Environ. Sci. Technol.* **2022**, *56*, 12380–12390. [CrossRef] [PubMed]
22. About Clarithromycin. Available online: <https://www.nhs.uk/medicines/clarithromycin/about-clarithromycin> (accessed on 30 March 2024).
23. Li, M.; Ji, D.; Pamudji, M.S.; Lui, K.H.; Zhao, Y.; Zhao, G.; Zhou, S.-Q.; Mo, C.-H.; Han, W.; Yeung, K.L. Occurrence, Risk, and Treatment of Ciprofloxacin and Clarithromycin in Drainage. *Chem. Eng. J.* **2023**, *466*, 142968. [CrossRef]
24. Sathishkumar, P.; Meena, R.A.A.; Palanisami, T.; Ashokkumar, V.; Palvannan, T.; Gu, F.L. Occurrence, Interactive Effects and Ecological Risk of Diclofenac in Environmental Compartments and Biota—A Review. *Sci. Total Environ.* **2020**, *698*, 134057. [CrossRef] [PubMed]
25. Fernández-Perales, M.; Sánchez-Polo, M.; Rozalen, M.; López-Ramón, M.; Mota, A.; Rivera-Utrilla, J. Degradation of the Diuretic Hydrochlorothiazide by UV/Solar Radiation Assisted Oxidation Processes. *J. Environ. Manag.* **2020**, *257*, 109973. [CrossRef] [PubMed]
26. Hydrochlorothiazide Removal from Water. Available online: <https://arviatechnology.com/pollutants/hydrochlorothiazide-removal-from-water> (accessed on 30 March 2024).
27. Mansor, N.A.; Tay, K.S. Potential Toxic Effects of Chlorination and UV/Chlorination in the Treatment of Hydrochlorothiazide in the Water. *Sci. Total Environ.* **2020**, *714*, 136745. [CrossRef] [PubMed]
28. Tajik, S.; Beitollahi, H.; Dourandish, Z.; Zhang, K.; Le, Q.V.; Nguyen, T.P.; Kim, S.Y.; Shokouhimehr, M. Recent Advances in the Electrochemical Sensing of Venlafaxine: An Antidepressant Drug and Environmental Contaminant. *Sensors* **2020**, *20*, 3675. [CrossRef] [PubMed]
29. Tang, Y.; Mi, P.; Li, M.; Zhang, S.; Li, J.; Feng, X. Environmental Level of the Antidepressant Venlafaxine Induces Behavioral Disorders through Cortisol in Zebrafish Larvae (Danio Rerio). *Neurotoxicol. Teratol.* **2021**, *83*, 106942. [CrossRef] [PubMed]
30. Sehonova, P.; Svobodova, Z.; Dolezelova, P.; Vosmerova, P.; Faggio, C. Effects of Waterborne Antidepressants on Non-Target Animals Living in the Aquatic Environment: A Review. *Sci. Total Environ.* **2018**, *631–632*, 789–794. [CrossRef] [PubMed]
31. Candesartan Sandoz 8 Mg Tablety. Available online: <https://www.adc.sk/databazy/produkty/detail/candesartan-sandoz-8-mg-tablety-508722.html> (accessed on 30 March 2024).
32. Candesartan Removal from Water. Available online: <https://arviatechnology.com/pollutants/candesartan-removal-from-water> (accessed on 30 March 2024).
33. Struk-Sokołowska, J.; Kotowska, U.; Piekutin, J.; Laskowski, P.; Mielcarek, A. Analysis of 1H-Benzotriazole Removal Efficiency from Wastewater in Individual Process Phases of a Sequencing Batch Reactor SBR. *Water Resour. Ind.* **2022**, *28*, 100182. [CrossRef]
34. Reemtsma, T.; Miehe, U.; Duennbier, U.; Jekel, M. Polar Pollutants in Municipal Wastewater and the Water Cycle: Occurrence and Removal of Benzotriazoles. *Water Res.* **2010**, *44*, 596–604. [CrossRef] [PubMed]
35. Voutsas, D.; Hartmann, P.; Schaffner, C.; Giger, W. Benzotriazoles, Alkylphenols and Bisphenol a in Municipal Wastewaters and in the Glatt River, Switzerland. *Environ. Sci. Pollut. Res.* **2006**, *13*, 333–341. [CrossRef]
36. Hem, L.J.; Hartnik, T.; Roseth, R.; Breedveld, G.D. Photochemical Degradation of Benzotriazole. *J. Environ. Sci. Health Part A* **2003**, *38*, 471–481. [CrossRef] [PubMed]
37. Hart, D.S.; Davis, L.C.; Erickson, L.E.; Callender, T.M. Sorption and Partitioning Parameters of Benzotriazole Compounds. *Microchem. J.* **2004**, *77*, 9–17. [CrossRef]
38. Cancilla, D.A.; Martinez, J.; van Aggelen, G.C. Detection of Aircraft Deicing/Antiicing Fluid Additives in a Perched Water Monitoring Well at an International Airport. *Environ. Sci. Technol.* **1998**, *32*, 3834–3835. [CrossRef]
39. Cancilla, D.A.; Baird, J.C.; Geis, S.W.; Corsi, S.R. Studies of the Environmental Fate and Effect of Aircraft Deicing Fluids: Detection of 5-Methyl-1H-Benzotriazole in the Fathead Minnow (*Pimephales promelas*). *Environ. Toxicol. Chem.* **2003**, *22*, 134–140. [CrossRef] [PubMed]
40. Shi, Z.-Q.; Liu, Y.-S.; Xiong, Q.; Cai, W.; Ying, G.-G. Occurrence, Toxicity and Transformation of Six Typical Benzotriazoles in the Environment: A Review. *Sci. Total Environ.* **2019**, *661*, 407–421. [CrossRef] [PubMed]
41. Cancilla, D.A.; Holtkamp, A.; Matassa, L.; Fang, X. Isolation and Characterization of Microtox<sup>®</sup>-Active Components from Aircraft De-Icing/Anti-Icing Fluids. *Environ. Toxicol. Chem.* **1997**, *16*, 430–434. [CrossRef]
42. Hu, J.; Zhao, L.; Luo, J.; Gong, H.; Zhu, N. A Sustainable Reuse Strategy of Converting Waste Activated Sludge into Biochar for Contaminants Removal from Water: Modifications, Applications and Perspectives. *J. Hazard. Mater.* **2022**, *438*, 129437. [CrossRef]
43. Gupta, A.; Singh, A.; Ilyas, T.; Chowdhary, P.; Chaturvedi, P. *Production and Environmental Applications of Activated Sludge Biochar*; Elsevier: Amsterdam, The Netherlands, 2022; pp. 387–406. [CrossRef]
44. Romero, V.; González, O.; Bayarri, B.; Marco, P.; Giménez, J.; Esplugas, S. Performance of Different Advanced Oxidation Technologies for the Abatement of the Beta-Blocker Metoprolol. *Catal. Today* **2015**, *240*, 86–92. [CrossRef]
45. Kaur, R.; Talan, A.; Tiwari, B.; Pilli, S.; Sellamuthu, B.; Tyagi, R.D. Chapter 5—Constructed wetlands for the removal of organic micro-pollutants. *Curr. Dev. Biotechnol. Bioeng.* **2020**, 87–140. [CrossRef]
46. Issaka, E.; AMU-Darko, J.N.-O.; Yakubu, S.; Fapohunda, F.O.; Ali, N.; Bilal, M. Advanced Catalytic Ozonation for Degradation of Pharmaceutical Pollutants—A Review. *Chemosphere* **2022**, *289*, 133208. [CrossRef]

47. Sgroi, M.; Snyder, S.A.; Roccaro, P. Comparison of AOPs at Pilot Scale: Energy Costs for Micro-Pollutants Oxidation, Disinfection By-Products Formation and Pathogens Inactivation. *Chemosphere* **2020**, *273*, 128527. [CrossRef] [PubMed]
48. Mousset, E.; Loh, W.H.; Lim, W.S.; Jarry, L.; Wang, Z.; Lefebvre, O. Cost Comparison of Advanced Oxidation Processes for Wastewater Treatment Using Accumulated Oxygen-Equivalent Criteria. *Water Res.* **2021**, *200*, 117234. [CrossRef]
49. von Gunten, U. Ozonation of Drinking Water: Part I. *Oxid. Kinet. Prod. Formation. Water Res.* **2003**, *37*, 1443–1467. [CrossRef] [PubMed]
50. Jesus, F.; Domingues, E.; Bernardo, C.; Pereira, J.L.; Martins, R.C.; Gomes, J. Ozonation of Selected Pharmaceutical and Personal Care Products in Secondary Effluent—Degradation Kinetics and Environmental Assessment. *Toxics* **2022**, *10*, 765. [CrossRef]
51. Nawrocki, J.; Kasprzyk-Hordern, B. The Efficiency and Mechanisms of Catalytic Ozonation. *Appl. Catal. B Environ.* **2010**, *99*, 27–42. [CrossRef]
52. Haag, W.R.; Hoigne, J. Ozonation of Bromide-Containing Waters: Kinetics of Formation of Hypobromous Acid and Bromate. *Environ. Sci. Technol.* **1983**, *17*, 261–267. [CrossRef]
53. Wang, J.; Chen, H. Catalytic Ozonation for Water and Wastewater Treatment: Recent Advances and Perspective. *Sci. Total Environ.* **2020**, *704*, 135249. [CrossRef]
54. Cuerda-Correa, E.M.; Alexandre-Franco, M.F.; Fernández-González, C. Advanced Oxidation Processes for the Removal of Antibiotics from Water. *Overview. Water* **2019**, *12*, 102. [CrossRef]
55. Lu, H.; Li, Q.; Feng, W. Application Progress of O<sub>3</sub>/UV Advanced Oxidation Technology in the Treatment of Organic Pollutants in Water. *Sustainability* **2022**, *14*, 1556. [CrossRef]
56. Kurokawa, Y.; Maekawa, A.; Takahashi, M.; Hayashi, Y. Toxicity and Carcinogenicity of Potassium Bromate—A New Renal Carcinogen. *Environ. Health Perspect.* **1990**, *87*, 309–335. [CrossRef] [PubMed]
57. Agrawal, S.; Chohadia, A.K.; Sherry, P.; Malhotra, G.; Verma, K. A Review on Wastewater Treatment Containing Organic Pollutants Using Advance Oxidation Processes. *Int. J. Sci. Res. Sci. Technol.* **2023**, *10*, 1. [CrossRef]
58. Urbina-Suarez, N.A.; López-Barrera, G.L.; García-Martínez, J.B.; Barajas-Solano, A.F.; Machuca-Martínez, F.; Zuurro, A. Enhanced UV/H<sub>2</sub>O<sub>2</sub> System for the Oxidation of Organic Contaminants and Ammonia Transformation from Tannery Effluents. *Processes* **2023**, *11*, 3091. [CrossRef]
59. Available online: <https://spartanwatertreatment.com/advanced-oxidation-uv-peroxide/> (accessed on 30 March 2024).
60. Zhu, T.; Deng, J.; Zhu, S.; Cai, A.; Ye, C.; Ling, X.; Guo, H.; Wang, Q.; Li, X. Kinetic and Mechanism Insights into the Degradation of Venlafaxine by UV/Chlorine Process: A Modelling Study. *Chem. Eng. J.* **2022**, *431*, 133473. [CrossRef]
61. Remucal, C.K.; Manley, D. Emerging Investigators Series: The Efficacy of Chlorine Photolysis as an Advanced Oxidation Process for Drinking Water Treatment. *Environ. Sci. Water Res. Technol.* **2016**, *2*, 565–579. [CrossRef]
62. Buxton, G.V.; Subhani, M.S. Radiation chemistry and photochemistry of oxychlorine ions. Part 2.—Photodecomposition of aqueous solutions of hypochlorite ions. *J. Chem. Soc. Faraday Trans. 1 Phys. Chem. Condens. Phases* **1972**, *68*, 958–969. [CrossRef]
63. Singh, P.; Jain, R.; Srivastava, N.; Borthakur, A.; Pal, D.B.; Singh, R.; Madhav, S.; Srivastava, P.; Tiwary, D.; Mishra, P.K. Current and Emerging Trends in Bioremediation of Petrochemical Waste: A Review. *Crit. Rev. Environ. Sci. Technol.* **2017**, *47*, 155–201. [CrossRef]
64. Pirkanniemi, K.; Sillanpää, M. Heterogeneous Water Phase Catalysis as an Environmental Application: A Review. *Chemosphere* **2002**, *48*, 1047–1060. [CrossRef]
65. Jiao, J.; Li, Y.; Song, Q.; Wang, L.; Luo, T.; Gao, C.; Liu, L.; Yang, S. Removal of Pharmaceuticals and Personal Care Products (PPCPs) by Free Radicals in Advanced Oxidation Processes. *Materials* **2022**, *15*, 8152. [CrossRef]
66. General Chemistry of Fenton Reagent. Available online: <https://h2o2.com/industrial/fentons-reagent.aspx?pid=143&name=General-Chemistry-of-Fenton-s-Reagent> (accessed on 28 February 2020).
67. Deng, Y.; Englehardt, J.D. Treatment of Landfill Leachate by the Fenton Process. *Water Res.* **2006**, *40*, 3683–3694. [CrossRef]
68. Navalon, S.; Alvaro, M.; Garcia, H. Heterogeneous Fenton Catalysts Based on Clays, Silicas and Zeolites. *Appl. Catal. B Environ.* **2010**, *99*, 1–26. [CrossRef]
69. Walling, C. Fenton's Reagent Revisited. *Acc. Chem. Res.* **1975**, *8*, 125–131. [CrossRef]
70. Yan, Y.; Wei, Z.; Duan, X.; Long, M.; Spinney, R.; Dionysiou, D.D.; Xiao, R. Pedro Merits and Limitations of Radical vs. Nonradical Pathways in Persulfate-Based Advanced Oxidation Processes. *Environ. Sci. Technol.* **2023**, *57*, 12153–12179. [CrossRef]
71. Su, C.-J.; Li, C.-L.; Wang, W.-H. Efficient Piezocatalytic Activation of Peroxydisulfate over Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub>: Thickness-Dependent Synergy Effect between Peroxydisulfate Activation and Piezocatalysis. *Rare Met. Rare Met.* **2023**, *42*, 4005–4014. [CrossRef]
72. Shi, P.; Yue, X.; Teng, X.; Qu, R.; Rady, A.; Maodaa, S.; Allam, A.A.; Wang, Z.; Huo, Z. Degradation of Butylated Hydroxyanisole by the Combined Use of Peroxymonosulfate and Ferrate(VI): Reaction Kinetics, Mechanism and Toxicity Evaluation. *Toxics* **2024**, *12*, 54. [CrossRef]
73. Lu, X.; Shao, Y.; Gao, N.; Chen, J.; Zhang, Y.; Xiang, H.; Guo, Y. Degradation of Diclofenac by UV-Activated Persulfate Process: Kinetic Studies, Degradation Pathways and Toxicity Assessments. *Ecotoxicol. Environ. Saf.* **2017**, *141*, 139–147. [CrossRef]
74. Deng, H. Ozonation Mechanism of Carbamazepine and Ketoprofen in RO Concentrate from Municipal Wastewater Treatment: Kinetic Regimes, Removal Efficiency and Matrix Effect. *Sci. Total Environ.* **2020**, *717*, 137150. [CrossRef]

75. Deng, H. A Review on the Application of Ozonation to NF/RO Concentrate for Municipal Wastewater Reclamation. *J. Hazard. Mater.* **2020**, *391*, 122071. [[CrossRef](#)]
76. Lee, W.; Choi, S.; Kim, H.; Lee, W.; Lee, M.; Son, H.-J.; Lee, C.H.; Cho, M.; Lee, Y. Efficiency of Ozonation and O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> as Enhanced Wastewater Treatment Processes for Micropollutant Abatement and Disinfection with Minimized Byproduct Formation. *J. Hazard. Mater.* **2023**, *454*, 131436. [[CrossRef](#)]
77. Edefell, E.; Falås, P.; Kharel, S.; Hagman, M.; Christensson, M.; Cimbritz, M.; Bester, K. MBBRs as Post-Treatment to Ozonation: Degradation of Transformation Products and Ozone-Resistant Micropollutants. *Sci. Total Environ.* **2021**, *754*, 142103. [[CrossRef](#)]
78. Jabbari, F.; Eslami, A.; Mahmoudian, J. Degradation of Diclofenac in Water Using the O<sub>3</sub>/UV/S<sub>2</sub>O<sub>8</sub> Advanced Oxidation Process. *Health Scope* **2020**, *9*, e99436. [[CrossRef](#)]
79. Shu, Z.; Bolton, J.R.; Belosevic, M.; Gamal El Din, M. Photodegradation of Emerging Micropollutants Using the Medium-Pressure UV/H<sub>2</sub>O<sub>2</sub> Advanced Oxidation Process. *Water Res.* **2013**, *47*, 2881–2889. [[CrossRef](#)]
80. Angosto, J.M.; Roca, M.J.; Fernández-López, J.A. Removal of Diclofenac in Wastewater Using Biosorption and Advanced Oxidation Techniques: Comparative Results. *Water* **2020**, *12*, 3567. [[CrossRef](#)]
81. Jaén-Gil, A.; Buttiglieri, G.; Benito, A.; Mir-Tutusaus, J.A.; Gonzalez-Olmos, R.; Caminal, G.; Barceló, D.; Sarrà, M.; Rodriguez-Mozaz, S. Combining Biological Processes with UV/H<sub>2</sub>O<sub>2</sub> for Metoprolol and Metoprolol Acid Removal in Hospital Wastewater. *Chem. Eng. J.* **2021**, *404*, 126482. [[CrossRef](#)]
82. Keen, O.S.; Baik, S.; Linden, K.G.; Aga, D.S.; Love, N.G. Enhanced Biodegradation of Carbamazepine after UV/H<sub>2</sub>O<sub>2</sub> Advanced Oxidation. *Environ. Sci. Technol.* **2012**, *46*, 6222–6227. [[CrossRef](#)]
83. Spyrou, A.; Tzamaria, A.; Dormousoglou, M.; Skourti, A.; Vlastos, D.; Papadaki, M.; Antonopoulou, M. The Overall Assessment of Simultaneous Photocatalytic Degradation of Cimetidine and Amisulpride by Using Chemical and Genotoxicological Approaches. *Sci. Total Environ.* **2022**, *838*, 156140. [[CrossRef](#)]
84. Jiménez-Holgado, C.; Calza, P.; Fabbri, D.; Dal Bello, F.; Medana, C.; Sakkas, V. Investigation of the Aquatic Photolytic and Photocatalytic Degradation of Citalopram. *Molecules* **2021**, *26*, 5331. [[CrossRef](#)]
85. Rapti, I.; Kosma, C.; Albanis, T.; Konstantinou, I. Solar Photocatalytic Degradation of Inherent Pharmaceutical Residues in Real Hospital WWTP Effluents Using Titanium Dioxide on a CPC Pilot Scale Reactor. *Catal. Today* **2023**, *423*, 113884. [[CrossRef](#)]
86. Vakros, J. Catalytic Processes for Water and Wastewater Treatment. *Catalysts* **2023**, *13*, 677. [[CrossRef](#)]
87. Valenzuela, L.; Pedrosa, M.; Bahamonde, A.; Rosal, R.; Torres-Pinto, A.; Silva, C.G.; Faria, J.L.; Adrián, M.T. Silva Carbon Nitride—PVDF Photocatalytic Membranes for Visible-Light Degradation of Venlafaxine as Emerging Water Micropollutant. *Catal. Today* **2023**, *418*, 114042. [[CrossRef](#)]
88. Schnabel, T.; Mehling, S.; Londong, J.; Springer, C. Hydrogen Peroxide-Assisted Photocatalytic Water Treatment for the Removal of Anthropogenic Trace Substances from the Effluent of Wastewater Treatment Plants. *Water Sci. Technol.* **2020**, *82*, 2019–2028. [[CrossRef](#)]
89. Hörsing, M.; Kosjek, T.; Andersen, H.R.; Heath, E.; Ledin, A. Fate of Citalopram during Water Treatment with O<sub>3</sub>, ClO<sub>2</sub>, UV and Fenton Oxidation. *Chemosphere* **2012**, *89*, 129–135. [[CrossRef](#)]
90. Ternes, T.A.; Stüber, J.; Herrmann, N.; McDowell, D.; Ried, A.; Kampmann, M.; Teiser, B. Ozonation: A Tool for Removal of Pharmaceuticals, Contrast Media and Musk Fragrances from Wastewater? *Water Res.* **2003**, *37*, 1976–1982. [[CrossRef](#)]
91. Naghizadeh, M.; Aghapour, A.A.; Khorsandi, H. The Degradation and Mineralization of Hydrochlorothiazide (HCTZ) Using Catalytic Ozonation Process (COP) with Al<sub>2</sub>O<sub>3</sub>/Granular Activated Carbon Composite. *React. Kinet. Mech. Catal.* **2022**, *135*, 1875–1889. [[CrossRef](#)]
92. Kosman, J.; Monteiro, L.; Lenart, V.M.; Los Weinert, P.; Regina, E. UV-Vis LED-Assisted Photo-Fenton Process for Mineralization of Losartan and Hydrochlorothiazide: Optimization Using Desirability Function. *Environ. Sci. Pollut. Res.* **2021**, *28*, 24046–24056. [[CrossRef](#)]
93. Luongo, G.; Saviano, L.; Libralato, G.; Guida, M.; Siciliano, A.; Previtiera, L.; Di Fabio, G.; Zarrelli, A. Secondary Effects of Hypochlorite Treatment on the Emerging Pollutant Candesartan: The Formation of Degradation Byproducts and Their Toxicological Profiles. *Molecules* **2021**, *26*, 3422. [[CrossRef](#)]
94. Li, R.; Liang, C.; Svendsen, S.B.; Kisielius, V.; Bester, K. Sartan Blood Pressure Regulators in Classical and Biofilm Wastewater Treatment—Concentrations and Metabolism. *Water Res.* **2023**, *229*, 119352. [[CrossRef](#)]
95. Pap, S.; Paunovic, O.; Prosen, H.; Kraševc, I.; Trebše, P.; Niemi, L.; Taggart, M.A. Maja Turk Sekulic Removal of Benzotriazole Derivatives by Biochar: Potential Environmental Applications. *Environ. Pollut.* **2023**, *334*, 122205. [[CrossRef](#)]
96. Alotaibi, M.D.; Patterson, B.M.; McKinley, A.J.; Reeder, A.Y.; Furness, A.J.; Donn, M.J. Fate of Benzotriazole and 5-Methylbenzotriazole in Recycled Water Recharged into an Anaerobic Aquifer: Column Studies. *Water Res.* **2015**, *70*, 184–195. [[CrossRef](#)]
97. Gatidou, G.; Oursouzidou, M.; Stefanatou, A.; Stasinakis, A.S. Removal Mechanisms of Benzotriazoles in Duckweed Lemna Minor Wastewater Treatment Systems. *Sci. Total Environ.* **2017**, *596–597*, 12–17. [[CrossRef](#)]
98. Kowalska, K.; Felis, E.; Sochacki, A.; Bajkacz, S. Removal and Transformation Pathways of Benzothiazole and Benzotriazole in Membrane Bioreactors Treating Synthetic Municipal Wastewater. *Chemosphere* **2019**, *227*, 162–171. [[CrossRef](#)]

99. Mazioti, A.A.; Stasinakis, A.S.; Pantazi, Y.; Andersen, H.R. Biodegradation of Benzotriazoles and Hydroxy-Benzothiazole in Wastewater by Activated Sludge and Moving Bed Biofilm Reactor Systems. *Bioresour. Technol.* **2015**, *192*, 627–635. [[CrossRef](#)]
100. Ahmadi, M.; Rahmani, K.; Rahmani, A.; Rahmani, H. Removal of Benzotriazole by Photo-Fenton like Process Using Nano Zero-Valent Iron: Response Surface Methodology with a Box-Behnken Design. *Pol. J. Chem. Technol.* **2017**, *19*, 104–112. [[CrossRef](#)]
101. Weiss, S.; Jakobs, J.; Reemtsma, T. Discharge of Three Benzotriazole Corrosion Inhibitors with Municipal Wastewater and Improvements by Membrane Bioreactor Treatment and Ozonation. *Environ. Sci. Technol.* **2006**, *40*, 7193–7199. [[CrossRef](#)]
102. Minella, M.; De Laurentiis, E.; Pellegrino, F.; Prozzi, M.; Dal Bello, F.; Maurino, V.; Minero, C. Photocatalytic Transformations of 1H-Benzotriazole and Benzotriazole Derivates. *Nanomaterials* **2020**, *10*, 1835. [[CrossRef](#)]
103. Yang, T.; Mai, J.; Wu, S.; Liu, C.; Tang, L.; Mo, Z.; Zhang, M.; Guo, L.; Liu, M.; Ma, J. UV/Chlorine Process for Degradation of Benzothiazole and Benzotriazole in Water: Efficiency, Mechanism and Toxicity Evaluation. *Sci. Total Environ.* **2021**, *760*, 144304. [[CrossRef](#)]
104. Malinović, B.N.; Markelj, J.; Žgajnar Gotvajn, A.; Kralj Cigić, I.; Prosen, H. Electrochemical Treatment of Wastewater to Remove Contaminants from the Production and Disposal of Plastics: A Review. *Environ. Chem. Lett.* **2022**, *20*, 3765–3787. [[CrossRef](#)]
105. Wagner, T.V.; Parsons, J.R.; Rijnaarts, H.H.M.; de Voogt, P.; Alette, A.M. Langenhoff Benzotriazole Removal Mechanisms in Pilot-Scale Constructed Wetlands Treating Cooling Tower Water. *J. Hazard. Mater.* **2020**, *384*, 121314. [[CrossRef](#)]
106. Nie, Y.; Qiang, Z.; Zhang, H.; Ben, W. Fate and Seasonal Variation of Endocrine-Disrupting Chemicals in a Sewage Treatment Plant with A/A/O Process. *Sep. Purif. Technol.* **2012**, *84*, 9–15. [[CrossRef](#)]
107. Qiang, Z.; Nie, Y.; Ben, W.; Qu, J.; Zhang, H. Degradation of Endocrine-Disrupting Chemicals during Activated Sludge Reduction by Ozone. *Chemosphere* **2013**, *91*, 366–373. [[CrossRef](#)] [[PubMed](#)]
108. Deblonde, T.; Cossu-Leguille, C.; Hartemann, P. Emerging Pollutants in Wastewater: A Review of the Literature. *Int. J. Hyg. Environ. Health* **2011**, *214*, 442–448. [[CrossRef](#)] [[PubMed](#)]
109. Singh, S.; Seth, R.; Tabe, S.; Yang, P. Oxidation of Emerging Contaminants during Pilot-Scale Ozonation of Secondary Treated Municipal Effluent. *Ozone Sci. Eng.* **2015**, *37*, 323–329. [[CrossRef](#)]
110. Bourgin, M.; Beck, B.; Boehler, M.; Borowska, E.; Fleiner, J.; Salhi, E.; Teichler, R.; von Gunten, U.; Siegrist, H.; McArdell, C.S. Evaluation of a Full-Scale Wastewater Treatment Plant Upgraded with Ozonation and Biological Post-Treatments: Abatement of Micropollutants, Formation of Transformation Products and Oxidation By-Products. *Water Res.* **2018**, *129*, 486–498. [[CrossRef](#)] [[PubMed](#)]
111. Marce, M.; Palacios, O.; Bartolomé, A.; Caixach, J.; Baig, S.; Esplugas, S. Application of Ozone on Activated Sludge: Micropollutant Removal and Sludge Quality. *Ozone Sci. Eng.* **2017**, *39*, 319–332. [[CrossRef](#)]
112. Council Directive 91/271/EEC Concerning Urban Waste Water Treatment. Available online: [https://www.europarl.europa.eu/doceo/document/A-9-2023-0276\\_EN.html](https://www.europarl.europa.eu/doceo/document/A-9-2023-0276_EN.html) (accessed on 30 March 2024).
113. Ak, M.S.; Muz, M.; Komesli, O.T.; Gökçay, C.F. Enhancement of Bio-Gas Production and Xenobiotics Degradation during Anaerobic Sludge Digestion by Ozone Treated Feed Sludge. *Chem. Eng. J.* **2013**, *230*, 499–505. [[CrossRef](#)]
114. Nie, Y.; Qiang, Z.; Ben, W.; Liu, J. Removal of Endocrine-Disrupting Chemicals and Conventional Pollutants in a Continuous-Operating Activated Sludge Process Integrated with Ozonation for Excess Sludge Reduction. *Chemosphere* **2014**, *105*, 133–138. [[CrossRef](#)] [[PubMed](#)]
115. Burzio, C.; Ekholm, J.; Modin, O.; Falås, P.; Svahn, O.; Persson, F.; van Erp, T.; Gustavsson, D.J.I.; Wilén, B.-M. Removal of Organic Micropollutants from Municipal Wastewater by Aerobic Granular Sludge and Conventional Activated Sludge. *J. Hazard. Mater.* **2022**, *438*, 129528. [[CrossRef](#)] [[PubMed](#)]
116. Albergamo, V.; Blankert, B.; Cornelissen, E.R.; Hofs, B.; Knibbe, W.-J.; van der Meer, W.; de Voogt, P. Removal of Polar Organic Micropollutants by Pilot-Scale Reverse Osmosis Drinking Water Treatment. *Water Res.* **2019**, *148*, 535–545. [[CrossRef](#)]
117. Boström, S. Occurrence and Fate of 7 APIs in Two Sewage Treatment Plants—And their Reactions to Tertiary Treatment. Dissertation. 2020. Available online: <https://urn.kb.se/resolve?urn=urn:nbn:se:umu:diva-194371> (accessed on 30 March 2024).
118. Büning, B.; Rechtenbach, D.; Behrendt, J.; Otterpohl, R. Removal of emerging micropollutants from wastewater by nanofiltration and biofilm reactor (MicroStop). *Environ. Prog. Sustain. Energy* **2021**, *40*, e13587. [[CrossRef](#)]
119. Hollender, J.; Zimmermann, S.G.; Koepke, S.; Krauss, M.; McArdell, C.S.; Ort, C.; Singer, H.; von Gunten, U.; Siegrist, H. Elimination of Organic Micropollutants in a Municipal Wastewater Treatment Plant Upgraded with a Full-Scale Post-Ozonation Followed by Sand Filtration. *Environ. Sci. Technol.* **2009**, *43*, 7862–7869. [[CrossRef](#)] [[PubMed](#)]
120. Wang, J.; Tian, Z.; Huo, Y.; Yang, M.; Zheng, X.; Zhang, Y. Monitoring of 943 Organic Micropollutants in Wastewater from Municipal Wastewater Treatment Plants with Secondary and Advanced Treatment Processes. *J. Environ. Sci.* **2018**, *67*, 309–317. [[CrossRef](#)] [[PubMed](#)]
121. Boehler, M.; Zwickenpflug, B.; Hollender, J.; Ternes, T.; Joss, A.; Siegrist, H. Removal of Micropollutants in Municipal Wastewater Treatment Plants by Powder-Activated Carbon. *Water Sci. Technol.* **2012**, *66*, 2115–2121. [[CrossRef](#)] [[PubMed](#)]
122. Margot, J.; Kienle, C.; Magnet, A.; Weil, M.; Rossi, L.; de Alencastro, L.F.; Abegglen, C.; Thonney, D.; Chèvre, N.; Schärer, M.; et al. Treatment of Micropollutants in Municipal Wastewater: Ozone or Powdered Activated Carbon? *Sci. Total Environ.* **2013**, *461–462*, 480–498. [[CrossRef](#)] [[PubMed](#)]
123. Sturm, M.T.; Myers, E.; Schober, D.; Thege, C.; Korzin, A.; Schuhen, K. Adaptable Process Design as a Key for Sustainability Upgrades in Wastewater Treatment: Comparative Study on the Removal of Micropollutants by Advanced Oxidation and Granular Activated Carbon Processing at a German Municipal Wastewater Treatment Plant. *Sustainability* **2022**, *14*, 11605. [[CrossRef](#)]

124. Kumar, M.; Sridharan, S.; Sawarkar, A.D.; Shakeel, A.; Anero, P.; Mannina, G.; Sharma, P.; Pandey, A. Current Research Trends on Emerging Contaminants Pharmaceutical and Personal Care Products (PPCPs): A Comprehensive Review. *Sci. Total Environ.* **2023**, *859*, 160031. [[CrossRef](#)]
125. Lember, E.; Kubliņa, A.; Kokorīte, I.; Putna, I.; Suzdalev, S. Recommendations for Wastewater Treatment Plants for Safe Removal of Pharmaceuticals and List of Pharmaceuticals to Be Monitored. *Latvijas Vides, Ģeoloģijas un Meteoroloģijas Centrs*. 2023. p. 6–56. Available online: <https://videscentrs.lv/gmc.lv/> (accessed on 1 April 2024).

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