Removal of Pharmaceutically Active Compounds (PhACs) in Wastewater by Ozone and Advanced Oxidation Processes

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Contents

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Abstract During the last decades, many water treatment processes have been proposed to deal with the increasing water quality requirements demanded for the urban wastewater effluents (UWWE). Among them, the so-called Advanced Oxidation Processes (AOPs) include a wide range of technologies based on the generation of very reactive and non-selective radical species with a strong oxidation potential that can readily remove not only PhACs but also other organic micropollutants. Together with ozone-based processes, these technologies constitute promising alternatives to be used as final barrier to remove these contaminants before the discharge of the effluents to the environment. This chapter focuses on the processes with higher potential to be implemented at large scale for the removal of PhACs in urban wastewater treatment plants: ozone-based, Fenton, and UV/H_2O_2 processes. Along the chapter, the fundamentals of these processes are introduced, including some of the more relevant modifications from the basic processes, and the more recent studies about their application for the removal of PhACs from UWWE at pilot and full scale are reviewed. From a scientific and technical point of view, the results from these researches confirm the successful removal of a wide range of PhACs and other micropollutants, although the absolute efficiency depends on the water matrix and the specific substances monitored along the treatment. As final remarks, other aspects are also included, such as the need to control the potential formation of by-products during the process and the required optimization of the processes to become competitive in economic terms.

Keywords Fenton, Hydrogen peroxide, Hydroxyl radicals, Ozone, UV

1 Introduction

The available technologies to remove contaminants in aqueous solution are very diverse. Physical treatments just concentrate the contaminants, whereas chemical and biochemical processes degrade these compounds, mainly oxidizing the contaminants. Glaze et al. [1] defined "the Advanced Oxidation Processes (AOPs) as those involved in the generation of hydroxyl radicals in sufficient quantity to affect water purification." Glaze referred to water treatments involving UV/H_2O_2/O_3 used in "light conditions," that is, room temperature and atmospheric pressure. Later on, the definition of AOPs was extended to the role of other radicals generated, as hydroperoxyl, persulfate, or peroxymonosulfate [2–4], and other treatments like Fenton, TiO_2 photocatalysis, electrochemistry, ultrasounds, non-thermal plasma, and wet oxidation were included in AOPs (Fig. 1). The distinction of applications at light conditions is nowadays questionable. The name AOPs is also doubtful because some of the named processes are used in the reduction instead of the oxidation attack to the contaminants. Nowadays, the applications to the AOPs have been extended from water to wastewaters, air, and soil, mainly at laboratory

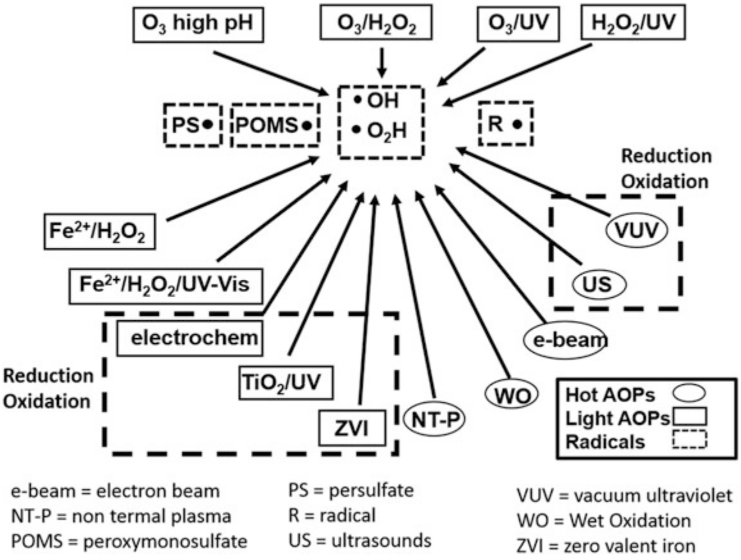

Fig. 1 Advanced oxidation processes

and pilot scales. Only ozone-based AOPs, Fenton, and UV/H_2O_2 are implemented at industrial scale for water and wastewater treatment.

AOPs involve chemical reactions promoting the degradation of the contaminants, and it is more a transformation of compounds than a simple fading. In addition, it is important to consider the possibility to generate by-products more harmful than the parent compounds. In consequence, biodegradability and toxicology tests of treated waters turn as important as the chemical analysis of the contaminant. The water matrix (pure, groundwater, wastewater) also influences in the efficiency and the removal rate of these contaminants [5], mainly because the oxidant is also consumed by other compounds in the water matrix (organic matter, ions, particulate matter). For most wastewaters, contaminant concentration and effluent toxicity decrease, and biodegradability increases as AOP treatment is extended. Because of this and the cost of chemicals and energy involved in AOP treatments, the combination of these technologies with other less costly treatments as biodegradation, adsorption, and membrane separation has been extensively studied [6].

Nowadays, there is major concern about the presence of PhACs in wastewater treatment plant effluents. These compounds are continuously released to the environment, and, in many cases, natural degradation is not enough to remove them efficiently. Consequently, PhACs remain in natural waters affecting the water quality and human health. Many reviews on the applications of AOPs for the treatment of water and wastewater containing PhACs compounds can be found in the literature [7–10]. Today it is possible to find extensive information on removal of PhACs in wastewater by AOPs, mainly at lab and pilot plant scale. Accordingly, this section aims to present a general vision of the removal of PhACs in wastewater by

AOPs. Specific care is devoted to the AOPs implemented at industrial scale, that is, ozone-based AOPs, Fenton, and UV/H_2O_2 processes.

2 Ozone-Based Processes

After more than 100 years of experience on industrial-scale applications of ozone, nowadays ozonation is already a chemical treatment process extensively applied on municipal and industrial wastewater disinfection and oxidation of recalcitrant organic microcontaminants (drugs, pesticides, phenolic compounds, etc.) and inorganic chemicals (iron, manganese, sulfites, etc.).

Among current environmental concerns, the accumulation of microcontaminants and particularly PhACs in natural waters has triggered numerous studies on ozonation and related technologies, like ozone/hydrogen (known as peroxone process) or catalytic ozonation of wastewaters. The effectiveness of ozone-based processes on the removal of PhACs strongly depends on chemical and engineering parameters, like ozone generation and transfer from the gas phase to the wastewater, PhACs reactivity with ozone, and, particularly, composition of the water matrix. This section summarizes the current knowledge on PhACs remediation in wastewaters by ozone-based processes.

2.1 Fundamentals

Ozone (O_3) is a pale blue gas with a robust oxidizing capacity ($E_0 = 2.07$ eV), slightly soluble in water. It easily decomposes to oxygen atoms and molecules; that is why in water treatment, ozone must be generated "in situ" [11]. This gas with high oxidation potential is produced by submitting oxygen molecules to high electrical voltages. There are different methods for producing ozone being the corona discharge one of the most used by far. This one consists of passing oxygen between two electrodes separated by a dielectric material and connected to a source of high voltage producing a corona discharge. The oxygen in the discharge gap is converted to ozone.

Once ozone is produced, it is bubbled into a reactor containing the solution to be treated. The ozone transfer efficiency from gas to liquid phase is fundamental to achieve optimal reaction kinetics rates between ozone and dissolved compounds. This transfer is mainly controlled by physical parameters, such as temperature, gas flow rate, bubble size, ozone partial pressure, and reactor geometry, and also chemical factors like pH, ionic strength, composition of aqueous solutions, etc. [12]. Therefore, it is important to distinguish between applied ozone dose and transferred ozone dose (TOD), which is defined by Eq. (1) and represents the accumulated amount of ozone that is transferred to the water sample per unit of volume and time:

$$TOD = \int_0^t \frac{F_{\text{gas}}}{V_{\text{liq}}} \cdot \left([O_3]_{\text{gas,in}} - [O_3]_{\text{gas,out}} \right) \cdot \mathrm{d}t \tag{1}$$

Ozone in the liquid phase can react with organic compounds in two ways, direct or indirect. These two reaction pathways lead to different oxidation products, and they are controlled by different reaction kinetics. Direct ozone reactions with organic water constituents (comprising PhACs) are quite selective mechanisms including cycloaddition, electrophilic substitution, and electron transfer reactions. Thus, molecular ozone preferably reacts with organic matter with double bonds, activated aromatic groups, or amines moieties [13, 14]. The indirect reaction pathway involves hydroxyl radicals (•OH), mainly generated by radical chain decomposition of ozone initiated by hydroxide ions (OH^-) in water. Reaction between O_3 and OH^- is very slow ($k = 70\ M^{-1}\ s^{-1}$); therefore indirect ozone reactions through hydroxyl radicals only contribute to pollutants removal at neutral or alkaline pH conditions. Hydroxyl radicals are extremely reactive transient species, more reactive, and significantly less selective than molecular ozone. Hydroxyl radicals' reactivity involves three main mechanisms: addition reactions, hydrogen abstraction reactions, and electron transfer reactions, being addition reactions to double bonds (like C=C, C=N, S=O) and aromatic rings the most common and fast [14].

Other •OH generation mechanism is ozone reactions with the dissolved organic matter (DOM) contained in wastewater matrices, particularly with DOM aromatic functional groups. The electron-rich aromatic components of DOM can undergo electron transfer with O_3 generating the intermediate ozonide anion ($O_3^{\bullet-}$) which can give rise to •OH generation. Similarly, phenolic moieties generated by hydroxylation of aromatic DOM moieties can also lead to •OH production by electron transfer with O_3. However, DOM present in water also acts as radical chain inhibitor, scavenging •OH or consuming O_3 without further •OH or chain carrier production [15]. Even with this dual behavior of DOM, organic matter content in wastewaters dramatically increases ozone consumption for pharmaceuticals depletion.

Moreover, some inorganic anions present in the wastewater can interfere in the ozonation process. Carbonate and bicarbonate anions are well-known •OH scavengers and radical chain inhibitors, since they contribute to the termination of the ozone decomposition mechanism [16]. Other important species is nitrite, contributing to ozone depletion of 3.4 g O_3 per g NO_2-N. Finally, organic particulate matter content of water consumes both O_3 and •OH, increasing overall ozone requirements.

Considering all the issues exposed, ozonation performance for the removal of PhACs in wastewaters hardly depends on the quantity and type of organic matter and inorganic constituents of the water matrix.

2.1.1 Ozonation Kinetics

There are many experimental shreds of evidence, at laboratory, pilot plant, and industrial scale, demonstrating the effectiveness of ozonation for the oxidation of

Table 1 Micropollutants classification and some PhACs with their second-order reaction rate constant with ozone and hydroxyl radical (adapted from [17])

Group of MPs	Reactivity	k_{O3} [M^{-1} s^{-1}]	$k_{\bullet OH}$ [M^{-1} s^{-1}]
I	*High with O_3 and $^{\bullet}OH$*	$>1 \times 10^5$	$>5 \times 10^9$
Triclosan	Antimicrobials	3.8×10^7	9.6×10^9
Diclofenac	NSAID	1.0×10^6	7.5×10^9
Sulfamethoxazole	Antibiotics	5.7×10^5	5.5×10^9
Carbamazepine	Anticonvulsant	3.0×10^5	8.8×10^9
Trimethoprim	Antibiotic	2.7×10^5	6.9×10^9
Naproxen	NSAID	2.0×10^5	9.6×10^9
II	*Moderate with O_3 and high with $^{\bullet}OH$*	$10^{-1} \times 10^5$	$>5 \times 10^9$
Gemfibrozil	Lipid regulator	5.0×10^4	10×10^9
Atenolol	B-blocker	1.7×10^3	8.0×10^9
III	*Low with O_3 and high with $^{\bullet}OH$*	<10	$>5 \times 10^9$
Ibuprofen	NSAID	9.6	7.4×10^9
Phenytoin	Antiepileptic	<10	6.3×10^9
Primidone	Anticonvulsant	<10	6.7×10^9
IV	*Low with O_3 and moderate with $^{\bullet}OH$*	<10	1×10^9–5×10^9
Meprobamate	Antianxiety drug	<1	3.7×10^9
V	*Low with both O_3 and $^{\bullet}OH$*	<10	$<1 \times 10^9$

PhACs in wastewaters. Since common municipal wastewater pH is neutral or slightly alkaline, ozonation efficiency directly depends on the second-order rate constants of reactions between the pharmaceutical (PhAC) and both ozone and hydroxyl radicals, as well as the ozone and •OH exposures ($\int[O_3]dt$ and $\int[\bullet OH]dt$) as described by Eq. (2):

$$-\ln\left(\frac{[\mathrm{PhAC}]}{[\mathrm{PhAC}]_0}\right) = k_{O3}\cdot\int[O_3]\mathrm{d}t + k_{\cdot OH}\cdot\int\left[{}^{\bullet}OH\right]\mathrm{d}t \qquad (2)$$

Most organic micropollutants, including PhACs, present high reactivity with •OH, with second-order rate constants higher than 10^9 M^{-1} s^{-1}. However, kinetics in direct ozone reactions largely depends on the structure of the target chemicals due to the specific reaction pathways of molecular ozone. Consequently, the second-order rate constants for ozone oxidation of organic compounds vary more than eight orders of magnitude, between 0.1 M^{-1} s^{-1} and 10^7 M^{-1} s^{-1}. Lee and coworkers classified micropollutants depending on their reactivity with ozone and •OH [17]. Classification goes for group I, including the most reactive compounds with both oxidants down to group V, containing the most resistant to ozonation treatment. The second-order kinetic constant of most common PhACs, both with ozone and •OH, is already available in the literature. Table 1 includes micropollutants classification and some examples of PhACs, together with their second-order reaction rate constant with ozone and hydroxyl radical.

The acid-base dissociation constant (pK_a) of a PhAC is also a key physicochemical parameter influencing ozonation performance. As the majority of drugs are weak acids and/or bases, the knowledge of their dissociation constant helps in understanding the ionic form a molecule will take across a range of pH values. This is particularly important since the reactivity of ozone with some organic dissociating compounds extraordinarily changes with pH by several orders of magnitude [13].

2.1.2 Peroxone

The promotion of in situ generation of •OH by combining ozone with hydrogen peroxide (H_2O_2) is known as peroxone process. The generation mechanism is based on the favored reaction of ozone with HO_2^-, the equilibrium deprotonated form of H_2O_2 [18]. On the other hand, H_2O_2 reaction with ozone is very slow ($k < 0.01\ M^{-1}\ s^{-1}$), while its reactivity with •OH is substantially faster ($k = 2.7 \times 10^7\ M^{-1}\ s^{-1}$). Consequently, increasing H_2O_2 concentration may result in an overall process efficiency decline, due to the reduction of the available amount of •OH in the reaction media [18].

There are many experimental pieces of evidence on the benefits of peroxone in terms of PhACs abatement and bromates production reduction, compared with single ozonation, for drinking water applications [19]. However, this enhancement in micropollutants abatement is not evident for urban wastewaters presenting a higher pollution load, at the current industrial ozone doses applied [20].

2.1.3 Catalytic Ozonation

Ozone combined with homogeneous and heterogeneous catalysts can also enhance •OH production. Homogeneous process, using transition metals in solution, and heterogeneous catalysts, like metal oxides, supported metals, and even minerals or metallic residues, have been widely studied demonstrating the benefits associated to the potential generation of •OH [21, 22].

However, several problems arise related to the use of catalysts that makes industrial application quite difficult. Thus, the homogeneous process requires metals removal from water effluents, increasing treatment costs. Heterogeneous systems deal with problems like catalyst fouling and deactivation, metals leakage into water media, and synthesis and/or preparation costs. All these drawbacks, together with the objective to improve the overall efficiency, are the reasons that, nowadays, catalytic ozonation is one of the main research topics in water treatment.

2.2 Removal of PhACs from Wastewaters by Ozonation

Although PhACs were not within the 45 substances/groups of substances included in the EU priority substances list (established in Directive 2013/39/EU), 5 out of 15 contaminants of emerging concern (CECs) in the latest watch list are antibiotics (Decision 2018/810/EU). Moreover, the Swiss Federal Office for the Environment (FOEN) established a list of 12 indicator substances to be removed by at least 80% in the upgraded wastewater treatment plants, among them are 11 PhACs (amisulpride, carbamazepine, citalopram, clarithromycin, diclofenac, metoprolol, hydrochlorothiazide, venlafaxine, candesartan, irbesartan, and mecoprop).

Although ozonation efficiency directly depends on the second-order rate constants of PhACs with ozone and •OH, urban wastewater effluents (UWWE) composition, mainly its effluent organic matter (EfOM) content, is the main parameter controlling overall process efficiency. This is the reason why ozone dosage for UWWE is commonly referred as specific ozone dose, that is, mg of ozone supplied per mg of dissolved organic carbon [mg O_3 mg C^{-1}]. Under the current applied specific ozone doses between 0.4 and 0.6 mg O_3 mg C^{-1}, there has been reported acceptable (50–80%) to good (>80%) efficiencies removal for PhACs belonging to groups I and II (i.e., triclosan, naproxen, trimethoprim, ciprofloxacin, clarithromycin, diclofenac, erythromycin, metoprolol, sulfamethoxazole, among others). PhACs with rate constants with ozone lower than 10 M^{-1} s^{-1} (from group III to V) are considered ozone-resistant compounds (like meprobamate, X-ray contrast agent iopromide, etc.). They are partially or poorly abated when applying ozone doses up to about 1.0 mg O_3 mg C^{-1} [23, 24]. Higher ozone doses would be necessary to improve their depletion, increasing ozone treatment cost. Figure 2 shows some PhACs removal obtained from concentrated municipal wastewaters at different applied specific ozone dose [25].

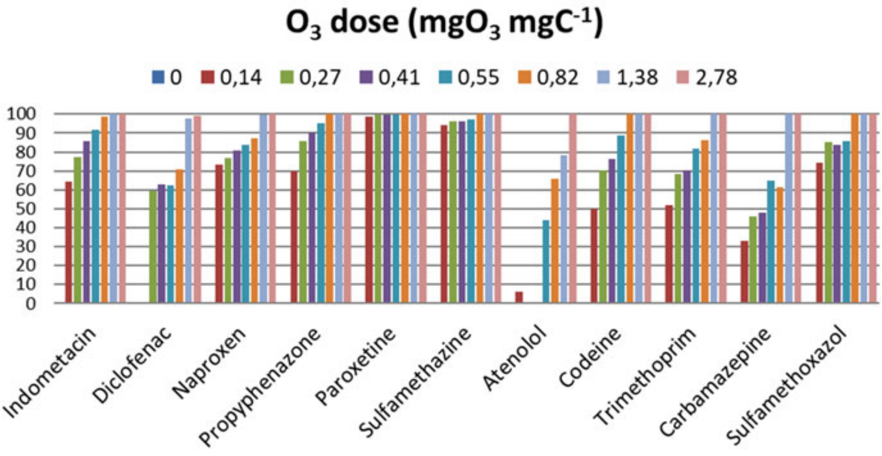

Fig. 2 PhACs removal at different ozone doses [25]

In UWWE ozonation, there is a competition for ozone between the PhACs and the wastewater constituents, that is, EfOM and some inorganic ions. These compounds rapidly consume transferred ozone in a process called primary ozonation or instantaneous ozone demand (IOD) stage. Wastewater organic and inorganic constituents also strongly scavenge the hydroxyl radicals formed through ozone decomposition reactions, resulting in poor availability of this oxidant in the reaction medium. After IOD completion, a secondary ozonation stage characterized by a slower ozone consumption and significantly lower •OH scavenging rate starts. However, UWWE ozonation typically employs ozone dosages below IOD fulfillment [26]; thus a satisfactory removal of recalcitrant PhACs is not accomplished. Application of peroxone (O_3/H_2O_2) process for the intensification of •OH oxidation neither appears to contribute significantly to recalcitrant PhACs removal in wastewaters, probably because the ozone decomposition process, at the current applied doses, is strongly controlled by reactions with EfOM [27].

As every year water resources become scarcer, wastewater reclamation and reuse gains prominence as an alternative to increasing water supplies in many areas of the world. Therefore, obtaining high-quality reclaimed water is already imperative. Ozonation is a water treatment technology with a proven capability to remove microcontaminants, including PhACs, from UWWE. However, efforts to further remove both highly reactive and also ozone-resistant micropollutants during ozonation and ozone-based processes are still necessary, especially for water entering the reuse cycle either in potable (drinkable) form or in non-potable (not drinkable) form.

2.2.1 Control of Ozonation By-products

Ozonation rarely leads to UWWE mineralization but to the so-called transformation products (TPs). A combination of advanced analytical techniques and the knowledge of mechanisms of ozone and •OH reactions with PhACs allows the elucidation of many of these products. Although the existence or not of the functional pharmacophores in the TPs structures can be an indicator of their potential hazard, their potential risks to humans and the environment associated to their presence in water matrices, particularly for water reuse, should be assessed. Protocols comprising a wide range of specific and unspecific toxicity bioassays have been developed over the last years, as well as computer-aided methods based on the existing knowledge for a number of model compounds [28].

The generation of bromate, an oxidation by-product from bromide, also needs to be carefully evaluated. Bromate is a highly carcinogenic compound, and its generation can be significant in the ozonation of industrial wastewaters and sewer systems with saline intrusion. Even though the process is still not fully understood due to its highly complicated chemistry, efficient strategies for its mitigation during wastewater ozonation are nowadays fairly well-known, such as low ozone dosage and the use of the peroxone process [29].

The generation of other oxidation by-products from water pollutants and EfOM transformations during ozonation can also bring some toxicity concerns – like

N-nitrosodimethylamine (NDMA) that originated, for example, from the oxidation of sulfonamide moiety of some antibiotics—and others, like aldehydes, ketones, and carboxylic acids, although in general less toxic, that are formed in significant concentrations. These compounds contribute to the increase of the biodegradability of ozonized effluents, which may trigger some technical and additional environmental problems, like formation of toxic disinfection by-products, bacterial growth in distribution systems, or eutrophication in receiving water bodies [30]. In order to mitigate problems with oxidation products, ozonation is integrated with post-treatments with other wastewater technologies, such as granular activated carbon and biofiltration strategies.

2.2.2 Municipal Wastewater Ozonation at Industrial Scale

UWWE have been proven as the main source of PhACs in natural water compartments. Protection of sensitive waters and drinking water resources together with load reduction for downstream water use has become a priority for some countries, like Switzerland. Moreover, the reclamation and reuse of municipal wastewater is a well-established practice in many areas of the world with water scarcity, like California and the southeast of Australia, and these activities will continue to increase.

High-quality effluents and water supplies can be obtained by further treatment of UWWE. Ozone is nowadays recognized as one of the best chemical oxidants for reducing the amount of micropollutants discharged with UWWE. This strategy is the one adopted by Switzerland and it is currently under development. By 2040, circa 100 wastewater treatment plants (out of a total of 650) will be upgraded with a tertiary treatment either with ozonation or powdered activated carbon [31]. In other European countries such as France, the Netherlands, or Germany, similar practices are currently under evaluation.

Ozonation is also one of the short- or medium-term future prospect technology in wastewater reclamation for water reuse. This technology can be employed after activated sludge when reuse is intended for agricultural and municipal applications or as part of a multibarrier advanced treatment in the case of indirect and direct potable reuse. Many cities have integrated reuse plans into their water management strategies, for example, to irrigate parks, playgrounds, and golf courses and for other non-potable uses such as toilet flushing, fire protection, street cleaning, and fountains. For example, Los Angeles has set the goal of reusing 40% of its municipal wastewaters within 20 years. St. Petersburg in Florida completely reuses all of its wastewater through a specific distribution system, at a cost about one-third less than the drinking-quality water. Many studies are being conducted on the feasibility of reclaiming wastewater to drinking quality. Although implementation results are still scarce, areas facing limited water availabilities and high costs of developing new supplies are considering reclaimed water as a potential source of potable water in the near future.

3 Fenton and Fenton-Like Processes

3.1 Fundamentals

Fenton reaction was described for the first time by Henry John Horstman Fenton, who discovered that H_2O_2 could be activated in the presence of ferrous ions to oxidize tartaric acid [32]. The mechanism of Fenton oxidation is quite complex [33]. Briefly, it relies on the reaction between ferrous iron (as catalyst) and H_2O_2 (as oxidant) generating •OH, as stated in the simplified sequence of reactions 3 and 4. The regeneration of ferrous iron from ferric iron by reaction 4 is the rate-limiting step in the catalytic iron cycle, if iron is added in small amounts. The values of the kinetic constants have been reported by Sychev and Isaak [34]. It has only been in 1968 that it has been first suggested as means for wastewater treatment by Bishop et al. [35]. In the presence of H_2O_2 and at $pH < 3$, the reaction system is autocatalytic, because Fe (III) reacts with H_2O_2 giving Fe(II), which is generated at a slow rate:

$$\mathrm{Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^-, k = 53 - 76\ M^{-1}s^{-1}} \tag{3}$$

$$\mathrm{Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + HO_2^{\bullet}, k = 1 - 2 \times 10^{-2}\ M^{-1}s^{-1}} \tag{4}$$

Many Fenton-based processes have risen in the last years, suggesting the future intensification of the use of the classical Fenton process coupled to radiation or electrochemistry, and/or involving heterogeneous catalysts. The optimization of the catalyst and oxidant doses makes the process capable of treating complex water matrices. It has long been demonstrated that the increase of H_2O_2 concentration results in a higher generation of •OH, which in turn leads to the increase of the degradation rate. Nevertheless, the use of excessive oxidant concentration is not encouraged either, since massive amount of H_2O_2 can induce antagonistic reactions (i.e., reaction of the oxidant with the produced hydroxyl radicals) and thus the formation of radicals that are less reactive than the hydroxyl radicals.

ZVI-based in situ chemical oxidation has been proposed as a potential alternative for the traditional Fenton reaction because ZVI would leach dissolved iron species regularly and activate molecular oxygen. ZVI can be used to oxidize organic and inorganic compounds in the presence of oxygen. The important oxidants are hydroxyl radicals, ferryl ions, and superoxide radicals [36]. In the oxidation of ZVI in aerobic water, hydrogen peroxide is produced as an intermediate product (reaction 5). Further reaction for the formation of H_2O_2 is the oxidation of ferrous iron by O_2 (reaction 6). H_2O_2 can react with ferrous iron by Fenton (reaction 3). Acidic conditions promote the production of highly reactive •OH (reaction 7), whereas neutral and basic conditions lead to the formation of oxidizing species such as ferryl iron (reaction 8). Moreover, fast recycling of ferric iron into ferrous species at the metal surface can take place (reaction 9). It has been also recently proposed [37] an analogous process using persulfate (reaction 10) for PhACs removal. Acidic conditions will be not discussed here, as an application for

UWWE containing PhACs would not be a consistent application, as stated in the following paragraphs.

$$Fe^0 + 2H_2O + O_2 \rightarrow Fe^{2+} + H_2O_2 + 2OH^- \quad (5)$$

$$Fe^{2+} + O_2^{\bullet -} + 2H^+ \rightarrow Fe^{3+} + H_2O_2 \quad (6)$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^- \quad (7)$$

$$Fe^{2+} + H_2O_2 \rightarrow FeO^{2+} + H_2O \quad (8)$$

$$2Fe^{3+} + Fe^0 \rightarrow 3Fe^{2+} \quad (9)$$

$$Fe^0 + S_2O_8^{2-} \rightarrow Fe^{2+} + 2SO_4^{2-} \quad (10)$$

Chelating agents are substances with several coordinating sites and can form bonds with metal ions. They can be used at pH higher than 3 to form complexes with Fe(III)/Fe(II), and keep it soluble, thus enhancing the production of oxidative species by the reaction of H_2O_2 with Fe(III)/Fe(II). The criteria to successfully achieve such goal have been recently defined by Clarizia et al. [38]: lowering costs, minimal increase of total organic carbon (TOC), low toxicity, and high biodegradability. Different chelating agents have been tested (most common have been humic acids, fulvic acids, citric acid, oxalic acid, aminopolycarboxylic acids).

3.2 Removal of PhACs from Wastewaters by Fenton and Fenton-Like Processes

Treating UWWE resulting in rapid and complete removal of pharmaceutically active compounds (PhACs) should take also into account that the process should be mild (to remove microcontaminants from huge streams of water not large quantities of catalyst, oxidant, or energy, keeping the environmental advantage of PhACs removal) and competitive with best available technologies (BAT) as ozonation and adsorption on active carbon (PAC and GAC) [24]. The subsequent use or reuse of water should be taken into account, for large quantities of iron could impede the reuse in irrigation of crops, the main application of treated water. Recommended maximum concentration in irrigation water is Fe <5.0 mg/L, as it is not toxic to plants in aerated soils [39]. However, FAO established the limit in Fe from 5 mg/L for long-term use until 20 mg/L for short-term use (periods of up to 20 years on fine-textured neutral or alkaline soil) [40]. Wastewater reuse for irrigation in agriculture is by far the most established end use in low-income countries as well as in arid and semi-arid ones [41]. Another important factor to take into account is the legislation that establishes environmental limits of iron emissions. Specifically, in Andalucia (Spain, Decree 109/2015), a limit of 3.3 and 2.2 mg/L is established for wastewater discharge in coastal or surface waters, respectively. High conductivity would not be also recommendable for reuse for irrigation.

BAT already applied at real scale in a few countries for PhACs removal in UWWE have been reported to range in 0.04–0.10 €/m^3 investment costs for ~50,000 population equivalent (PE) and 0.03–0.09 €/m^3 operation costs. Therefore, for mid-scale plants (~50,000 PE), the costs range from 0.10 to 0.15 €/m^3. Capitalized investment-related and operation cost yield to the annual costs for the given life cycle are stated in Rizzo et al. [24], decreasing further with the increasing plant size. Therefore, Fenton for PhACs removal in UWWE should be applied at low iron concentration (in the range of a few mg/L) and minimizing the use of additional chemicals to improve the efficiency, as it would dramatically increase costs up to the available BAT.

Because of the low solubility product of ferric iron hydroxide ($K_S(Fe(OH)_3) \approx 10^{-37}$), precipitation starts at pH 2.5–3.5 depending on the iron concentration and the temperature. The precipitation process starts with the formation of dimers and oligomers, which at continuation gradually polymerize further and lose water until forming finally insoluble iron hydroxides (e.g., goethite or hematite). At pH above 4, the formation and precipitation of ferric oxyhydroxides inhibit both the production of •OH radicals and the regeneration of Fe(II) [42]. The precipitation and aging processes are also temperature-dependent, and more and faster precipitation takes place at higher temperatures [43]. The precipitate is difficult to re-dissolve through acidification and insoluble above pH 1–1.5 [44]. Therefore, conventional Fenton should be applied at acidic pH.

However, urban wastewater effluents containing PhACs also contain inorganic carbon as carbonates, mainly as hydrogen carbonate (HCO_3^-), in the range of hundreds of mg/L. Roughly, HCO_3^- 250 mg/L needs around 200 mg/L H_2SO_4 for being balanced and 50 mg/L H_2SO_4 for attaining pH < 3. Therefore, 250 kg H_2SO_4 are needed per 1,000 m^3 of urban wastewater effluent. Before water disposal or reuse, pH 7–8 should be recovered, using at least NaOH 40 mg/L, or other neutralizing agents. The salinity of effluent would increase >0.5 mS/cm, leading also to considerable loads of iron-containing sludge that will require further management. Applying conventional Fenton to urban wastewater effluents would dramatically increase effluent salinity, environmental impact, and treatment costs. Therefore, from the point of view of the authors, it could be disregarded for PhACs removal.

It has also been demonstrated that by adding iron at different steps (i.e., sequential iron dosage), it is possible to operate Fenton at initial neutral pH but substantially increasing iron dosing and decreasing the reaction rate compared to Fenton at acidic pH [45]. Using Fenton at neutral pH is not viable without adding large quantities of iron and long treatment times, as Fe(II) 30 mg/L and 90 min or 72 min of reaction for eliminating 51 or 32 microcontaminants (ranging from tens of nanogram per liter to micrograms per liter) detected in urban wastewater effluents from two different treatment plants [46]. Similar results were obtained by Soriano-Molina et al. [47] as only 35% of PhACs and other microcontaminants were removed from UWWE with $FeSO_4$ (Fe 20 mg/L) at circumneutral pH. Increasing iron concentration >5 mg/

L would impede proper reuse of treated water in many crops, as stated earlier. It can contribute to soil acidification and loss of availability of essential phosphorus and molybdenum and may result in unsightly deposits on plants, equipment, and buildings [48]. But when using Fe <5.0 mg/L, Fenton could not remove almost any PhACs [49].

Another important factor that strongly influences Fenton performance concerning the removal of PhACs is the complex chemical composition of organic matter present (OM) in UWWE. OM components react readily with hydroxyl radicals, thus reducing the radical concentration and the direct attack of HO• toward the PhACs. Under the inherent wastewater pH, Fe(III) can be complexed by DOM resulting in the formation of stable and soluble complexes that can participate in further reactions [50]. Humic substances are the largest fraction of dissolved organic matter in natural water, and an important fraction of UWWE, as they result from microbiological and chemical transformation of organic debris. They contain carboxylic acids, phenolic compounds, alcoholic quinine, and amino and amido groups which enable them to support ion exchange and redox processes and to form complexes. They can also facilitate the reduction of Fe(III) to Fe(II) due to the presence of quinone moiety [51].

The occurrence of inorganic anions (i.e., chlorides, sulfates, carbonates) in wastewater can influence the degradation rate of PhACs during the Fenton treatment by consuming HO•. They can also complex the iron species ($FeCl_2^+$, $FeCl_2^+$, and $Fe(SO_4)^{2-}$) interfering with the reduction of Fe(III) to Fe(II) that is required to sustain Fenton mechanism. The inorganic anions scavenge the hydroxyl radicals to generate inorganic radicals ($Cl^\bullet$, $SO_4^{-\bullet}$, and $CO_3^{\bullet-}$) which, in turn, react with the organic contaminants, albeit at a slower rate [5]. $SO_4^{-\bullet}$ have recently gained great attention due to the high redox potential [52], reacting preferentially through an electron transfer mechanism. Phosphate is a specific case as it can precipitate the iron catalyst as iron(III) phosphate in a wide range of pH.

In conclusion, conventional Fenton or Fenton at circumneutral pH seems to be not suitable for PhACs removal in UWWE. Other available processes based on electrochemical processes [53] would be also disregarded due to a lack of efficiency (and therefore high costs) with usual UWWE due to the low salt content (0.9–2.2 mS/cm conductivity). Therefore, other research line has been explored and are now hot topics in Fenton and Fenton-like processes: zero-valent iron (ZVI) and application of chelating agents to form complexes with Fe and permit Fenton reaction at high pH.

The use of waste-metallic iron shavings instead of commercial ZVI powders showed promising results for the elimination of PhACs [54] but always after activation by immersion in acid solution to remove the surface layer of the oxidized iron (Fig. 3).

It has been demonstrated the negligible effect of the air/ZVI system for the treatment of the wastewater, unlike the promising results reported in the degradation of model pollutants. It is clear the significant role of both ZVI and H_2O_2 together in the reaction system. The formation of iron oxides supported on the metallic iron

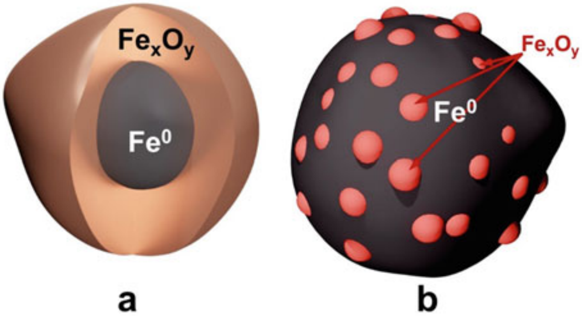

Fig. 3 Waste-metallic iron with Fe^0 inside (**a**). Formation of iron oxides supported on the metallic Fe^0 surface at circumneutral pH (**b**)

surface (Fig. 3b) is plausible at circumneutral pH, which would also reduce the presence of the iron species in the treated aqueous solution [55].

Many chelating agents presented important drawbacks to be applied for PhACs removal in UWWE. Carboxylic acids (citric acid, oxalic acid) add an important extra dissolved organic carbon and reduced final pH; humic substances resulted in low degradation rates due to the quite low amount (few mg/L) that can be found in UWWE. Therefore, it is required extracting and concentrating actions from water which is not easy and does not fulfill the “lowest-cost” principle. Aminopolycarboxylic acids (APCAs) act similarly to polycarboxylic acids, and they are used widely in domestic products, industrial applications, and soil remediation. APCAs contain several carboxylate groups linked to one or more nitrogen atoms and can chelate metal ions by forming one or more heteroatomic rings around the ions [56].

EDTA, as one of the most common APCAs, has been used widely. However, the concern about the potential of toxicity and low biodegradability makes it a persistent organic pollutant and limits its applicability as iron chelate [57] for treatment of UWWE by Fenton processes. EDDS (ethylenediaminedisuccinic acid) is a structural isomer of EDTA and is reported to have metal-complexing properties similar to EDTA [58]. Complete and rapid biodegradation of [S,S]-EDDS (SS-ethylenediaminedisuccinic acid) has been described in many environmental matrices as water [59] and soil [60], being easily biodegraded by activated sludge [61]. Therefore, [S,S]-EDDS is safe when used as Fe-chelating agent during Fenton treatment of UWWE. Currently, 80% of fertilizers used in agriculture are synthetic iron chelates. In addition, the effect of the sub-products generated by photodecomposition has been previously investigated resulting non-toxic for crops [62]. Therefore, its use as a possible iron chelate for wastewater treatment and further reuse in agriculture seems to be a plausible option.

The removal of PhACs in the EDDS-driven Fenton reaction was successful at pH between 8 and 9 [63]. Therefore, that of EDDS application may be limited by its rapid reaction with •OH that involves the decomposition of EDDS and the decrease in efficiency of Fenton process. It is important to highlight that the treatment of several grams of PhACs per cubic meter of UWWE should be achieved in just a few minutes to be an alternative to the previously mentioned BAT. In conclusion, it would be possible to apply EDDS-iron complex only in these circumstances.

4 UV/Peroxide Processes

4.1 Fundamentals

The system UV/hydrogen peroxide (UV/H_2O_2) is one of the most extensively studied AOPs for the removal of water pollutants, both chemical and biological [64, 65]. In this case, the generation of the •OH comes from the photolysis of the hydrogen peroxide, specifically through the cleavage of the peroxide bond (O-O). Baxendale and Wilson [66] reported the formation of two hydroxyl radicals per absorbed photon with a quantum yield close to 1.0 at 254 nm according to reaction 11:

$$H_2O_2 \xrightarrow{h\nu} 2^{\bullet}OH, \phi_{254nm} = 1.0 \text{ mol Einstein}^{-1} \quad (11)$$

The photolysis of H_2O_2 is controlled by certain parameters such as H_2O_2 concentration, UV-C dose, UV wavelength, pH, and alkalinity of water. The optimal control of these parameters allows maximizing the efficiency of the treatment. Obviously, the increase of the UV dose leads to an increase in the efficiency of the generation of •OH. In contrast, the concentration of H_2O_2 is a critical parameter. Since the molar absorption coefficient of H_2O_2 is low ($\varepsilon_{254nm} = 18.6\ M^{-1}\ cm^{-1}$), a high concentration is required to absorb a significant fraction of UV in the range of 200–300 nm (the maximum absorbance of hydrogen peroxide is around 220 nm). However, excessive dosage can cause scavenging of •OH according to the reactions (12)–(14):

$$^{\bullet}OH + H_2O_2 \rightarrow HO_2^{\bullet} + H_2O \quad (12)$$

$$HO_2^{\bullet} + H_2O_2 \rightarrow {}^{\bullet}OH + H_2O + O_2 \quad (13)$$

$$HO_2^{\bullet} + HO_2^{\bullet} \rightarrow H_2O_2 + O_2 \quad (14)$$

Besides, the activation of H_2O_2 is affected by the UV transmittance of the medium, or in other words, the effectiveness of UV/H_2O_2 process is susceptible to water matrix. Alkaline pH favored the process, as the molar absorption coefficient of the HO_2^- conjugate base is much higher ($\varepsilon_{254nm} = 240\ M^{-1}\ cm^{-1}$), improving significantly the efficiency of the photon absorption step. However, water alkalinity strongly affects the yield of the process, as carbonates and bicarbonates present act as •OH scavengers (reactions 15 and 16), reducing the net availability of •OH for the degradation of pollutants:

$$^{\bullet}\mathrm{OH} + \mathrm{CO_3^{2-}} \rightarrow \mathrm{OH^-} + \mathrm{CO_3^{\bullet -}}\ \mathrm{k} = 2 \times 10^8\ \mathrm{M^{-1}\ s^{-1}} \tag{15}$$

$$^{\bullet}\mathrm{OH} + \mathrm{HCO_3^-} \rightarrow \mathrm{OH^-} + \mathrm{HCO_3^{\bullet}}\ \mathrm{k} = 1.5 \times 10^7\ \mathrm{M^{-1}\ s^{-1}} \tag{16}$$

Among the advantages of the UV/H_2O_2 processes for the removal of chemical pollutants, it can be mentioned that their degradation might occur also via direct photolysis and the possibility of carrying out the simultaneous disinfection of water by the damages produced by the UV-C on the DNA of microorganisms [67]. In addition, the design of the treatment facilities is simple [68], and existing facilities can be adapted [69], taking advantage of the high degree of maturity and widely full-scale application of UV disinfection processes. Moreover, UV/H_2O_2 minimizes the formation of by-products, as trihalomethanes (THMs) and haloacetic acids (HAAs) generated as a consequence of reaction of chlorine used as oxidant with natural organic matter (NOM) [70]. Finally, UV/H_2O_2 is an AOP with a relative low cost if it is compared with other advanced treatments. This low cost gives it great versatility, being useful as a single or complementary treatment to other treatments (coupled with filtration processes, adsorption, etc.) [70–72]. The cost of the UV/H_2O_2 process is associated with the intensity required from the UV lamps and their low energy efficiency [69]. The introduction of UV-LED lamps promises to reduce the associated costs, although now they are not competitive because of the associated cooling costs [73].

As main limitations of the process, it can be mentioned the strong sensitivity of the efficiency to water turbidity, reducing UV transmittance, and water matrix effects, especially radical scavenging substances. For this reason, the application of this technology is especially of interest as a tail-end technology treating the final effluent before discharge. It is also worth noting that H_2O_2 is a powerful oxidizing substance, so its handling and storage require some specific precautions.

Recently, the scientific community has focused their interest in the application of a modification of UV/H_2O_2 system, based on substituting the H_2O_2 by persulfate salts as sodium or potassium persulfate and potassium peroxymonosulfate [74]. The substantial difference with UV/H_2O_2 system is the additional generation of sulfate radicals, with a comparable redox potential to hydroxyl radicals (2.5–3.1 V vs. 1.8–2.7 V for $SO_4^{\bullet -}$ and •OH, respectively) [75]. The reactions 17 and 18 show the generation of hydroxyl and/or sulfate radicals by cleavage of the O-O bond of persulfate (PS) and peroxymonosulfate (PMS) anion [76]:

$$\mathrm{S_2O_8^{2-}} \xrightarrow{h\nu} 2\mathrm{SO_4^{\bullet -}},\ \ \phi_{254\mathrm{nm}} = 1.4\ \mathrm{mol/Einstein} \tag{17}$$

$$\mathrm{HSO_5^-/SO_5^{2-}} \xrightarrow{h\nu} \mathrm{SO_4^{\bullet -}} + {}^{\bullet}\mathrm{OH}, \phi_{254\mathrm{nm}} = 1.04\ \mathrm{mol/Einstein} \tag{18}$$

These treatment systems are as simple to apply as UV/H_2O_2, with the only difference that persulfate salts are solids and hydrogen peroxide is liquid. In both cases, the oxidizing character of both substances forces precautions for storage and handling.

4.2 Removal of PhACs from Wastewaters by UV/H_2O_2

As it has been previously mentioned, the UV/H_2O_2 process is a promising technology with a high level of maturity thanks to the extensive bench-scale studies carried out during the last decades. However, the study of the process continues nowadays due to the current challenges and associated human risks, such as the formation of by-products [77], the presence of substances of emerging concern [78], and antibiotic resistance genes [79].

The high level of bench-scale tests of the UV/H_2O_2 system has helped through the scaling up of pilot- and even full-scale application, as a feasible technology for the removal of PhACs. Along this section, it will be shown the state of the art about pilot- and full-scale application of UV/H_2O_2 system for the removal of PhACs and other micropollutants or emerging concern. Table 2 summarizes recent reports about the application of UV/H_2O_2, UV/PS, and UV/PMS processes at pilot scale, whereas Table 3 summarizes some recent studies at full scale. As it can be observed, there is an important variety of working conditions in the presented researches, such as different water matrices, working pH, UV dose, concentration of hydrogen peroxide, flow rates, kind of reactor, or even the studied PhACs, making difficult the direct comparison of the results. Nevertheless, there is a common trend, that is, the use of UV/H_2O_2 system as a final step in a tertiary treatment in a wastewater treatment plant, in some cases treating directly the effluent after the secondary treatment and in other cases treating the effluent after some previous stages as microfiltration, ultrafiltration, reverse osmosis, adsorption, etc. Besides, there is a common pattern in most of the cases, which is the comparison of the process with other AOPs, including UV/Cl_2 system.

Miklos et al. [68] reported the viability of applying UV-C/H_2O_2 as a tertiary treatment for municipal wastewater, studying the removal efficiency of this technology over 15 different organic pollutants occurring at trace level in UWWE. The study included the optimization of working conditions at bench scale and the scaling up at pilot scale. Using a dose of 10 mg/L of hydrogen peroxide, these authors reported the UV-C/H_2O_2 system as a successful option to remove water PhACs. Between the most important remarks, they pointed out the important variations of •OH exposure as a consequence of the fluctuations on nitrite concentration and the scavenging effect of substances in water. A common feature in most of the studies is the significant differences in the removal efficiency depending on the specific substance, as a direct consequence of their chemical structure and properties. For instance, Miklos et al. [68] reported the total removal of diclofenac (DCF) but a null efficiency over tris(2-carboxyethyl)phosphine (TCEP).

On the other hand, Zhang et al. [70] reported the comparison between UV/H_2O_2, UV/free chlorine, and UV/chloramines in the removal of 0.5 log units of 1,4-dioxane

Table 2 Summary of recent pilot-scale UV/H_2O_2 studies for the removal of PhACs and other micropollutants in different water matrices

Reference	Location	Water matrix	[Oxidant]	pH	Operation mode	Reactor characteristics	UV dose	Flow rate (m^3/h)	Reactor volume (L)	Pollutants	Yield (%)
Sarathy et al. [80]	Canada	Surface water	$H_2O_2 =$ 10 mg/L	N.S.	Continuous	Trojan UVSwift 4L12 Trojan UVPhox 8AL20	N.S.	MP reactor: 22–65 LP reactor: 11–22	N.S.	Natural organic matter	> 58%
Sichel et al. [81]	Germany	Tap water	$H_2O_2 = 5$ mg/L	7	Continuous	WTL 40, 80, and 200, Siemens AG	N.S.	0.25	N.S.	BTA, TTA, DEA, CBZ, SMX, DCF, IPM	50–100%
Lester et al. [82]	Boulder (USA)	Secondary effluent wastewater	$H_2O_2 =$ 10 mg/L	N.S.	Continuous	Trojan 100 W LP Trojan 400 W MP	750 mJ/cm^2 1,500 mJ/cm^2	0.11–0.23	N.S.	SCL, LMT, GMB, CLAR, ATN, 2,4-D, CBZ, MTP, TMP, VEN, DPD	750 mJ/cm^2: 18–54% 1,500 mJ/cm^2: 37–71%
Chu et al. [83]	Singapore	Fresh water	$H_2O_2 = 0.5$–10 mg/L	6.3	Continuous	Trojan UVSwift 4 MP UV lamps; each of 3 kW	N.S.	40–60	N.S.	BPA, E2, PFOA, PFOS, NDMA, DCF	45–100%, except for PFOS and PFOA, 5–20%
Miralles-Cuevas et al. [84]	Almería (Spain)	Simulated fresh water	$H_2O_2 = 10$, 25, and 50 mg/L PS = 10, 25, and 50 mg/L	N.S.	Continuous	3 UV-C lamps, 230 W	115 W/m^2 (254 nm)	1.2	5.21	AP, CFN, CBZ, CPX, SMX	65–99%

(continued)

Table 2 (continued)

Reference	Location	Water matrix	[Oxidant]	pH	Operation mode	Reactor characteristics	UV dose	Flow rate (m^3/h)	Reactor volume (L)	Pollutants	Yield (%)
Sarasidis et al. [85]	Thessaloniki (Greece)	Tap water	$H_2O_2 = 10$–80 mg/L	7.8	Continuous	PURO 4S, 4 UV-C lamps	N.S.	0.027	15	DCF	100%
Krystynik et al. [86]	Czech Republic	Groundwater	$H_2O_2 =$ 2 mM/h	7.62	Continuous	TUV UVC TL-D 36 W G13 Philips	N.S.	1.27	42.4	TCE, PCE	100%
Miklos et al. [68]	Munich (Germany)	Secondary effluent wastewater	$H_2O_2 =$ 10 mg/L	N.S.	Continuous	WEDECO LBX 90e WEDECO LBX 10	800 mJ/cm^2 (254 nm)	LBX 90e: 35 LBX 10: 11	LBX 90e: 45 LBX 10: 13	DCF, IOP, SMX, CLI, TRA, BZN, VEN, SOT, PRI, CBZ, GBP, TCEP	44–99.6% 1–90% 1–81%
Baresel et al. [87]	Stockholm (Sweden)	Wastewater	$H_2O_2 = 10$–50 mg/L	6.8–7	Continuous	Van Remmen UV Technology	3,000–10,000 mJ/m^2 (254 nm)	1–2	50	Sum of pharmaceuticals	50–80%
Rodríguez-Chueca et al. [74]	Madrid (Spain)	Secondary effluent wastewater	H_2O_2; PS and PMS $= 0.01$–5 mM	7.23	Continuous	Philips TUV PL-L 95 W/4 P HO 1CT/25	5.7–57 J/L	0.06–0.6	0.47	DCF, IBP, SMX, CBZ, ATN, SMZ, ATZ, TCS, CFN, SCL	23–100%
Wünsch et al. [88]	Germany	Rhine river	$H_2O_2 = 4$ mg/L	8.1 ± 0.1	Continuous	N.S.	6,000 mJ/m^2 (254 nm)	N.S.	N.S.	EDTA, ACE, IPA, IME, MET, BTZ, IPR	10–95%
Zhang et al. [70]	Fountain Valley (USA)	Permeate reverse osmosis	$H_2O_2 = 3.1$–6.2 mg/L	5.7 and 7	Continuous	Trojan 257 W LPHO	≈1,000 mJ/cm^2 (254 nm)	1.33	9.7	1,4-Dioxane	65–78%

N.S., Not specified

Table 3 Summary of recent full-scale UV/H_2O_2 studies for the removal of PhACs and other micropollutants in different water matrices

Reference	Location	Water matrix	pH	Operation mode	Reactor characteristics	[Oxidant]	UV dose	Flow rate (m^3/h)	Reactor volume (L)	Pollutants	Yield (%)
Wang et al. [89]	Cornwall (Canada)	St. Lawrence River	6.5, 7.5, and 8.5	Continuous	Trojan UVSwift 8 L24	$H_2O_2 = 1$, 2.9, 4.8 mg/L	2,000 ± 150 mJ cm^{-2} (200–400 nm)	360	720	Geosmin, MIB, CFN	93% for geosmin; 83% for MIB; 77% for CFN
Rodríguez-Chueca et al. [69]	Toledo (Spain)	Secondary effluent wastewater	7.17 ± 0.04	Continuous	WEDECO LBX400e	H_2O_2; PS and PMS =0.05–0.5 mM	42–170 J/L	28, 75, 114	140	LDC, TRA, ODT, VLX, NVNF, CBZ, OCBZ, MIR, GBP, METO, SFX, BTR, TT, DEET, TBY, TCEP, TCPP, TPP, HHCB, HHCB-I, HHCB-II, AHTN, ATII, OTNE	Average removal of 48% with PMS; 55% with H_2O_2
Wetterau et al. [72]	California (USA)	Permeate reverse osmosis	5.6	Continuous	Trojan 30AL50 UVPhox Trojan 72AL75 UVPhox	$H_2O_2 = 1$–4 mg/L	N.S.	568–947	N.S.	1,4-Dioxane	1.2 log
Rodríguez-Chueca et al. [90]	Toledo (Spain)	Secondary effluent wastewater	7.17 ± 0.04	Continuous	WEDECO LBX 400e	H_2O_2; PS and PMS	42–170 J/L	28, 75, 114	140	Antibiotics (AB): AZT, CLAR,	AB: average removal

(continued)

Table 3 (continued)

Reference	Location	Water matrix	pH	Operation mode	Reactor characteristics	[Oxidant]	UV dose	Flow rate (m^3/h)	Reactor volume (L)	Pollutants	Yield (%)
						=0.05–0.5 mM				CPFX, OFX, SMX, SFD, SFP, TMP, MTZ, CLI Antibiotic resistance genes (ARG): intI1, sul1, sul2, blaOXT, blaTEM, qnrS	of 29% with PMS; 36% with H_2O_2 ARG: average removal of 0.31 log with PMS; 0.55 log with H_2O_2
Wang et al. [71]	Mississauga (Canada)	UF effluent	6.5 and 8	Continuous	Trojan UVSwift ECT16L30	H_2O_2 = 5–10 mg/L	16 medium-pressure lamps (12.3 kW). Three UV ballast power levels (50, 70, and 100%)	625	316	SCL, CFN, DBP (THMs, HAA, and AOX)	At pH 6.5, 0.3–1 log; at pH 8, 0.2–0.8 log

N.S., Not specified

(1,4-D) to regenerate wastewater, as well as the assessment of the generation of disinfection by-products (DBPs). Their main conclusion is that the UV/free chlorine system is the most efficient at pH 5.7, while at pH 7, because of the scavenging caused by the OCl^-, the most efficient treatment was UV/H_2O_2. In any case, the UV/free chlorine system achieved a cheaper cost than UV/H_2O_2 and UV/chloramines treatments, and the generation of DBPs was similar in all the cases but promoting the generation of different substances. Other authors, as Baresel et al. [87], also reported a good efficiency of UV/H_2O_2 in removing micropollutants but confirm that they are still not economically competitive regarding other technologies such as ozonation or activated carbon.

Miralles-Cuevas et al. [84] compared from the economical point of view the application of UV/H_2O_2 using UV-C and solar radiation. They concluded that the main contribution to the operating costs comes from reagents and electricity from lamps operation. However, according to their results, the main difference between using solar and UV systems on the removal of PhACs is the optimal concentration of the oxidant. Rodríguez-Chueca et al. [74] compared the efficiency of UV/H_2O_2 with modification treatments using PS and PMS as oxidants with very low residence times. In general, the use of PMS and PS as oxidants led to higher removal yield than using hydrogen peroxide. Both persulfate anions allowed to reach the total removal of some PhACs under the most demanding operating conditions. Just the removal of sucralose (SCL) was more effective by using H_2O_2.

Other authors, such as Sarasidis et al. [85], studied the efficiency of UV/H_2O_2 to regenerate powdered activated carbon (PAC) used on the removal of PhACs. With promising results on the removal of DCF, the authors proposed a further investigation on the mechanisms of regeneration of PAC because it involves adsorption, desorption, and oxidation. Some authors reported the use of UV/H_2O_2 on the treatment of fresh surface water, as it is the case of Wünsch et al. [88], studying the impact of a UV/H_2O_2 before soil aquifer treatment (SAT). They assessed the efficiency on the abatement of different PhACs and other micropollutants present in Rhine river water, using a pilot plant consisting of a UV-C reactor and two parallel soil columns. These coupled systems enhanced the removal of micropollutants by an additive effect of the unit processes. However, in almost all cases, the UV/H_2O_2 system is responsible for the abatement of the studied micropollutants, being only the metformin primarily abated by SAT.

The disadvantages reported by some authors in terms of efficiency and cost of UV/H_2O_2 in comparison with other AOPs have slowed down the implementation of technology on a full scale. Despite this, there are reports about the application of UV/H_2O_2 at full-scale, in some cases as research studies, but in others in real water facilities using this technology in the removal of PhACs and other micropollutants (Table 3). For instance, Wang et al. [71] compared the efficiency of UV/H_2O_2 and UV/Cl_2 on the removal of micropollutants in water adapting the tertiary treatment of the Lorne Park Water Treatment Plant in Canada. Both AOPs were applied over the permeate of the filtration step. The conclusions obtained are quite similar to the ones showed by Zhang et al. [70] at pilot scale. At pH 6.5, the generation of •OH was almost twice by UV/Cl_2 than UV/H_2O_2, but at pH 8.0, •OH formation was negligible during UV/Cl_2 system. Similar conclusions comparing UV/Cl_2 and UV/H_2O_2 were reached by other authors, such as Wang et al. [89] applying the technologies in the Cornwall Water Purification Plant (Canada) and Wetterau et al. [72] in WRD Leo J. Vander Lans Advanced Water Treatment Facility in California (USA). In this last case, Wetterau et al. [72] pointed that the same level of 1,4-dioxane reduction can be achieved with UV/Cl_2 at roughly one-third the dose as UV/H_2O_2, reducing the use of reagents or the size of the UV reactor.

Finally, Rodríguez-Chueca et al. [69] modified the tertiary treatment of municipal wastewater treatment plant in Toledo (Spain) to test different UV-driven AOPs in the existing UV-C equipment. Among them, UV/H_2O_2, UV/PMS, and UV/PS were tested using different flow rates, or in other words different UV-C doses and UV-C contact time. In general, photolysis of H_2O_2 and PMS led to similar results considering the average removal of the sum of the studied micropollutants, with a slightly higher performance using H_2O_2 (55% with H_2O_2 vs. 48% with PMS). These results, together with the lower cost of H_2O_2, made UV/H_2O_2 more attractive than the use of PMS for the removal of micropollutants. In a similar study, Rodríguez-Chueca et al. [90] analyzed the removal of antibiotics and antibiotic resistance genes from the effluents. In general, the addition of the oxidants improved significantly the efficiency of the removal of the antibiotics in comparison with the UV alone. However, the removal of antibiotic resistance genes was maximum when only UV is dosed, without oxidants. This fact suggested a compromising situation because the highest antibiotics removal corresponded to the lowest removal of genes. The reason is that the generation of hydroxyl and sulfate radicals, triggered by light absorption of the oxidants, actually reduces the availability of photons for the direct damages on the DNA. Consequently, although in theory both processes can take place simultaneously, to achieve a high efficiency in the removal on the PhACs and the antibiotic resistance genes, much higher UV doses have to be used.

5 Concluding Remarks

In this chapter the fundamentals of several advanced oxidation processes for the removal of PhACs in urban wastewater effluents have been summarized, remarking that the most suitable oxidation technique would depend mainly on the water matrix and the final use of the effluent.

Nowadays, O_3, O_3/H_2O_2, and UV/H_2O_2 treatments constitute good options to succeed in the removal of PhACs as tertiary treatments in municipal wastewaters. Modified processes such as catalytic ozonation or the use of alternative peroxides are under study.

Applying conventional Fenton at acidic pH to urban wastewater effluents would dramatically increase effluent salinity, environmental impact, and treatment costs disregarding it as an option for PhACs removal from this type of effluents. Many iron-chelating agents (carboxylic acids, humic substances, EDTA) to operate Fenton-like processes at circumneutral pH presented important drawbacks to be applied for PhACs removal in UWWE. EDDS appears as a possible iron chelate for UWWE treatment, and further reuse in agriculture seems to be a plausible option if the treatment would be completed in just a few minutes. Modifications of Fenton and Fenton-like processes at circumneutral pH are under study in many research labs, but they are still far away from their application.

Independently on the oxidation treatment used to remove PhACs, it should be considered the potential formation of by-products during the oxidative treatment.

Treating urban wastewater effluents for removal of PhACs should be mild, minimizing the use of additional chemicals, and economically competitive with best available technologies as ozonation and adsorption on active carbon, reported to range between 0.10 and 0.15 €/m^3.

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