Advanced oxidation processes for removal of organic micropollutants from wastewater

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Abstract

Treatment of emerging pollutants is one of the global necessities in the water sector aimed at water and wastewater treatment sustainability. This is a key action from the point of view of the safety of the environmental water bodies and the reuse of wastewater for economic purposes. Water bodies are systematically polluted by municipal, industrial and agricultural effluents which contain numerous hazardous pollutants, including organic micropollutants (OMPs). This is because most of the existing wastewater treatment plants (WWTPs) are not adapted to be able to remove OMPs from wastewater. In a typical WWTP, some of the micropollutants are biodegradable, much of them are adsorbed in the sewage sludge but, unfortunately, some of them flow with the effluent into natural receiving bodies and cause serious environmental problems. Recently, there has been growing interest in using advanced oxidation processes (AOPs) to remove emerging micropollutants from wastewater. Numerous literature reports and the results of full-scale application demonstrate the suitability of AOP methods for the removal of OMPs. This paper reviews a wide range of AOPs methods used for the degradation of selected OMPs, such as pharmaceuticals, organic dyes, pesticides, and microplastic in wastewater. The role of treatment process parameters, including input power, reaction time, chemicals addition, and the concentration of micropollutants on degradation efficiency was discussed. In addition, the degradation kinetics and the possibilities of creating intermediate products by AOP were reported.

Keywords: Organic micropollutants; Wastewater treatment; Advanced oxidation processes; Emerging contaminants removal

1. Introduction

The intensively developing pharmaceutical industry and the growing trend of drug consumption year by year lead to an increase in the concentration of pharmacological products and their metabolites in wastewater. Poland is one of the world's leading countries in terms of the number of used drugs per capita [1]. The migration of these pollutants in the environment is very dangerous due to the threat to the health and life of humans and animals. In addition, the presence of antibiotics in surface waters contributes to the acquisition of bacteria resistance, which results in an increase in drug-resistant populations [2].

Dyes are also common organic pollutants in wastewater. Every year, huge amounts of this compounds are discharged into the wastewater, which poses a serious threat to the environment. Dyes in sewage also pose a risk to human health due to the possibility of bioaccumulation, due to which they can enter the food chain. Therefore, treatment of wastewater from the textile industry containing significant amounts of dyes has received a lot of interest. Many studies concern the use of advanced oxidation processes...
(AOP) methods using oxidants such as ozone, Fenton and photo-Fenton reagents and hydrogen peroxide [3,4].

Another important group of pollutants are pesticides, and other plant protection products, that are intended to protect crops against fungi (fungicides), insects (insecticides) and weeds (herbicides) [5]. The use of these plant protection products is common in agriculture, horticulture and orchards. Therefore, their presence in sewage is not surprising. According to official data, in 2017 in Poland, 2.5 kg of the active substance was used per hectare of cultivation, which ranked as 13th among European Union countries [6].

The next major environmental problem are microplastics, which are particles with sizes ranging from 1 µm to 5 mm. During the treatment of raw wastewater, about 90% of microplastics are removed (remains in sewage sludge), the remaining part discharged with effluent to natural reservoirs poses a serious threat to the environment, for example, due to the sorbing of organic micropollutants in the form of, for example, PAHs (polycyclic aromatic hydrocarbons) on the surface of the microplastic. Studies show that microplastic particles are ubiquitous and dangerous to fauna and flora [7,8]. In 2016, the production of plastic exceeded 330 million tons, and in 2019 it reached a figure close to 370 million tons, of which in Europe alone the amount reached almost 58 million tons, indicating the scale of the dissemination of this material in the environment [9]. In addition, microplastic particles interact with pollutants such as dyes and heavy metals, which allow them to act as vectors for the accumulation and transport of organic and inorganic pollutants that adhere to their surfaces [10].

Conventional methods of wastewater treatment involving mechanical, biological or chemical treatment are no longer effective enough to guarantee the elimination of micropollutants found in wastewater in the form of pharmaceuticals, organic dyes, pesticides or microplastics, the concentrations of which in treated wastewater raise increasing concerns. This entire mixture is discharged to natural receivers, for example, rivers, from where it migrates further in the natural environment, posing a huge risk to the health and life of people and animals. That is why it is so important to introduce new technologies that allow for higher efficiency in removing these pollutants.

The lack of adequate efficiency in removing organic micropollutants from wastewater has led to increased interest in using advanced oxidation processes (AOP) for this purpose. A common feature of all variants of the AOP technique is the oxidizing agent, mainly very reactive hydroxyl radicals with high oxidation–reduction potential. The use of advanced oxidation processes allows the mineralization of pollutants present in sewage into carbon dioxide and water and inorganic compounds [11,12].

### Table 1

<table>
<thead>
<tr>
<th>Advanced oxidation processes</th>
<th>Classification of advanced oxidation processes (based on Neczaj [11])</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₃ and H₂O₂ oxidation</td>
<td>UV photolysis</td>
</tr>
<tr>
<td>Fenton reaction</td>
<td>Processes using UV/O₃</td>
</tr>
<tr>
<td>Electrochemical oxidation</td>
<td>Processes using UV/H₂O₂</td>
</tr>
<tr>
<td>Wet air oxidation</td>
<td>Processes using UV/O₂/H₂O₂</td>
</tr>
<tr>
<td>Supercritical water oxidation</td>
<td>Photo-Fenton reaction</td>
</tr>
<tr>
<td></td>
<td>Photocatalytic degradation in aqueous suspensions of semiconductors</td>
</tr>
<tr>
<td></td>
<td>Ultrasonic processes</td>
</tr>
</tbody>
</table>

### 2. Advanced oxidation processes

Conventional methods of wastewater treatment are not able to fully eliminate the pollutants that are identified in the wastewater both flowing into the treatment plant and those that are discharged to receivers. As a result, advanced oxidation processes have been recognized as one of the most promising methods that can be used to mineralize complex organic pollutants [13]. AOP methods are based on the use of strong oxidants, characterized by a high oxidation potential [14]. Oxidation processes are mainly based on the use of OH⁺ hydroxyl radicals, the oxidation potential is 2.8 V. Hydroxyl radicals are the strongest oxidants used in wastewater and water treatment [12]. They are characterized by non-selective oxidation of organic compounds to carbon dioxide (CO₂) and water (H₂O) and reaction speed [15]. Hydroxyl radicals can be formed during the decomposition of ozone in an aqueous environment, the photolysis of hydrogen peroxide, an aqueous solution of iron(III), chlorine in an aqueous environment, in the Fenton reaction as well as under the influence of ionizing radiation [16]. The OH⁺ radical can react with organic compounds in three ways:

- splitting a hydrogen atom,
- electrophilic addition,
- electron transfer.

Each of these processes leads to the formation of organic radicals with an unpaired electron on the carbon atom, which reacts quickly with dissolved oxygen, resulting in superoxide radicals, which is the first stage of oxidation of organic compounds [17]. The efficiency of AOP processes is mainly dependent on the type of pollutants present in the wastewater and the oxidation parameters. They are recognized as an effective method in removing hazardous pollutants by mineralizing them to inorganic aliphatic acid, carbon dioxide and water [13].

Among the AOP methods, chemical processes and photochemical processes that are induced by light are distinguished (Table 1).
2.1. Chemical processes

2.1.1. O₃ and H₂O₂ oxidation

Ozone is most often used to remove pollutants that are difficult to biodegrade or are toxic. It is an oxidant characterized by selective action. In addition, it has disinfecting properties and deactivates the cells of pathogenic microorganisms. Ozone itself is unstable and quickly converts to molecular oxygen, which reduces the level of its use. Most often, O₃ is used for the treatment of drinking water, water in swimming pools, municipal and industrial wastewater and leachates [18,12]. Moreover, the ozonation process generates high costs and poses a corrosion risk [19,20]. The oxidation process with the use of ozone causes the formation of a number of by-products, which include: low-molecular organic compounds, for example, aldehydes; brominated organic compounds, for example, bromoacetic acids; inorganic compounds, that is, bromates and oxidized, highly polar organic compounds [21]. The oxidation potential of O₃ is 2.07 V, while that of H₂O₂ is 1.77 V. Therefore, hydrogen peroxide can also be successfully used in wastewater treatment. Often these two oxidants are used in combination with each other due to the fact that hydrogen peroxide significantly reduces the cost of the process. The approximate reaction mechanism is shown below [12]:

\[
\text{H}_2\text{O}_2 \rightarrow \text{HOO}^- + \text{H}^+
\]

\[
\text{HOO}^- + \text{O}_3 \rightarrow \text{HOO}^* + \text{O}_3^-
\]

It is assumed that ozone reacts with excess HO₂⁻ and generates hydroxyl radicals. Too low and too high concentrations of hydrogen peroxide should be avoided. There exists an "ozone dose threshold" below which the addition of H₂O₂ yielded no noticeable increase in the rate of OH⁻ production [18].

2.1.2. Fenton’s reaction

The Fenton reaction involves the use of Fe²⁺ ions and hydrogen peroxide. Modifications of the classic Fenton’s reagent are also used by using iron(III) ions in combination with an excess of H₂O₂. Thanks to such a modification, it is possible to recover Fe³⁺ ions together with obtaining hydroxyl radicals. This allows for the oxidation and reduction of organic compounds [14]. Most organic compounds containing hydrogen can be successfully reduced using Fenton’s reagent. The advantages of the process undoubtedly include: reaction speed with high efficiency, simplicity, no H₂O₂ residue in the post-reaction system, availability of reagents and moderate costs of the process [22,23]. However, the limitation of the method is: a specific pH (3–4), as well as a large consumption of substrates related to the non-selectivity of the process [24].

The Fenton reaction produces an iron ion, a hydroxyl radical, and a hydroxyl ion. The decomposition of H₂O₂ catalyzed by Fe²⁺ ions is represented by the following reaction:

\[
\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{OH}^- + \text{OH}^-
\]

In the next stages of the reaction, Fe³⁺ ions are regenerated from Fe²⁺ ions [25]. Oxidation of industrial wastewater most often takes place in unpressurized batch reactors. A typical reactor is a non-pressurized tank with a stirrer (Fig. 1) [12,23].

The efficiency of the oxidation reaction increases with the increase in the concentration of iron ions and hydrogen peroxide. However, too high concentrations of both substrates may cause a decrease in the reaction rate (Fig. 2). The Fenton process is used for several types of wastewater: refinery wastewater, wastewater from the production of polymers containing, for example, phenol, wastewater from the wood industry, wastewater from soil treatment and process waters generated during the synthesis of, for example, drugs and pesticides [12].

Research conducted by Krzemieńska et al. [27] regarding the use of the Fenton reaction for support biological wastewater treatment from the dairy industry, showed that the efficiency of eliminating organic compounds and the biodegradability increases with the increase in the reagents concentration. The maximum value was obtained for a dose of 1.2 g·Fe²⁺/L and 2 g·H₂O₂/L. Moreover, it was found that a further increase in the concentration of reagents decreased the treatment efficiency.

2.1.3. Electrochemical oxidation

Electrochemical oxidation is quite rarely used due to the high cost of the process. Moreover, the reaction mechanism itself is very complicated. The following stages can

![Fig. 1. Simplified scheme of the system for conducting the Fenton reaction based on the study of Pawar and Gawande [26].](image-url)
be distinguished: electrocoagulation, electroflotation and electrooxidation [28]. It is a method that does not increase the number of chemical compounds in the environment, which results from the production and consumption of electrons on the surface of the electrodes. In addition, the nature of the reaction causes the gradual corrosion of the electrodes, which forces their replacement [14, 25].

The application of the electrochemical oxidation process for hospital wastewater treatment was studied by Petrovic et al. [29]. The process was based on the electrochemical generation of sulphate and hydroxyl radicals. Strongly oxidizing radicals were formed by applying a current to the anode at atmospheric temperature and pressure. Initial studies have shown an increase in reaction rate up to 80 times that of hydroxyl radicals alone. Sulfate radicals react mainly by electron transfer, therefore they are less susceptible to matrix capture. This allows them to accumulate in the solution, which significantly increases the efficiency of oxidation.

2.1.4. Wet air oxidation

The process is carried out in the liquid phase, at elevated temperature (100°C–300°C) and under increased pressure (0.5–20 MPa) [12]. Wet air oxidation (WAO) is characterized by a non-selective effect on organic and inorganic compounds. Thanks to the high temperature, a high degree of intermediates and intermediate products is achieved [30]. Wet air oxidation is most often used to treat industrial wastewater that is too concentrated to be biologically treated or contains compounds that adversely affect activated sludge. There are three main steps in the process: transfer of oxygen from the gas phase to the gas–liquid interface; transport of dissolved oxygen from the gas–liquid interface to the liquid mass; chemical reaction between dissolved oxygen and substrates [30].

The mechanism of the process is very complex (Fig. 3). Generally, it can be assumed that it proceeds in two stages. The first is thermohydrolysis. However, when the oxidant is introduced into the system, the second stage begins – destructive oxidation of organic compounds. The main factor affecting the efficiency of the process is temperature. For example, at a temperature of 200°C, the efficiency of the process is at the level of 40%. However, at the temperature of 280°C it increases to nearly 80% [31]. WAO is used for:

- removal of detergents, phenols, glycols, naphthol's, pesticides, oils, synthetic resins from sewage,
- treatment of wastewater from the spirits industry,
- oxidation of wastewater containing cyanides and nitriles (galvanizing processes), from coke ovens, from the pharmaceutical industry,
- regeneration of activated carbons.

Currently, several companies in the world sell ready-made installations for wet air oxidation. One of the most popular is the installation designed by ZIMPRO®, operating on the basis of a tower flow reactor. In recent years, Mannesmann Anlagenbau AG (Germany) has been intensively promoting the VERTECH® technology, which is based on a vertical tubular reactor [12, 31].

2.1.5. Supercritical water oxidation

Supercritical oxidation takes place in water. Oxidation is carried out above the H₂O critical point. Water in the supercritical state changes its properties as a solvent, from ionic to non-ionic [12]. The use of such conditions allows for the conversion of impurities at the level of 99.99% [14]. The use of water as a catalyst and reaction medium with changes in temperature and pressure makes it an effective medium for the treatment of resistant organic compounds [32]. The basis of the supercritical water oxidation (SCWO) process is a reactor in which organic waste is oxidized to small harmless particles. SCWO is particularly suitable for disposing of organic wastewaters with high toxicity, high concentration, and bio-refractory components. Despite a number of advantages, the process has its disadvantages. The key problems are corrosion, plugging triggered by salt precipitation, and high running cost [33].

Tank F contains a solution or a fine suspension of organic matter. The oxidant (tank O) is pumped by a high-pressure pump through the evaporator (P). Both streams meet in reactor R. The post-reaction stream gives off heat in the heat exchange system H. The installation also includes systems for final cooling C and separation of reaction products P1 and P2 (Fig. 4) [12].
2.2. Photochemical processes

2.2.1. UV photolysis

Direct photolysis can only be applied to a selected type of wastewater – the contaminants must be able to absorb UV radiation. During direct photolysis, chemical compounds are degraded by direct light excitation [34]. This is the process that is used in the final stage of treatment. In general, the technique is characterized by low efficiency and is most often used in combination with other methods [14]. UV radiation is considered as a potential method of disinfection. UV photolysis is recommended as a substitute for chemical additives in wastewater treatment against a wide range of environmental pollutants, especially to control antibiotic contamination. The decomposition of β-lactams, fluoroquinolones and tetracyclines induced by UV photolysis proceeds with a high efficiency of degradation [35]. Highly fluorinated or chlorinated saturated aliphatic compounds can be effectively removed by hemolysis of carbon–halogen bonds. The excitation energies are below <190 nm for C–F bonds and 210–230 nm for C–Cl bonds. The process is used to eliminate: nitrated and chlorinated aromatic compounds, halogenated aliphatic compounds and phenols [12]. In contrast to chemical methods (with particular emphasis on chlorination) UV radiation does not cause the formation of by-products of the reaction of disinfectants with water components (e.g., humic compounds), such as trihalomethanes. However, the use of this type of disinfection can cause the formation of nitrates, which are the result of the reaction of UV rays with a wavelength below 240 nm with the nitrate present in the water [36].

2.2.2. UV/O₃ processes

The combination of ultraviolet radiation with ozone is much more effective than using the two methods separately. Ozone absorbs UV at a wavelength of 253.7 nm. The essence of the process is the photolysis of ozone generating the formation of by-products of the reaction of disinfectants with water components (e.g., humic compounds), such as trihalomethanes. However, the use of this type of disinfection can cause the formation of nitrates, which are the result of the reaction of UV rays with a wavelength below 240 nm with the nitrate present in the water [36].

2.2.3. UV/H₂O₂ processes

The combination of UV radiation with hydrogen peroxide enables complete mineralization of organic compounds to CO₂ and H₂O [14]. Hydroxyl radicals are formed as a result of photolysis of hydrogen peroxide. It is assumed that the mechanism of H₂O₂ photolysis consists in the homolysis of the oxygen–oxygen bond with the formation of two OH⁺ radicals [38]. The advantage of using hydrogen peroxide as an oxidant is its widespread availability, thermal stability, total solubility in water and low cost [12]. The process that combines ultraviolet radiation with hydrogen peroxide is the most popular AOP method used to degrade and disinfect organic compounds. The course of the reaction is illustrated by the following equation [39]:

\[
\text{H}_2\text{O}_2 + \text{hv} \rightarrow 2\text{OH}^+ 
\]

The generated OH⁺ radicals react non-selectively with all components of the matrix. The conversion of target compounds in wastewater or water competes with the oxidation of other organic and inorganic compounds. The occurrence

Table 2

<table>
<thead>
<tr>
<th>Factor</th>
<th>Water disinfectant</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>UV</td>
</tr>
<tr>
<td>Contact time</td>
<td>1–10 s</td>
</tr>
<tr>
<td>Exploitation</td>
<td>Easy</td>
</tr>
<tr>
<td>Installation</td>
<td>Easy</td>
</tr>
<tr>
<td>Impact on water parameters:</td>
<td></td>
</tr>
<tr>
<td>- Temperature</td>
<td>No</td>
</tr>
<tr>
<td>- pH</td>
<td>No</td>
</tr>
<tr>
<td>Corrosivity</td>
<td>No</td>
</tr>
<tr>
<td>Toxicity</td>
<td>No</td>
</tr>
<tr>
<td>Costs</td>
<td>Low</td>
</tr>
</tbody>
</table>

Fig. 4. Simplified diagram of the supercritical water oxidation installation based on reference [12].
of the so-called radical scavengers that interrupt radical chain reactions can significantly reduce the oxidation efficiency in AOP. In addition, changes in UV transmittance directly affect \( \text{H}_2\text{O}_2 \) activation. Therefore, the efficiency of the process is very susceptible to changes in the water matrix [40]. Research conducted by Zylla et al. [41] showed that the use of pre-oxidation with \( \text{H}_2\text{O}_2/\text{UV} \) reduces the membrane fouling effect, and thus increases the efficiency of nanofiltration in the case of wastewater containing cationic and non-ionic surfactants derived from polysiloxanes.

2.2.4. UV/O₃/H₂O₂ processes

The use of three factors at the same time increases the level of pollution removal efficiency, but in terms of process chemistry it does not differ from the use of UV radiation in combination with ozone. Only the concentration of \( \text{H}_2\text{O}_2 \) in the system is higher [12,14,38]. Research conducted by the team of Demir-Duz et al. [42] showed that the use of a combination of ozone with hydrogen peroxide and UV radiation to treat process water from oil sands allows for mineralization while reducing the toxicity resulting from the presence of such organic compounds as naphthenic acids. Four reaction variants were carried out: using only \( \text{O}_3 \), \( \text{O}_3/\text{H}_2\text{O}_2 \), UV/O₃, and UV/O₃/H₂O₂. However, taking into account the energy demand of the tested treatment method, it was found that treatment with \( \text{O}_3/\text{H}_2\text{O}_2 \) is the most realistic for large-scale applications. Therefore, it can be concluded that \( \text{O}_3/\text{H}_2\text{O}_2 \) provides effective treatment with lower electricity costs, while UV/O₃/H₂O₂ provides better quality effluent that can be reused instead of discharged.

The balance between operating costs and purification efficiency is very important if the purification processes are to be viable. While various combinations of UV-C, \( \text{O}_3 \), and \( \text{H}_2\text{O}_2 \) can provide a high degree of mineralization, operating costs must also be considered. The final use of wastewater should also be taken into account [42,43].

2.2.5. Photo-Fenton reaction

Photo-Fenton reaction (UV/\( \text{Fe}^{2+}/\text{H}_2\text{O}_2 \)) is based on the classic Fenton reagents in combination with UV radiation. Thanks to the use of radiation, photocatalytic regeneration of oxidized iron takes place. In addition, the reaction is also a source of new hydroxyl radicals [44]. It was observed that the reduction of the removed compounds occurs from the beginning of the reaction, and not as in the case of the method using ultraviolet radiation in combination with hydrogen peroxide, where significant changes in concentration were observed with a delay of several minutes from the moment of introducing the oxidant [45]. In the Fenton photo process, hydroxyl radicals are formed as a result of photolysis of \( \text{H}_2\text{O}_2 \) molecules with the participation of radiation in the range \( \lambda < 300 \text{ nm} \). The \( \cdot \text{OH} \) produced in this way take part in direct reactions oxidation of organic compounds and in a circular cycle with \( \text{Fe}^{2+} \) ions. Moreover, they are also possible reactions of photochemical decomposition of \( \text{Fe}^{3+} \) complexes with \( \cdot \text{OH} \):

\[
\text{Fe(OH)}^{2+} + \text{hv} \rightarrow \text{Fe}^{2+} + \cdot \text{OH}
\]

According to the literature, it is possible to regenerate \( \text{Fe}^{3+} \) ions by supporting the reaction with UV radiation cyclic conduction of the reaction, and thus improving the efficiency and effectiveness of the process [46].

2.2.6. Photocatalytic degradation in aqueous suspensions of semiconductors

The method is based on the use of suspensions of semiconductors. Heterogeneous photocatalysis uses suspensions of semiconductors of metal oxides, sulfides, selenides and tellurides [12]. \( \text{TiO}_2 \) is most commonly used due to its low price, non-toxicity and high oxidation potential. These processes are carried out under ambient conditions. No additional chemical compounds that could burden the environment are introduced into the system [47]. The first stage of the reaction consists in the absorption of radiation, and this involves the transfer of an electron from the valence band to the conduction band. An electron gap is formed in the valence band. \( \cdot \text{OH} \) radicals are formed as a result of an oxidation reaction between the gap and a water molecule or hydroxyl anion. The oxygen anion can generate \( \text{H}_2\text{O}_2 \) and \( \cdot \text{OH} \) [12,48]. Many factors affect the efficiency of the process. The most important include: selection of the appropriate semiconductor and proper preparation of its surface, light intensity, type of solvent, degradation conditions (e.g., temperature, pH), chemical properties of pollutants [47].

2.2.7. Ultrasonic processes

The use of ultrasound, most often in the form of mechanical vibrations with a wide frequency range, allows for the decomposition of pollutants in sewage and the improvement of biodegradation [11]. The advantage of this method is simplicity, the possibility of automation and monitoring, as well as a positive impact on a number of unit processes, such as combating the swelling effect [49]. The use of ultrasound is particularly useful in the removal of hardly biodegradable pollutants, as it facilitates their oxidation, disinfection and destabilization. However, it generates high costs, for example, for ultrasonic generators [14]. The cavitation bubbles formed during the reaction are filled with gas, grow and explode intensively under the influence of overpressure. Very high temperatures (approx. 5,000 K) and high pressures (approx. 500 atm), micro-jets and shock waves are generated locally. ROS are then produced by pyrolysis of water molecules in the collapsing bubbles and oxidize the substrates in the water. Among those formed ROS (Reactive Oxygen Species), \( \cdot \text{OH} \) is a very important, very strong and non-specific oxidizing radical. In addition, hydrophobic volatile compounds also undergo thermal decomposition in hot spots, both of which contribute to the degradation of organic pollutants [50]. Sonochemical reactions take place inside, on the surface and in the immediate vicinity of the cavitation bubbles. However, the most intense course is observed at the interface. This is due to the highest concentration of radicals at the bubble–liquid interface [11].
3. AOP in removing pharmaceuticals from wastewater

Pharmacologically active substances belong to the group of the most dangerous pollutants found in wastewater. When they reach conventional municipal sewage treatment plants, they are not fully eliminated in classic treatment systems. Their presence in treated wastewater poses a threat to the life and health of humans and animals. In addition, the presence of antibiotics in surface waters contributes to the acquisition of resistance by bacteria, which results in the selection of drug-resistant bacteria [2,51].

The source of pharmaceuticals in wastewater are hospitals, pharmaceutical companies producing medicines, veterinary facilities, diagnostic and medical facilities and households [52]. It should be mentioned that not only the use of pharmaceuticals contributes to their presence in wastewater, but the improper disposal of expired, unused drugs is also a significant source in the environment. According to the data of the Central Statistical Office, in the last quarter of 2020, 74.3% of respondents used at least one drug or dietary supplement. This is a similar value compared to 2016. The highest percentage was recorded for dietary supplements, nearly 67%. On the other hand, the lowest (6.7%) was noticed for anti-allergy drugs [53]. The report prepared by the Organization for Economic Co-operation and Development (OECD) and the European Center for Disease Prevention and Control, the European Food Safety Authority and the European Medicines Agency showed an upward trend in the consumption of antibiotics in 2011–2020. Poland is among the top ten OECD countries that use the most antibiotics. The average for OECD countries was 17 doses of antibiotics per 1,000 inhabitants/d. Poland was above this average with 22 doses, which made our country 17th in this ranking. The countries with the highest rates were Greece and Australia. Estonians and Swedes used the least amount of antibiotics [54].

The most common pharmacological substances identified in wastewater are: non-steroidal anti-inflammatory drugs (NSAIDs), antibiotics, hypolipidemic drugs, psychotropic drugs, β-blockers, hormonal agents and others like caffeine [51]. The concentration of pharmaceuticals in wastewater is also conditioned by seasonal variability. In the autumn and winter period, higher concentrations of drugs are recorded in contrast to the summer season. This is related to the increased consumption of drugs during the increased period of influenza. In the summer season, the phenomenon of photolysis additionally occurs, which can have a significant impact on the decomposition of a given compound if it is sensitive to light [1,51].

Table 3 presents the average values of concentrations of selected pharmaceuticals in raw and treated wastewater.

The above data indicate that the reduction of these pollutants from wastewater is not sufficient. In some cases, the concentration of pharmaceutical compounds in the treated effluent may exceed the concentration in the raw effluent, a recurring phenomenon attributed to the sampling method used for the study, namely random sampling which is not representative (temporary samples) rather than daily averages. In addition, the retention time of wastewater throughout the treatment plant system is often overlooked during sampling. In order to ensure accurate results and thus confirm the efficiency of the treatment plant in terms of treatment, it becomes necessary to monitor the concentration levels in both the inlet and wastewater over an extended period of time. In addition, concentrations show seasonal variations that are often overlooked in the literature, contributing to higher pharmaceutical values at the wastewater inlet compared to the outlet.

The efficiency of elimination of pharmacological substances from wastewater by AOP methods is presented in Table 4. Using photocatalytic degradation in aqueous suspensions of semiconductors with the use of TiO₂, as a method of degradation of sulfamethoxazole Oluwole et al. [13] used irradiation with a xenon lamp for 1 h, obtaining the effect of 99.5% antibiotic reduction. A slightly smaller reduction effect was found during the elimination of diclofenac in the study of Bourke et al. [68] when 3 h irradiation was applied. Mathew et al. [69] also used a 3-h irradiation time, obtaining a high degree of sulfamethoxazole elimination, but only above 50% reduction of carbamazepine was observed. In the case of estrone and β-blocker elimination, the degree of reduction was 80% [70,71]. High efficiency of elimination of diclofenac and sulfamethoxazole was obtained by photocatalytic degradation in aqueous suspensions of semiconductors with the use of TiO₂ [13,72]. However, this method failed to remove the estrone (below 60%) [73]. The use of the photo-Fenton reaction gave the best results (above 98%) in the reduction of sulfamethoxazole [69]. Also processes using

<table>
<thead>
<tr>
<th>Drug group</th>
<th>Active substance</th>
<th>Raw wastewater</th>
<th>Treated wastewater</th>
<th>Sources</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-steroidal anti-inflammatory drugs</td>
<td>Diclofenac</td>
<td>&lt;10–19,000</td>
<td>4.5–7,000</td>
<td>[55,56]</td>
</tr>
<tr>
<td></td>
<td>Naproxen</td>
<td>11,000–217,000</td>
<td>3,590–14,000</td>
<td>[57–59]</td>
</tr>
<tr>
<td></td>
<td>Sulfamethoxazole</td>
<td>500–2,600</td>
<td>400–2,100</td>
<td>[56,60]</td>
</tr>
<tr>
<td>Antibiotics</td>
<td>Erythromycin</td>
<td>360–3,500</td>
<td>85–1,000</td>
<td>[56,61,62]</td>
</tr>
<tr>
<td>Hypolipidemic drugs</td>
<td>Bezafibrate</td>
<td>780–4,000</td>
<td>96–2,000</td>
<td>[51,52]</td>
</tr>
<tr>
<td></td>
<td>Bezafibrate</td>
<td>1,780–6,300</td>
<td>33–2,000</td>
<td>[56,63]</td>
</tr>
<tr>
<td></td>
<td>Atorvastatin</td>
<td>100–2,359</td>
<td>70–1,000</td>
<td>[64,65]</td>
</tr>
<tr>
<td>Hormones</td>
<td>Estrone</td>
<td>6.54–1,008</td>
<td>1.04–307</td>
<td>[66,67]</td>
</tr>
</tbody>
</table>
UV/\text{O}_3/\text{H}_2\text{O}_2 brought very good results. Sulfamethoxazole and atenolol were more than 90% removed [52,74]. The above results show the advantage over traditional methods of eliminating pharmaceuticals from wastewater, where elimination can be achieved at a level [51]:

- diclofenac – from 20 to 70%,
- sulfamethoxazole – about 20%,
- bezafibrate – from 80 to 90%,
- carbamazepine – about 10%,
- \(\beta\)-blockers – from 85 to 95%,
- estrone – to 10%.

Significantly higher effectiveness using AOP methods was obtained for diclofenac, sulfamethoxazole, carbamazepine and estrone. In the case of the hypolipidemic drug (bezafibrate) and the \(\beta\)-blocker, the degree of removal was at a similar level (Table 4).

4. AOP in removing organic dyes from wastewater

Dyes are the main source of pollutants in wastewater from the textile industry. They are organic compounds with a complex structure that are poor in biodegradation. Their presence disturbs aquatic ecosystems into which they get along with discharged sewage [3]. Wastewater from the textile industry contains not only dye residues, but also other chemicals that change biochemical oxygen demand (BOD) and chemical oxygen demand (COD) values over a wide range [4].

Perkowski et al. [89] checked the degree of colorization of aqueous solutions of azo dyes (violet, red, black, yellow), for example, through the use of UV radiation in combination with ozone and the combination of \(\text{UV/O}_3/\text{H}_2\text{O}_2\). They also used a photocatalytic oxidation process involving TiO\(_2\). A 15 W mercury lamp emitting UV light with a wavelength of 254.2 nm was used in the tests. The degree of decolorization was determined by spectrophotometric measurement. The most favorable course of the process was observed when \(\text{UV/O}_3/\text{H}_2\text{O}_2\) was used together (complete discoloration of the most favorable course of the process was observed when UV/\text{O}_3/\text{H}_2\text{O}_2 was determined by spectrophotometric measurement. The 254.2 nm was used in the tests. The degree of decolorization was confirmed by Bilińska [3]. The effectiveness of the UV/\text{H}_2\text{O}_2 process, oxidation with Fenton’s reagent and ozonation were tested. The paper draws attention to the presence of sodium chloride and surfactant, which are characteristic of wastewater from the textile industry. Their presence inhibited the decolorization processes with Fenton’s reagent and UV/\text{H}_2\text{O}_2. It is therefore to justified to use an increased dose of reagents. Promising results were obtained using ozone. After an hour of reaction, 85% of the tested samples were discolored and reduced COD by 13%.

Thanavel et al. [92] proposed to combine AOP methods with biological decolorization of textile wastewater. They used a strain of \textit{Aeromonas hydrophila} bacteria isolated from soil contaminated with dyes. Test samples containing dyes were treated with 4% hydrogen peroxide and irradiated for 6 h. Simultaneously, degradation reactions were carried out using a bacterial strain. Both treatments were then combined: the biomass was removed after biodegradation by centrifugation, and the remaining solution was treated with UV/\text{H}_2\text{O}_2. The obtained results confirmed the effectiveness of the combination of AOP with biological degradation. Significant levels of sample discoloration (close to 100%) were achieved, but COD and BOD in the effluent were also reduced. None of these treatments used alone achieved this level of dye degradation.

The results obtained by Thanavel et al. [92] were also confirmed in the Ambaye and Hagos [93]. They used a sequential combination of AOP methods with biological treatment of textile wastewater. The research involved the use of TiO\(_2\), irradiation and hydrogen peroxide. After the end of photocatalysis, oxygen biological treatment (bacterial and yeast extract) was carried out. Thanks to these treatments, more than 93% of the color was removed and COD was reduced by 90%. The pH of the samples was not adjusted.


decolorization of wastewater from the textile industry was also investigated using UV/\text{O}_3/\text{ZnO} as an immobilized catalyst. Reaction yield was assessed based on pH retention time, catalyst concentration, and initial dye concentration [94]. Dye reduction at the level 97% was
<table>
<thead>
<tr>
<th>Process</th>
<th>Active substance</th>
<th>Didofenac</th>
<th>Sulfamethoxazole</th>
<th>Bezafibrate</th>
<th>Carbamazepine</th>
<th>Atenolol</th>
<th>Estrone</th>
<th>Sources</th>
</tr>
</thead>
<tbody>
<tr>
<td>Photolysis</td>
<td></td>
<td>5 mg/L</td>
<td>99%</td>
<td>20–25 mg/L</td>
<td>45%–90%</td>
<td>5 mg/L</td>
<td>93%–99%</td>
<td>2–2.5 µg/L</td>
</tr>
<tr>
<td>Photocatalytic degradation with a semiconductor</td>
<td></td>
<td>32 mg/L</td>
<td>56%–100%</td>
<td>50,000 mg/L</td>
<td>40%–100%</td>
<td>10–30 mg/L</td>
<td>50%–80%</td>
<td>10 µg/L</td>
</tr>
<tr>
<td>Fenton and photo-Fenton Processes using UV/O&lt;sub&gt;3&lt;/sub&gt;/H&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;</td>
<td></td>
<td>2 µg/L–10 mg/L</td>
<td>80%–98%</td>
<td>20–40 mg/L</td>
<td>23%–100%</td>
<td>50–70 mg/L</td>
<td>61%–92%</td>
<td>10–2000 mg/L</td>
</tr>
<tr>
<td></td>
<td></td>
<td>100–400 ng/L</td>
<td>70%–80%</td>
<td>1–80 mg/L</td>
<td>&gt;90%</td>
<td>1.3–1.6 µg/L</td>
<td>45%–90%</td>
<td>100–500 mg/L</td>
</tr>
</tbody>
</table>

I.c. – Initial concentration; Rem. – Removal.
observed at pH 5, contact time 40 min, catalyst concentration 3 g/L and an initial dye concentration of 25 mg/L.

5. AOP in removing pesticides from wastewater

Pesticides are classified as persistent organic pollutants (POPs - Persistent Organic Pollutants) characterized by high toxicity and low susceptibility to biodegradation [95]. AOP methods used to remove these compounds are an alternative to traditional methods.

Malakootian et al. [96] used AOP (photocatalysis, UV/H2O2, Fenton reaction) to remove organophosphate pesticides. The mechanism of degradation of organophosphate pesticides by AOP may be the formation of hydroxylated intermediates as the first reaction step, followed by the formation of aliphatic compounds. Test results showed the effectiveness of AOP methods in removing pesticides (chlorpyrifos, diazinon) at the level of 70%. The main disadvantage of this technology is the formation of periodic oxidation by-products, which is the reason for the lack of complete degradation of the organic compound.

According to Saleh et al. [97] some of the most common pesticides are removed with high efficiency, for example, methyl parathion (insecticide) using ozone and activated carbon at 100%. Similarly with 2,4-dichlorophenoxyacetic acid (2,4-D), its 100% removal results in ozonation in combination with adsorption on activated carbon. However, the use of O3/H2O2 allows for the reduction of about 95% of synthetic auxin. The herbicide isoproturon was also most effectively removed by O3 in combination with activated carbon. The ozonation process alone allowed for a 70% reduction of the substance. In the study by Akinapally et al. [98] three sequential methods of removing pesticides from industrial wastewater containing pesticide intermediates were used. Option one was to use distillation, a Fenton process with an anaerobic biological process. The second approach differed from the first variant by using the photo-Fenton process instead of the Fenton reaction alone. The last variant was the most extensive and combined the coagulation process, Fenton, electrooxidation and anaerobic biological process. Among the presented methods, the second variant resulted in the highest percentage reduction of COD (95.77%). However, the technology using the Fenton reagent gave a slightly lower result (95%), therefore, in order to reduce the cost of the process (compared to the photo-Fenton reaction), it can be successfully used to treat industrial wastewater containing pesticide intermediates.

In the work of Brill [99] the use of single and complex electrochemical AOP processes for the treatment of wastewater and soils contaminated with herbicides was presented. Among others, anodic oxidation (AO), AO/H2O2, electro-Fenton, photo-electro-Fenton were tested. A atrazine, 2,4-D and diuron were mainly studied. Research on the reduction of herbicides from wastewater were carried out on a laboratory scale. Faster degradation and mineralization of pesticides was obtained. However, the use of EAOP (electro-AOP) methods on a large scale requires a lot of research on, for example, technical and economic research to demonstrate their cost-effectiveness and economic benefits in relation to commercial technologies.

Jatoi et al. [100] in their work, based on the literature, presented the degree of advancement of the use of AOP methods for the elimination of pesticides. It follows that most advanced oxidation processes are only used on a laboratory scale. With the exception of the UV/H2O2 process, which is carried out on a pilot scale in Poland and is characterized by a 95% removal of synthetic auxin (2,4-D). The degree of degradation of selected pesticides varies depending on the type of method used. This indicates that careful technical judgment has been performed. Each pesticide has different properties, so it is important to choose the right technology to avoid the formation of toxic by-products. Solubility, molecular weight and reactivity with free radicals should be tested beforehand.

The effectiveness of the photo-Fenton method, as in the case of Akinapally et al. [98], on the degradation of pesticides is also confirmed by the studies of Radović Vučić et al. [101]. Tests were carried out using UV/H2O2, Fenton, photo-Fenton reactions and UV/TiO2. Urban model wastewater based on water taken from a local river was subjected to treatment. The following pesticides were analyzed: atrazine, cyprodinil, dicamba and clomazone. Photodegradation turned out to be most effective in the first 10 min of the process. It has been proven that the precise determination of the correlation between the processes used, as well as the determination of the impact of the structure on the degradation efficiency, allow for a more accurate selection of the appropriate technique, especially in the case of interference. It was noted that the greatest energy savings are obtained by using the most effective process of removing pollutants.

In order to compare the effectiveness of pesticide removal with AOP methods, it is also worth presenting research on the degradation of these pollutants from rainwater. Such studies were conducted by Zheng et al. [102]. For the degradation of selected pesticides (atrazine and diuron) photolytic oxidation, electrochemical oxidation and photoelectrochemical oxidation were used. The best results were achieved for photoelectric oxidation, and each herbicide was degraded 90% within 2 h reaction time at 5 V. The lowest reduction degree was observed for photooxidation; only 20% for diuron and about 1% for atrazine. The efficiency of the electrochemical oxidation also resulted in a high reduction rate of close to 90%. The additional use of voltage aided the degree of reduction.

The effectiveness of removal of selected pesticides and an attempt to assess the risk associated with the potential toxicity of by-products resulting from the reaction were examined by Kudlek [95]. Reduction processes of triclosan, tri- alate and oxadiazone using UV rays, ozone and chlorination were carried out. The tested samples were prepared on the basis of aqueous solutions of pesticides. Among the methods used, the highest efficiency (above 90%) was achieved by the process using ultraviolet radiation. Reactions were carried out at time intervals of 5, 10, 20, 30, 40 and 60 min. As the reaction time increased, the efficiency increased. A similar effect was observed in the case of increasing the dose of the reagent. During the decomposition of pollutants, a number of by-products were formed. Toxicity tests were performed with Aliivibrio fischeri bacteria. Irrespective
of the method of degradation used, solutions containing triclosan were characterized by the highest toxicity.

6. AOP in removing microplastics from wastewater

Microplastics were found in wastewater that comes from cosmetics, fabrics, paints and varnishes. It can get to the wastewater treatment plant along with domestic wastewater and from surface runoff. Raw wastewater contains the so-called primary microplastic, which is fragmented during the wastewater treatment process, creating the so-called secondary microplastic [7]. Increasing the degree of removal of microplastics from wastewater may only enable the introduction of the 3rd degree of treatment.

Ukić et al. [103] indicate the Fenton and photo-Fenton process, photocatalysis, photooxidation using hydrogen peroxide. However, the authors point out that there is little knowledge about the reaction mechanisms of microplastics with some oxidants. Therefore, a number of studies on the reaction mechanism, kinetics and rate constants should be conducted. This is important due to the large impact on the overall efficiency of the degradation process. It may be important to combine AOP methods with biological treatment.

In the study by Tagg et al. [104] the impact of Fenton’s reagent as a quick and effective method of isolating microplastics from wastewater were studied. Polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC) and nylon, which were treated with Fenton’s reagent, were used in the tests. The reaction time was about 10 min. Post-reprocessed microplastic particles were rinsed with water and 80% ethanol, followed by Fourier-transform infrared spectroscopy analysis. Fenton’s reagent has proven to be a beneficial entry method for the efficient and precise analysis of microplastics. It is a practical method of isolating microplastic particles from wastewater, but also from other complex matrices such as soil.

The effectiveness of advanced oxidation techniques in the degradation of microplastics is demonstrated by Ricardo et al. [10]. Authors also confirm the use of techniques based on the Fenton reaction (electro-Fenton, the use of oxidants, for example, persulfate, peroxymonosulfate) or heterogeneous photocatalysis (based on, for example, ZnO, TiO2). The work emphasized not only the efficiency of microplastic degradation by AOP methods (30%-95%), but also the emphasis on the lack of sufficient knowledge about the mechanisms that occur during the oxidation reaction of these compounds. The incredible advantage is definitely the mineralization of microparticles, and not just the phase transition.

Study by Chen et al. [105] indicate the effectiveness of AOP methods based on the use of sulphate and hydroxyl radicals. Thanks to this modification, it was possible to reduce polyethylene (PE) first to intermediates: aldehydes, ketones and carboxylic acids with short hydrocarbon chain lengths. As the reaction progressed, the intermediates were further degraded to low molecular weight organic compounds and then mineralized to carbon dioxide and water.

Degradation efficiency of polyester microfibers in laundry wastewater from a hospital facility was tested using UV-induced photodegradation and UV/H2O2-based oxidation. The COD value was also monitored to assess the degree of degradation of dissolved organic material from the microplastic. Easton et al. [106] observed that the degradation of fibers occurs through the formation of shallow cracks, pits and holes on their surface, as well as changes in the relative amount of oxygen-containing functional groups. Increasing the initial UV dose resulted in increased molecular weight removal with UV/H2O2. The weight loss was mainly due to surface degradation and fiber fragmentation. The authors of the work indicate the technology used as the final stage of microplastic removal.

7. Summary

Advanced oxidation processes significantly increase the efficiency of removing selected pharmaceuticals from the wastewater. However, each variant of AOP methods requires appropriate selection of process parameters such as exposure time, lamp power or reagent dose. Only precisely selected process parameters are able to ensure high efficiency. Attention should also be paid to the possible formation of reaction by-products. Therefore, it is important to monitor the entire process.

Conventional technologies cannot cope with the treatment of wastewater from the textile industry. AOP methods have become an alternative, attracting more and more interest due to the formation of highly reactive radicals in situ at ambient temperature and pressure [107]. The use of individual variants of AOP techniques brings satisfactory results (Fenton reaction, UV/O3/H2O2), but the research also shows the positive effect of combining advanced oxidation methods with biological treatment, which significantly affects the degree of reduction of dyes and COD. Using AOP methods in the decolorization of textile wastewater, UV/O3/H2O2, Fenton reaction, photocatalytic oxidation with the participation of TiO2 are most often used. Wastewater treatment using the Fenton process is characterized by low energy consumption and low reagent costs. Processes related to the use of ozone are very effective, but they generate higher costs.

AOP processes can be also used to degrade pesticides from wastewater. They are used as individual unit processes or in sequential or hybrid systems. Photocatalytic processes and Fenton reactions are most often used in the degradation of organophosphate pesticides. Removing a particular pesticide requires a thorough understanding of its physical and chemical properties, as this is key to selecting the right technology.

Increasingly, AOP processes are seen as an alternative to removing microplastics from wastewater. This is a relatively new branch of science that is just beginning to study the mechanisms of oxidation reactions of these pollutants. More research needs to be done to assess the impact of advanced oxidation techniques on microplastic degradation in real matrices. However, it is a method with great potential. Specific organic pollutants, which include microplastics, are more difficult to degrade due to their much higher molecular weight than other organic pollutants discussed in the article.
Acknowledgments

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