Introduction to Photochemical Advanced Oxidation Processes for Water Treatment

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Abstract In this chapter, an overview of Photochemical Advanced Oxidation Technologies (PAOTs) is given, together with recent relevant literature examples and references. Short-UV and VUV photolysis, UV/H_2O_2, UV/O_3, $UV/O_3/H_2O_2$, photo-Fenton and iron-based technologies, photo-ferrioxalate and UV/periodate, are exposed, together with a brief introduction of heterogeneous photocatalysis. Fundamental grounds with mechanistic pathways are described in each case. Combination of PAOTs with other treatments (espe-

cially biological methods) is also illustrated. Limitations, advantages and drawbacks are pointed out, together with different examples of real cases.

Abbreviations

$^1O_2$	singlet oxygen
2,4,5-T	2,4,5-trichlorophenoxyacetic
2,4-D	2,4-dichlorophenoxyacetic acid
2,4-DNT	2,4-dinitrotoluene
2,6-DNT	2,6-dinitrotoluene
4-CP	4-chlorophenol
AMBI	5-amino-6-methyl-2-benzimidazolone
AOPs	Advanced Oxidation Processes
AOTs	Advanced Oxidation Technologies
BOD_5	biological oxygen demand during an incubation period of 5 days at 37 °C
$C_2O_4{}^{\bullet-}$	oxalyl radical
COD	chemical oxygen demand
CPC	compound parabolic solar collector
DOC	dissolved organic carbon
EDTA	ethylenediaminetetraacetic acid
FBR	fixed bed reactor
FeOx	ferrioxalate
GAC	granular activated carbon
$HO^{\bullet}$	hydroxyl radical
$HO_2{}^{\bullet}$	hydroperoxyl radical
LMCT	ligand to metal charge transfer
MTBE	methyl *tert*-butyl ether
NB	nitrobenzene
NOM	natural organic matter
NTA	nitrilotriacetic acid
$O_2{}^{\bullet-}$	superoxide radical
OM	organic matter
PAOPs	photochemical Advanced Oxidation Processes
PAOTs	photochemical Advanced Oxidation Technologies
PCBs	polychlorinated biphenyls
PET	polyethyleneterephthalate
RB	rose bengal
Sens	sensitizers
TCE	trichloroethylene
THM	trihalomethanes
TNT	trinitrotoluene
TOC	total organic carbon
VUV	vacuum ultraviolet

1
Introduction

The growing demand from society for disinfection and detoxification of polluted waters from different sources, materialized in very strict governmental regulations, has led, in the last few decades, to the development of new and more effective water purification technologies. In most cases, anthropogenically polluted water can be efficiently treated by biological methods, activated carbon adsorption or other adsorbents, or by conventional physical and chemical treatments (flocculation, filtration, thermal oxidation, chlorination, ozonation, potassium permanganate, etc.). Nevertheless, in some cases, these procedures are not adequate to reach the degree of purity required by law or by the final use. In those cases, Advanced Oxidation Technologies or Processes (AOTs, AOPs) are efficient novel methods for water treatment, which have afforded very good results in industrialized countries and are beginning to be employed in developing regions [1–5].

AOTs are based on physicochemical processes that produce profound changes in the structure of chemical species. The concept was initially established by Glaze et al. [2, 6, 7], who defined AOPs as processes involving generation and use of powerful transitory species, principally the hydroxyl radical (HO$^\bullet$). This species can be generated by photochemical means (including solar light) or by other forms of energy, and has a high efficiency for organic matter (OM) oxidation. Some AOTs, such as heterogeneous photocatalysis, radiolysis and others, can also produce reducing agents, allowing the transformation of pollutants that are difficult to oxidize, such as some metal ions or halogenated compounds. AOTs are usually divided into non-photochemical and photochemical processes, as listed in Table 1. In this article, only photochemical technologies (PAOTs, PAOPs) will be reviewed, with some references to the non-photochemical process in the cases of ozonation and the Fenton reagent. For other technologies, the references indicated in Table 1 can be consulted, as well as references [8] and [9]. Concerning heterogeneous photocatalysis, this subject will be treated in detail in another article of this book, and we will only make a brief mention in this chapter. Examples and references are principally those covering the last five years, with the exception of the most relevant papers on the subject. Older references may be consulted in the referenced papers.

The high efficiency of AOPs is supported on thermodynamic and kinetic grounds, due to the participation of radicals. The hydroxyl radical can attack **virtually all organic** compounds and it reacts 10^6–10^{12} times more rapidly than alternative oxidants such as O$_3$. In Table 2, it can be observed that, after fluorine, HO$^\bullet$ is the most energetic oxidant. Table 3 shows that the reaction constant rates of different compounds with HO$^\bullet$ are several orders of magnitude higher than those with O$_3$. However, we must emphasize that

Table 1 Advanced Oxidation Technologies and other related processes

Non-photochemical processes	Photochemical processes
Alkaline ozonation (O_3/OH^-) [2, 7, 35, 41, 45]	Water photolysis in vacuum ultraviolet (VUV)
Ozonation with hydrogen peroxide (O_3/H_2O_2) [42, 45]	UV/ hydrogen peroxide
Fenton and related processes (Fe^{2+}/H_2O_2)	UV/O_3
Electrochemical oxidation [124, 125]	Photo-Fenton and related processes
γ-Radiolysis and electron-beam treatment [126–128]	UV/periodate
Non-thermal plasma [129]	Heterogeneous photocatalysis
Electrohydraulic discharge—ultrasound [2, 130–133]	
Oxidation in sub/and supercritical water [134–137]	
Zero-valent iron [94, 138, 139]	
Ferrate (K_2FeO_4, Fe(VI)) [140]	

Table 2 Redox potentials of some oxidants [1]

Species	E^0 (V, 25 °C)[1]
Fluorine	3.03
Hydroxyl radical	2.80
Atomic oxygen	2.42
Ozone	2.07
Hydrogen peroxide	1.78
Perhydroxyl radical	1.70
Permanganate	1.68
Chlorine dioxide	1.57
Hypochlorous acid	1.49
Chlorine	1.36
Bromine	1.09
Iodine	0.54

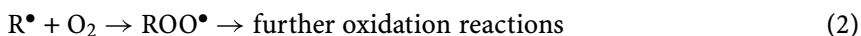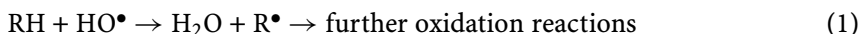[1] Redox potentials referred to normal hydrogen electrode (NHE)

the efficiency of AOTs resides in the generation of high concentrations of hydroxyl radicals in the steady state.

Another active oxygen species is the superoxide radical, $O_2^{\bullet-}$, and its conjugate acid form, the hydroperoxyl radical, $HO_2^\bullet$, and these are also produced in many AOTs, but they are far less active than $HO^\bullet$.

Table 3 Rate constants (k in $M^{-1}s^{-1}$) for some organic compounds with hydroxyl radical and ozone [4]

Compound	HO$^\bullet$	O$_3$
Chlorinated alkenes	10^9–10^{11}	10^{-1}–10^3
Phenols	10^9–10^{10}	10^3
Aromatics	10^8–10^{10}	1–10^2
Ketones	10^9–10^{10}	1
Alcohols	10^8–10^9	10^{-2}–1
Alkanes	10^6–10^9	10^{-2}

When a target pollutant compound is attacked by HO$^\bullet$, three main mechanisms may be involved in the degradation of organics: hydrogen abstraction, OH addition or substitution, and electron transfer. Hydrogen abstraction is generally the first step in many acid compounds [1, 4]:

$$RH + HO^\bullet \rightarrow H_2O + R^\bullet \rightarrow \text{further oxidation reactions} \qquad (1)$$
$$R^\bullet + O_2 \rightarrow ROO^\bullet \rightarrow \text{further oxidation reactions} \qquad (2)$$

If the target is an aromatic compound, the first stage is ring hydroxylation, but further HO$^\bullet$ attack leads to the opening of the ring and the formation of open conjugated structures:
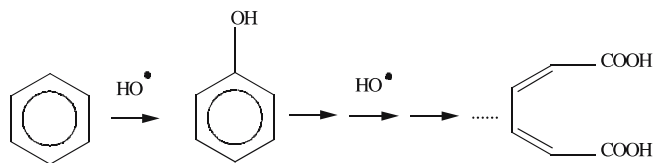
Scheme 1

The majority of AOTs can be applied to the remediation and detoxification of low or medium volumes of waters. Ground, surface, and wastewater can be treated, giving rise to the destruction or transformation of hazardous or refractory pollutants. Point sources of toxic pollutants such as pesticides, heavy metals and others can be treated in small-scale mobile treatment units, easy to install in industrial plants. The methods can be used alone or combined with other AOTs or with conventional methods. The use of modular units allows the selection of the best technology or combination of technologies to treat a specific wastewater. AOTs can also be applied to pollutants in the air and soil, and they may even allow disinfection or sterilization of bacteria, viruses, and other microorganisms.

AOTs offer several advantages over conventional methods of treatment. One of the most important characteristics is that pollutants are not merely

transferred from one phase to another (as in air stripping or activated carbon treatment), but they are chemically transformed, leading, in many cases, to complete mineralization (destruction) of the pollutant. In consequence, Advanced Oxidation Processes are very useful for treating refractory pollutants resistant to other treatments such as, for example, biological technologies. AOTs can treat contaminants at very low levels (ppb), and reaction by-products are generally not formed. The technologies are also useful for improving the organoleptic properties of water, or can just be used to discolor dark industrial wastes. In most cases, they consume much less energy than some conventional methods such as, for example, incineration. Nevertheless, it must be taken into account that wastes with relatively high chemical oxygen demand (COD) contents ($> 5.0\ gL^{-1}$) cannot be suitably treated by AOTs because they would require large amounts of expensive reagents or electrical energy for irradiation [10].

As the total destruction of the pollutant is not always required, AOTs are especially useful in two cases: (a) as a **pre-treatment** to transform recalcitrant pollutants in more biodegradable compounds; or (b) as a **post-treatment**, to polish waters before their discharge to the receptor bodies [11]. The main idea of the combination is the use of a more expensive technology only in the first or final step of the treatment, to reduce costs.

PAOTs are developed and commercialized to a variable degree and are undergoing constant change as technological advances take place. At present, UV/H_2O_2, UV/O_3, $UV/H_2O_2/O_3$, UV/Fenton and UV/TiO_2 are totally or partially commercialized.

2
Photochemical Advanced Oxidation Technologies

To produce photochemical changes in a molecule, irradiation of light in the UV–visible range must occur within the system. The visible spectrum covers wavelengths between 400 and 800 nm. The UV range is usually divided into four regions, UV-A (also called near-UV light, long-wave light or black-light), UV-B, UV-C (short-UV light) and VUV (vacuum ultraviolet light), as shown in Table 4. Sunlight irradiation may be used in some applications, but it must be taken into account that only 3–5% of UV light is present in the solar spectrum.

Usually, light appreciably increases the reaction rate of AOTs in comparison with the same technology in the absence of illumination. As a source of light, high-pressure mercury or xenon arc lamps, with good emission in the near-UV range, can be used. Some applications require short-UV irradiation, as we will see later and, in this case, cheap germicide lamps are easily available. Operative costs are reduced due to a lower power consumption to generate HO$^\bullet$ compared to other rather more expensive AOPs such as radiolysis or supercritical technologies. If solar light can be used, a consequent

Table 4 Regions of the UV-Vis electromagnetic spectrum and their application in Photochemical Advanced Oxidation Technologies for water treatment

Type	λ (nm)	Energy (kJ mol^{-1})	Uses
UV-A*	315–400 (365)**	380–299 327	Almost all photochemical AOTs
UV-B	280–315	427–380	Some AOTs
UV-C*	190–280 (254, 185)	629–427 (471, 646)	Disinfection and sterilization, H_2O_2
VUV*	< 190 nm (172)**	> 629 695	Some applications

* Used in environmental applications ** The most used wavelength

saving of electrical power will be produced, with safer industrial installations. As the light is totally directed to the system, the photochemical industrial equipment used is more compact, and smaller tanks can be employed. As we will see later, the use of light increases the flexibility of the system, allowing the use of a variety of oxidants and operational conditions. Another advantage of the photochemical technologies is that pH changes in the effluents need not be as drastic as for example with alkaline ozonation.

It is worthwhile to point out, however, that light-mediated AOPs, especially the homogeneous processes, are not adequate for treating mixtures of substances of high absorbance, or containing high amounts of solids in suspension, because the quantum efficiency decreases through loss of light, dispersion and/or by competitive light absorption.

2.1
Direct Photolysis

It is possible to use a direct photolytic process for the treatment of waters and effluents, without the addition of chemical reagents. It is worthwhile to bear in mind that, for example, a 254-nm photon is equivalent to 4.89 eV, enough energy to produce homolytic or heterolytic breakages in the molecules. Direct irradiation leads to the promotion of a molecule from the fundamental state to an excited singlet state, which may then intersystem cross to produce triplets. Such excited states can undergo homolysis, heterolysis or photoionization, among other processes. In most cases, homolytic rupture produces radicals:

$$R - R + h\nu \rightarrow R - R^* \rightarrow 2R^\bullet \tag{3}$$

These radicals initiate chain reactions to produce the final low-weight products. In the presence of oxygen, additional reactions generating the superoxide radical are possible:

$$R - R^* + O_2 \rightarrow R - R^{\bullet+} + O_2^{\bullet-} \tag{4}$$

Although its oxidizing power is not very high, the superoxide radical is able to degrade substituted aromatic compounds with high absorption in the UV range.
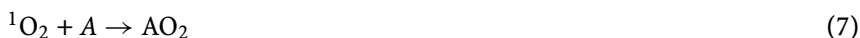
Direct photolysis is important for compounds that react very slowly with $HO^{\bullet}$ or do not react at all, for example nitrophenols, NO_2^-, and halogenated compounds. Some pesticides can be degraded by direct short-UV photolysis with good yield [12]. Degradation of trihalomethanes (THM), chloromethanes, chloroethanes, chlorinated aromatics and chlorinated phenols by the use of 254 nm irradiation is well documented in the literature [1, 4]. For irradiation at this wavelength, low-pressure mercury germicidal lamps are easy to employ. Irradiation with KrCl excimer lamps (222 nm) is used for chlorinated aliphatics such as CCl_4 or 1,1,1-trichloroethane, because the rupture of the C – Cl bond takes place at 210–230 nm. Generally, the technology is combined with other conventional methods. Limitations of the process are: (i) low efficiency; (ii) application only to compounds absorbing at 200–300 nm; (iii) only one target compound can be treated with reasonably good results. The mechanism and products of UV radiation decomposition have been described for important pollutants such as DDT, lindane, PCP, TNT and atrazine ([13] and references therein).

Direct 254-nm UV photolysis is effective for discoloring textile dyes at low concentrations, as seen in the recently described case of Solophenyl Green BLE 155% [14]. When direct photolysis was compared with other processes as 254-nm UV/TiO_2 and combined TiO_2 photocatalysis/activated carbon, it was demonstrated that, at low dye concentrations (5–10 mgL^{-1}), the photolytic treatment is 2–3 times faster than the other processes for color removal.

2.2
Sensitization

In many cases, direct photolysis may be favored in the presence of oxygen and substances which can act as photosensitizers. Sensitizers (Sens) are compounds that absorb visible light and are excited to a higher energy state from which an energy transfer occurs, the excess energy then being transferred to other molecules present in the system [15]. In this sense, some dyes like Rose Bengal (RB), phthalocyanines or methylene blue promote singlet oxygen ($^1O_2$) formation in excellent quantum yield [16]; singlet oxygen is an oxidant powerful enough to attack OM and microorganisms [3]:

$$\text{Sens} + h\nu \rightarrow {}^1\text{Sens}^* \rightarrow {}^3\text{Sens} \tag{5}$$

$$^3\text{Sens} + {}^3O_2 \rightarrow \text{Sens} + {}^1O_2 \tag{6}$$

$$^1O_2 + A \rightarrow AO_2 \tag{7}$$

For water purification, the efficiency is strongly dependent on the production rate of singlet oxygen in the aqueous solution.

Significant degradation of compounds can also be obtained in the presence of electron-acceptor sensitizers. In a very recent example, triadimenol, a systemic pesticide widely applied in horticulture and viticulture that is very difficult to degrade by direct UV photolysis, could be significantly decomposed in the presence of electron acceptors such as 9,10-dicyanoanthracene or 2,4,6-triphenylpyrylium tetrafluoroborate. Decomposition was accelerated by the presence of oxygen [17].

This process has not been commercialized yet; one of the main problems is the necessity of removing the dye from the water after the treatment. For this reason, attempts at immobilization to different supports have been reported recently, but this process leads to a decrease in the efficiency of $^1O_2$ production. For example, when RB is immobilized on a polymer, its efficiency is reduced one hundred-fold compared with the sensitizer in a homogeneous water solution [18]. More research is needed to improve this technology, taking into account that the system demonstrates an effective disinfection ability for drinking water.

2.3
Photolysis of Water in the Vacuum Ultraviolet (VUV)

This process uses light irradiation of wavelengths lower than the UV-C, i.e., lower than 190 nm. Generally, Xe excimer lamps (λ_{exc} = 172 nm) are used. The excitation leads, in the majority of the cases, to the homolytic breakage of chemical bonds, degrading OM in condensed and gaseous phases (for example, fluorinated and chlorinated hydrocarbons) [1, 3]. However, its application is limited, and the most important use of VUV radiation is in water photolysis (Eq. 8):

$$H_2O + h\nu \rightarrow HO^\bullet + H^\bullet \tag{8}$$

This process generates hydroxyl radicals and hydrogen atoms in situ, without the addition of external agents[1]. Due to the high absorption cross-section of water, the total incident radiation is absorbed within a very narrow layer around the lamp shaft [19]. The quantum yield of reaction 8 depends on the irradiation wavelength, varying between 0.33 at 185 nm and 0.72 at 147 nm [20]. Aqueous electrons (strong reductants) are also produced, but with a lower quantum yield (0.05), almost independent of the irradiation wavelength in the range 160–190 nm [19].

$$H_2O + h\nu \rightarrow HO^\bullet + H^+ + e^-_{aq} \tag{9}$$

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[1] A similar in situ HO$^\bullet$ generation can be obtained using high power ultrasound sources or by processes using subcritical or supercritical water (at very high temperatures or pressures). [9] and other references therein and in Table 3 can be consulted.
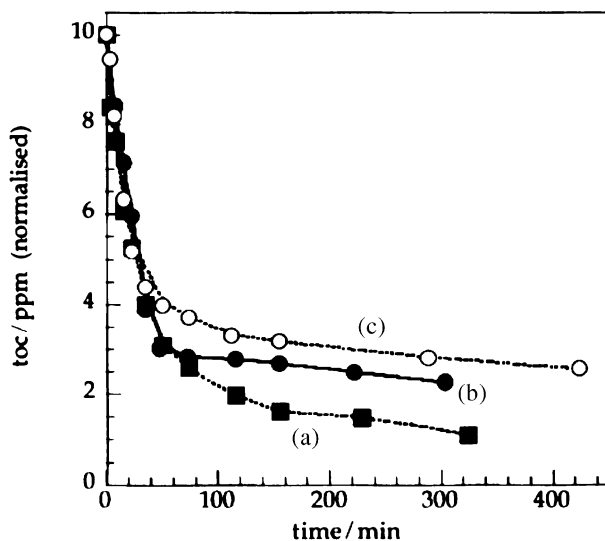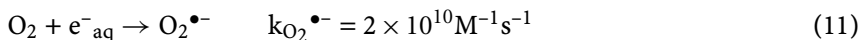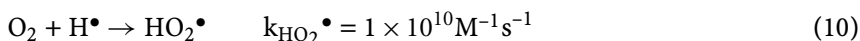
Fig. 1 Degradation of atrazine by photolysis of water under VUV irradiation in argon (**a**), air (**b**), and oxygen (**c**); [atrazine]$_0$ = 0.1 mM [23]

In aerated solutions, HO$_2$$^\bullet$ and O$_2$$^{\bullet-}$ are rapidly generated from the primary active species:

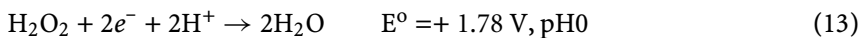$$O_2 + H^\bullet \rightarrow HO_2^\bullet \qquad k_{HO_2}{}^\bullet = 1 \times 10^{10} M^{-1} s^{-1} \tag{10}$$

$$O_2 + e^-_{aq} \rightarrow O_2^{\bullet-} \qquad k_{O_2}{}^{\bullet-} = 2 \times 10^{10} M^{-1} s^{-1} \tag{11}$$

The generated oxidants (HO$^\bullet$, HO$_2$$^\bullet$, O$_2$$^{\bullet-}$) and reductants (H$^\bullet$, e$^-_{aq}$, HO$_2$$^\bullet$, O$_2$$^{\bullet-}$) make possible simultaneous reductions and oxidations in the chemical system. The technology can be used for the degradation of pollutants in water and in a current of air with a high humidity content, for ultrapure water production and for treating oxidizable compounds that are difficult to treat, such as chlorinated and fluorinated hydrocarbons (for instance, ClCH$_3$). The process is highly efficient because VUV lamps generally have a high radiant power of illumination and water has a high cross-section of absorption in the wavelength range. This technology does not require the addition of chemical agents, and is simple and competitive. However, it requires an oxygen supply, the use of quartz and high power provisions. The technology has not yet been commercialized, and is presently in the development stage. González and Braun have thoroughly studied various systems submitted to this process, such as nitrate and nitrite photolysis [21, 22] and mineralization of the very resistant pesticide atrazine [23]. The results of this work are shown in Fig. 1.

2.4
UV/H$_2$O$_2$

H$_2$O$_2$ is a weak acid, a powerful oxidant and an unstable compound that disproportionates with a maximal rate at the pH of its pK$_a$:

$$H_2O_2 \Leftrightarrow HO_2^- + H^+ \qquad pK_a = 11.6 \tag{12}$$

$$H_2O_2 + 2e^- + 2H^+ \rightarrow 2H_2O \qquad E^o = +1.78 \text{ V, pH0} \tag{13}$$

$$H_2O_2 \rightarrow H_2O + \frac{1}{2}O_2 \tag{14}$$

$$H_2O_2 + HO_2^- \rightarrow H_2O + O_2 + HO^- \tag{15}$$

Hydrogen peroxide has been widely used in the removal of low levels of pollutants from wastewaters (chlorine, nitrites, sulfites, hypochlorites, etc.) and as a disinfectant [24]. However, low reaction rates make its use—at reasonable concentrations—in the treatment of high levels of refractory pollutants, such as highly chlorinated aromatic compounds and some inorganic compounds (e.g. cyanides), ineffective. The oxidizing power of hydrogen peroxide can be sensibly improved by HO$^\bullet$ generation through cleavage of the O–O union with photons of enough energy (higher than 213 kJ mol^{-1}, the energy bond, which corresponds to wavelengths lower than 280 nm). The reaction has a low quantum yield ($\phi_{HO^\bullet} = 0.5$) due to strong recombination of the radicals in solution [19, 25], and produces almost quantitatively one HO$^\bullet$ per quantum of radiation absorbed in the 200–300 nm range:

$$H_2O_2 + h\nu \rightarrow 2HO^\bullet \tag{16}$$

H$_2$O$_2$ photolysis is usually performed with low- or medium-pressure mercury vapor lamps. Almost 50% of the energetic consumption is lost in the form of heat or emissions less than 185 nm, which are absorbed by the quartz jacket. Generally, cheap germicidal lamps are used; however, as H$_2$O$_2$ absorption is maximal at 220 nm, it is more convenient to use Xe/Hg lamps that—although more expensive—emit in the 210–240 nm range.

In addition to H$_2$O$_2$ ($\varepsilon = 18.6$ M^{-1} cm^{-1} at 254 nm), other species can absorb photons at these short wavelengths, and can act as light filters. However, if the contaminants can be directly photolyzed, this may improve the efficiency of the oxidative destruction process. As the intensity of UV radiation decays exponentially towards the bulk of the solution, it is necessary to establish conditions of turbulent flow to continuously renew the solution surrounding the luminous source.

In the presence of oxygen, multiple pathways are operative in the UV/H$_2$O$_2$ system, as shown in Fig. 2 [1].

The photochemical process is more efficient in alkaline media because the concentration of the conjugate anion of hydrogen peroxide increases with pH (reaction 12), and this species has a higher absorption coefficient
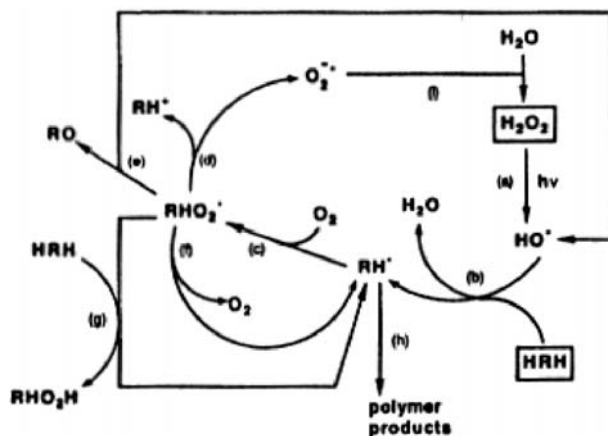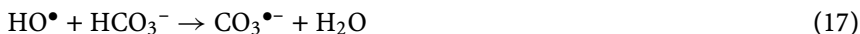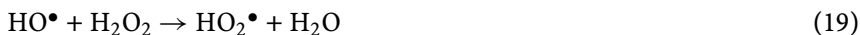
Fig. 2 Sequence of reactions occurring in the UV/H_2O_2 system [1]

($\varepsilon_{254} = 240 \, M^{-1} \, cm^{-1}$) than H_2O_2, favoring light absorption and increasing $HO^\bullet$ production [1, 26]. However, a high pH should be avoided because bicarbonate and carbonate ions (coming from the mineralization or present in the waters) are competitive $HO^\bullet$ trapping species:

$$HO^\bullet + HCO_3^- \rightarrow CO_3^{\bullet-} + H_2O \tag{17}$$

$$HO^\bullet + CO_3^{2-} \rightarrow CO_3^{\bullet-} + HO^- \tag{18}$$

Of course, this will occur in every AOT involving $HO^\bullet$ in carbonated solutions. As a general rule, pH changes due to mineralization processes should be taken into account in almost all AOTs because they may affect reaction rates [8].

In most degradations performed by UV/H_2O_2, it has been found that the rate is very dependent on the concentration of H_2O_2, increasing to an optimum value, beyond which an inhibitory effect takes place [19, 27]. At high $HO^\bullet$ concentrations, competitive reactions occur because these radicals are prone to recombination, regenerating H_2O_2 (reverse of reaction 16), or react in accordance with the following scheme [28]:

$$HO^\bullet + H_2O_2 \rightarrow HO_2^\bullet + H_2O \tag{19}$$

$$HO_2^\bullet + H_2O_2 \rightarrow HO^\bullet + H_2O + O_2 \tag{20}$$

$$2HO_2^\bullet \rightarrow H_2O_2 + O_2 \tag{21}$$

$$HO_2^\bullet + HO^\bullet \rightarrow H_2O + O_2 \tag{22}$$

Reactions 19 and 22 consume $HO^\bullet$ and decrease the probability of oxidation. $HO_2^\bullet$ radicals are produced through reaction 19, but one must remember that they are much less reactive than $HO^\bullet$. In all cases, it is necessary to determine the optimal H_2O_2 concentration, to avoid an excess that could retard the degradation, and this depends on the concentration and chemical nature

of the pollutants in the effluent stream. Consequently, treatability tests are needed to determine the right amount of H_2O_2 and to validate the technology. López et al. [19] were able to determine the optimal concentration of hydrogen peroxide that led to the fastest degradation of 4-chloro-3,5-dinitrobenzoic acid as a function of the initial concentration of the organic compound.

If low-pressure mercury vapor lamps are used, a high $[H_2O_2]$ is needed to generate enough $HO^\bullet$, making the process less effective. To overcome this limitation, high-intensity UV lamps can be employed.

The use of UV/peroxide offers some advantages: the oxidant is commercially accessible, thermally stable, and can be stored in the site of use (with the required precautions). As H_2O_2 has an infinite solubility in water, it is an effective source of $HO^\bullet$, producing $2HO^\bullet$ per each H_2O_2. There are no mass transfer problems associated with gases, as we will see in the case of ozone. The capital investment is minimal and the operation is simple. In contrast, due to the low H_2O_2 cross-section absorption at 254 nm, high concentrations of the oxidant are required, and depletion of the reagent must be controlled throughout the reaction span. The method has a low efficiency for treating waters of high absorbance at $\lambda < 300$ nm, or containing substances that compete with $HO^\bullet$ generation. In these cases, a large amount of H_2O_2 is again needed.

The UV/H_2O_2 technology is one of the oldest AOPs and has been successfully used in the removal of contaminants from industrial effluents, including organochlorinated aliphatics, aromatics, phenols (chlorinated and substituted) and pesticides [1, 8]. It has been considered a very good treatment for the reuse of wastewater from the dye industry [29]. A recent example is the case of Hispamin Black CA, a dye widely used in the Peruvian textile industry [27]. Using UV/H_2O_2, it was possible not only to decolorize but also to mineralize the dye in reasonable reaction times (Fig. 3). A strongly absorbing solution was completely decolorized after 35 min, and an 82.1% reduction of the total organic carbon (TOC) was obtained after 60 min.

Care must be taken to control the formation of toxic compounds during the process, as has been observed during the degradation of Remazol Black-B. However, an absence of toxicity was reported as occurring at the end of the process [29].

At present, UV/H_2O_2 technology is totally commercialized. The method can be sensibly improved by combination with ultrasound [30] or by pretreatment with ozone [31]. The combination $UV/H_2O_2/O_3$ has also been proposed, as we will see later.

Recently, the degradation kinetics of two pharmaceutical intermediates [5-methyl-1,3,4-thiadiazole-2-methylthio (MMTD-Me) and 5-methyl-1,3,4-thiadiazole-2-thiol (MMTD)] has been studied in order to assess the effectiveness and the feasibility of UV processes. For both substrates, the results showed that no degradation occurred when H_2O_2 was used alone and that UV and UV/H_2O_2 processes were both effective for degrading the substrates, but
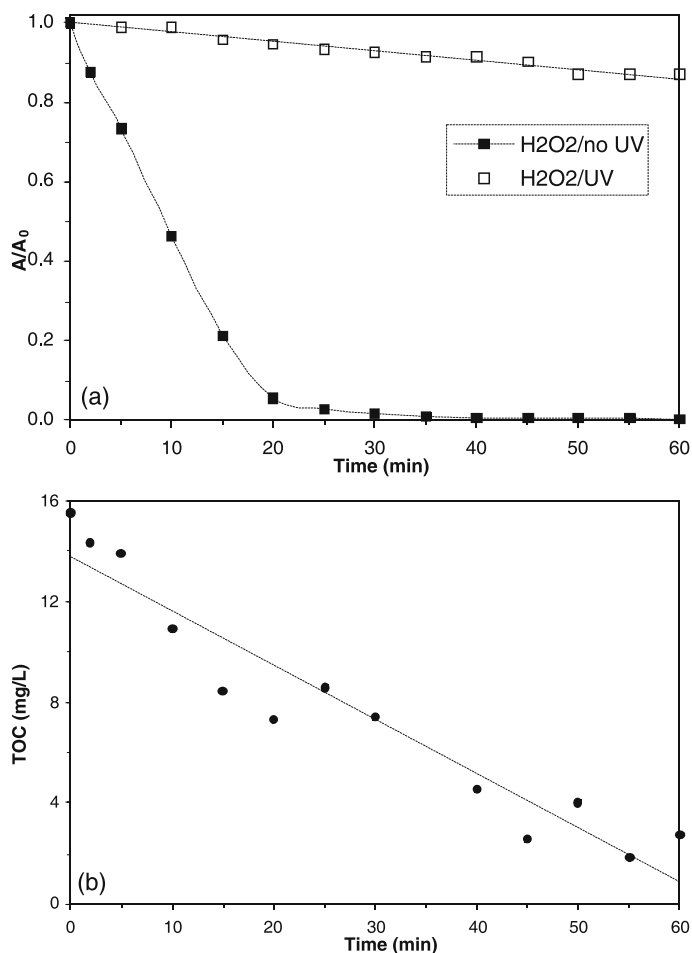
Fig. 3 Treatment of Hispamin Black CA by UV(366 nm)/peroxide: (**a**) Variation of the normalized absorption at 471 nm with irradiation time under UV irradiation and under UV irradiation in the presence of hydrogen peroxide; (**b**) variation of TOC during reaction with UV/peroxide. Conditions: [Hispamin Black CA] = 40 mg L^{-1}, pH 7.5, [H$_2$O$_2$] = 565.8 mg L^{-1} [27]

photo-oxidation was always faster than direct photolysis. The results showed that to remove 99% of some µg L^{-1} of the pharmaceutical intermediates with a H$_2$O$_2$ dose of 1 mg L^{-1}, 55 min for MMTD-Me and 2.6 min for MMTD are necessary, showing the feasibility of the decontamination process suggested in this study [32].
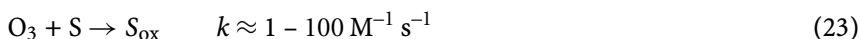
2.5
UV/O$_3$

2.5.1
Thermal Ozonation

Ozone is a powerful oxidant (see Table 2) and an efficient bactericide. Lately, ozone has been increasingly used for the treatment of drinking water, because the method does not produce THM or other chlorinated compounds that can be generated through disinfection with chlorine or chlorine oxide. The use of ozone allowed a remarkable improvement of organoleptic properties, filtration characteristics and biodegradability of drinking water. Additionally, the use of ozone decomposition by different initiators for the decontamination of water has triggered a study of the different mechanisms taking place in the chemical processes.
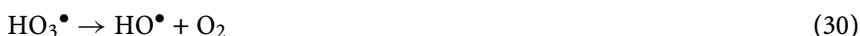
Ozone is industrially applied for water treatment either alone or in combination with hydrogen peroxide and/or activated carbon. Recent reviews describe improvements of the ozone technology, including combinations with catalysts and AOTs [33, 34].

In the absence of light, ozone can react directly with an organic substrate, through a slow and selective reaction 23, or through a fast and non-selective radical reaction that produces HO$^\bullet$, Eq. 24 [2, 35–37]:

$$O_3 + S \rightarrow S_{ox} \qquad k \approx 1 - 100 \, M^{-1} \, s^{-1} \tag{23}$$

$$2O_3 + 2H_2O \rightarrow 2HO^\bullet + O_2 + 2HO_2^\bullet \qquad k \approx 10^8 - 10^{10} \, M^{-1} \, s^{-1} \tag{24}$$

As stated earlier, the rate constants of ozone with organic compounds differ greatly for both types of processes (Table 3). The first reaction is important in acid media and for solutes that react very fast with ozone such as, for example, unsaturated compounds and compounds containing amine or acid groups. The results support the electrophilic nature of the reaction, either by electrophilic substitution or by dipolar cycloaddition [37]. This route leads to a very limited mineralization of the organic compounds, and its use for the removal of pollutants must be reinforced by modification of the method.

It has been demonstrated that ozone decomposition in aqueous solution forms HO$^\bullet$, especially when initiated by OH$^-$ [10]:

$$O_3 + HO^- \rightarrow O_2 + HO_2^- \tag{25}$$

$$HO_2^- + O_3 \rightarrow O_3^{\bullet-} + HO_2^\bullet \tag{26}$$

$$HO_2^\bullet \Leftrightarrow O_2^{\bullet-} + H^+ \tag{27}$$

$$O_2^{\bullet-} + O_3 \rightarrow O_3^{\bullet-} + O_2 \tag{28}$$

$$O_3^{\bullet-} + H^+ \rightarrow HO_3^\bullet \tag{29}$$

$$HO_3^\bullet \rightarrow HO^\bullet + O_2 \tag{30}$$

$$O_3 + HO^\bullet \Leftrightarrow O_2 + HO_2^\bullet \tag{31}$$

In some cases, singlet oxygen is formed when ozone reacts by O-atom transfer, for example with sulfides, disulfides, methanesulfinic acid, nitrite, etc. A detailed description of these results is beyond the scope of this paper; for more information see [38].

Ozonation follows a rapid zero-order initial step, limited by the mass transfer of the gas to water. A second step takes place when the aqueous medium is saturated by ozone, and the rate of this step is limited by slower reaction pathways [39]. The increase of the ozone dose plays a relevant role in enhancing the reaction efficiency. Typical ozone doses are $3-15\,mg\,L^{-1}$, depending on the initial concentration of the target compound.

The indirect pathway is less selective, because the species formed in the process have a higher oxidant ability than the ozone itself, especially $HO^{\bullet}$. The route can be initiated in different ways, by HO_2^-, $HCOO^-$, Fe^{2+}, humic substances or principally by HO^-. This is why, in principle, ozonation is more efficient in alkaline media, presenting an optimum around pH 9. Figure 4 shows a scheme of the main species of ozone decomposition in pure water initiated by hydroxide ions [7].

The addition of Fe(II), Mn(II), Ni(II), Co(II) or Ag(I) salts as well as solid oxides such as $Fe(III)/Al_2O_3$, goethite, MnO_2, TiO_2, Cu/Al_2O_3 or Cu/TiO_2 (Catazone process) improve the technology [37] (see Sect. 2.6.6).

The combination of both direct and indirect routes enhances sensibly OM degradation. This obviously depends on the composition and pH of the solution, and on the ozone dose. The pH should be carefully controlled due to the already mentioned $HO^{\bullet}$ scavenging action of bicarbonate and carbonate ions produced as mineralization takes place (reactions 17 and 18). Intermedi-
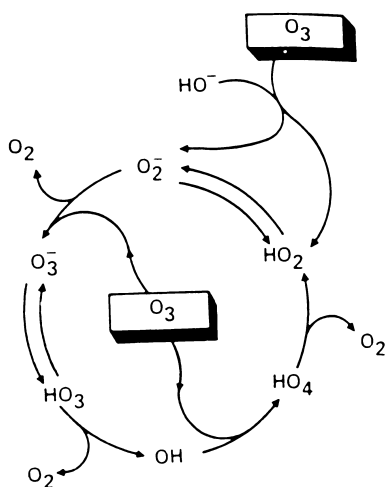

Fig. 4 Scheme of the main species of ozone decomposition in pure water initiated by hydroxide ions [7]

ate oxidation products, like acetic and oxalic acids, are refractory compounds that often resist mineralization.

In a relatively recent example, total depletion of 5×10^{-6} M nitrobenzene (NB) and 2,6-dinitrotoluene (2,6-DNT), model compounds of nitroaromatic hydrocarbons, could be accomplished with ozone in 10 and 40 min respectively at neutral or weakly basic pH. The rate constants of the direct reaction between ozone and NB or DNT are very low, indicating that the process develops in these cases more through hydroxyl radicals than through the direct reaction [40].

Ozonation is a very well-known commercialized technology for water treatment. It has been successfully used in the discoloration of kaolin and cellulose pulp and, in general, in the treatment of extremely polluted aqueous effluents. It must be highlighted that ozone is transformed merely into O_2 and H_2O, making the method less toxic when compared with other conventional treatments that use Cl_2 or chromic acid. Ozonation is a good pre-treatment to a biological treatment, because complex organics are transformed into aldehydes, ketones or carboxylic acids, all easily biodegradable compounds. Ozonation is versatile and can be combined with other conventional or Advanced Oxidation Technologies. Ozone can be simply produced in situ by electric discharge in a current of oxygen or air, leaving neither odors nor residual tastes. In contrast, from the operational point of view, the use of ozone is not as trivial as the use of a totally water miscible oxidant such as hydrogen peroxide, and there are mass transfer limitations due to the difficult access of the gaseous molecule to the aqueous phase [41]. Consequently, the process requires efficient stirring, the use of line mixers, venturis, contact towers, etc. To improve the process, another possibility is to increase the retention time in the reactor by large bubble columns or to increase the solubility of ozone by increasing the pressure to several atmospheres. However, any additional modification adds high investment costs. Furthermore, a rather high O_3/pollutant molar ratio (more than 5 : 1) is generally needed for the complete destruction of a compound, which makes the treatment even more expensive. As an additional drawback, in some cases, the method does not lead to complete mineralization. Care must be taken to control the temperature, because of the risk of volatilization of initial or intermediate compounds. Final degassing devices in the circuit are necessary to completely deplete ozone, which will be deleterious in a possible biological post-treatment; this also increases the costs.

2.5.2
O_3/H_2O_2

The addition of hydrogen peroxide to the ozonation system provides a better result [42]. The process, called Perozone, combines the direct and indirect ozone oxidation of organic compounds. H_2O_2 initiates O_3 decomposition by

electron transfer [2]; alternatively, the reaction can be envisaged as the activation of H_2O_2 by ozone. The set of reactions already seen (27 to 31) is initiated by the $HO^\bullet$ producing reaction 32 [43]:

$$O_3 + H_2O_2 \rightarrow HO^\bullet + O_2 + HO_2^\bullet \tag{32}$$

The process is expensive but fast, and can treat organic pollutants at very low concentrations (ppb), at a pH between 7 and 8; the optimal O_3/H_2O_2 molar ratio is $\cong 2:1$. It has been suggested that the acceleration of ozonation is due to the fact that H_2O_2 increases ozone transfer within water [44].

The treatment is effective for decomposing organochlorinated compounds such as trichloroethylene (TCE), tetrachloroethylene, etc. It is excellent for the post-treatment of water submitted to disinfection treatments with chlorine or chlorine dioxide because it can decompose THM or related compounds. One of the principal fields of application is in the degradation of pesticides [45].

2.5.3
Photoinduced Ozonation

The UV irradiation of ozone in water produces H_2O_2 quantitatively:

$$O_3 + h\nu + H_2O \rightarrow H_2O_2 + O_2 \tag{33}$$

The generated hydrogen peroxide is photolyzed (see Eq. 16), generating $HO^\bullet$ radicals, and also reacts with the excess of ozone, according to Eq. 32. This method might be considered in principle as just an expensive way of generating H_2O_2 and then $HO^\bullet$. Indeed, it is a combination of UV/H_2O_2 and O_3/H_2O_2, but the advantage is that the ozone has a higher absorption coefficient than H_2O_2 ($\varepsilon_{254} = 3300\ M^{-1}\ cm^{-1}$), and can be used to treat water with a high UV absorption background. The efficiency is higher than that of O_3 or direct UV, and the reactor does not need to be in quartz because UV-B light (280–315 nm) can be used. The method has been applied to potable water, to treat highly contaminated wastewater, in disinfection, in discoloration of waters from the paper industry, in the degradation of chlorinated aliphatic hydrocarbons (saturated and unsaturated), etc. In [43], the first applications of the technology are mentioned.

If wavelengths lower than 300 nm are used, photolysis of O_3 takes place, generating additional $HO^\bullet$ and other oxidants, with a subsequent increase in the efficiency [46]:

$$O_3 + h\nu \rightarrow O_2(^1\Delta g) + O(^1D) \tag{34}$$
$$O(^1D) + H_2O \rightarrow 2HO^\bullet \tag{35}$$
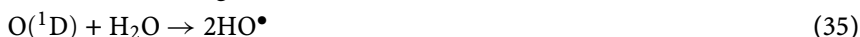
Gurol and Akata [43] studied the kinetics of ozone photolysis following a conceptual model based on possible reaction pathways. They obtained experimentally the primary quantum yield of ozone photolysis at 254 nm (0.48).

The rate of ozone photolysis increased with increasing light intensity, ozone concentration and pH, and decreased with increasing inorganic carbon concentration. As the formation of $HO^\bullet$ is tied to ozone decomposition, this model can be extended to predict the oxidation rates of water contaminants by $HO^\bullet$ generated in the process.

Generally, an increase of the ozone concentration increases the degradation rate of the pollutant, as demonstrated for the case of atrazine [47]. Although direct ozonation can contribute, 87% of the oxidation process proceeds, in the atrazine case, through the radical pathway.

In contrast with the results in the absence of light, alkaline pH reduces the reaction rate, as has been observed in the case of 2,6-DNT degradation. The decrease of the rate is due to the dissociation of the hydroxyl radical in the less active oxygen anion radical (Eq. 36) and to the lower solubility of ozone at high pH [40].

$$HO^\bullet \rightarrow O^{\bullet-} + H^+ \tag{36}$$

Although ozonation is improved under UV light, it was found that the use of high initial concentrations of ozone ($1000 \, mg \, L^{-1}$) (without irradiation) was more effective than the combination UV/O_3 to treat formulated pesticides like atrazine, alachlor, carbofuran, etc., because of the presence of large amounts of hydroxyl radical scavengers in the formulations [39].

It was recently demonstrated that solar light is also valuable for enhancing ozonation, as proved in the degradation of two model organic compounds, phenol and malic acid. This process has been called Heliozon. The rates of OM removal were also higher and faster, and complete mineralization was achieved even at high initial TOC values (as high as $49\,000$ ppm). This provides a possible way of increasing ozone reactivity at low cost. The simultaneous presence of sunlight and Fe(II) in solution also produced a beneficial effect in the mineralization; this was, however, less effective with other metal ions like Cu(II), Ni(II), Mn(II) and Co(II) [49].

Ozonation is greatly improved when UV irradiation is combined with a heterogeneous photocatalyst such as TiO_2 (see Sect. 2.8).

2.5.4
$UV/O_3/H_2O_2$

The addition of light to the H_2O_2/O_3 process produces a net increase in the efficiency. The thermal process is accelerated, especially the very slow reaction (32). The three separate processes, UV/H_2O_2, UV/O_3 and $UV/H_2O_2/O_3$, have been shown to be very effective for the decontamination of groundwater and for soil remediation [2, 3]. In contrast to UV/O_3 and UV/H_2O_2 technologies, which are commercially available [3], $UV/H_2O_2/O_3$ application studies are at present only at the pilot plant scale.

2.6
Photo-Fenton and Related Reactions

2.6.1
Fenton Reaction

Fenton's well-known experiments at the end of the 19th century demonstrated that solutions of hydrogen peroxide and ferrous salts were able to oxidize tartaric and malic acids as well as other organic compounds [50]. Haber and Weiss suggested later that $HO^\bullet$ was formed through reaction (37) [2, 51]:

$$Fe^{2+}_{aq} + H_2O_2 \rightarrow Fe^{3+}_{aq} + HO^- + HO^\bullet \tag{37}$$
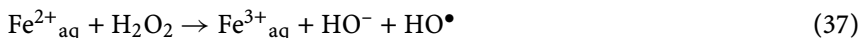
The attack of $HO^\bullet$ radicals on OM was proposed, in principle, as the oxidizing pathway according to Eqs. 1–3 (see however Sect. 2.6.9). Radicals produced by these processes can be additionally oxidized by Fe^{3+}, reduced by Fe^{2+} or dimerized, according to the following sequence [24, 52]:

$$R^\bullet + Fe^{3+} \rightarrow R^+ + Fe^{2+} \tag{38}$$

$$R^\bullet + Fe^{2+} \rightarrow R^- + Fe^{3+} \tag{39}$$

$$2R^\bullet \rightarrow R - R \tag{40}$$

$HO^\bullet$ can also oxidize Fe^{2+}, leading to the following unproductive reaction:

$$Fe^{2+}_{aq} + HO^\bullet \rightarrow Fe^{3+}_{aq} + HO^- \tag{41}$$

At pH < 3, the reaction system is autocatalytic, because Fe^{3+} decomposes H_2O_2 in O_2 and H_2O through a chain mechanism [51, 53–57]:

$$Fe^{3+} + H_2O_2 \Leftrightarrow Fe - OOH^{2+} + H^+ \tag{42}$$

$$Fe - OOH^{2+} \rightarrow HO_2^\bullet + Fe^{2+} \tag{43}$$

$$HO_2^\bullet + Fe^{2+} \rightarrow Fe^{3+} + HO_2^- \tag{44}$$

$$HO_2^\bullet + Fe^{3+} \rightarrow Fe^{2+} + O_2 + H^+ \tag{45}$$

$$HO^\bullet + H_2O_2 \rightarrow HO_2^\bullet + H_2O \tag{46}$$

As can be seen, the process can be initiated by Fe^{3+}, and it is then known as Fenton-like or as a Fenton-type process. This reaction is, however, slow and, as stated, $HO_2^\bullet$ is much less reactive than $HO^\bullet$. The Cu(II)/Cu(I) couple can play the same role as the Fe(III)/Fe(II) couple.

  The Fenton process is very effective for $HO^\bullet$ generation, but an excess of Fe^{2+}, H_2O_2, hydroperoxyl radicals or halogens (if present) can act as $HO^\bullet$ scavengers.

  In the presence of an excess of peroxide, the Fe^{2+} concentration is small compared with that of Fe^{3+}, because Fe^{2+} is quickly oxidized to Fe^{3+} (in seconds or minutes)[53]. It is believed that the destruction of wastes by the

Fenton reagent is simply due to the catalytic cycle of H_2O_2 decomposition, a process that generates $HO^\bullet$ radicals.

Generally, the degree and rate of total mineralization are independent on the initial oxidation state of iron. Conversely, the efficiency and the initial mineralization rate are higher when starting from Fe^{2+}; as a counterpart, Fe^{3+} salts produce a stationary Fe^{2+} concentration.

The application of the Fenton process to the destruction of toxic organic material began in 1960 [2]. In [58], several applications have been reported, including a large pilot plant for wastewater treatment. The method is effective for the treatment of water from the manufacturing or processing of chemicals, pharmaceuticals, insecticides, from petroleum refineries and fuel terminals, for color removal in effluents from the dye industry [59], for explosives such as trinitrotoluene (TNT), etc. The Fenton process degrades chlorinated aliphatic and aromatic compounds, polychlorinated biphenyls (PCBs), nitroaromatics, azo dyes, chlorobenzene, pentachlorophenol, phenols, chlorinated phenols, octachloro-p-dioxine, formaldehyde and many others. Compounds that cannot be attacked by this reaction are few but include acetone, acetic acid, oxalic acid, paraffins and organochlorinated compounds [60]. It has been successfully applied in the COD reduction of municipal and groundwaters and in the treatment of lixiviates. It is useful as a pre-treatment for non-biodegradable compounds [55]. Recently, it has begun to be effectively applied to the treatment of soils as a good oxidant of herbicides and other contaminants such as hexadecane or Dieldrin (see for example [61, 62]).

The advantages of the method are various: Fe^{2+} is abundant and non-toxic, hydrogen peroxide can be easily handled and it is an environmentally friendly compound. No chlorinated compounds are formed as in other oxidative techniques, and there are no mass transfer limitations because all of the reagents are in solution. The design of reactors for technological application is rather simple [60]. At variance, it requires a high iron concentration and the continuous or intermittent addition of H_2O_2 and Fe^{2+}. However, one must remember that an excess of both reagents, Fe^{2+} and H_2O_2, cause $HO^\bullet$ trapping. Although the degradation rate increases with Fe^{2+} concentration, no effect is observed above a certain value; oppositely, a large amount should be avoided because it contributes to an increase in the content of total dissolved salts in the effluent stream [8]. Generally, the reaction rate is high until full H_2O_2 depletion. Theoretically, the H_2O_2/substrate molar ratio needed for destruction of soluble compounds oscillates between 2 and 10. However, in practice, this ratio may be sometimes as high as 1000, because in environmental samples there are usually other $HO^\bullet$ competing species. Obviously, hydrogen peroxide must be completely eliminated before passing the effluent on for biological treatment [8].

The maximum catalytic activity of the Fe(II)/Fe(III) – H_2O_2 system is at a pH of about 2.8–3.0. At pH > 5, particulate Fe(III) is generated and at a lower pH, the complexation of Fe(III) with H_2O_2 (reaction 42) is inhib-
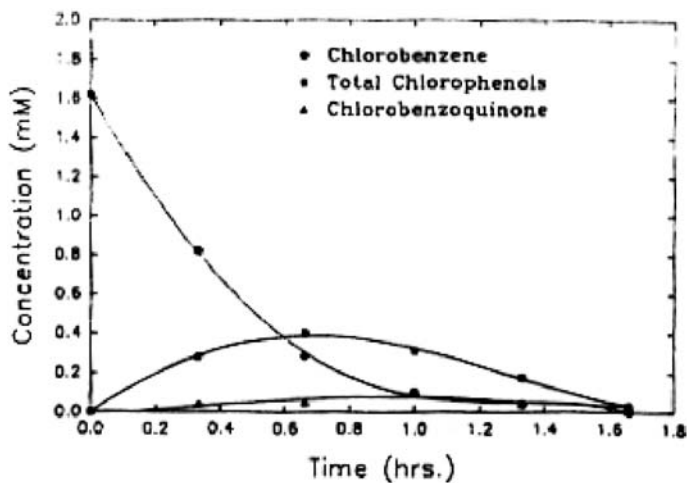
Fig. 5 Oxidation of chlorobenzene by Fenton reagent (excess H_2O_2). Initial conditions: [chlorobenzene] = 1.6 mM; [Fe^{2+}] = 5.0 mM; pH 3.0 [64]

ited [55]; therefore, the pH must be kept constant. The type of buffer used also has an effect on the degradation efficiency. Phosphate and sulfate buffers are the worst, probably due to formation of stable Fe(III) complexes, which decreases the concentration of free iron species in solution and inhibits the formation of free radicals [53]. At the end of the process, even though this means further management of the generated sludge, it is common to alkalinize the waters, with the simultaneous addition of a flocculant to eliminate the remaining iron.

In the laboratory, the metal is traditionally added as pure ferrous salts, but at a larger scale, the use of these salts becomes prohibitively expensive, and normally $Fe(NH_4)_2(SO_4)_2$, which contains 20% of active iron, is used. Other iron compounds have been employed, including solids such as goethite, which has been used, for example, for TCE destruction [63].

In Fenton reactions, complete mineralization cannot generally be achieved; resistant intermediates such as carboxylic acids, which react very slowly with $HO^\bullet$, are formed, with the unproductive reaction (41) predominating. Sometimes, as Fig. 5 shows, products more toxic than the initial ones—a quinone in this example—can be formed, whose presence must be carefully monitored until total depletion [64].

2.6.2
The Photo-Fenton Reaction and Other Iron-Based Photoprocesses

As mentioned in the previous section, Fenton processes do not generally lead to mineralization, the recycling of Fe^{2+} is slow, and a scavenging of $HO^\bullet$ or

other competitive reactions take place. Complexation of Fe(III) with organic compounds in the system, mainly carboxylic acids, leads to the formation of very stable iron (III) compounds, whose further oxidation and mineralization is difficult. One example is oxalate, a common intermediate in many oxidative degradations.

The photochemistry of the Fe(III) species in solution is a very common process in natural waters, and can also be of interest for use in oxidation processes for water treatment. The chemistry implicated in photoinduced processes of Fe(III)-complexes has been recently reviewed, together with the degradation of organic compounds in aqueous solutions initiated by them [65]. Fe(III)-hydroxocomplexes undergo photochemical reduction to Fe(II) under UV irradiation, and Fe(II) is reoxidized by oxidants like dissolved oxygen, giving rise to the basic Fe(III)/Fe(II) redox cycle. $Fe(III)(OH)^{2+}$ is the dominant complex from pH 2.5 to 5 and it absorbs light in the UV range with higher absorption coefficients than that of aqueous Fe^{3+}. Its photolysis leads to Fe(II) and $HO^\bullet$, as shown in Eq. 47. The quantum yield of this reaction is low and depends on the irradiation wavelength, but it is higher than that of other Fe(III)-aquo or -hydroxo species in solution [65]:

$$Fe(III)(OH)^{2+} + h\nu \rightarrow Fe(II) + HO^\bullet \tag{47}$$

A set of recent results [66–74] shows that the iron(III)-photoinduced degradation by itself is a homogenous photocatalytic process, efficient under solar light and useful to be employed in decontamination systems. It can be used as a physicochemical pre-treatment to transform biorecalcitrant pollutants or as a complete treatment leading to mineralization. The advantage of this process is that it only needs the addition of iron at low concentrations, compatible with the environment (ca. 5 ppm). The process must be rationalized as follows:

1. If there is no interaction between Fe(III) and the pollutant, Fe(III)-hydroxocomplexes are the source of $HO^\bullet$, according to reaction (47). The interest of this process resides in its catalytic aspect. $HO^\bullet$ radicals react with iron (II) at a high rate, according to reaction (41), which allows the regeneration of the absorbing species. The aqueous $FeOH^{2+}$ complex plays a fundamental role in this process. The efficiency of this system in degrading benzene, phenols, chloro-organic carboxylates and triazines was tested under either UV or solar light (for a list of references, see [65]).

2. If the pollutant is a carboxylic acid such as oxalic acid or others used in the formulation of detergents (ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA), etc.), Fe(III) forms stable complexes or associated ionic pairs that exhibit ligand-to-metal charge transfer (LMCT) bands in the UV-Vis spectrum; these complexes are, in general, photochemically active and, under irradiation, they generate Fe(II):

$$Fe(III)(O_2CR)^{2+} + h\nu \rightarrow Fe(II) + CO_2 + R^\bullet \tag{48}$$
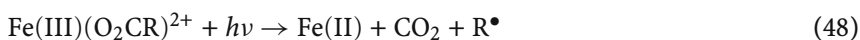
Light irradiation of these complexes can be used to promote an important enhancement of the degradation of organic compounds [53–56, 75]. We will return to ferrioxalate in Sect. 2.6.3.

Recently, Park and Choi [76] reported the visible light ($\lambda \geq 420$ nm) and Fe(III)- mediated discoloration of Acid Orange 7 (AO7) in the absence of H_2O_2. Ferric ions form complexes with AO7 mainly through the azo chromophoric group of the dye and, under irradiation, production of ferrous ions accompanies AO7 photodegradation. The reaction was not inhibited in the presence of an excess of an $HO^\bullet$ scavenger (2-propanol), which indicated that $HO^\bullet$ radicals were not responsible for the dye degradation. From the evidence that addition of an excess of sulfites and sulfates, which inhibit complex formation, decreased the photodegradation efficiency, it was suggested that the actual active species was the Fe(III)-AO7 complex. Although the process does not reduce TOC concentration, it does not require hydrogen peroxide addition and it can be proposed as an economically viable method to pre-treat or decolorize azo dye wastewaters using sunlight.

The above-mentioned processes in the absence of H_2O_2 also take place in the presence of the oxidant, making both Fenton and Fenton-like reactions more efficient due to radical generation through Eqs. 47 and 48 and iron recycling. In these photo-Fenton processes, wavelengths from 300 nm up to the visible can be used, in contrast to UV/H_2O_2, which needs short-UV light. As expected, irradiation under 360 nm produces H_2O_2 photolysis (Eq. 16), yielding also $HO^\bullet$.

However, as in the case of thermal Fenton systems, H_2O_2 must be continuously added and acid conditions are needed. Iron concentrations can be orders of magnitude lower than in the conventional Fenton reaction; either Fe^{3+} or Fe^{2+} can be used, in the 5–15 mg L^{-1} range, supplied as $FeSO_4$, $Fe(ClO_4)_3$ or $FeCl_3$. Iron salts must be eliminated after the treatment by neutralization and precipitation of $Fe(OH)_3$, as in classic Fenton processes.

The most frequent use of the photo-Fenton technology has been the treatment of industrial waters and lixiviates. Nitroaromatics, polychlorinated phenols, herbicides (2,4,5-trichlorophenoxyacetic (2,4,5-T), 2,4-dichlorophenoxyacetic acid (2,4-D)) and pesticides have been successfully degraded [39].

When comparing different technologies, photo-Fenton is generally the most efficient. An interesting example is the comparative efficiency of three different AOP systems, direct photolysis, UV/H_2O_2 and UV/Fenton reagent, for the degradation of 2,4-dinitrotoluene (2,4-DNT, 100 ppm) [77]. While direct photolysis resulted in incomplete and slow 2,4-DNT decomposition, UV/H_2O_2 was faster (98% degradation in 60 min, 88 mM optimal H_2O_2 concentration). However, 94% TOC reduction after 2 h and complete mineralization after 60 min occurred with the Fenton reagent (3 : 1 H_2O_2 to $FeSO_4.7H_2O$ molar ratio), while 96% TOC reduction after 2 h was observed with UV photo-Fenton oxidation using a 125W UV lamp and the same ratio of reagents.

One practical use of Fenton and photo-Fenton processes is the removal of natural organic matter (NOM) from organic rich waters before the chlorine disinfection of drinking water. It was observed that, under optimal conditions, both processes achieved more than 90% TOC removal, leading to the potential formation of trihalomethanes at concentrations below $10 \, \mu g \, L^{-1}$, well under UK and US standards [78].

2.6.3
Photo-Ferrioxalate and Other Fe(III) Complexes

Oxalic acid forms complexes with Fe(III) that absorb strongly from 254 to 442 nm. The absorption corresponds to a LMCT band, with ε_{max} values around 10^3–$10^4 \, M^{-1} \, cm^{-1}$. Photolysis of trisoxalatoferrate(III) (ferrioxalate, FeOx) constitutes the most used chemical actinometer; the quantum yield of Fe^{2+} formation is high ($\phi = 1.0 - 1.2$) and almost independent of the wavelength [79].

If H_2O_2 is added, the photochemical reduction of the Fe(III)-complex will be coupled to a Fenton reaction (Eq. 37) [56, 80]. Thus, the use of illuminated mixtures of H_2O_2 and FeOx is very efficient for the photodegradation of organic contaminants: the energy required to treat the same volume of a selected wastewater is ca. 20% of the energy required by the common photo-Fenton system [56, 81, 82].
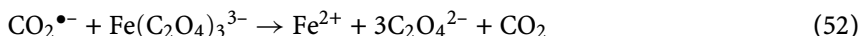
The main reactions in the photo/FeOx/H_2O_2 system are described by the following sequence of reactions [83]. After light absorption, oxalyl radical ($C_2O_4^{\bullet-}$) is produced through a LMCT:

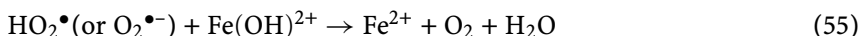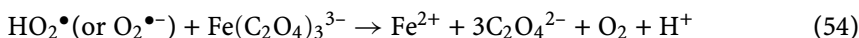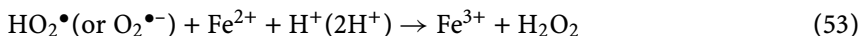$$Fe(C_2O_4)_3^{3-} + h\nu \rightarrow Fe^{2+} + 2C_2O_4^{2-} + C_2O_4^{\bullet-} \tag{49}$$
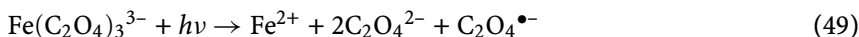
Then, a rapid decarboxylation takes place from the oxalyl radical:

$$C_2O_4^{\bullet-} \rightarrow CO_2^{\bullet-} + 2CO_2 \tag{50}$$

The fate of $CO_2^{\bullet-}$ depends on the competitive reactions between dissolved oxygen and ferrioxalate:

$$CO_2^{\bullet-} + O_2 \rightarrow O_2^{\bullet-} + CO_2 \tag{51}$$
$$CO_2^{\bullet-} + Fe(C_2O_4)_3^{3-} \rightarrow Fe^{2+} + 3C_2O_4^{2-} + CO_2 \tag{52}$$

The superoxide radical (or its conjugate acid) has three reaction pathways, depending on the oxidation state of iron or the H_2O_2 concentration and the pH:

$$HO_2^{\bullet}(or\ O_2^{\bullet-}) + Fe^{2+} + H^+(2H^+) \rightarrow Fe^{3+} + H_2O_2 \tag{53}$$
$$HO_2^{\bullet}(or\ O_2^{\bullet-}) + Fe(C_2O_4)_3^{3-} \rightarrow Fe^{2+} + 3C_2O_4^{2-} + O_2 + H^+ \tag{54}$$
$$HO_2^{\bullet}(or\ O_2^{\bullet-}) + Fe(OH)^{2+} \rightarrow Fe^{2+} + O_2 + H_2O \tag{55}$$

Reaction (54) is the predominant one at high $[H_2O_2]$ (in the mM range) and acid pH, while at low $[H_2O_2]$ (μM range), reaction (53) is the preferred path. $HO_2^\bullet$ can produce H_2O_2 and O_2 by disproportionation:

$$HO_2^\bullet + HO_2^\bullet (\text{or } O_2^{\bullet-} + H^+) \rightarrow H_2O_2 + O_2 \tag{56}$$
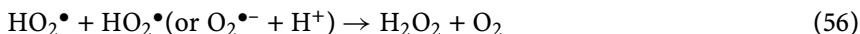
Then, the Fenton reaction (37) takes place.

The method is useful to treat waters with high absorbance at $\lambda < 300$ nm, because of the high ferrioxalate absorption cross-section in the 200 to 400 nm range. Solar light can be used, and that makes the technology very attractive from the economical point of view. As said, the energy required to treat the same volume of a wastewater is about 20% of the energy required by the photo-Fenton system [56], and this high efficiency is attributed to the broad range of absorbance of the reagent, and the high quantum yield of Fe^{2+} formation. The reagents are totally water soluble, and there are no mass transfer limitations. The process is cheap and the oxidant is accessible.

Ferrioxalate technology has been used for the treatment of aromatic and chloroaromatic hydrocarbons, chlorinated ethylenes, ethers, alcohols, ketones and other compounds. Figure 6 compares the destruction of 2-butanone by three different AOTs, and shows the high efficiency of ferrioxalate. Figure 7 compares solar photo-Fenton and solar FeOx for toluene treatment.

Nevertheless, it must be stated that total mineralization is seldom attained and that the contaminants are only transformed into other organic compounds. Aromatic pollutants producing hydroxyderivatives as intermediates that strongly absorb in the same UV range as H_2O_2 and Fe^{3+}, present a low rate of destruction [10].
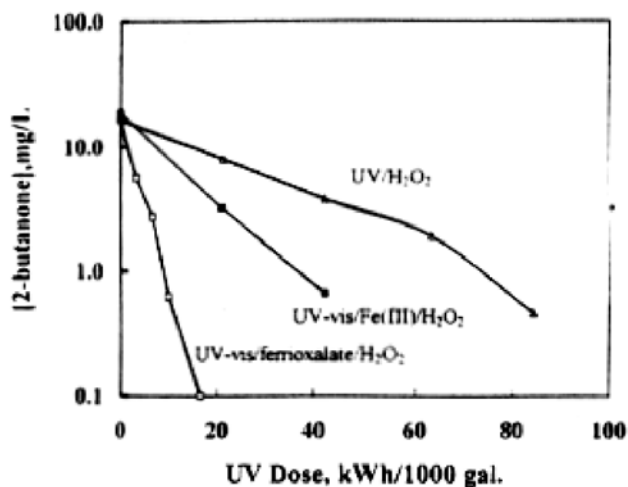

Fig. 6 Destruction of 2-butanone in a contaminated groundwater with different UV treatment processes [55]
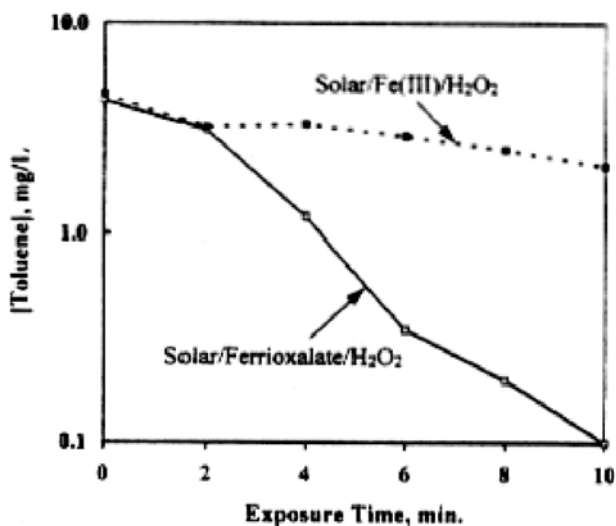
Fig. 7 Comparison of toluene destruction in a polluted groundwater by solar irradiation in the presence of ferrioxalate/H_2O_2 and Fe(III)/H_2O_2 [55]

A recent paper [84] presents a very complete study of the influence of different operational parameters on the FeOx process, such as light intensity, concentration of the reagents, and the presence of anions and HO• scavengers. The case study was the herbicide 2,4-D. It was demonstrated that the system presented a higher efficiency than the photo-Fenton process, that the removal rate increased with light intensity and that ferrioxalate concentration determined the light absorption fraction, then controlling the removal rate.

Iron carboxylates other than oxalate were tested [81, 85]. For example, an enhancement of the TiO_2-photocatalytic degradation of 4-chlorophenol (4-CP) was found when Fe(III)-NTA was added, this effect being larger than that in the presence of non-complexed Fe(III) [86]. However, when the carboxylate is itself the target pollutant, the addition of oxalate only causes a competition for Fe(III). This has been observed when EDTA degradation (in the mM range) at pH 3 was treated with the FeOx/H_2O_2 process under solar irradiation. A rapid TOC removal was attained in all cases, reaching almost 100% after 1 h solar exposure under the best conditions. However, the extent of degradation was found to decrease at high ferrioxalate concentrations, probably because of the competition of oxalate with EDTA or its degradation products. In the absence of oxalate, EDTA could also be degraded to a reasonably good extent, with a TOC removal only slightly lower than that obtained when using ferrioxalate; this constitutes a good advantage from the economical point of view [87].

2.6.4
SORAS Technology

The Solar Oxidation and Removal of Arsenic (SORAS) method is a very simple process in which As can be removed in the presence of iron and citric acid; the technology has been applied with relatively good success in the poorer regions of the planet such as in Bangladesh, India and other countries [88–90]. Water contained in transparent polyethyleneterephthalate (PET) bottles, to which some drops of lemon or lime juice have been added, are irradiated with sunlight for a few hours. Generally, natural water contains an amount of iron salts or they are intentionally added in proper quantities to the water. Although As(III) is partly oxidized in the dark by the addition of Fe(II) to aerated water, presumably by reactive intermediates formed in the reduction of oxygen by Fe(II), over 90% of As(III) can be oxidized photochemically after 2–3 h solar illumination. In the SORAS process, where Fe(III) citrate complexes participate, Fenton-like reactions strongly accelerate As(III) oxidation. The resulting As(V) is adsorbed or incorporated into the precipitating solid in a better way than As(III); clear water is then obtained by decantation or filtration.

Topics that have been recently explored include the way in which the nature of the solids formed under solar irradiation differ from those obtained by the normal hydrolysis of Fe(III) salts, and how the presence of complexing agents such as citrate influence the nature of solids formed by oxidative hydrolysis. It was concluded that the role of solar energy is to direct the pathway of the formation of solids towards structures that are adequate for As(V) uptake, and to achieve these reactions in time spans that permit coupling with the photocatalyzed oxidation of As(III) [91].

2.6.5
Zero-Valent Iron

The use of zero-valent iron (Fe(0)) as a reducing agent to treat compounds recalcitrant to oxidative treatments (e.g., halogenated olefins such as TCE to ethylene) is an emerging technology, which can also convert metal ions (for example Cr(VI) to Cr(III)). For details of this promising new technology, see [92] and references therein.

The combined action of UV and Fe(0) or H_2O_2 and Fe(0) has been assessed in these systems, and this actually transforms the technology into a Fenton-based process. The role of UV light is to affect Fe(0) dissolution. Recent examples are the enhancement of atrazine degradation [93] and the improvement of discoloration of three reactive dyes, C.I. reactive red 2, C.I. reactive blue 4 and C.I. reactive black 8, using Fe(0) and 254-nm UV irradiation [94].

However, information is still rare regarding the effects of ultraviolet light on the zero-valent iron system. In the case of nitrate reduction by Fe(0), a detrimental effect of 254-nm irradiation on ferrous ion dissolution and ni-

trate removal was reported. It seems that the role of UV light is strongly dependent on the solution composition [95]. These processes deserve profound further research.

2.6.6
Photo-Fenton and Ozonation

The combination of photo-Fenton and ozonation results in an important enhancement of the destruction efficiency of organic compounds like phenol [96], 2,4-D [97], aniline or 2,4-chlorophenol ([33] and references therein). As mentioned in Sect. 2.5.1, metal ions catalyze ozone decomposition. In the dark, Fe(II) catalyzes O_3 degradation giving the ferryl intermediate (FeO^{2+}, see Sect. 2.6.9), which can directly oxidize the organic pollutant or evolve to a hydroxyl radical:

$$Fe^{2+} + O_3 \rightarrow FeO^{2+} + O_2 \tag{57}$$

$$FeO^{2+} + H_2O \rightarrow Fe^{3+} + HO^\bullet + HO^- \tag{58}$$

The combination of ozone with UV light and iron as the catalyst improves the oxidative capability of the system due to regeneration of Fe(III). In the presence of UV light, Fe(III) ions can be reduced to Fe(II) by a photo-Fenton process, closing a loop mechanism where Fe species act as catalysts while generating additional $HO^\bullet$ and ferryl radicals. Irradiation with UV light also causes $HO^\bullet$ generation by the direct UV/O_3 pathway and photo-Fenton reactions. The interaction of Fe(III) and ligand species in solution, which ends in photochemical active complexes, can also take place in these complex systems.

2.6.7
Photoelectro-Fenton

The photoelectro-Fenton method [98] complements the photo-Fenton and electro-Fenton reactions. In the latter, a potential is applied between two electrodes immersed in a solution containing Fenton reagent and the target compound. The recent study of the herbicide 2,4,5-T, performed in an undivided cell with a Pt anode and an O_2-diffusion cathode, showed that the photoelectrochemical process was more powerful than the electro-Fenton process, which can yield only about 60–65% of decontamination. The electro-Fenton method provides complete destruction of all reaction intermediates, except oxalic acid, which, as already mentioned, forms stable complexes with Fe^{3+} that remain in the solution. The fast photodecarboxylation of such Fe(III)-oxalate complexes by UV light explains the highest oxidative ability of the photoelectro-Fenton treatment, which allows a fast and total mineralization of highly concentrated acidic aqueous solutions of 2,4,5-T at low current and temperature. A similar behavior was found for the herbicide 3,6-dichloro-2-methoxybenzoic acid [99].

2.6.8
Immobilized Photo-Fenton Systems

As has been already mentioned, homogeneous Fe^{3+}/H_2O_2 reactions need up to 50–80 ppm of iron ions in solution, a value far above the established regulations in industrial countries (around 2 ppm). Moreover, Fenton systems require working at acid pH to avoid iron precipitation, but additional alkalinization and redissolution steps, required to eliminate and recover iron, elevate the costs of the process. To avoid these drawbacks, supported Fenton catalysts, with iron containing membranes or beads, have been developed in recent years. The supporting material needs to be a good complexing agent for Fe^{2+} and Fe^{3+}, stable in aqueous solution, resistant to oxidative conditions and transparent to UV/Vis radiation. In this sense, Fe-containing Nafion® [100] and perfluorinated Nafion® membranes [101, 102] were reported useful in degrading Orange II, 2,4-dichlorophenol and other chlorophenols at a pH between 2.8 and 11 with rates similar and even faster than those of homogeneous photo-Fenton reactions [102]. Nafion-silica composites [103], C-Nafion structured fabrics [104], polyethylene copolymers [105], alginate gel beads [106], structured silica fabrics [107], brick grain [108], MgO [109], SiO_2 [110] and zeolites [111] have also been successfully tested as supports. Another advantage of these systems is that it is possible to work at a pH at which it is not necessary to make a final adjustment before a biological post-treatment. Interestingly, when industrial wastewaters were treated with Fe-containing silica fabrics, the final BOD_5/TOC ratio was higher than that obtained with a homogeneous photo-Fenton process, indicating a higher biodegradability extent [107].

2.6.9
## Active Species in Fenton and Photo-Fenton Systems

Although several studies indicate that $HO^\bullet$ is formed in Fenton systems according to Eq. 37 and it is responsible for the efficiency of degradative reactions, it is presently believed that other Fe(IV) or Fe(V) species like FeO^{3+} and ferryl complexes, are also active agents in the processes [53–55, 58, 112]. For example, Kremer [112] identified a mixed valence binuclear species, $\{FeOFe\}^{5+}$, and proposed a new mechanism for the Fenton reaction, in which FeO^{2+} acts as the key intermediate.

Bossmann et al. [58] proposed the initial formation of a hydrated Fe(II)–H_2O_2 complex, leading to a steady-state concentration of iron(II) bound to H_2O_2, according to:
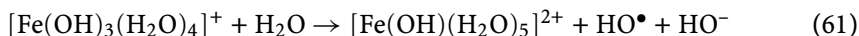
$$[Fe(OH)(H_2O)_5]^+ + H_2O_2 \Leftrightarrow [Fe(OH)(H_2O_2)(H_2O)_4]^+ + H_2O \qquad (59)$$
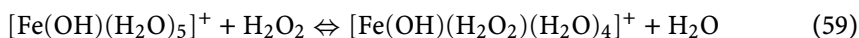
The authors based their argument on the fact that an outer-sphere electron-transfer reaction between Fe^{2+}_{aq} and H_2O_2, as indicated in the classical re-
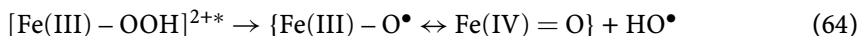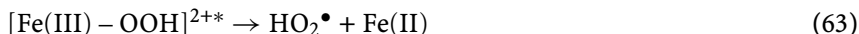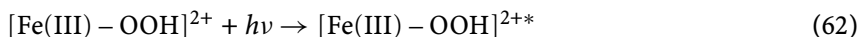
action (37), is thermodynamically not possible, because the formation of the $H_2O_2^-$ species is not favorable. Subsequently, an inner-sphere two-electron-transfer reaction takes place, with the formation of a Fe(IV) complex:

$$[Fe(OH)(H_2O_2)(H_2O)_4]^+ \rightarrow [Fe(OH)_3(H_2O)_4]^+ \tag{60}$$
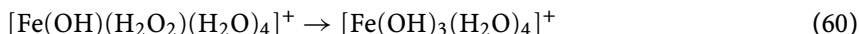
This complex may give rise to $HO^\bullet$ and Fe(III):

$$[Fe(OH)_3(H_2O)_4]^+ + H_2O \rightarrow [Fe(OH)(H_2O)_5]^{2+} + HO^\bullet + HO^- \tag{61}$$

Pignatello et al. [54] performed nanosecond laser flash photolysis experiments with a 355-nm laser pulse in the Fe(III)/H_2O_2 system in the absence of organics. They observed a broad positive signal in the visible region, indicative of the formation of a light-induced transient. They proposed different possible species in agreement with the observed signal, such as $H_3Fe(V)O_4$, FeO^{3+}, FeO^{2+} or a triplet excited state of the $[Fe(III) - OOH]^{2+}$ peroxo complex. The decay of this species produces $HO_2^\bullet$ radicals and new high valent oxoiron, ferryl-like species, which can be precursors of the Fenton reaction, although their identity remained undetermined:

$$[Fe(III) - OOH]^{2+} + h\nu \rightarrow [Fe(III) - OOH]^{2+*} \tag{62}$$

$$[Fe(III) - OOH]^{2+*} \rightarrow HO_2^\bullet + Fe(II) \tag{63}$$

$$[Fe(III) - OOH]^{2+*} \rightarrow \{Fe(III) - O^\bullet \leftrightarrow Fe(IV) = O\} + HO^\bullet \tag{64}$$

$$[Fe(III) - OOH]^{2+*} \rightarrow Fe(V) = O + OH^- \tag{65}$$

In summary, it could be emphasized that both $HO^\bullet$ as well as ferryl species coexist in the Fenton systems; depending on the experimental conditions (type of substrate, iron-H_2O_2 ratio, presence or addition of scavengers, etc.), one of them will predominate.

2.7
UV/Periodate

Periodic acid, H_5IO_6, and periodate, IO_4^-, are strong oxidants:

$$H_5IO_6 + H^+ + 2e^- \rightarrow IO_3^- + 3H_2O \qquad E^0 = + 1.60 \text{ V} \tag{66}$$

Irradiation of periodate solutions under short-UV light generates radicals ($IO_3^\bullet$, $HO^\bullet$, $IO_4^\bullet$) and other oxidative species (IO_3^-, HOI, I_2, H_2O_2, O_3). The oxidation of a system containing this reagent under UV light is less selective but more efficient than other AOTs. The proposed mechanism may be very complex, as illustrated in Fig. 8 [113].

With this technology, a wide variety of compounds at low concentrations can be destroyed. It can be used for discoloration of dye-containing waters and for the treatment of other wastewaters. For improved effectiveness, waters should have a low absorbance. So far, there are no legislated discharge requirements for iodine compounds, from which I_2 and I^- are the
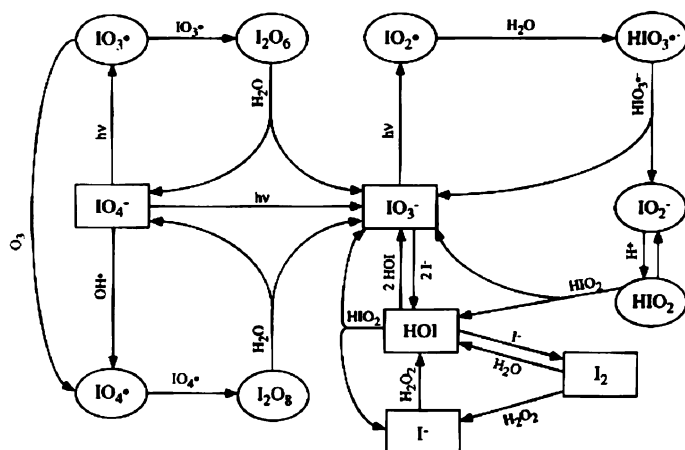
Fig. 8 Possible reduction pathway of periodate to iodide based on radiolysis studies and UV irradiation of iodine species [113]

more toxic (but still of low toxicity). Iodine can be recovered by ionic exchange, and periodate can be electrochemically regenerated. For example, the treatment of a real wastewater of high COD containing triethanolamine with UV/periodate reduces COD to acceptable values in relatively short times. The technology is faster than other photochemical AOTs and seems very promising, although there are no more recent references in the literature concerning its use.

2.8
Heterogeneous Photocatalysis

This AOT will be discussed later in this book; therefore, only a brief introduction is included here. Heterogeneous photocatalysis is a process based on the direct or indirect absorption of visible or UV radiant energy by a solid, normally a wide-band semiconductor. In the interfacial region between the excited solid and the solution, destruction or removal of contaminants takes place, with no chemical change in the catalyst.

Figure 9 shows a scheme of processes occurring in a particle of semiconductor when it is excited by light of energy higher than that of the band gap. Under these conditions, electron-hole pairs are created, whose lifetime is in the nanosecond range; during this time interval, electrons and holes migrate to the surface and react with adsorbed species, acceptors (A) or donors (D) [114]. Electron-hole pairs that cannot separate and react with surface species, recombine with energy dissipation. The net process is the catalysis of the reaction between the oxidant A and the reductant D (for example, between O_2 and OM).
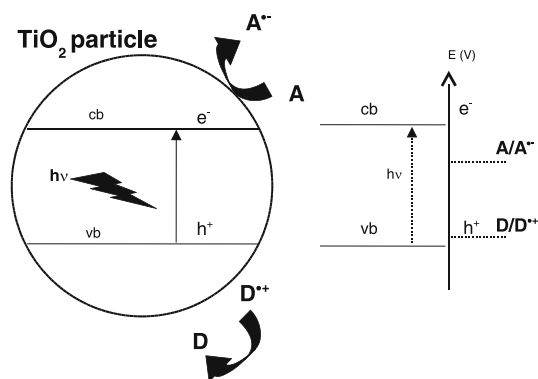
Fig. 9 Processes occurring in the semiconductor-electrolyte interface under irradiation with light of $E > E_g$

Various materials are candidates to act as photocatalysts such as, for example, TiO_2, ZnO, CdS, iron oxides, WO_3, ZnS, etc. These materials are economically available, and many of them participate in chemical processes in nature. Besides, most of these materials can be excited with light of a wavelength in the range of the solar spectrum ($\lambda > 310$ nm); this increases the interest in the possible use of sunlight. So far, the most investigated photocatalysts are metallic oxides, particularly TiO_2; this semiconductor presents a high chemical stability and can be used in a wide pH range, being able to produce electronic transitions by light absorption in the near ultraviolet range (UV-A).

The driving force of the electron transfer process in the interface is the difference of energy between the levels of the semiconductor and the redox potential of the species close to the particle surface. The thermodynamically possible processes occurring in the interface are represented in Fig. 9: the photogenerated holes give rise to the $D \rightarrow D^{\bullet+}$ oxidative reaction while the electrons of the conduction band lead to the $A \rightarrow A^{\bullet-}$ reductive process. The most common semiconductors present oxidative valence bands (redox potentials from +1 to + 3.5 V) and moderately reductive conduction bands (+ 0.5 to – 1.5 V) [115]. Thus, in the presence of redox species close or adsorbed to the semiconductor particle and under illumination, simultaneous oxidation and reduction reactions can take place in the semiconductor-solution interface.

Holes react with adsorbed substances, in particular with adsorbed water or OH^- ions, generating $HO^{\bullet}$ radicals and/or other radicals, as in other AOTs. Normally, in environmental applications, the photocatalytic processes take place in aerobic environments, and adsorbed oxygen is the principal electron acceptor species:

$$O_2 + e_{cb}^- \rightarrow O_2^{\bullet-} \tag{67}$$

If noble or heavy metal ions are present in solution, they can be reduced by conduction band electrons to a lower oxidation state:

$$M^{z+} + n\,e_{cb}^- \rightarrow M^{(z-n)+} \tag{68}$$

Reduction to the zero-valent state or formation of other metal solid phases like oxides, causes the element to deposit onto the semiconductor surface. The efficiency of the photocatalytic reaction depends on different factors. One of the most critical aspects is the high probability of electron-hole recombination, which competes with the separation of the photogenerated charges. On the other hand, as there is no physical separation between the anodic reaction site (oxidation by holes) and the cathodic one (reduction by electrons), back reactions can be of importance. The low efficiency is one of the most severe limitations of heterogeneous photocatalysis.

Heterogeneous photocatalysis over TiO_2 can be also combined with other AOTs. For example, addition of Fe(III) and H_2O_2 combines UV/TiO_2 with photo-Fenton; in this way, the destruction of some resistant pollutants can be improved. For example, EDTA, NTA and other oligocarboxylic acids are more rapidly mineralized in the presence of Fe(III)/H_2O_2 than when using TiO_2 alone [116–118]. Similarly, the presence of photochemical Fe(III) complexes such as Fe(III)-NTA helps the photocatalytic degradation of 4-CP [86]. In these cases, an important effect of the Fe(III)-complexes formed with the initial compound or with possible degradation intermediates takes place: these complexes can be photolyzed and even photocatalyzed in the reaction medium, generating Fe(II) and other active radical species.

Combination of UV/TiO_2 and ozone is also possible. Ozone acts as a powerful oxidant in place of oxygen, which has a slow electron transfer from TiO_2 (reaction 67) [33, 119]. In the presence of TiO_2, ozone generates $HO^\bullet$ through the formation of an ozonide radical in the adsorption layer:

$$O_3 + e_{cb}^- \rightarrow O_3^{\bullet-} \tag{69}$$

Then, direct and indirect ozonation reactions take place, with $HO^\bullet$ generation:

$$O_3^{\bullet-} + H^+ \rightarrow HO_3^\bullet \tag{70}$$

$$HO_3^\bullet \rightarrow HO^\bullet + O_2 \tag{71}$$

$HO^\bullet$ generation from O_3 is pH dependent and increases with decreasing pH. This avoids the use of high alkaline pH to induce $HO^\bullet$ formation from O_3. Photocatalytic ozonation of organic compounds such as 2,4-D, glyoxal, pyrrole-2-carboxylic acid, p-toluenesulfonic acid, monochloroacetic acid, phenol, aniline and others was found to be much faster than UV/TiO_2, UV/O_3 or ozonation alone ([33] and references therein). In many cases, higher extents of mineralization than with single AOTs are reached.

Another interesting combination is heterogeneous photocatalysis with ultrasonic irradiation, because this process hinders the inactivation of the catalyst by reaction intermediates, which usually block the catalyst. Ultrasound also reduces mass transfer limitations occurring in the case of immobilized catalysts (see [8] for a detailed description of this combined process).

2.9
Comparative Practical Examples

Two recent interesting examples will be briefly commented upon to evaluate AOTs in real application cases. However, it is worthwhile to point out that it is not possible to generalize the results due to variable experimental conditions.

In a recent work, different AOPs (O_3, O_3/H_2O_2, UV, UV/O_3, UV/H_2O_2, UV/O_3/H_2O_2, Fe^{2+}/H_2O_2 and UV/TiO_2) have been compared for the degradation of the model pollutant phenol [120]. Different variables (pH, oxidant, catalyst and reagent concentration) were studied to select the best conditions for each process, and pseudo-first order constants were calculated and compared among the cases. None of the ozone combinations improved the degradation rate of the single ozone process and even inhibited it. The UV/H_2O_2 process was almost five-times faster than photocatalysis and UV alone. Fenton reagent showed the fastest degradation, 40-times faster than UV and photocatalysis and 5-times faster than ozonation. Nevertheless, the relatively high degradation rate combined with lower costs made ozonation the most suitable choice for phenol degradation under the studied conditions.

Another interesting case is the study of the treatability of methyl *tert*-butyl ether (MTBE) in five groundwaters with highly variable water quality characteristics. Air stripping, granular activated carbon (GAC) adsorption, O_3/H_2O_2 and UV/H_2O_2 were compared in a mobile water treatment pilot plant under a variety of conditions. For high-flow rates, air stripping showed the lowest treatment costs, although relatively tall towers were required. However, at low flow rates and low COD, AOTs were the least expensive treatments [121].

2.10
Combination of PAOTs with Biological Treatments

Reference [122] offers an overview of recent works (1998–2002) where photoassisted AOPs and biological processes were coupled for wastewater treatment. This overview confirms the beneficial effects of such two-step treatments at the laboratory scale and the lack of studies carried at a field scale with the same approach.

A general strategy to develop combined photochemical and biological systems for biorecalcitrant wastewater treatment was proposed, taking into ac-

count the following points: the biodegradability of the initial solutions, the operation mode of the coupled reactor, the chemical and biological character-istics of the phototreated solutions, the evaluation of different photoassisted AOPs, the optimal conditions for both the photochemical and biological processes, and the efficiency of the coupled reactor. The strategy to couple photochemical and biological processes is illustrated by case studies of four different biorecalcitrant pollutants: p-nitrotoluene-ortho-sulfonic acid, a pol-lutant derived from the manufacture of dyes, surfactants and brighteners, metobromuron and isoproturon, two of the most commonly used herbicides in Europe and 5-amino-6-methyl-2-benzimidazolone (AMBI), a model biore-calcitrant compound of the dye industry. Three kinds of combined systems were developed using either photo-Fenton, Fe^{3+}/UV, or TiO_2 supported on glass rings for the photocatalytic pre-treatment and, in all cases, immobi-lized biomass for the biological step. However, the authors indicate that this strategy is not a universal solution. Chemical, biological, and kinetic studies must always be carried out to ensure that the photochemical pre-treatment increases the biocompatibility of the treated wastewater. Some field experi-ments using a solar reactor indicated that a coupled photochemical-biological treatment system at the pilot scale is a possible way to achieve the complete mineralization of the biorecalcitrant pollutant compounds, but it can only be justified if the resulting intermediates are easily degradable in a further biological treatment [123].

An innovative coupled solar-biological system at field pilot scale for the treatment of biorecalcitrant pollutants has been described in [122]. The strat-egy to develop this system implicates the choice of the most appropriate solar collector and the most efficient AOP, the optimization of this AOP, the choice of the biological oxidation system, the monitoring of the chemical and biological characteristics of photo-treated solutions and the evaluation of the performance of the coupled solar-biological flow system. The coupled system is conformed by a Compound Parabolic Solar Collector (CPC) and a Fixed Bed Reactor (FBR). AMBI was selected for tests. The results showed that CPC was the most appropriate photoreactor to be coupled with a bio-logical reactor and that the photo-Fenton system was the most appropriate AOT for the degradation of the model pollutant, generating a biocompatible effluent. The coupled reactor operated in semicontinuous mode, and a min-eralization performance between 80 and 90% was reached in the range of initial dissolved organic carbon (DOC) concentration of $300-500 \, mg \, C \, L^{-1}$. With this coupled system, wastewaters coming from textile, pulp and paper, surfactants, explosive military industries, and from olive washing, as well as effluents contaminated with pesticides, were tested. For the 16 cases studied, two of them were previously biologically pre-treated to remove the easily biodegradable fraction before leading to the classical AOT-biological treat-ment schema, in which the main aim of the AOT is to produce biodegradable intermediates or partial mineralization. This result indicates the plausibility
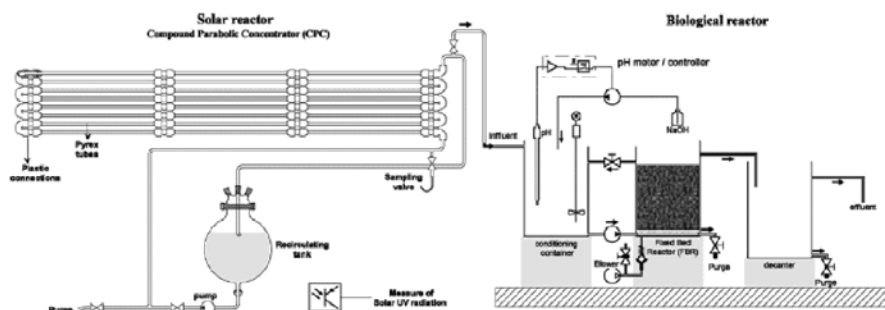
Fig. 10 Schematic representation of the coupled solar-biological flow reactor, according to [122]

of using the coupled approach at the pilot scale to treat real industrial wastewaters. Figure 10 shows a scheme of the proposed coupled system.

3
Conclusions

The relevant parameter that determines if a photochemical AOT can result in an effective alternative to traditional processes (e.g., chlorination, biological treatment) is mostly the concentration of the pollutants. In general, AOTs are more adequate for the treatment of small flows (or volumes) and not too high concentrations. Small COD contents, not higher than $5\,g\,L^{-1}$, can be suitably treated. Higher concentrations would require high concentrations of expensive reagents and/or high electrical power consumption [10]. The great utility of the technologies resides in the fact that they can process wastewaters resistant to conventional treatments and are complementary to them. However, the selection of the technology to be used must be based on its effectiveness and cost. The effectiveness depends on the nature of the contaminants to be destroyed, and the cost is strongly determined by the required equipment, the amount of energy required and the necessity for further treatment. Among the chemical reagents, the advantages of using O_2 or H_2O_2 as oxidants are clear, they are cheap, easy to handle and do not generate substances that must be removed later. Ozone shares the last advantage, but its manipulation is not as simple.

A generalization on the application of an AOT can never be made. Each effluent must be previously characterized, and treatability tests at the laboratory scale must be performed to choose the most appropriate method in economical and efficiency terms. It is important to evaluate the existing options to choose the most adequate. A knowledge of the kinetics, with establishment of the limiting step and limiting reagent(s), and a comparison with other conventional treatments should be available before applying

the technology. With a study of the kinetics, reliable information about substrate decay can be obtained, using analytical techniques such as HPLC or spectrophotometric measurements. Continuous TOC measurements should be performed to follow the degree of mineralization during the process. Obviously, a complex chemical composition always has a higher difficulty than simple mixtures, and HO$^{\bullet}$ scavengers are usually the main source of efficiency reduction.

From the technical point of view, suitable UV sources and appropriate photochemical reactors must be chosen and designed. A more extended exploitation of solar radiation would ensure a reduction of the costs of photochemical AOTs. In the case of photoreactors, a proper design should warrant the highest possible absorption of light by the reaction system. If an ozone-based technology is used, a rather expensive ozone generator is needed, with a cooling system, air-dryer and abatement of residual ozone at the end of the treatment. Furthermore, gas-liquid contactors, bubbling devices and good stirring must be provided to reduce mass transfer limitation problems. The use of ozone also requires resistant materials that cannot be attacked by the reagent, such as stainless steel.

It should be remembered that each AOT has an optimum working pH value and that in addition to adjusting the initial pH, the variation of pH during the reaction must be continuously controlled. Of course, this is dependent on the composition of the mixture: some pollutants are transformed to acid intermediates and give rise to a pH decrease, while others such as amino compounds produce amines or ammonia that increases pH. As constantly repeated in this article, carbonate or bicarbonate, either initially present in the treated water or formed during the reaction, are strong HO$^{\bullet}$ scavengers. At the end of the process, another pH adjustment will be needed in many cases before a biological treatment or to comply with local regulations before discharge of the effluent to receiving bodies.

The use of toxicological tests (Microtox, Amphitox, etc.), to control the formation of noxious by-products along the process path is mandatory. The purpose is to use the technology until toxicity is reduced to a certain level, beyond which a conventional, less expensive method, can bring about the mineralization process with the obvious reduction of costs.

Although much research has been done to understand the mechanistic and kinetic aspects of AOTs, which can be improved in the future by new investigations, some requirements are still needed for wide commercialization. These requirements refer mainly to reactor optimization and modeling from the point of view of chemical engineering. In the case of solar light, fluctuation in solar irradiation through the year or because of varying weather conditions on different days, makes reactor design difficult. Another important point is the control of variables that can affect the reactivity. This last task needs the support from expertise coming from varied scientific areas. Research in solid state physics can lead to an improved semiconductor activity;

development of analytical techniques would allow the discovery of methods for evaluating very low concentrations of the target and intermediates, and there are many other examples.

As possible future actions in the area, it is necessary to widely disseminate photochemical AOTs, especially in the less industrially developed countries, as alternative technologies of treatment that can be successfully used instead of other more expensive or less productive ones. These underdeveloped countries are fortunate in that they possess the highest sunlight irradiation powers on the planet, in contrast to the richest countries. From the point of view of scientific research, knowledge of the mechanisms taking place in PAOTs is extremely important as a way of improving existing drawbacks that hinder the use of the technology.

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