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Advanced oxidation processes in the removal of organic substances from produced water: Potential, configurations, and research needs

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ABSTRACT

Produced water is the main by-product generated by fossil fuel extraction activities. This wastewater is often heavily contaminated and associated with significant health, safety, and environmental risks; thus, adequate treatment systems are required to bring these streams to a quality that may be suitable for their recycling, reuse, or discharge into the environment. Advanced oxidation processes (AOPs) are increasingly studied to purify produced waters, and specifically for the removal of organic pollutants in the aqueous and non-aqueous phases. This review evaluates Fenton-based oxidation, heterogeneous catalysis, electro-oxidation, photo-assisted processes, and homogeneous advanced oxidation processes to remove organic contaminants in produced water. The efficiency and applicability of the reviewed approaches are discussed with particular attention to the configurations within the water purification train. Ozonation, Fenton-based techniques, heterogeneous photocatalysis, and anodic oxidation techniques are the most widely researched AOPs in produced water treatment. Photo-assisted processes and electrochemistry have been shown to significantly improve the effectiveness of decontamination of more traditional processes. Oxidation can be exploited as polishing stage of already pre-treated effluents with the final goal of reuse with closing of the water cycle, or as a primary/secondary treatment step to facilitate subsequent biological processes and membrane separation steps. The combination of two oxidation approaches or the oxidation with a membrane-based treatment within the same hybrid system is particularly promising. Challenges, research needs, and future perspectives are thus examined to guide efforts aimed at improving the application of advanced oxidation in produced water treatment and accelerate its implementation at real scale.

Keywords: produced water; advanced oxidation processes; Fenton; reuse; oil and grease.

Highlights

- Advanced oxidation processes (AOPs) effectively remove organics from produced water
- Both homogeneous and heterogeneous processes are reviewed and evaluated
- Photo-assisted techniques and electrochemistry increase the efficiency of oxidation
- AOPs are flexible in terms of configuration and combination with other treatment steps
- The most effective processes need important development for real-scale implementation

Table of Contents

1. INTRODUCTION

Accessibility to reliable energy and to safe water is essential to guarantee the well-being and the development of societies worldwide. Proper management of the two resources is also essential to maintain and improve the health of the environment where human communities flourish [1]. A challenging circle characterizes the water-energy nexus, as growing availability of one resource is required to warrant that of the other. The extraction of natural resources is but one example of this apparent deadlock that restrains numerous trajectories aimed at sustainability. By simply considering the worldwide production of crude oil, large volumes of water are injected into the subsoil to mine this resource; the water-to-oil ratios are expected to reach values well above 10 within the next five to ten years for onshore resources [2, 3]. At the other end of the line, once separated from extracted fossil fuels, the by-product of this activity is the so-called produced water (PW), which includes both the formation water and the injection water, and which is laden with other substances. The production of PW worldwide currently amounts to almost 50 millions of cubic meters per day [4-6].

PW may contain different organic and inorganic substances, some of which are actually added for extraction purposes. The characteristics of PW vary considerably if this wastewater is associated to the production of oil, natural gas, or coal, but they also depend strongly on the geochemistry of the producing formation, the characteristics of the producing well, and those of the extraction method [3, 7-9]. To complicate the picture, PW properties and volumes may differ from well to well in the same production field, and may even vary over time with the ageing of the same well. The main components are typically suspended particulates and colloids, salts and hardness, organic matter, heavy metals, and radioactive species [10, 11], resulting in a wastewater stream with high pollution and health risk potential [4, 12, 13]. To reduce the environmental impacts of the extractive activity associated with freshwater withdrawals and wastewater discharge, PW should be suitably treated to be recycled within the extraction process, or for reuse with beneficial purposes, such as livestock watering, steam production, aquifer storage, or other civil or industrial consumption [7, 14]. Specific treatments are needed according to the requirements of each application and a fit-for-purpose treatment approach should be adopted to promote the economic feasibility of PW reuse. As indicated recently by Coonrod *et al.* [3], such a strategy revolves around higher discrimination for the removal of specific contaminants of chief concern, and around multifunctionality to remove different families of contaminants in combined treatment steps. However, the purification of PW is still today a unique and outstanding technological challenge due to the typically high concentration of contaminants and the complexity of this matrix. Among all components, organic compounds usually present more demanding restrictions according to the legislation and constitute the main focus of the treatment [6]. These organics comprise most notably oil and grease, but also other toxic substances, such as BTEX, polycyclic aromatic hydrocarbons (PAHs), organic acids, and phenols [6, 10].

PW is traditionally treated by means of gas-water-oil separation, sedimentation or cyclones, and coarse depth filtration; the final effluent is discharged into the sea in offshore platforms or reinjected into the soil in onshore ones. Commercial PW treatment trains are currently limited and often aimed at the removal of a few families of compounds, in order to achieve the specific treatment objectives of each production site. However, if the goal is to improve PW management through water reuse, additional and more robust treatment steps are required [6, 13, 15, 16]. Jiménez *et al.* [6] provided a review of different treatments applied to polish PW with this purpose, which include membrane-based separation, as well as biological, thermal, and chemical treatments. The potential of advanced oxidation processes (AOPs) to remove toxic organic compounds has also been highlighted and preliminarily demonstrated through experimental investigation [17]. The application of such tertiary and advanced purification techniques is becoming increasingly important as stricter legislation is being enforced, more stringent controls are performed, and more parameters are taken into account.

Currently, AOPs are applied to effectively remove pollutants in plants for the production of drinking water, to remove biorecalcitrant micro-pollutants in wastewater treatment systems, and in disinfection strategies (including photo-assisted ones) [18-20]. These processes are based on the production of powerful reactive species (usually radicals), which can virtually attack and mineralize almost all oxidizable substances. The benefit of AOPs is noteworthy in engineering solutions where different processes need to be integrated to abate a large variety and concentrations of target contaminants and in a multiple barrier treatment strategy [21-23]. AOPs represent valuable pre-treatment options for various processes, as they effectively eliminate substances that may be toxic to microorganisms, which are sometimes exploited in subsequent biological treatment. Moreover, AOPs reduce the amount of foulants that may impair membrane separation. AOPs are thus promising processes specifically in the light of zero liquid discharge approaches, because they accomplish the partial or complete degradation of the target substances and not simply their separation from the main effluent and concentration in a waste stream or in another phase (*e.g.*, partitioning of pollutants on adsorbents). However, AOPs have also some intrinsic limitations that are especially important when treating streams containing radical scavenging species (*e.g.*, chloride, carbonate species), as well as refractory contaminants [24], all of which substances are typically present in PW. Consequently, AOPs themselves require effective pre-treatment to perform reliably.

This critical review focuses on the application of selected AOPs in the removal of organic contaminants in PW. The results reported on the basis of a somewhat limited but rapidly growing literature on this topic are here evaluated. Both homogeneous and heterogeneous processes are considered, including Fenton-based reactions, photo- and electro-catalysis, as well as the use of ozone, anodic oxidation, and other more novel techniques. The different roles of AOPs within integrated or hybrid systems are discussed, with special attention to the needs and benefits of possible coupling and combined configurations. Finally, the advantages, challenges, and perspectives around the application of AOPs in PW treatment are highlighted to guide future research and development in both academia and industry.

2. EVALUATION OF AOPS

2.1 SUMMARY OF AOP OBJECTIVES AND CURRENT RESEARCH STATUS

Produced water (PW) contains a wide variety of substances that need to be removed in order to properly manage this effluent. Typical substances include organic contaminants (*e.g.*, oil & grease, hydrocarbons, natural organic matter, surfactants), suspended solids, heavy metals, hardness, and dissolved solids giving rise to salinity values that are often far exceeding that of seawater. Depending on the nature of the field, PW may also contain other contaminants, including sulfides, ammonia, naturally occurring radioactive material (NORM), and microorganisms. Therefore, the PW treatment trains commonly consist of an initial removal of non-aqueous substances and suspended solids, followed by further removal of suspended and dissolved organics and, when needed, a final desalination step. For example, some authors reported innovative systems including flotation and granular media filtration, followed by biological treatment and reverse osmosis. Other novel trains include oil removal, coagulation, adsorption, ultrafiltration, and reverse osmosis [15, 16, 25]. The main objective of advanced oxidation processes (AOPs) in the treatment of PW is the partial or complete degradation of organic contaminants. The degradation may result in the formation of still oxidizable but safe products or, if the oxidation is complete, into mineralization (*i.e.*, the transformation of all organic compounds into CO_2 and mineral salts). Partial degradation gives rise to compounds that, compared to the parent pollutants, are electron-poorer, usually smaller in terms of molecular mass, more hydrophilic, and often biodegradable. For these reasons, these substances are often more easily handled by subsequent treatment steps. The amount and the nature of organic molecules contained in PW may vary considerably, as shown in **Table 1**, which reports the approximate concentration range of the most common organic PW components based on values found in the literature. **Table 1** also includes the concentration ranges of sodium, chloride, total dissolved solids (TDS), total suspended solids (TSS), and the main composition of five specific PWs from different basins.

Table 1. Approximate concentration range of the main cations, anions and organic PW components and examples of specific PW samples from different basins.

Component [Main sources referenced in square brackets]	Approximate concentration range from literature survey (mg/L)	Examples				
		PW from CO_2-enhanced oil recovery, Illinois Basin [26]	Shale-oil PW, Permian Basin [27]	Oilfield PW, Sergipe, Brazil [28]	PW average composition, Pennsylvania and West Virginia Basin [29]	PW, offshore North Sea, Brage Platform, Norway [30]
pH [31]	<1 - >13 Avg.: 7.1 ± 1.1 Median: 7.2					
Na^+ [26, 28, 31]	< *LOD*-210,000	22,732		9,200	23,500	
Cl^- [26, 28, 31]	< *LOD*-330,000	40,657		17,800	56,900	
Br^- [31]	< *LOD*-10,600					
HCO_3^- [31]	< *LOD*-242,000					
SO_4^{2-} [31]	< *LOD*-185,000					
CO_3^{2-} [31]	< *LOD*-170,000					
PO_4^{3-} [31]	< *LOD*-9,200					
N-NH_4 [26, 31, 32]	0.017-6305	17				
Total dissolved solids (TDS) [26, 27, 31]	0.1-530,000	65,252	106,540		63,800	
Chemical oxygen demand (COD) [31, 33]	10-51,000				5,645	
Total suspended solids (TSS) [4, 26, 27, 31, 32]	1-7,000	63	6,850		129	
Total organic carbon (TOC) [4, 27, 31, 32, 34]	< *LOD*-5,700		86.25		449	
Total O&G [4]	2-560				17	

Saturated hydrocarbons [35]	17-30					
Total BTEX [30, 36]	0.73-24.1					9
Benzene [27, 28, 30, 31, 34, 36]	0.032-500		1.50	1.397	0.4795	4.5
Toluene [10, 27, 28, 30, 31, 34, 36]	0.00097-78		0.11	1.263	0.833	3.5
Ethyl benzene [10, 27-30, 36]	0.01-400		2	0.148	0.0536	0.3
m-Xylene [28, 34, 36]	0.015-1.29			0.216	0.444	0.7
p-Xylene [27, 28, 30, 36]	0.02-0.34		0.02			
o-Xylene [28, 36]	0.09-1.06			0.096		
Xylenes [31]	0.0047-327					
Total NPD [30, 36]	0.766-10.4					0.93
Naphthalene [28, 30, 36]	0.01-0.841			0.0103	0.0113	0.35
C1-naphthalenes [30, 36]	0.2-2.9					0.26
C2-naphthalenes [30, 36]	0.145-3.21					0.15
C3-naphthalenes [30, 36]	0.056-2.08					0.10
Phenanthrene [28, 30, 36]	0.002-0.11			0.0023		0.0164
C1-phenanthrenes [30, 36]	0.017-0.32					0.0203
C2-phenanthrenes [30, 36]	0.005-0.365					0.0063
C3-phenanthrenes [30, 36]	0.007-0.27					0.0079
Dibenzothiophene [30, 36]	0.001-0.023					0.0025
C1-dibenzothiophene [30, 36]	0.005-0.103					0.0057
C2-dibenzothiophene [30, 36]	0.004-0.12					0.0061
C3-dibenzothiophene [30, 36]	0.003-0.089					0.0032
Total 16 EPA PAH [36]	0.0058-0.129					
Fluorene [30, 36]	0.0041-0.067					0.0089
Acenaphthene [28, 30, 36]	0.0003-0.015			0.002		0.0018
Chrysene [28, 30, 36]	0.0005-0.015			0.0079		0.0005
Phenols [30-32]	0.006-85				0.191	6.12
Total organic acids [30, 35]	0.001-10,000					757

Formic acid [30]	0.26-584					282
Acetic acid [30, 31]	8-9,700					
Propanoic acid [30, 31]	0.09-98					53
Butanoic acid [30]	*N.D.*-46					28
Pentanoic acid [30]	*N.D.*-33					5
Hexanoic acid [34]	*N.D.*-3.3					
Oxalic acid [37]	*N.D.*-495					
Malonic acid [37]	*N.D.*-1,540					
Aliphatic acids [38]	1.8-120					
Benzoic acid [38]	0.13-16					
C1-benzoic acids [38]	0.089-16					
C2-benzoic acids [38]	0.043-3.8					

N.D.: not determined; < *LOD*: below limit of detection of the employed analytical method

The main mechanism of oxidation in most of the AOPs is related to the production of highly reactive radicals, which can react non-selectively with oxidizable organic compounds following fast reaction kinetics. This feature is advantageous in as much as a rapid and broad-spectrum treatment is desired. These latter assets are the main rationale for the use of AOPs in PW treatment, whose interest has started roughly 20 years ago, with a surge in recent years; see **Fig. 1a**.

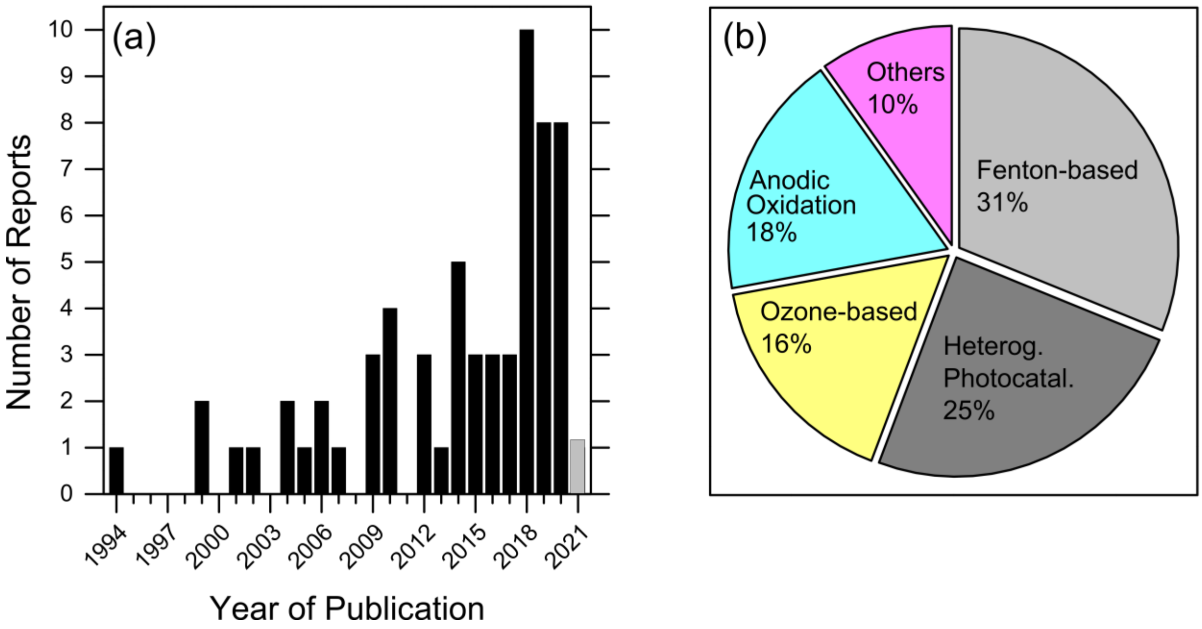


Fig. 1. Reports on AOPs applied specifically to the treatment of produced and flowback water on the basis of the literature analyzed and cited in this work: (a) number of reports published from the 1990s to the year 2020 (because the year 2021 is still ongoing, its associated value is incomplete); (b) classification of the studies based on the process of interest.

This section of the article summarizes the results reported in literature studies about the application of AOPs in the treatment of PW; it focuses on the efficiency of the various processes in terms of contaminant removal and reaction rate, but it also takes reaction conditions and target substances into account. The chapter is divided into five main subsections, each devoted to a family of AOPs: the first sub-section discusses Fenton-based reactions, which account for almost a third of the prevailing literature (**Fig. 1b**), while the second and the third sub-chapters discuss heterogeneous catalysis and the use of ozone, respectively. The fourth sub-chapter deals with anodic oxidation, while the last one with other processes that have been less applied for PW treatment so far.

2.2 FENTON REACTION

2.2.1 GENERAL CHARACTERISTICS AND MECHANISMS OF REACTION

The Fenton process has been known since over a century and its classic account is based on the Haber-Weiss reaction (Eq. 1), which describes the activation of hydrogen peroxide promoted by ferrous ions [18, 39-43]. In addition to the primary reaction (1), the recycling of Fe(III) to Fe(II) by H_2O_2 and $HO_2^{\bullet}/O_2^{\bullet-}$ plays a major role in Fenton-based degradation and it is often the rate-determining step of the catalytic cycle [44, 45]. The general scheme of Fenton reaction mechanism is reported below:

$$\mathrm{Fe(II)} + H_2O_2 \rightarrow \mathrm{Fe(III)} + {}^{\bullet}OH + OH^{-} \qquad (1)$$

$$\mathrm{Fe(III)} + H_2O_2 \rightarrow \mathrm{Fe(II)} + HO_2^{\bullet} + H^{+} \qquad (2)$$

$${}^{\bullet}OH + H_2O_2 \rightarrow HO_2^{\bullet} + H_2O \qquad (3)$$

$${}^{\bullet}OH + \mathrm{Fe(II)} \rightarrow \mathrm{Fe(III)} + OH^{-} \qquad (4)$$

$$\mathrm{Fe(III)} + HO_2^{\bullet} \rightarrow \mathrm{Fe(II)} + O_2 + H^{+} \qquad (5)$$

$$\mathrm{Fe(II)} + HO_2^{\bullet} + H^{+} \rightarrow \mathrm{Fe(III)} + H_2O_2 \qquad (6)$$

$$HO_2^{\bullet} + HO_2^{\bullet}\ (HO_2^{\bullet} + O_2^{\bullet-} + H^{+}) \rightarrow H_2O_2 + O_2 \qquad (7)$$

The Fenton process occurs through a radical mechanism, hence all the reactions from 1 to 7 take place simultaneously. Due to the prominent radical behavior of the Fenton process, it is generally somewhat improperly considered a catalytic process, by virtue of the cyclic regeneration of Fe(II) from Fe(III). However, a plethora of parasitic reactions can occur outside the catalytic cycle. The most critical parasitic reaction is the precipitation of Fe(III) as hydroxide, creating iron sludge. This mechanism explains the importance of controlling the pH during the process (*vide infra*). Some questions about the Fenton reaction are still debated, such as those around the nature of the transient species [46] and the role of superoxide radicals. On the other hand, adequate understanding of (*i*) the role of pH, (*ii*) the optimum [H_2O_2]/[Fe(II, III)] ratio, and (*iii*) the role of inorganic ions is available, with useful implications for a discussion of the Fenton process applied for PW treatment:

(i) Studies on the application of the classic Fenton reaction in water treatment indicate that substrate degradation is most effective under acidic pH conditions. De Laat and Gallard observed a peak in the rate of the Fenton reaction at approximately pH 3.2 [44]. The decrease of kinetics above this value is reasonably due to the precipitation of Fe(III), which prevents its recycling to Fe(II). An acidic pH limits the kinetics of precipitation of Fe(III) as hydroxide during the process. However, the formation of the iron sludge (iron hydroxides) cannot be avoided, and this by-product needs to be disposed of at the end of the process.

(ii) The rate of H_2O_2 decomposition has a peak as a function of the [H_2O_2]/[Fe(II)] ratio; De Laat and Gallard suggested that at pH 3 this ratio should be between 50 and 500 to maximize the kinetics [44]. This effect is due to the interconnected ability of Fe(II) and H_2O_2 to work as both sources and scavengers of hydroxyl radicals in the Fenton reaction, as well as to the ability of H_2O_2 and derived species to reduce Fe(III) into Fe(II) that takes part again in reaction 1. Indeed, a merely stoichiometric Fe(II)/H_2O_2 ratio, while optimizing reaction 1, would not allow for an efficient recycling of Fe(III) and would prevent the Fenton process from being effectively catalytic.

(iii) Inorganic anions are always present in PW (TDS: 100-400,000 mg/L) and they may significantly affect the Fenton reaction in several ways: (a) complexation of Fe(II, III), which avoids the interaction between iron species and H_2O_2 through the formation of inner-sphere complexes and limits the formation of $^{\bullet}OH$ in reaction 1, especially in the presence of sulfate; (b) precipitation reactions in the presence of phosphate or carbonate, which remove Fe(II, III) from the solution; (c) direct scavenging of hydroxyl radicals and formation of less reactive inorganic radicals, especially in the presence of chloride. The most troublesome anions for the Fenton reaction in PW treatment may be chloride and sulfate, due to their concurrent typically high concentration in the matrix and ability to affect Fenton reaction compared to other anions [47].

Sulfate ions reduce the reactivity of Fe(II, III) through the coordination of the iron species [45]. H_2O_2 cannot easily exchange the sulfate anion from Fe(III)–sulfato complexes and the Fenton reaction is not as easily activated. Sulfate ions may also react with $^{\bullet}OH$ (it is especially true for HSO_4^-, which prevails at $pH < 2$) [43], but they cannot be defined as direct scavengers because of the formation of $SO_4^{\bullet -}$, which has a redox potential that is only slightly lower than that of $^{\bullet}OH$ (2.4 vs. 2.7 V vs. NHE) [48]. Actually, from a kinetic point of view, $SO_4^{\bullet -}$ is only slightly less reactive than the hydroxyl radical itself (the second-order reaction rate constants with pollutants range within 10^6–10^9 M^{-1} s^{-1} and 10^7–10^{10} M^{-1} s^{-1} for $SO_4^{\bullet -}$ and $^{\bullet}OH$, respectively) [49, 50]. On the other hand, chloride ions inhibit the Fenton reaction by directly scavenging $^{\bullet}OH$ (the scavenging process occurs best at $pH < 5$, thus precisely under typical Fenton conditions) with the formation of consistently less reactive $Cl_2^{\bullet -}$ radicals (in this case, the second-order reaction rate constants with pollutants are 10^3–10^7 M^{-1} s^{-1}) [51]. Coherently, authors observed noticeable inhibition of the Fenton reaction by chloride scavenging above 0.01 M Cl^- at pH 2.8 [45].

The presence of dissolved organics may trigger a number of complex and competing processes when a Fenton reaction occurs. For example, Voelker *et al.* [52] in 1996, in a model system containing dissolved Fe, hydrogen peroxide, and Suwannee River fulvic acid, observed the increase of the Fenton reaction rate due to the formation of Fe(II)-fulvate complexes, which activated H_2O_2 more rapidly than the Fe(II)-aqua complexes. However, this phenomenon was accompanied by scavenging of $^{\bullet}OH$ by fulvic acid with the generation of the superoxide radical, $HO_2^{\bullet}/O_2^{\bullet-}$. While less reactive than $^{\bullet}OH$, $HO_2^{\bullet}/O_2^{\bullet-}$ may still enhance Fenton degradation by promoting Fe(III) recycling to Fe(II) [53].

The major drawbacks in the practical application of a Fenton process are the formation of iron sewage and the possible generation of by-products that are more toxic than the starting contaminants [54-56]. The latter can occur if a complete mineralization of the organic content in the stream is not achieved. The current attempts to overcome this possibility of the Fenton process are currently based on a careful monitoring of the treated effluent. An iron ligand may help overcome some of the limitations described above, by maintaining iron in solution at circumneutral or basic pH [57, 58], thus avoiding the formation of iron sludge, and by creating a complex with iron that may inhibit the scavenging effect of dissolved anions. Also, iron-ligand complexes give production of transient species (such as ferryl or other superoxidized iron species) other than solely $^{\bullet}OH$ [58-61]. A metal-based mechanism can induce a more selective oxidation path, allowing better control on the oxidation by-products compared to a classic Fenton process [58]. More information on the Fenton reaction with and without iron ligands can be found in the Supplementary Information (SI).

2.2.2 LITERATURE REPORTS

Table 2 presents a summary of the Fenton process applied for the degradation of organic substrates in PW. The pH value of PW can vary between 4 and 10 [4], although most of the samples are within the 6-8 range [62-64]. Before Fenton treatment, it is usually necessary to acidify the solution. As a high concentration of Cl^- and SO_4^{2-} is already present in the PW sample, HCl [65, 66] and concentrated H_2SO_4 [62-68] are often chosen for this purpose.

Studies have shown that the application of the Fenton reaction to PW treatment usually leads to adequate removal efficiencies. Based on an optimization procedure, Afzal *et al.* [67] have found that the best conditions to remove COD were a concentration of H_2O_2 of 10 mM and a $[H_2O_2]/[Fe^{2+}]$ molar ratio of 10 at pH 3.5. After 2 h of reaction, they observed a plateau in the decrease of COD, corresponding to a removal efficiency of 91%. Additionally, Yang J. *et al.* [64] evaluated the optimal reaction conditions, finding that the same maximum efficiency of roughly 50% COD removal was achieved with either (*i*) $[Fe^{2+}] = 1$ mM, $[H_2O_2] / [Fe^{2+}] = 2$ and a reaction time of 60 min, or (*ii*) $[Fe^{2+}] = 4$ mM, molar ratio of 1, and reaction time of 40 min. The first option required lower amount of chemicals, but needed a slightly longer reaction time. The discrepancy in COD removal in these first two studies can be rationalized mainly with the difference in reagent concentrations and possibly also with the higher COD concentration in the latter study, which was approximately three times higher compared to the former one. Jimenez *et al*. [17] studied the TOC reduction in a synthetic PW under different conditions, finding the best removal efficiency with $[H_2O_2]/[COD] = 2.1$ and $[H_2O_2]/[Fe^{2+}] = 0.5$ after a reaction time of 2 h. Furthermore, increasing the temperature from 20 °C to 70 °C led to an increase in TOC reduction from 18% to 32%. Ricceri *et al.* [23] used a Fenton process to degrade organic compounds in a synthetic PW containing 100 g/L NaCl. They showed a TOC reduction of up to 28%. The treated stream had significantly lower fouling potential in the subsequent membrane step, thereby suggesting a significant oxidation of the dissolved organic substrates. Note that the COD includes all oxidizable substances, such as organics, dissolved metals, and sulfides; however, its reduction does not necessarily mean the mineralization of organics. On the other hand, a significant reduction in TOC means that most of the organic carbon has been completely oxidized to CO_2. Zhang *et al.* [69] proposed a heterogeneous Fenton process with the use of Fe-Co/γ-Al_2O_3 catalysts to abate the COD in a coalbed methane PW. At pH = 3.5, with $[H_2O_2] = 40$ mM and a catalyst concentration of 4 g/L, 72% COD removal was achieved after 90 min of reaction. Therefore, similar conditions to the traditional (homogeneous) Fenton process produced similar efficiencies, but the heterogeneous process has the potential to more easily recover the catalyst after the oxidation.

Table 2. Summary of the AOPs and their efficiency reported in the literature, as of December 2020.

Process	**Target or reported substance/parameter with indicated concentration value before AOPs, when available**	**Conditions**	**Removal efficiency**	**Reference**
Fenton	COD (1,382 mg/L)	pH = 3 $[H_2O_2]$ = 2 mM $[Fe^{2+}]$ = 1 mM t = 60 min	47%	[64]
	Naphthalene	t = 60 min	98%	[70]
	Oil and grease (30 mg/L) Phenol (5 mg/L)	pH = 3 $[H_2O_2]$ = 1662.5 mg/L $[Fe^{2+}]$ = 133 mg/L t = 6 h	58% 80%	[21]
	COD (3,200 mg/L)	pH = 3.5 $[H_2O_2]$ = 0.01 M $[H_2O_2]/[Fe^{2+}]$ = 10 t = 120 min	91%	[67]
	COD (1865 mg/L) TOC (764 mg/L)	pH = 3 $[Fe^{2+}]$ = 13.8 mM $[H_2O_2]/[Fe^{2+}]$ = 25 t = 60 min	70% 58%	[71]
	COD (368 mg/L)	pH = 3.5 $[H_2O_2]$ = 40 mM [Fe heterogeneous catalyst] = 4 g/L T = 25°C t = 90 min	72%	[69]
	TOC (444 mg/L with SDS) (495 mg/L without SDS)	pH = 3 $[H_2O_2]$ = 32 mM $[Fe^{2+}]$ = 19 mM t = 60 min	0.4% (in the presence of surfactants) 28% (in the absence of surfactants)	[23]
	TOC (92 mg/L)	pH = 3 $[H_2O_2]/[COD]$ = 2.1 $[H_2O_2]/[Fe^{2+}]$ = 0.5 T = 70°C t = 120 min	32%	[17]

Photo-Fenton	TOC (86 mg/L, as C)	pH = 3 $[H_2O_2]$ = 100 mM $[Fe^{2+}]$ = 1 mM T = 30°C t = 4.5 h 450 W Hg vapor lamp	96%	[65]
	TOC (84 mg/L, as C)	pH = 3 $[H_2O_2]$ = 100 mM $[Fe^{2+}]$ = 1 mM T = 25-60°C t = 4.5 h Solar energy apparatus	80%	[66]
	TOG (Total oil and grease) (30 mg/L)	pH = 3 $[H_2O_2]$ = 10 mM $[Fe^{2+}]$ = 0.44 mM T = 20°C t = 45 min 400 W Hg vapor lamp	84%	[63]
	Oil and grease (30 mg/L) Phenol (5 mg/L)	pH = 3 $[H_2O_2]$ = 600 mg/L $[Fe^{2+}]$ = 300 mg/L T = 30-35°C t = 3 h 2500 W Xe lamp	74% 95%	[21]
	TOC (44 mg/L, as C)	pH = 3 $[H_2O_2]$ = 100 mM $[Fe^{2+}]$ = 1 mM T = ~40°C t = 45 min Solar energy apparatus	76%	[68]
	COD (1,865 mg/L) TOC (764 mg/L)	pH = 3 $[Fe^{2+}]$ = 13.8 mM $[H_2O_2]/[Fe^{2+}]$ = 25 t = 60 min 15 W Hg UV lamp	82% 73%	[71]
	TOC (92 mg/L)	pH = 3 $[H_2O_2]/[COD]$ = 2.1 $[H_2O_2]/[Fe^{2+}]$ = 0.5 T = 20°C t = 120 min 2,500 W Xe lamp	22%	[17]
	Total PW chemicals	Parameters not known	*Qualitative*	[72]
Electro-Fenton	COD Oil	pH = 3 $[Fe^{2+}]_i$ = 1 mM	78% 90%	[73]
	COD (457 mg/L)	pH = 3 $[Fe^{2+}]_i$ = 0.306 mM I = 156.6 mA t = 81 min	73%	[62]
Photo-electro-Fenton	COD (457 mg/L)	pH = 3 $[Fe^{2+}]_i$ = 0.306 mM I = 156.6 mA t = 81 min 2x 3W UVA lamps	81% (1 lamp) 86% (2 lamps)	[62]

Heterogeneous photocatalysis	GC/MS peaks and peak area	pH = ~10 [TiO_2] = 0.5 g/L t = 1 h T = 25° C 250 W Hg lamp	*Qualitative*	[74]
	Total alkanes (0.26 mg/L) Total phenolics (2.5 mg/L)	pH = 7 [TiO_2] = 2 g/L t = 1 h 500 W Hg lamp	82% 30%	[75]
	PAHs (0.06 mg/L)	[TiO_2] = 100 mg/L t = 200 min High pressure Hg lamp	*Not reported*	[76]
	Naphtalene (0.01 mg/L)	pH = 6.86 [P25] on glass = 0.8 g/m^2 t = 12 h Ambient Temperature Pen-ray light source (peak max at 254 nm)	~85%	[77]
	Oil (59.6 mg/L)	pH = 6.5 [TiO_2] = 35 ppm Room temperature t = 1.5 h 8x 18W UV tubes (365 nm)	100%	[78]
	BTEX (600 mg/L)	pH = 3 [γ-Fe_2O_3] = 150 mg/L t = 5 days 225 W Fluorescent (Vis) lamp	95%	[79]
	BTEX (600 mg/L)	pH = 3 [γ-Fe_2O_3] = 150 mg/L t = 1.5 h 100 W UV lamp	97%	[79]
	COD (~ 1,400 mg/L)	pH = 6 [TiO_2] on membranes = 2 wt% ABFR = 0.41 L/min 8 W black light blue UVA lamp	67%	[80]
	TOC (92 mg/L)	pH = 4.8 [TiO_2] = 500 mg/L t = 3 h 2,500 W Xe lamp	16%	[17]
	BTEX (10 mg/L)	Commercial FO membranes loaded with TiO_2 and graphene oxide t = 180 min T = 25°C Visible light	80%	[81]
	COD (~1135 mg/L)	pH = 6 [composite] = 80 g/L %TiO_2 on composite = 60% Stirring speed = 200 rpm t = 1 h Natural sunlight (10AM-12PM)	77-88% (depending on sunlight intensity)	[82]

	COD (927 mg/L) Extractable oil content (28 mg/L)	pH = 7.65 PVDF membrane loaded with TiO_2 0.1 MPa transmembrane pressure Stirring speed = 350 rpm 10 W UV irradiation (λ_{max} at 365 nm)	20% 98%	[83]
Heterogeneous Photo-electro-catalysis	COD (645 mg/L)	pH = 7 $[TiO_2]$ = 2 g/L $[H_2O_2]$ = 10 mM t = 1 h Cell voltage = 30 V 500 W Hg lamp	89%	[84]
	Total alkanes (0.26 mg/L) Total phenolics (2.5 mg/L)	pH = 7 $[TiO_2]$ = 2 g/L t = 1 h Cell voltage = 30 V 500 W Hg lamp	96% ~ 100%	[75]
	COD (1,104 mg/L)	pH = 7.3 t = 120 min 36 W UV lamp	67%	[85]
Ozonation	Perchloroethylene-extractable materials	O_3 added = *not known* t = 3 days	*Qualitative*	[86]
	COD (325 mg/L)	pH = 11 O_3 flow rate = 5 L/min Compression time = 28 s Number of cycles = 30 T = 25°C Stirring speed = 60 rpm	65%	[87]
	COD (270 mg/L)	pH = 10 O_3 added = 4.6 g $L^{-1}h^{-1}$ t = 60 min T = 30°C	29%	[88]
	PAH (9 μg/L)	pH = 3 O_3 flow rate = 250 mL/min O_3 dose = 40 ppm Bubble size = 104 μm T = 50°C t = 60 min	~100%	[89]
	COD (1,872 mg/L)	O_3 flow rate = 2 L/min Contact time = 5 min $[O_3]$ = 0.3 mg/L	58%	[90]
	COD (1,104 mg/L)	pH = 7.3 O_3 added = 3.85×10^{-4} mol/min t = 120 min	73%	[85]
	TOC (92 mg/L)	pH = 10 O_3 added = 4 g/h $[H_2O_2]$ = 1,500 mg/L T = 20°C t = 120 min Agitation rate = 500 rpm	85%	[17]
	COD (927 mg/L)	pH = 7.65 O_3 added = 28 mg/L t = 2 min	11%	[83]

Ozonation combined with photocatalysis	COD (2,865 mg O_2/L) Oil and grease (315 mg/L) Phenol (2.45 mg/L)	O_3 added = 300 mg/L h^{-1} [TiO_2] = 1 g/L T = 25°C t = 60 min 100 W Hg lamp	89% 98% 100%	[91]
	PAHs (0.016 mg/L)	O_3 added = 15 mg/L O_2 [TiO_2 nanotube arrays] = 0.1 g/L t = 60 min 34 V UV-LED light source	~100%	[92]
Anodic oxidation	COD (5,500 mg/L)	M/C/Fe electrodes (10 m^2) Voltage = 15 V Current = 120 A t = 9 min	98%	[93]
	BTEX (30 mg/L) Phenol (5 mg/L)	Ti/RuO_2-TiO_2-SnO_2 DSA anode Current density = 89 mA/cm^2 T = 25°C Flow rate = 0.25 L/h	98% (BTX) 47% (Ethylbenzene and phenol)	[94]
	COD (1,588 mg/L)	Current density = 30 mA/cm^2 Inter-electrodes gap = 1.5 cm Na_2SO_4 added = 10 g/L T = 60°C t = 9h Agitation rate = 400 rpm	50% (Ti/Pt anode) 87% (BDD anode)	[95]
	COD (11,541 mg/L)	Current density = 10 mA/cm^2 Inter-electrodes gap = 1.0 cm T = 25°C Flow rate = 160 L/h	50% (Ti/IrO_2-Ta_2O_5 anode) 44% (BDD anode)	[96]
	COD (2,746 mg/L)	Current density = 60 mA/cm^2 Inter-electrodes gap = 10 mm T = 25°C t = 8h Flow rate = 151 L/h	94% (Ti/Pt anode) 97% (BDD anode)	[97]
	COD (19,842 mg O_2/L)	pH = 6.9 Current density = 30 mA/cm^2 T = 25°C t = 8h Agitation rate = 400 rpm	~70% (Ta/PbO_2 anode) 96% (BDD anode)	[98]
	PAH (0.114 mg/L)	Ti/IrO_2 DSA anode Inter-electrodes gap = 2 cm pH = 5.7 Current density = 8.82 mA/cm^2 t = 3.9 h	95%	[99]
	PAH (0.16 mg/L)	Ti/SnO_2-Sb_2O_5-RuO_2 anode Inter-electrodes gap = 2 cm	95%	[100]

		pH = 3 Current density = 9 mA/cm^2 t = 3.7 h		
	COD (2,485 mg O_2/L)	Flow-by graphite electrode pH = 7.3 Current density = 1.41 mA/cm^2 Flow rate = 50 mL/min	67%	[101]
	COD (960 mg/L)	Ti/Sb-SnO_2 GO modified anode Inter-electrodes gap = 10 mm pH = 4 Current density = 10 mA/cm^2 t = 2 h	59%	[102]
	COD (622 mg/L)	Ti/TiO_2 anode and steel stainless plate cathode pH = 11 Current density = 30 mA/cm^2 T = 25°C t = 50 min	86%	[103]
Micro-electrolysis	COD (274 mg/L) TOC (136 mg/L)	pH = 6 [Iron filings and shavings] = 80 g/L [Active carbon] = 40 g/L T = 32 °C t = 8h	38% 24%	[104]
Catalytic wet oxidation (CWAO and CWPO)	TOC Sample A: 1,249 mg/L Sample B: 1,442 mg/L	CWAO process Cu/CeMnO catalyst = 0.8 g/L Synthetic air (99.99% pure) as oxidant O_2 partial pressure = 1 MPa t = 80 min T = 160 °C	~80%	[105]
	Phenol (100 ppm)	CWPO process PdAu/Al_2O_3 catalyst = 200 mg/L O_2 flow = 50 mL/min [HCOOH] = 0.2 M pH_i = 2 t = 8h Room temperature Stirring rate = 1,000 rpm	16%	[106]
Sonolysis and sono-assisted processes	COD (1865 mg/L) TOC (764 mg/L)	Sono-Fenton process pH = 3 [Fe^{2+}] = 13.8 mM [H_2O_2]/[Fe^{2+}] = 25 Ultrasonic power = 200 W t = 120 min	79% 70%	[71]
	TOC (92 mg/L)	Sono-Fenton process pH = 3 [H_2O_2]/[COD] = 2.1 [H_2O_2]/[Fe^{2+}] = 0.5	26%	[17]

		T = 20°C Sonication frequency = 24 kHz Acoustic power density = 105 W cm^{-2} t = 120 min		
Radiolysis	Benzene (~1,500 mol/L) Toluene (~1,950 mol/L) Ethylbenzene (~750 mol/L) Xylene (~3,750 mol/L) Phenol (~27 mol/L)	Electron beam accelerator with 1.5 MeV energy and 37 kW power Adsorbed dosed = 200 kGy	~100%	[107]

The application of a UV light source to aid the Fenton reaction (photo-Fenton process) usually leads to higher removal efficiencies. Using a UV lamp, Jimenez *et al.* [21] increased the removal of oil and grease from 58% to 74% and that of phenol from 80% to 95% from a synthetic PW with similar salinity as seawater, while the reaction time was halved (from 6 to 3 h). Although the optimal working parameters for the two processes (Fenton vs. photo-Fenton) were different, the increase in efficiency was marked even under the same conditions. The photo-Fenton process was also observed to achieve a significant reduction in TOC. Jimenez *et al*. [17] tested the removal efficiency of TOC in a synthetic PW under different conditions. They reported TOC removal of 22% after 2 h of reaction working at $[H_2O_2]/[COD] = 2.1$, $[H_2O_2]/[Fe^{2+}] = 0.5$, and using a 2,500 W Xe lamp. Moraes *et al.* [65] observed a TOC reduction of 96% after 4.5 hours in a photo-Fenton process under UV light. Using a solar energy apparatus instead of artificial UV lights led to a TOC reduction of around 80% [66]. More recently, Mota *et al.* [68] showed that under the same experimental conditions, but with a new solar energy apparatus, similar removal efficiencies towards TOC (76% vs. 80%) can be achieved in significantly shorter times (45 min vs. 4.5 h). Zhai *et al.* [71] noted a higher TOC and COD reduction using a photo-Fenton process compared to a traditional Fenton reaction for a PW from a natural gas drilling field (after coagulation as primary treatment). After 1 h under UV light with $[H_2O_2]/[Fe^{2+}] = 25$, the TOC removal increased from 58% to 73% while the COD reduction moved from 70% to 82%. Da Silva *et* *al.* [63] have tested the removal efficiency of oil and grease by the combination of induced air flotation and photo-Fenton oxidation. For these experiments, a synthetic PW was prepared by dispersing crude oil in a saline aqueous solution containing different salts at average concentration values found in the literature for oilfield PWs. The flotation step reduced these contaminants by 90% in 10 min, and the photo-Fenton process at pH 3 led to a further 84% abatement in 45 min, for a final total removal of 98%. The importance of combining flotation and photo-Fenton oxidation was also pointed out by Jin *et al*. [72] where this treatment train (under optimum conditions) was suggested to remove solids and chemicals from PW to enable reuse of 85% of the PW in other subsequent processes.

An alternative to the already examined processes is the electro-Fenton technique, an electrochemical process based on in situ generation of $^{\bullet}OH$, whereby the reagents are formed or regenerated by electrochemistry. Here, Fe(III) is regenerated as Fe(II) at the cathode and hydrogen peroxide can also be generated in-situ at the cathode via reduction of oxygen, This allows for a lower addition of reagents compared to the traditional chemical Fenton process and a better dosage of H_2O_2 itself [48]. Al-Khafaji *et al.* [62] achieved a 73% reduction in COD through this process in a real PW sample, while Li *et al.* [73] obtained COD and oil removal efficiencies of 78% and 90%, respectively, starting from an initial Fe(II) concentration of 1 mM. The result of the former study was enhanced to 86% COD degradation with the use of a UV radiation source (photo-electro-Fenton process), suggesting that also the electro-Fenton process can be enhanced with the use of UV radiation.

2.3 HETEROGENEOUS PHOTOCATALYSIS

2.3.1 GENERAL CHARACTERISTICS AND MECHANISMS OF REACTION

The term "photocatalysis" usually denotes the photoactivation of a chemical reaction through the absorption of a quantum of light from a species (an inorganic or organic material, a molecule) that is unchanged at the end of the chemical process (*i.e.*, the photocatalyst) [108-

110]. Although photocatalytic processes activated by organic materials or single molecules have been investigated for the abatement of biorecalcitrant pollutants, only photocatalysis with inorganic semiconductors (*e.g.*, TiO_2, ZnO) has found real application. From a thermodynamic point of view, a photocatalyzed process can be an endo- or exoergonic process, but the transformation of a pollutant (at least up to its mineralization) in the presence of O_2 over an irradiated semiconductor is typically exoergonic [111]. In contrast, the photocatalytic production of a highly energetic product (*e.g.*, H_2, through photocatalyzed water splitting [112]) is an endoergonic process.

The first step in a photocatalytic process is the absorption by the semiconductor of a photon with $h\nu \geq E_g$ (E_g is the energy gap of the semiconductor). Absorption generates a bound electron/hole couple that can either recombine (and dissipate energy) or dissociate to generate thermalized conduction band electron (e^-_{cb}) and valence band hole (h^+_{vb}). The e^-_{cb} and h^+_{vb} can migrate to the surface where they are trapped in localized surface sites, can recombine, or be transferred to acceptor species adsorbed at the surface or in solution. The e^-_{cb} reacts with electron acceptors (the ubiquitous oxidant in photocatalysis is O_2, unless it is removed on purpose from the system), while h^+_{vb} reacts with electron donors (*e.g.*, the substrate to be degraded). The electron/hole transfer at the surface can generate different reactive species, whereby their concentration and chemical nature is strictly related to the position of the semiconductor bands and to the physico-chemical properties of the photocatalyst [113].

The photocatalytic process under UV-irradiated semiconductors as an AOP suffers from low quantum yield related to the quite efficient recombination processes operating in the bulk solid as well as at the solid/electrolyte interface and from matrix effects. Indeed, it is quite complex to obtain a selective oxidation of the target pollutant or pollutants in the presence of other oxidizable organic substrates. Selectivity is intended as the ability of the oxidants (in the heterogeneous photocatalytic processes these are h^+_{vb} and/or $^{\bullet}OH$) to discriminate among the various organic substrates present in solution. For instance, it is highly difficult to selectively oxidize benzene or other BTEX compounds, in the presence of high content of DOM. Furthermore, inorganic components can behave as scavengers of reactive species (*e.g.*, chloride ions are directly oxidized by h^+_{vb} into $Cl^{\bullet}$ radicals that react with further chloride ions to give the radical anions $Cl_2^{\bullet-}$; $Cl_2^{\bullet-}$ is a less strong oxidant than h^+_{vb} /$^{\bullet}OH$ and is also able to promote the formation of toxic chlorinated compounds). Moreover, if adsorbed at the surface, inorganic components can act as recombination centers in the case of species with more than one redox state. Furthermore, high ionic strength usually destabilizes the semiconductor colloids and promotes their aggregation, with dramatic changes in the optical properties of the system (increase of the back scattering) that result in a decrease of the light absorption and, consequently, of the transformation rate of the contaminant(s) [114, 115]. Furthermore, the application of nanometric colloid catalysts (and in general of unsupported catalysts) imposes a separation step after the photocatalytic treatment (*i.e.*, a nanofiltration) to eliminate the nanoparticles from water, thus allowing their reuse. Differently from the Fenton reaction, photocatalysis generally leads to a cleaner effluent in terms of by-products [116-118], due to its higher efficiency in the complete mineralization of the substrates. Additional information on the mechanisms of photocatalysis can be found in the Supplementary Information.

2.3.2 LITERATURE REPORTS

The use of heterogeneous photocatalysis as a PW treatment is documented by several articles, with the most widely adopted catalyst being titanium dioxide (**Table 2**). This process does not require adjustment of the pH. In general, studies show that by increasing the catalyst concentration, the removal efficiency toward target pollutants increases. However, at high catalyst loadings, the degradation efficiency usually reaches a plateau or is even reduced because the suspended catalyst thwarts the penetration of light through the solution (shield effect).

One of the first articles about the possible use of photocatalysis on irradiated TiO_2 in PW treatment was published by Bessa *et al.* [74] in 2001. The work was based on a qualitative analysis of all the compounds detected through GC/MS in an oil field PW sample: the chromatogram of the raw effluent (real PW subject to flocculation and filtration prior to the photocatalytic process) showed more than 145 peaks; after 30 min of photocatalytic treatment, the number of peaks dropped to 21. Furthermore, it was noted that compounds with high retention times were converted into others with shorter retention times, which were mainly branched alkanes with low molecular weight. The addition of H_2O_2, despite its role as oxidant (H_2O_2 is able to efficiently scavenge e^-_{cb} to give $^{\bullet}OH$), had a negative effect on the degradation of the organics because of UV absorption by H_2O_2 itself and hydroxylation of aromatic rings with formation of phenol. Hassan *et al.* [78] reached a maximum oil percentage removal of 71% after 90 min by a continuous-flow photocatalytic process at pH 6.5 and with $[TiO_2] = 35$ mg/L, starting with a real PW sample containing high TDS concentration (nearly 138 g/L). Jimenez *et al.* [17] found that the best conditions for TOC reduction in a synthetic PW were pH = 4.8 and $[TiO_2] = 500$ mg/L, corresponding to a removal efficiency of 16% after a reaction time of 3 h. A study conducted by Liu *et al.* [76] assessed the effects of the water matrix in relation to PAHs removal efficiencies. In a synthetic salt-free solution, anthracene was completely eliminated within 10 min, while the complete disappearance of all 16 studied PAHs occurred at times close to 3 h. However, the pollutant removal rate constants decreased sharply in the real PW sample, especially for the degradation of high molecular weight PAHs, indicating inhibition of the TiO_2-based process.

Research has also been performed to incorporate TiO_2 (or other photocatalysts) into inert substrates, such as glass or polymers, most notably to resolve post-treatment catalysts recovery problems. Liu *et al*. [77] compared the removal efficiency of naphthalene in real offshore PW achieved by the catalyst suspended or immobilized on glass slides. Even if naphthalene reduction after 12 h was around 85%, immobilized TiO_2 promoted a larger removal rate, mainly due to a much lower increase in system turbidity upon catalyst addition. Syed *et al*. [82] studied the feasibility of using the natural solar light in a photocatalytic process with a composite consisting of nano-TiO_2 supported on epoxy resin. Under the best photocatalytic conditions (pH 6, composite concentration of 80 g/L, TiO_2 percentage of 60 wt%, 1 h contact time, and 200 rpm stirring speed), real offshore PW samples showed a 77%-88% COD reduction, depending on sunlight intensity. The main problem with polymers might be their progressive degradation under photocatalytic conditions, which could thwart prolonged reuse of the relevant composite materials and the release of the nanometric photocatalyst in the environment.

Other studies involved the use of catalysts other than classic TiO_2. Sheikholeslami *et al.* [79] studied the removal efficiency of BTEX compounds using γ-Fe_2O_3 nanoparticles. At the optimal catalyst concentration of 150 mg/L and pH 3, a 97% decrease in COD was achieved after 90 min of irradiation. Differently from TiO_2, even a light source in the visible range can activate the iron oxide semiconductor, although with significantly reduced kinetics of COD degradation (almost 2-order of magnitude difference) and with operational mechanisms also different from the classic photocatalytic scheme (*e.g.*, Fenton based mechanism).

In the so-called photo-electro-catalysis, the applied voltage accelerates the separation and suppresses the recombination of the photogenerated holes and electrons, thus leading to higher production of strong oxidants (*e.g.*, h^+_{vb} and/or adsorbed $^\bullet OH$) and better removal efficiency. With an optimal TiO_2 concentration of 1.5-2 g/L, Li *et al.* [84] achieved increased COD removal from 38% for classic photocatalysis to roughly 47% with an applied electric field, using a real PW sample following natural sedimentation. This result is rationalized partly with the electrochemical formation of additional oxidants (mainly active chlorine) in the photo-electro-catalytic treatment. Furthermore, contrary to what was previously mentioned, Li *et al.* [75] highlighted that addition of H_2O_2 led to a better COD removal for shorter treatment times (up to 88.9% after 60 minutes). The same authors observed that the alkane removal efficiency was significant for both the photocatalytic treatment (82%) and photo-electro-catalysis (96%), while the removal efficiency of phenolic compounds with high mutagenic potential was excellent for photo-electro-catalysis (~100%), but poor after simple heterogeneous photocatalysis (30%).

In the last few years, the use of membrane processes in which the membrane is loaded with the semiconductor (*i.e.*, photocatalytic membranes) is also emerging. Rawindran *et al.* [80] proposed a TiO_2-loaded membrane capable of separating and simultaneously degrading the surfactants contained in a real PW, with a high initial COD concentration of 1.4 g/L. At pH 6, with an optimal TiO_2 loading of 2 wt.%, and with introduction of air bubbles in the stream, a COD rejection of around 67% was achieved. In the work by Taghizadeh *et al.* [81], cellulose triacetate membranes were loaded with TiO_2 and/or graphene oxide. Due to a reduction in the band-gap energy, the TiO_2/GO membrane can also be activated by visible light. This membrane allowed for the best BTEX removal of 80% after 3 h, at salinity levels of up to 100 g/L NaCl. Veréb *et al*. [83] proposed a PVDF ultrafiltration membrane loaded with TiO_2 for the purification of a real PW effluents following primary treatments, namely, chemical destabilization and sand filtration. Even if COD reduction (~20%) in the permeate stream was similar for PVDF membranes with and without TiO_2 (due to a high amount of dissolved oxidizable compounds in the PW), catalyst-modified membranes showed better fouling resistance ability. However, as in the case of polymer-based composite materials containing TiO_2 or ZnO, the potential issue of membrane damaging after prolonged use should be seriously considered in view of practical applications.

2.4 OZONATION

2.4.1 GENERAL CHARACTERISTICS AND MECHANISMS OF OZONATION

Ozone (O_3) is a strong oxidant (reduction potential E_o = 2.07 V vs NHE) that can be used to directly oxidize a number of contaminants, or as a precursor of other reactive species (most notably, $^\bullet$OH) [119]. O_3 is too unstable and reactive to be stocked or transported, thus it should be produced on site starting from dry air (to avoid side reactions induced by the presence of water vapor) or pure O_2 [120].

The direct reactions of O_3 are particularly important in the case of compounds with double carbon bonds, due to the facility with which O_3 adds to C=C bonds to finally break them. The reactivity of O_3 extends to other classes of organic compounds, among which are electron-rich aromatics, alcohols and aldehydes, but the reaction rate constants are lower compared to alkenes [121]. Aqueous matrices may contain contaminants that do not react with O_3 (*e.g.*, carboxylic acids or compounds with only C-C single bonds) or react poorly with it, in which case it may still be convenient to produce O_3 and use it as an $^\bullet$OH precursor. There are several ways to generate $^\bullet$OH from $O_{3:}$: basification, UV photolysis (UVC radiation is particularly suitable to this purpose), addition of H_2O_2, or any combination of these [122]. The main drawback in the use of O_3 for direct oxidation or as an $^\bullet$OH precursor, is related to the possible presence of bromide in the water matrix. In the presence of Br^-, O_3 can produce carcinogenic bromate (BrO_3^-) [123]; moreover, Br^- can act as a catalyst in the oxidation of N-containing precursors into carcinogenic N-nitrosamines [124]. In waters with a high content of bromide, such as saline and brackish water, as well as PW, the formation of bromate can be prevented by the initial formation of hypobromite, which leaves only a limited residual ozone concentration to be involved in the subsequent oxidation reactions of hypobromite to bromite, and ultimately to bromate [125]. In cases with high initial bromide concentration and the presence of DOM, a main drawback of ozonation is the formation of trihalomethanes or other brominated by-products [125-127].

2.4.2 LITERATURE REPORTS

The abatement yields that emerge from the literature when using ozone as oxidant in PW treatment are usually slightly lower than those reported so far for the other AOPs (**Table 2**). Horn *et al.* [128] proposed a mobile unit based on the coupling of ozonation and ultrasonic transducers (to oxidize heavy metals, soluble and insoluble organics) with reverse osmosis (RO), with promising results. Jing *et al.* [89] worked with a real offshore PW spiked with 16 PAHs, achieving their complete abatement. Authors also pointed out that an increase in temperature and ozone dose (higher reaction rates and ozone levels), or a decrease in pH and bubble size (higher surface area), led to higher removal efficiencies. Jimenez *et al.* [17] evaluated the optimal operational conditions for TOC reduction in a synthetic PW. After a reaction time of 2 h with an O_3 dose of 4 g/h, the observed TOC decrease was around 20%. Increasing the pH to 10 and adding H_2O_2 at a concentration of 1,500 mg/L (both intended to produce $^{\bullet}OH$ from O_3), increased the removal to 85%. Klasson *et al.* [86] monitored the concentration of perchloroethylene-extractable materials and of CO_2 before and after 3-day ozonation of real PW samples. The mineralization of some of the organic fractions was observed, but the conversion was not complete, even at high ozone loadings. Cha *et al.* [87] tested pressure-assisted ozonation on a synthetic PW. After 30 compression and decompression cycles, the COD removal was 65%. If ozonation was followed by sand filtration, removal efficiency was higher (69%), although the best results were obtained after two ozonation-sand filtration cycles, corresponding to a COD reduction of around 82%. Aryanti *et al.* [90] studied ozonation in combination with ultrafiltration (UF). Upon 5 min ozonation, the COD was reduced by 58% (from 1,872 to 790 mg/L) in the feed solution. Also Veréb *et al.* [83] studied a treatment train where ozonation was a pre-treatment for UF with

TiO_2-loaded PVDF membranes. After only 2 min of ozonation, the COD removal was around 11%.

Shokrollahzadeh *et al.* [88] applied an oxidation treatment after primary de-oiling, comparing ozone with other oxidants. H_2O_2 performed poorly with 15% COD reduction after 4 h. On the other hand, ozonation achieved better efficiencies of up to 25% with 1-h treatment. Using $Ca(ClO)_2$ between 300 and 7,100 mg/L afforded a COD removal of 36-70%; however, the residual active chlorine from the use of this reagent needs subsequent treatments and may promote the generation of harmful halogenated substances. Recently, Tang *et al.* [129] applied ozonation in the treatment of wastewater from the Weiyuan shale gas play (Sichuan, China), containing approximately 40 mg/L dissolved organic carbon, COD of roughly 400 mg/L, and 16 g/L TDS. They obtained COD removal percentages of 12%, 27%, and 31% with a flux of ozone of 0.2, 0.4, and 0.6 L/min, respectively, at an initial ozone concentration of 32 mg/L. The relatively low abatement was attributed to the presence of chloride (9.4 g/L) and bromide (67.5 mg/L). Interestingly, the BOD_5/COD ratio was almost double at the highest ozone stream flow rate, proof that at the end of the treatment with the highest O_3 concentration, the wastewater contained more biodegradable compounds.

Corrêa *et al.* [91] applied a combination of ozonation and photocatalysis on a real PW sample with 38 g/L salinity and an initial COD of 2.87 g/L. O_3 was introduced in a reactor that comprised a UV lamp to activate the titanium dioxide catalyst. The conditions were $[TiO_2] = 1$ g/L and an addition of 300 mg O_3 L^{-1} h^{-1}. After 60 minutes, the COD showed 89% reduction, while oil, grease, and phenol were nearly completely eliminated. Ozone can act as an e^{-}_{cb} scavenger with the formation of the ozonide anion (O_3^{-}) that operates as an additional source of hydroxyl radicals according to the reaction $O_3^{-} + H^{+} \rightarrow {}^{\bullet}OH + O_2$. Liu *et al.* [92] combined ozonation with TiO_2-nanotube arrays photocatalysis to treat a real PW spiked with 16 PAHs, achieving complete removal of nearly all of these compounds within 1 h of treatment. An increase in the ozone dose led to higher removal efficiencies, while an increase in the TiO_2-nanotube arrays load above 0.1 g/L led to a greater PAHs absorption on the nano-catalyst (*i.e.*, very low or no traces of PAHs in the treated PW, but high concentrations on the catalyst surface). Also de Brito *et al.* [85] combined heterogeneous photocatalysis (in this case, a photo-electro-catalytic system) with ozonation, showing that the coupling of these techniques led to higher removal efficiencies compared to the individual processes. Experiments showed that the least efficient process was heterogeneous photocatalysis. Photo-electro-catalysis and ozonation led to better results (COD reduction of roughly 65%), but the combination of the two processes led to the largest removal efficiency (73%).

2.5 ANODIC OXIDATION

2.5.1 GENERAL CHARACTERISTICS AND MECHANISMS OF ANODIC OXIDATION

Anodic oxidation is an oxidative process that occurs at the anode of an electrolytic system [94, 95, 130, 131]. Its main mechanism is based on monoelectronic oxidation of water at the electrode surface to give physisorbed $^{\bullet}OH$ radicals (Eq. 8):

$$H_2O + M \rightarrow M[^{\bullet}OH] + H^+ + e^- \qquad (8)$$

In the presence of chloride, which is typical in PW, the formation of chlorohydroxyl radicals also contributes to the abatement of the organic compounds within the solution (Eq. 9):

$$H_2O + M + Cl^- \rightarrow M[^{\bullet}ClOH] + H^+ + 2e^- \qquad (9)$$

Furthermore, the reactions between water and the radicals lead to primary oxidants, such as oxygen, chlorine, and hydrogen peroxide (Eqs. 10-12)

$$H_2O + M[^{\bullet}OH] \rightarrow M + O_2 + 3H^+ + 3e^- \qquad (10)$$

$$H_2O + M[^{\bullet}ClOH] + Cl^- \rightarrow M + O_2 + Cl_2 + 3H^+ + 4e^- \qquad (11)$$

$$H_2O + M[^{\bullet}OH] \rightarrow M + H_2O_2 + H^+ + e^- \quad (12)$$

Then, molecular oxygen and free chlorine can further react to produce ozone and chlorine dioxide as secondary oxidants (Eq. 13-14).

$$O_2 + M[^{\bullet}OH] \rightarrow M + O_3 + H^+ + e^- \quad (13)$$

$$H_2O + M[^{\bullet}ClOH] + Cl_2 \rightarrow M + ClO_2 + 2Cl^- + 3H^+ + e^- \quad (14)$$

Finally, the use of boron doped diamond (BDD) anodes in chloride- and/or sulfate-rich water at high temperatures can lead to the reactions shown in Eqs. 15-17, with the formation of further oxidizing species [95].

$$2\ Cl^- \rightarrow Cl_2 + 2e^- \quad (15)$$

$$2\ SO_4^{2-} \rightarrow S_2O_8^{2-} + 2e^- \quad (16)$$

$$2\ ^{\bullet}OH \rightarrow H_2O_2 \quad (17)$$

Optimization of the operational parameters, including electrode material, distance between the electrodes, current density, temperature, pH, reaction time, or flow rate, is of fundamental importance in order to achieve good removal efficiencies. In general, the increase in current density, temperature, and reaction time leads to higher removals of organic contaminants [95, 96, 98, 102, 103]. The role of pH is more complex: although the highest conductivities are obtained at low or high pH (due to a greater amount of ions in solution), often the optimal conditions are obtained around circumneutral pH [98, 99, 101]. Regarding the nature of the anode, it is important that no strong interactions exist with the electrogenerated hydroxyl radicals, otherwise the oxidation and mineralization of organic contaminants would compete with the side reaction of oxygen formation (Eq. 18) [98]:

$$2\ ^{\bullet}OH_{ads} \rightarrow \tfrac{1}{2}\ O_2 + H_2O \quad (18)$$

Anodic oxidation may also be enhanced by the cathodic production of hydrogen peroxide using a porous gas-diffusion electrode [132]. As noted by Coonrod et al. [3], anodic oxidation is particularly interesting for PW treatment since native ions may form powerful oxidants (*e.g.*, active chlorine, although the possible formation of harmful by-products cannot be ruled out in all cases). Furthermore, the high salinity of several PWs will promote charge transfer effects, necessary to guarantee contaminant oxidation.

2.5.2 LITERATURE REPORTS

Several authors have proposed anodic oxidation as a promising PW treatment to achieve suitable removal efficiencies toward organic contaminants (see **Table 2**). Yaqub *et al.* [99] studied the degradation of 16 PAHs contained in real PW samples using a Ti/SnO_2-Sb_2O_5-RuO_2 anode. The optimum conditions for PAHs removal were found at pH 5.7 with a current density of 8.82 mA/cm^2 and a reaction time of 3.9 h. Under these conditions, the PAHs removal was 95%. In another work [100], the same authors also investigated PAHs degradation through a dimensionally stable Ti/IrO_2 anode. Also in this case, under optimum conditions (pH 3, current density 9 mA/cm^2 and a reaction time of 3.7 h), PAHs removal was around 95%. Zhu *et al.* [103] achieved 86% reduction of COD in a PW previously treated with gel breaking and magnetic-enhanced coagulation. The optimal conditions for the oxidation were a reaction time of 50 min and a current density of 30 mA/cm^2 at pH 11 using a Ti/TiO_2 anode and a stainless-steel plate cathode. Pahlevani *et al.* [102] tested the COD removal efficiency using a Ti/Sb-SnO_2 anode modified with graphene oxide to improve its electrical conductivity. Under optimum conditions, the electro-oxidation treatment led to a 59% abatement after 2 h, while total COD removal occurred at 235 min. Ma *et al.* [93] proposed a laboratory M/C/Fe pilot-scale plant consisting of double anodes made with active metal and graphite, and of an iron electrode as the cathode. COD removal efficiency was around 98% after a reaction time of only 9 min.

Rocha *et al.* [95] compared the oxidation performance obtained with Ti/Pt and BDD anodes in a real PW effluent. Higher COD elimination rate and COD removal were observed using the BDD anode, due to reduced passivating film formation at the electrode surface caused by surfactants in solution. Working at higher temperature and after the addition of Na_2SO_4 (10 g/L), COD removal was higher (around 87%) due to the electro-generation of peroxydisulfates as secondary oxidants. Gargouri *et al.* [98] evaluated the difference between Ta/PbO_2 and BDD anodes. Also in this case, the BDD electrode led to a more rapid COD removal (85% in 5 h vs. 11 h), while consuming less energy (24 vs. 46.2 kWh/m^3). Similar results were also achieved by the scale-up of an electrochemical system proposed by dos Santos *et al.* [97]. COD reductions were 94% and 97%, using a Ti/Pt and a BDD anode, respectively. The removal efficiencies were proportional to the current density and the temperature, while the addition of Na_2SO_4 seemed to have a little effect due to the high concentration of sulfates present in the initial sample. Da Silva *et al.* [96] compared the COD removal efficiencies in PW at three different salinities (namely, fresh, brine, and saline) and COD contents, with a Ti/IrO_2-Ta_2O_5 and with a BDD anode. In fresh and brine PW, BDD led to better removal efficiencies, with COD removal rates increasing at higher temperatures and current densities. Saline PW (characterized by higher chloride and COD concentrations) showed instead similar removal rates at different temperatures, current density values, and electrode materials.

Abdel-Salam *et al.* [101] evaluated the optimal reaction conditions for a continuous-flow electrochemical cell equipped with flow-by porous graphite electrodes (*i.e.*, a system where current and flow are perpendicular to each other). A maximum COD removal of around 67% was achieved with a flow rate of 50 mL/min and a current density of 1.41 mA/cm^2 at pH 7.3. In particular, the removal efficiency decreased at higher flow rate, due to the shorter residence time that prevented the complete oxidation of organic compounds. These results were in agreement with previous work by Ramalho *et al.* [94], whereby the anodic oxidation of a real PW sample using a RuO_2–TiO_2–SnO_2 anode led to the complete abatement of benzene, toluene, and xylenes, and a 47% reduction of ethylbenzene and phenol.

2.6 OTHER PROCESSES

2.6.1 BRIEF DESCRIPTIONS AND LITERATURE REPORTS IN PW TREATMENT

Micro-electrolysis is an electrochemical technique where active carbon acts as the cathode while iron is the anode. Microscopic galvanic cells are formed where iron and carbon pieces are in contact with the electrolyte solution. The semi-reactions involved in the process are summarized in Eqs. 19-20:

$$Fe \rightarrow Fe^{2+} + 2e^{-} \qquad (19)$$

$$2H^{+} + 2e^{-} \rightarrow H_2 \qquad (20)$$

Li *et al.* [104] tested the COD and TOC removal efficiency in a real PW sample after oil separation and flotation as pre-treatments. The best COD reduction (around 38%) was achieved using iron filings and shavings at a concentration of 80 g/L and active carbon at 40 g/L after a reaction time of 8 h.

Among electrochemical treatments, bio-electrochemical systems are raising interest due to the possibility of removing organics with the concomitant production of electric power. They are not strictly AOPs, because radicals are not the active species, but they are worth mentioning here for completeness. They consist of a bacteria-covered anode in a bioreactor (*i.e.*, the microbial fuel cell, MFC), where bacteria act as catalysts for the oxidation of organic and inorganic compounds: the electrons produced by the oxidation are transferred to the conductive support and then flow to the cathode in a Galvanic cell. These systems have been tested for the abatement of organic compounds in PW samples. Mohanakrishna *et al*. [133] achieved a 55% COD reduction with a dual-chamber MFC and a 90% COD reduction by integrating an electrochemical and a bio-electrochemical system [134]. Jain *et al.* [135] observed COD and hydrocarbons removals of 91% and 77%, respectively, while Mousa [136] obtained a total petroleum hydrocarbons abatement of 75%.

In catalytic wet air oxidation (CWAO), air is the oxidant [137] and is mixed with the wastewater, which is thus circulated over a catalyst, often of heterogeneous nature, such as metal oxides or supported precious metals. The operational conditions require a temperature above the boiling point of water (*i.e.*, 100 °C) and an air pressure between 0.5 and 20 MPa to avoid excessive water evaporation. In catalytic wet peroxide oxidation (CWPO), H_2O_2 is used as oxidant and the process takes place at mild operational conditions (temperatures in the range of 20-80 °C and atmospheric pressure). Posada *et al.* [105] studied a CWAO method to treat two different PW samples, reaching in both cases 80% of COD reduction after 80 min in a reactor where 0.8 g/L of Ce-Mn-O catalyst was introduced at 160°C and with an oxygen partial pressure of 1 MPa. Yin *et al.* [106] studied the degradation of phenol in a synthetic moderately-saline PW, using a PdAu/Al_2O_3 catalyst to generate *in situ* H_2O_2 and $^{\bullet}OH$ from formic acid and O_2. The bimetallic catalyst was more active than monometallic Pd or Au catalysts in terms of initial $^{\bullet}OH$ production rate, leading to a 16% phenol reduction after a reaction time of 8 h. The degradation rate dropped by increasing the pH (no degradation observed above pH 4) and the salinity of the sample.

Sonolysis is another option for PW treatment, which requires little or virtually no pre-treatment of the influent water [19]. Using ultrasonic waves at high frequency, cavitation bubbles are formed in solution. Due to the high temperature (~5500 K) and pressure (~500 atm) reached inside the bubbles, when these collapse they promote the dissociation of water into $H^{\bullet}$ and $^{\bullet}OH$ and/or the direct degradation of the pollutants (the dominant degradation mechanism is strongly affected by the hydrophilic/hydrophobic properties of the molecules to be degraded). T. The reaction between these species and O_2 dissolved in solution can lead to the formation of other oxidants, such as $HO_2^{\bullet}$ and H_2O_2. Seth *et al.* [138] proposed that the combination of electrocoagulation with ultrasounds could promote the oxidation and the destruction of aromatic compounds in PW. Ultrasound can also be coupled with other AOPs. Jimenez *et al.* [17] tested a sono-Fenton process, reaching a maximum TOC removal of 26% after 2 h with a $[H_2O_2]/[COD]$ ratio of 2.1 and a $[H_2O_2]/[Fe^{2+}]$ ratio of 0.5 at room temperature. Zhai *et al.* [71] also applied a sono-Fenton process on a raw PW after oil separation. The authors noted that increasing the ultrasonic power decreased the removal efficiency. At optimal conditions (200 W), the TOC reduction was around 70% after a treatment time of 2 h. Ultrasound-assisted Fenton led to better performance than conventional Fenton, but it was less active than photo-Fenton treatment. A major drawback of sonolysis is the elevated concentrations of reactive radicals (*e.g.*, $^{\bullet}OH$, $H^{\bullet}$, $O_2^{\bullet-}$) confined in a small volume, which favors radical-radical recombination and dissipates ultrasound energy. Interestingly, high concentrations of anions as those occurring in saline PW may inhibit such recombination and produce secondary radicals ($CO_3^{\bullet-}$, $Cl_2^{\bullet-}$, $^{\bullet}NO_2$) that may be involved in pollutant degradation [139], although with the potential to form harmful by-products. A second important drawback of sonolysis is the difficulties to scale up reactors for ultrasonic treatment from the lab (or small) scale to higher dimensions (essential to treat large flows of wastewater).

Electron beam irradiation is another emerging technique that is able to remove organic pollutants in aqueous media and decrease their toxicity, with minimal pre-treatment required [19]. The use of a ionizing radiation produced by a radioactive material, such as ^{60}Co, or an electron beam accelerator, promotes water radiolysis, leading to the production of $^{\bullet}OH$ radicals (the main responsible species for the oxidation of organic compounds) as well as e_{aq}^{-} that can further react with dissolved O_2 to generate $O_2^{\bullet-}$ radicals. Duarte *et al.* [140] tested radiolysis on two real PW samples and monitored the decrease in BTEX and phenol concentrations, obtaining almost complete removal when irradiating the samples with an adsorbed dose of 200 kGy.

3. ROLES OF AOPS AND POSSIBLE SYSTEM CONFIGURATIONS

While AOPs are applied in the treatment of PW to degrade organic substances, the goal within the effluent purification scheme may not always be the same. For example, oxidation may have the purpose of polishing a high-quality stream that was already subject to primary, secondary, and possibly desalination treatments. In this case, the influent to the AOP step would be engineered to allow removal of trace contaminants for the production of water with reuse potential in a finishing step. On the other hand, AOPs may be specifically applied to obtain effluents with sufficient quality to enhance the performance of subsequent treatment processes (*e.g.*, decrease the toxicity of an effluent to allow a successive biological treatment). In this case, the influent to the AOP step may be of varying quality, at times being even a relatively raw stream, and the oxidation will be brought to the minimum necessary extent or will target only a fraction of substances, to guarantee a quality or composition suitable for further treatment. As a matter of fact, oxidative degradation of organic contaminants may be deployed, with different designs, both as a pre-treatment unit and as a polishing step within the same treatment train. The efficacy of the treatment scheme to purify PW and to produce an effluent for specific intended uses depends on how well the various processes are combined. This chapter discusses the possible configurations involving the application of AOPs, in light of the influent and effluent quality that one requires and expects.

3.1 QUALITY OF THE INFLUENT WATER

Studies about the application of AOPs to treat real water samples indicate that pre-treatment is often necessary to obtain a stream of sufficient quality to enhance the efficiency of oxidation and to minimize chemicals consumption. The need or extent of pre-treatment is possibly minimal for some of the AOPs discussed above, such as sonolysis or radiolysis; on the other hand, the application of an extensive pre-treatment may be required for the effective application of other processes, especially those assisted by light and based on the use of heterogeneous catalysts or electrodes whose surface should remain clean. The most frequently applied pre-treatment discussed in the literature is flotation [141]. Flotation is a physical technique in which solid and/or non-aqueous liquid particles are separated by interaction with fine gas bubbles. Flotation is based on particle accumulation on the surface of the liquid phase, and final removal with skimmers. It is applied for the removal of suspended solids, oils and hydrocarbons in the undissolved and non-volatile phase, and of iron, manganese, and aluminum. Volatile organics (VOCs) may also be partially or completely removed during this process through stripping. The advantages of this technique are the high rate of separation in often short residence times and low operating cost. Induced air flotation was successfully applied with the addition of small quantities of surfactant to remove 84% of total oil and grease (300 mg/L) from a relatively raw influent wastewater, thus producing a stream with a residual concentration of 49 mg/L of oil and grease to be further oxidized. The Fenton process then led to a further reduction of 69%, with a residual content of oil and grease of 15 mg/L [63].

Flocculation with settling is also a useful pre-treatment for AOPs. The process of coagulation-flocculation is typically used for the removal of suspended solids, including fine colloids and organic macromolecules. It consists of a first addition of a coagulant (*e.g.*, iron or aluminum salts or oligomers, with or without addition of organic polyelectrolytes), adjustment of the pH to maximize aggregation (the pH should be near the point of zero charge of the colloids to allow the particles agglomeration), followed by a mixing phase aiming at increasing the size of the flocs, and by their final removal from the effluent [141]. When a base is also dosed, heavy metals and alkaline earth metals (*e.g.*, Be, Ca, Mg, Sr, Ba) can be removed as precipitates. In the study by Yang *et al.* [64], polymeric aluminum chloride and polyacrylamide were used as coagulants with optimal concentrations of 40 mg/L and 4 mg/L, respectively, as pre-treatment for a Fenton reaction; see **Fig. 2b**. The pre-treatment achieved a COD removal efficiency of about 55% following sedimentation, facilitating the degradation in the subsequent Fenton process. In a different study, flocculation was studied in combination with flotation or with settling as pre-treatment options for a photo-Fenton process. Specifically, three flotation-based techniques were investigated, including traditional dissolved air flotation (DAF), enhanced flotation in which glass microspheres were used instead of gas bubbles, and combined DAF with glass microspheres. The initial coagulation-flocculation step was performed with the addition of $FeCl_3$ (**Fig. 2e**). Among the various alternatives, in the case that reaction time is not a limiting factor, the system comprising flocculation and settling was the most suitable pre-treatment, leading to a COD removal of 69%, turbidity removal of 90%, and oil and grease removal of 86%. This step allowed for a high efficiency of the subsequent photo-Fenton process, with the goal to produce a final effluent for reuse. Enhanced flotation without insufflation of gas (which may break up the flocs) is also advantageous when the reduction of reaction volumes and times is important [21]. In a study by Zhu *et al*. [103], the combination of gel breaking and magnetic enhanced coagulation was proposed as a pre-treatment for the subsequent electrochemical oxidation. The pre-treatment train led to a COD removal of 85% (from 4,230 to 622 mg/L), removing substantial portions of organic matter and suspended solids and enhancing the subsequent AOP. Finally, in a study by Aryanti *et al.* [90], effluent already treated with pre-ozonation and ultrafiltration allowed for the near complete degradation of oil and grease as well as toluene in a final ozonation polishing step, also thanks to the previous significant abatement of COD and oil and grease in the membrane-based treatment. The latter step enhanced the efficiency of the post-treatment oxidation; see **Fig. 2d**.

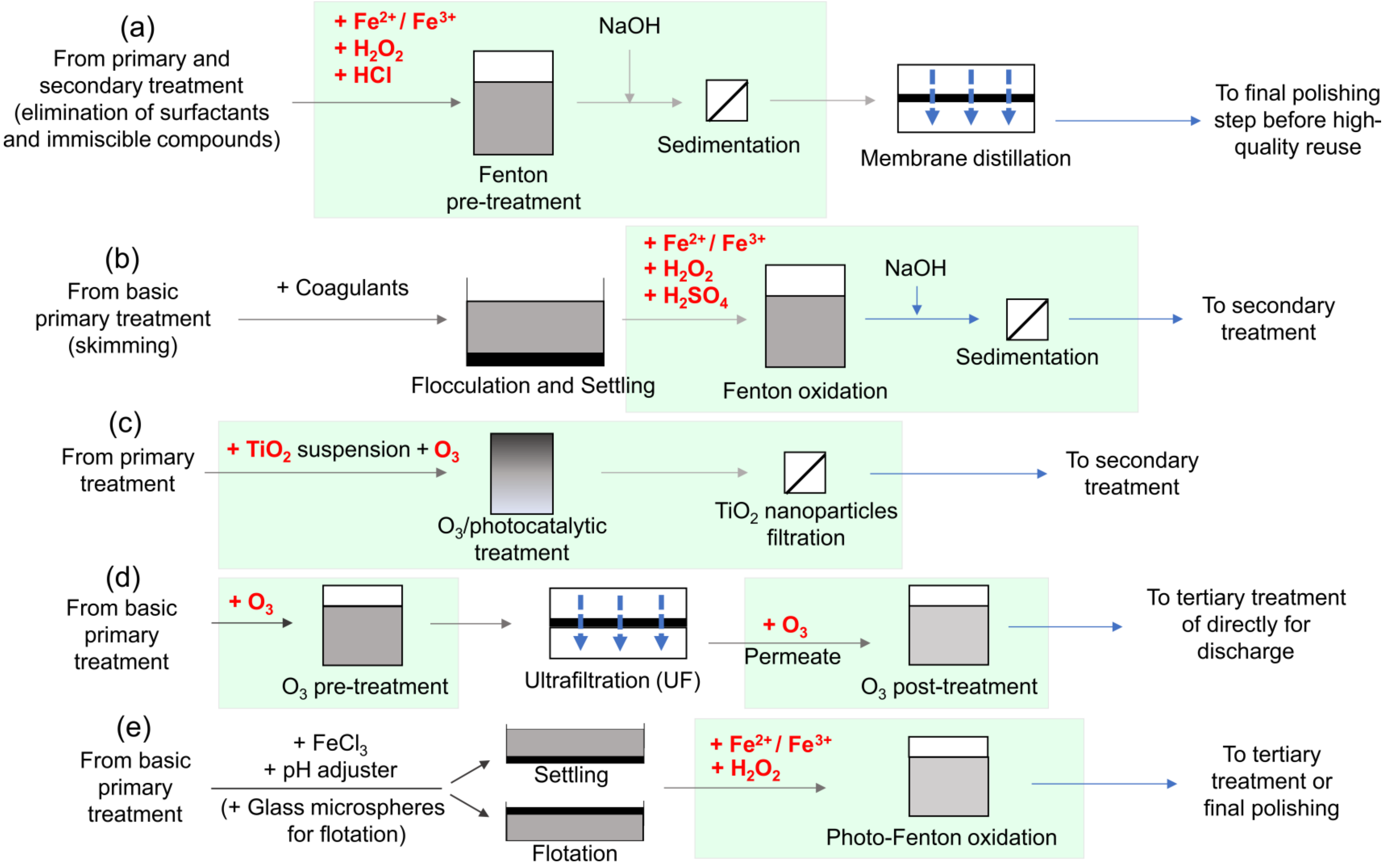


Fig. 2. Possible configurations of PW treatment trains including advanced oxidation processes (AOPs). The AOP steps are highlighted in green shade, while reagents added to allow their functioning are in red font.

When PW contains large amounts of oil and grease, volatile organics, and low-density organic solvents, applying AOPs without any pre-treatment step is not usually feasible or advantageous due to the too large concentration of reactive species scavengers. In summary, flotation, with the possible combination of a previous or concurrent coagulation-flocculation process, is an ideal pre-treatment for AOPs because it provides reliable removal of a large fraction of interfering contaminants in a simple operation. These pre-treatment options are able to considerably reduce the COD and TOC of the stream and simplify further removal of organic contaminants in the oxidation step.

Flocculation and flotation processes may also be designed to remove metals, inorganic particles, and colloids, which may be responsible for turbidity and in general complicate the engineering and the efficiency of the oxidation step. They can also be designed to separate small oil droplets, even if emulsified, which may not be easily attacked by oxidants in the aqueous phase [141]. At the same time, these suggested pre-treatments when used alone do not offer the possibility to reach the desired standard for safe effluent discharge or reuse. This is especially true with respect to dissolved small organic compounds, such as phenols, and other contaminants or parameters, such as BTEX, naphthalene, cyanide, nitrite, manganese, color, and odor. However, following pre-treatment, the AOP step can be more easily designed to target such smaller and more refractory oxidizable substances, even at trace amount, with reduced addition of chemical reagents. With respect to the engineering implementation of flotation and flocculation, one limitation is the presence of surfactants (that produce difficult-to-manage foams), the PW salinity, and the lower solubility of air in this type of matrix. Another issue is the generation of large quantities of sludge that must be managed carefully due to its high toxicity. It may also be useful to note that flotation is specifically recommended in conjunction with a gravity oil-water separator in the case of PW [142-144].

3.2 AOPS AS PRE-TREATMENT STEP

In numerous treatment configurations, AOPs are applied to reduce the concentrations of organic pollutants and aid subsequent purification steps. A chief example is the removal of organic foulants to improve the performance of membrane-based treatment and desalination. This was the main purpose of ozonation in the study by Aryanti *et al.* [90]; see **Fig. 2d**. Pre-ozonation was capable of breaking up large organic molecules and complex compounds present in crude oil, also rendering them more polar. The flux reduction in the UF apparatus was remarkably slower compared to the feed solution that had not been previously oxidized, coherently with SEM analysis of the UF membranes following filtration, which showed substantial foulant deposition in the latter case. Following ozone pre-treatment, foulants that deposited onto the membrane were of smaller size and density. Similar results were obtained by Veréb *et al*. [83], where the flux reduction during the ultrafiltration step was significantly lower if the influent was pre-ozonized. During the ozonation pre-treatment, the negative surface charge of the oil droplets rapidly increased (as shown by an increase in the zeta-potential), leading to a decrease of oil adhesion on the membrane surface. Another example of successful application of AOPs as a pre-treatment technique for the feed solution of a membrane purification step is discussed by Ricceri *et al.* [23]. While not significantly decreasing the TOC of the solution, the Fenton process facilitated desalination of the synthetic PW feed containing 105 g/L of TDS using membrane distillation, with high water recovery achieved in this step; see **Fig. 2a**. Hydrophobic organic compounds are responsible for wetting of microporous membranes in this process, a phenomenon that allows undesired passage of salt water across the membrane into the permeate and is arguably the primary barrier to the widespread industrial application of membrane distillation. Specifically, when the synthetic PW was used as feed solution without any pre-treatment, wetting occurred almost immediately in the filtration step. The more polar and oxygen-rich organic compounds of the oxidized feed solution had lower affinity with the hydrophobic membrane, thus reducing fouling and subsequent membrane wetting. This effect was even more pronounced when the feed solution was free of surfactants, sometimes present in PW. Considering these results, the most practical figure of performance of AOPs when used as pre-treatment units might not be the mere oxidation efficiency of the process itself, but rather the partial oxidation of troublesome substances and the overall reduction of contaminants achieved in combination with the subsequent treatment process. This conclusion was also offered by a recent investigation by Tang *et al.* [129], whereby a system comprising ozonation, ultrafiltration, and reverse osmosis in series was studied to purify a wastewater stream from shale gas extraction activities, for beneficial reuse purposes of irrigation, livestock watering, and surface discharge. Despite the low COD removal rate (<32%), pre-ozonation decreased the average molecular weight of organic substances and thus significantly mitigated the UF membrane fouling, thereby allowing for high overall rejection rates of the ozonation-UF-RO train to respect stringent limits for beneficial reuse. The cost of water purification using the entire train was estimated as falling in the range of 3.67–5.17 $\$/m^3$.

In summary, the rationale of applying AOPs as pre-treatment steps is justified when they allow for the degradation (or transformation) of substances that would otherwise impair subsequent process, such as membrane-based separation or even biological treatment. Specifically, oxidation degrades organic foulants and inactivates biological foulants; even when complete degradation is not achieved, oxidation renders these components more hydrophilic, thus significantly reducing their fouling potential. This translates into an overall higher productivity of the membrane-based step and a lower frequency of membrane cleaning (hence, less system down time and use of chemicals), which in turn means lower capital and operations costs. Furthermore, lower fouling phenomena are related to a better quality of the membrane permeate stream. When they precede a biological treatment, chemical oxidation processes may be applied to reduce the amount of non-biodegradable compounds, transforming them into less toxic and readily biodegradable compounds, and to remove substances that may disturb, harm, or overload the downstream biological processes.

3.3 HYBRID SYSTEMS

Hybrid treatment techniques, whereby both separation of pollutants and their simultaneous degradation by AOPs are performed within the same treatment step, have developed significantly in recent years. With respect to PW management, this approach is particularly interesting in offshore platforms, where compactness of the treatment plant is critical. An example of such strategy was presented by Rawindran *et al.* [80], in a study involving the use of a separation membrane loaded with TiO_2 catalytic nanoparticles for the removal of surfactants. As mentioned above, surfactants have high wetting potential and may impair the membrane separation process. The presence of the semiconductor and the concurrent insufflation of air bubbles promoted the removal of surfactants, enhanced the separation performance of the membrane, and increased the quality of the permeate stream. In a study presented by Taghizadeh *et al.* [81], TiO_2 and graphene oxide (GO) were loaded onto a cellulose triacetate membrane applied in forward osmosis, an innovative process that provides high rejection of contaminants by exploiting the osmotic pressure as the driving force for mass transport across the membrane. The TiO_2/GO nanocomposite had better hydrophilicity, antifouling ability, thermal stability, and mechanical strength compared to the conventional polymeric membrane. The GO extended the light response of TiO_2 to longer wavelengths and improved the efficiency of the photocatalysis under both UV and visible light, promoting suitable separation and degradation of pollutants with overall high membrane water flux.

Another example of a hybrid system is that tested by de Brito *et al.* [85], whereby photo-electro-catalysis and ozonation were combined in a single step to achieve higher removal efficiencies compared to the individual processes; see **Fig. 2c**. As it has been shown frequently, photocatalysis alone hardly achieves high removal efficiencies under conditions like those found in PW, often characterized by turbid, colored, and highly concentrated solutions. Ozonation helped with color removal to maximize the absorption of the photons that create photo-generated holes and electrons on the semiconductor. The integration of ozonation with photocatalysis through TiO_2 nanotube arrays was also tested by Liu *et al.* [92]. Ozone seemed to be the main responsible for PAHs degradation, while the enhancement of pollutants degradation by added TiO_2 was not significant. Furthermore, increasing the photocatalyst concentration above 0.2 g/L decreased the overall removal rates, due to the attenuation of light intensity by the catalyst itself. However, under optimal conditions, a higher concentration of reactive species was achieved, which led to better oxidation efficiency as also observed by Corrêa *et al.* [91] in a similar study. There, the treated PW presented an adequate BOD5/COD ratio for the subsequent purification step, through a biological system comprising macroalgae.

In general, the use of hybrid systems allows for multiple complementary treatment objectives to be achieved in a single step, effectively reducing the time required for the overall treatment and the space occupied by the equipment. In particular, immobilization of the semiconductor on a membrane potentially decreases the cost of water treatment, because it avoids the subsequent complicated step of separating the nanometric catalyst from the solution (**Fig. 2c**). The integration of several AOPs within the same reactor also seems to lead to synergetic mechanisms and greater removal rates and kinetics, although the increase in the cost of treatment should be assessed in relation to the increase in efficiency achieved (*vide infra*). Moreover, despite major advantages, the combination of TiO_2 with membranes has the caveat of membrane performance over time, which should be monitored due to possible damage to the polymer caused by photocatalytically produced reactive transients.

4. POTENTIAL, CHALLENGES, AND IMPLEMENTATION PERSPECTIVES

4.1 POTENTIAL AND RESEARCH NEEDS

Advanced oxidation processes exploit the formation of highly reactive species, especially hydroxyl radicals, to convert pollutants into similar but less harmful or hazardous compounds or into short-chained, more hydrophilic, and more easily degradable or biodegradable organic compounds. Because the action of the most reactive species is non-specific, AOPs can be applied for the removal of numerous organic compounds at once, all typically present in PW, including oil and grease, phenols, mono- and polycyclic aromatic hydrocarbons, naphthalenes, chlorophenols, and other halogenated pollutants. While this review focuses on organic substances, inorganic compounds usually present in PW can also be removed or transformed into less toxic species by AOPs, including cyanides, sulfides, sulfites, nitrites, and some heavy metals (such as Cr, for which detoxification may be achieved by a change in redox state). AOPs are also applied to degrade compounds causing odor, taste, color, and for disinfection purposes. Chemical oxidation may be specifically attractive when small flow rates or quantities of PW are involved, when compactness is a principal factor of the system design, particularly in offshore activities, and because the poisonous level of the PW stream is high, such that installation of biological-based oxidation is usually not feasible. Other typical advantages to the most common AOPs are that they operate at atmospheric pressure and temperature, that they are effective over a wide range of COD values, often with the use of small residence times and thus small tank volumes, and that large fluctuations in flow rate or composition can be managed. These features are all specifically attractive in the treatment of PWs, which are often characterized by variability in composition and volume over space and time, and by high salinity and toxicity levels. Therefore, AOPs have high potential in this application, which justifies the recent increase in the attention of related investigations. Furthermore, the quality of the effluent achievable by AOPs may be as high as required in light of the purpose and final use, and of the various legislations enforced in different parts of the world. That being said, the current state of the art of the various AOPs hardly allows for their immediate and cost-effective implementation for the treatment of PW at an industrial scale. It is worth listing some of the most important limitations of the different processes, with the main aim of suggesting some opportunities for research and development. Please see **Table 3** for a summary of advantages, challenges, and opportunities of the various AOPs applied for PW treatment.

The classic Fenton process has shown adequate effectiveness in PW treatment; its deployment requires acidic pH conditions, which may necessitate acidification and subsequent re-basification of the aqueous matrix. The evolution of the Fenton process to work at near-neutral pH, for example with the use of iron ligands or by using heterogeneous processes based on zero-valent iron (ZVI-Fenton) or other iron-based materials [145, 146], should be pursued to improve the Fenton-based purification of PW and wastewaters in general. Applying the Fenton reaction at near-neutral pH, by virtue of a different reaction mechanism, can also curtail the scavenging effects of halides, usually dissolved in PW at high to very high concentrations.

An important side effect of the Fenton reaction is the precipitation of Fe(III), which gives rise to a large quantity of sludge, although mostly inert. The use of iron ligands reduces this effect, but also implies the need to remove and recover the dissolved metal catalyst from the effluent. Please note that the use of hydrogen peroxide requires appropriate storage and handling to avoid risk of explosive decomposition, and the concentration of this oxidant per reactor cannot normally exceed 4% [144]. Additional research should also look into the use of different oxidants [147] and into the possibility of energy recovery if the reaction produces excess heat, which may be the case for TOC removal when this parameter is higher than 3 g/L, which requires large additions of oxidant.

Heterogeneous photocatalysis can also provide suitable effluents starting from PW streams, and it has similar advantages and limitations as the Fenton process in PW treatment. While current catalysts are typically more expensive than iron salts, the advantages of this technique are mostly related to the possibility to more easily recover the catalysts, which usually come in the form of nano- or micro-particles, and to better versatility in a wider range of solution conditions in terms of pH, salinity, and organic content. The vast majority of the approaches are based on the use of TiO_2 semiconductors, but further research should be conducted to study more economical and available materials, such as zerovalent iron. Interesting developments involve the coating or doping of fixed supports with semiconductors; in the case of membranes, this approach allows for the simultaneous degradation and separation of contaminants from the stream.

In general, the application of electro-Fenton and heterogeneous electro-catalysis, as well as the implementation of photo-assisted techniques, such as photo-Fenton or photo-electro-catalysis, can significantly increase the degradation rate of organic substances in PW. Other advantages associated with the exploitation of an electric field are a lower cost of reagents, which may be efficiently generated in-situ at the cathode (*e.g.*, Fe(II), H_2O_2) together with other compounds with high oxidation potential and/or the direct oxidation of the compounds at the anode or the anodic production of further oxidants (*e.g.*, active chlorine following chloride oxidation at the anode). The scavenging effect of halides is virtually absent in these processes, which also generally reduce the recombination in the case of photocatalytic processes (direct or mediated reactions between the photogenerated electrons and holes). Clearly, these benefits are accompanied by several challenges, which are currently related to the general applicability of these techniques with PW and any other wastewater matrix. The implementation of UV light and/or electric potentials entails higher investment and operating costs, as well as appropriate (photo/electro)-reactors or system designs, which may even result into larger footprint compared to classic catalysis despite the larger removal kinetics provided by the electrochemical or photo-assisted processes. A photo-assisted oxidation does not usually result in efficiency gain when high contaminant concentrations are expected, because large amounts of reagent are required and because contamination usually relates with turbidity and poor transmission of light. Therefore, more extensive pre-treatment is usually required with photo-assisted compared to irradiation-free processes. Finally, the effective use of solar light instead of UV-lamps as a source of energy would represent a significant leap forward for an energy-efficient implementation of photo-assisted processes.

Anodic oxidation is also a particularly promising electrochemical technique for the treatment of PWs, and has shown similar removal efficiency toward organic contaminants as Fenton-based and heterogeneous photocatalytic processes. Some of the challenges of other AOPs are instead advantages of this process, such as high salinity and chloride content. Nevertheless, anodic oxidation requires the development of robust, selective, and efficient electrodes, and common issues of electrochemical processes are the chemical poisoning of electrodes and electrode passivation.

Ozonation is a straightforward technique and it is already implemented as PW purification technology. It has shown sufficient capability to handle the removal of organics in PW, although with efficiencies that are slightly lower than those guaranteed by other AOPs. Ozonation is especially useful as a support for a second combined AOP, specifically to exploit ozone as electron scavenger in heterogeneous photocatalysis. Ozone is an unstable compound that cannot be stored or transported and has to be generated on site, necessitating specific equipment. Safety requirements to handle ozone are usually strict and surplus ozone, if any, must be eliminated after treatment.

To conclude the discussion on limitations of AOPs, one must keep in mind that, like with any other oxidation-based degradation, attention should be paid when incomplete oxidation produces intermediate contaminants. These may sometimes be more harmful than parent substances for the quality of the effluent or for subsequent treatment steps. A further avenue of research to avoid some of the issues related to the exploitation of hydroxyl radicals, is the application of AOPs to produce instead sulfate radicals, $SO_4^{\bullet-}$, for example from the activation of peroxymonosulfate or persulfate or from the anodic oxidation of sulfate anion in an electrocatalytic cell. The mechanism and effectiveness of the reaction mediated by $SO_4^{\bullet-}$ is still amply debated and numerous accounts of its potential have been reported [148-150]. The following reactions account for the activation of persulfate ($S_2O_8^{2-}$) and peroxymonosulfate (HSO_5^{2-}) in the presence of Fe^{2+}, and for the direct photolysis of $S_2O_8^{2-}$:

$$S_2O_8^{2-} + Fe^{2+} \rightarrow SO_4^{\bullet-} + SO_4^{2-} + Fe^{3+} \qquad (21)$$

$$HSO_5^{-} + Fe^{2+} \rightarrow SO_4^{\bullet-} + FeOH^{2+} \qquad (22)$$

$$S_2O_8^{2-} + h\nu \rightarrow 2\ SO_4^{\bullet-} \qquad (23)$$

The $SO_4^{\bullet-}$ radical is only slightly less reactive than $^{\bullet}OH$, but it is considerably more selective. Indeed, the reaction rate constants between organic compounds and $SO_4^{\bullet-}$ span a couple of orders of magnitude more than those involving $^{\bullet}OH$ (see SI, Figure S1 [49, 50]). This means that, if a compound (*e.g.*, an aromatic one) reacts rapidly with $SO_4^{\bullet-}$, this transformation undergoes less interference from other organic chemicals (*e.g.*, aliphatics), compared to the equivalent process that involves $^{\bullet}OH$. Although they are applicable to fewer pollutants compared to $^{\bullet}OH$, the techniques involving $SO_4^{\bullet-}$ are more suitable for use with organic-rich matrices, especially if one is interested in the degradation of a minority of $SO_4^{\bullet-}$-reactive compounds and if the remaining ones are little reactive towards $SO_4^{\bullet-}$.

4.2 REDUCTION OF EFFLUENT TOXICITY BY MEANS OF AOPS

Laboratory tests show that PW causes toxicity problems on many biological systems. Salinity, dispersed and dissolved oil and organic compounds, heavy metals, radionuclides, and pathogens are responsible for the observed toxicity, but assessing the contribution of each class to the total toxicity is complex. Furthermore, PW chemical composition (and relative toxicity) changes significantly in relation to many factors. For example, the age of the wells and the formation geology strongly affect the concentrations of heavy metals (such as cadmium, chromium, lead, mercury) [4], while gas production-associated PW are typically more toxic due to the higher levels of aromatic hydrocarbons [151]. Even the production chemicals (*e.g.*, scaling and corrosion inhibitors, biocides) added during extraction to avoid operational problems can influence PW toxicity: even if no direct toxicity problems have been detected in their normal dosage concentration, some of these agents can increase the partition of oil toxic organic components (such as PAHs) in the aqueous phase, making them more accessible to aquatic organisms [152].

Some authors have discussed the ability of AOPs in reducing PW toxicity. De Brito *et al.* [85] evaluated the acute toxicity of PW on Zebrafish (*Danio rerio*) after photocatalysis, photo-electro-catalysis (PEC), and PEC combined with ozonation for a reaction time of 2 h. Photocatalysis seemed to be the best treatment, with a 90% reduction of hatching failure compared to raw PW. In general, photocatalysis, as well as PEC combined with O_3, were able to reduce lethal and sublethal effects, even if they were not totally successful. Li *et al.* [84] compared the effects towards two strains of *S. typhimurium* of a raw PW and of a sample treated with PEC for 4 h, achieving a notable decrease in mutagenic activity (Ames test). The same authors [75] also investigated toxicity effects after 1 h treatment by photocatalysis, PEC, and electro-oxidation. PEC showed the greatest genotoxicity reduction, due to the best decrease in COD and phenolic compounds concentration. Jimenez *et al.* [17] compared the residual toxicity toward *Vibrio fischeri* bacteria after Fenton-based, photocatalysis, and ozonation treatments, showing that ozonation (with and without the addition of H_2O_2) was the most efficient method to decrease acute toxicity, while Fenton-based and photocatalytic treatments only led to a slight increase in EC_{50} value. Corrêa *et al.* [91] evaluated the effluent toxicity before and after a O_3/UV/TiO_2 treatment with respect to *Vibrio fischeri* and to a fish, namely, *Poecilia vivipara*. They achieved, respectively, a 20- and 1.3-times increase in EC_{50} after the AOP (note that higher EC_{50} corresponds with lower toxicity). By coupling the AOP with a subsequent biological treatment, the value of EC50 was increased further, due to the enhanced absorption/transformation of metals and ammonia compounds. Liu *et al.* [92] also obtained an increase in EC_{50} from 3% to 50% in a *Vibrio fischeri* assay after 1 h photocatalytic ozonation. When considering the effect of anodic oxidation, Gargouri *et al.* [98] compared the cytotoxicity reduction on HeLa cell lines achieved with a Ta/PbO_2 and with a BDD anode. The treatment with BDD led to a better reduction of cytotoxicity, but it should be noted that both treated samples showed lower toxic effects than the raw PW. Finally, Posada *et al.* [105] employed the *Pseudomonas putida* growth inhibition test to evaluate toxicity during a catalytic wet air oxidation treatment. Inhibition rapidly decreased from 80% to 40% in the first 30 minutes, then it was almost constant until 1.5 h, when the inhibition value finally dropped to 0.

Overall, studies confirm the beneficial effect of AOPs to lower the toxicity and/or mutagenicity of PW effluents, thus increasing the sustainability of their ultimate environmental discharge following treatment. The lower toxicity associated with oxidized matrices is due to a combined removal or inactivation effect by AOPs toward organic content, heavy metals, radionuclides, microorganisms, and other oxidizable toxic compounds. Moreover, there is some statistical evidence that oxidized (and, as a consequence, more polar) organics are often less acutely and chronically toxic compared to their parent counterparts [153].

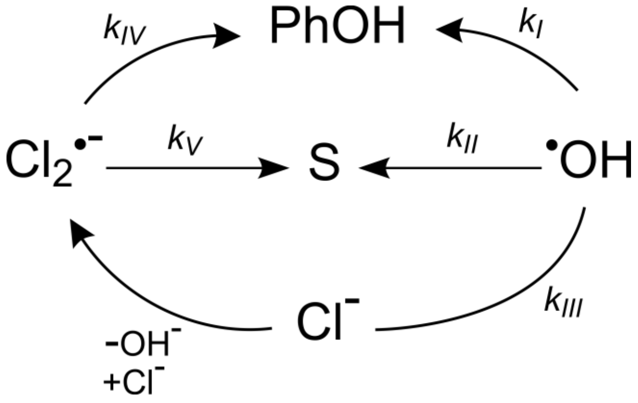
4.3 Effect of Chloride on AOPs Based on $^{\bullet}$OH

It is worth providing more insight into the role of chloride as an interfering agent, also given the importance of chloride anions in typical PWs. Chloride is known to be an interfering agent in several AOPs, due to its ability to transform $^{\bullet}$OH into the less reactive transient species $Cl_2^{\bullet-}$ at pH < 5. However, the impact of chloride on $^{\bullet}$OH reactions may be more complex than usually thought. When the AOP is applied to target a specific contaminant, chloride might slow down or even speed up the degradation process, depending on the relative reactivity with $^{\bullet}$OH and $Cl_2^{\bullet-}$ of the target contaminant and other substrates. This issue can be exemplified by considering a reaction system where $^{\bullet}$OH occurs together with phenol (PhOH, here assumed to be the target pollutant), chloride, and an additional substrate, S. Here, it is assumed that S = 2-propanol (PrOH), methanol (MeOH), hydroquinone (HQ), or 4-methoxyphenol (MeOP). The shown reaction scheme applies (**Fig. 3**), where $^{\bullet}$OH is transformed by Cl^- into $Cl_2^{\bullet-}$, and both $^{\bullet}$OH and $Cl_2^{\bullet-}$ can react with PhOH and with S (k_I-k_V are second-order reaction rate constants between the transient - $^{\bullet}$OH and $Cl_2^{\bullet-}$ - and the phenol, the considered organic substrates S, and Cl^-). By applying the steady-state approximation to $^{\bullet}$OH and $Cl_2^{\bullet-}$, one gets the following expression for the degradation rate of phenol (R_{PhOH}):

$$R_{PhOH} = R_{^{\bullet}OH}(k_{I}[PhOH]+k_{II}[S]+k_{III}[Cl^{-}])^{-1}\left(k_{I}[PhOH]+\frac{k_{III}k_{IV}[PhOH][Cl^{-}]}{k_{IV}[PhOH]+k_{V}[S]}\right)(24)$$

where $R_{^{\bullet}OH}$ is the formation rate of $^{\bullet}$OH in the system. The trend of $R_{PhOH}/R_{^{\bullet}OH}$ as a function of chloride concentration, for fixed concentration values of PhOH (10 μmol/L) and

S (500 μmol/L), is shown in **Fig. 3**. It is apparent that chloride enhances phenol degradation in the presence of PrOH and MeOH, because PhOH competes better with the alcohols for reaction with $Cl_2^{\bullet-}$ than it does for reaction with $^{\bullet}OH$ (k_{II} / k_V > k_I / k_{IV}). In contrast, chloride inhibits degradation in the presence of HQ and MeOP because these two compounds react faster than phenol with $Cl_2^{\bullet-}$, compared to what they do with $^{\bullet}OH$ (k_{II} / k_V < k_I / k_{IV}). Therefore, it would not be surprising to find that, contrary to expectations, for some pollutants in some matrices chloride actually enhances degradation instead of inhibiting it. For additional details concerning the kinetic system , the derivation of equation 3, and the numerical values of the kinetic constants (k_I-k_V) used for the modeling, see section SI.4 of the Supplementary Information.



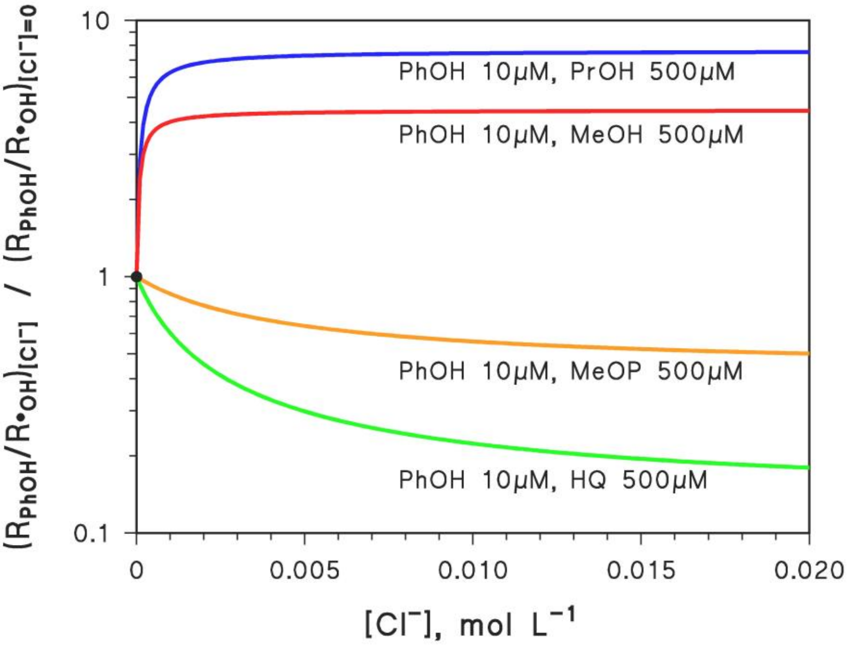


Fig. 3. Reaction scheme and trends of the ratio $R_{PhOH}/R_{\bullet OH}$ (normalized to its value at $[Cl^-] = 0$) as a function of chloride concentration according to eq. 3, in the presence of 10 µM phenol and of the other organic compounds (2-propanol, PrOH; methanol, MeOH; hydroquinone, HQ; 4-methoxyphenol, MeOP) at 500 µM concentration.

4.4 IMPLEMENTATION AND TECHNOLOGY READINESS LEVEL

AOPs have been investigated for various purposes within systems aimed at purifying PW. In fact, the same AOP may be designed as a pre-treatment or as a polishing step within a train, depending on the specific treatment rationale and objective. As discussed above, AOPs are effective in increasing the (bio)degradability or in reducing the fouling potential of raw PW. Moreover, their efficiency increases significantly when they are preceded by removal systems that minimize the detrimental effect of scavengers or other agents that interfere with oxidation. When applied to polish pre-treated streams of good quality, AOPs can guarantee the production of high-quality effluents, suitable for beneficial reuse.

Fig. 4 evaluates the various AOPs in light of the efficiency demonstrated so far in the removal of organic substances from PW, specifically classified as oil & grease, TOC, and COD in **Fig. 4a**, **4b**, and **4c**, respectively. In **Fig. 4d**, the readiness level of the technologies is thus summarized. In this latter graph, the size of the dots refers to the average organics removal efficiencies reported in the literature for PW treatment and summarized in **Table 2**. The parameter referred to as “maturity” is related to the knowledge of each technique in terms of reaction mechanism, process control and intensification; “feasibility” is instead related to the current implementation at an industrial scale, as well as to the ease and economy of installation. This latter assessment is based on the comprehensive report by Miklos *et al.* [19], who classified the various AOPs in three categories based on their current developmental stage.

Apparently, the most mature and feasible processes, ozonation and classic Fenton, are also associated with lower efficiency in PW treatment. Electrochemical and photo-assisted processes provide the best performance but still require significant development to increase their technology readiness level and significantly decrease operational costs. The current challenges and the analysis provided above suggest that, while AOPs have clearly high potential for the treatment of PW, their widespread implementation will follow only sustained academic and industrial efforts, aimed at the intensification and at the increase of their reliability and cost-effectiveness.

Table 3. Current advantages and limitations of AOPs and their application in the treatment of produced water.

Process	Advantages	Limitations	Open Questions and Research Needs
Common features	- Applicable to produced water of different composition in terms of organics due to non-specific oxidation mediated by $OH^{\cdot}$ - Capacity of removing also inorganic compounds (cyanides, sulfides, sulfites, nitrites, heavy metals) - Abatement of compounds responsible for odor, taste and color - Applied at atmospheric pressure and (often) at room temperature - High quality of the final effluent - Capacity of increasing the degradability or reducing the fouling potential of a raw PW	- Possible scavenging effects by Cl^- - Concerns about possible incomplete degradation (possible production of by-products that are more toxic and harmful than the parent compound) - General need for pre-treatment steps in order to minimize the detrimental effect of scavengers or other interfering agents of the oxidation reaction - Low implementation at industrial scale due to cost-effectiveness problems	- Development of AOPs based on other radical species (*e.g.*, $SO_4^{\bullet-}$ from the activation of peroxymonosulfate or persulfate)
Fenton	- Good removal efficiency in relatively short time - Reagents easily available - Low cost	- Need for acidic pH conditions (requiring acidification and final re-basification of the aqueous matrix) - Precipitation of Fe(III) as hydroxide in the final basification step - Safety concerns at high $[H_2O_2]$	- Use of iron ligands (possibility of working at near-neutral pH values and limiting scavenging effects by halide ions) - Use of heterogeneous Fenton, such as zerovalent iron (easier recovery of the catalyst) - Use of different (greener) oxidants - Possibility of recovering energy from the reaction (e.g. heat excess)
Photo-Fenton	- Higher removal efficiency in shorter times compared to the traditional Fenton process - Higher concentration of $OH^{\cdot}$ due to photolysis with	- Same as traditional Fenton processes - Need for appropriate tanks or system designs	- Feasibility of using solar light as irradiation source (energy-efficient implementation of photo-assisted processes)

	the same amount of hydrogen peroxide - Reagents easily available	- Necessity for more extensive pre-treatment for improving light transmission inside the reactor - Higher costs compared to the traditional Fenton process, due to electrical energy consumption for irradiation (except for experiments under solar light)	
(Photo-)Electro-Fenton	- Higher removal efficiency in shorter times compared to the traditional Fenton process - Need for lower iron concentration (it is constantly and rapidly regenerated as Fe(II) at the cathode) - Lower costs of reagents due to the in-situ generation of H_2O_2 at the anode - Reduction of suppression rate for photogenerated electrons and holes - No scavenging effects by Cl^- - Enhancement of removal efficiency also due to the generation of active chlorine from chloride ions	- Same as photo-Fenton - Need for electrical energy source	- Research need for real applicability of this technique with PW and other wastewater matrices - Design of efficient reactors in terms of configuration and flow pattern
Heterogeneous Catalysis	- Complete sample mineralization often reached - Feasibility of loading TiO_2 on membranes (desalination and removal of organic pollutants at the same time)	- - Low quantum yield as a consequence of the high rate of recombination of the charge couple - Need for a post-treatment filtration step of the photocatalyst (TiO_2 or other nanoparticles) - Higher costs due to energy consumption (light source always needed) - Purification of the catalyst required before re-	- Research needs for improving the applicability in real systems , especially about the problem of low quantum yields and the visible sensitization of the photocatalyst - Need to better check the long-term compatibility between TiO_2 and the membrane polymers.

		use, in order to reach the same efficiency in a new process	
(Photo-)Electro-catalysis	- Removal efficiency higher than classic catalysis and photocatalysis - Moderately high removal efficiency for short time treatments - Reduction of the recombination rate for photogenerated electrons and holes - No scavenging effects by Cl− - Enhancement of removal efficiency also due to the generation of active chlorine from chloride ions	- - Need for appropriate tanks or system designs - Necessity for more extensive pre-treatment for improving light transmission inside the reactor - Higher costs compared to the traditional electrocatalytic process, due to electrical energy consumption for irradiation (except for experiments under solar light) - Need for a post-treatment filtration step of the photocatalyst - Higher electrical energy consumption compared to traditional photocatalysis	- Research need for real applicability of this technique with PW and other wastewater matrix - Design of efficient reactors in terms of configuration and flow pattern - Economic feasibility still under evaluation
Ozonation	- Currently most used technique among AOPs treatment strategies (easy applicability) - Useful as support for a second combined AOP - Safe and easy in use (ozone produced on-site, no storage of dangerous chemicals) - Low maintenance and operational costs - No need for controlled pH (ozone is effective in a wide pH range) - High efficiency also as disinfectant (No need for additional disinfectants or cocktails of them)	- Need for an ozone-generator apparatus - A bit lower removal efficiency compared to other AOPs - Need to eliminate surplus ozone at the end of the treatment	- Research need for improving the organics removal efficiencies - Efficient combination of hybridization with other oxidation processes or treatment steps

Anodic oxidation	- No chemicals needed (environmentally friendly) - Wide variety of electrode materials - Little or no sludge production - High efficiency and flexibility - Safe and easy in use (simple equipment, easy operation) - Compactness (*in-situ* operation at offshore platforms) - Amenability of automation	- High cost of the electrodes - High energy requirements - Long reaction times - Anode instability - Deposition of substances onto anode surface (e.g., due to the foam produced by surfactants and corrosion inhibitors) - Removal efficiencies depending significantly on influent flow rate and COD initial concentration	- Research need for new electrode materials with high removal efficiencies in shorter times - Research for new sources of electrical power, to make the process more sustainable
CWAO and CWPO	- No or little chemicals needed (only H_2O_2 in CWPO) - Wide variety of catalyst materials - Easy recovery of the catalyst after treatment, when needed	- Very few applications in PW treatment - High temperature and high pressure required (for CWAO)	- Research need for catalysts with higher removal efficiencies
Sonolysis	- No chemicals needed - No pre-treatment of the effluent required - Possibility of coupling sonolysis with other techniques (*e.g.*, sono-Fenton process) - Suitable especially for volatile and hydrophobic organic compounds	- Very few applications in PW treatment - High energy consumption	- Research need for improving the removal efficiencies combining sonolysis with other AOPs
Radiolysis	- No chemicals needed - No pre-treatment of the effluent required - Very high efficiency at high absorbed dose	- Very few applications in PW treatment - Need for an electron beam accelerator (high cost) or radioactive materials - Safety problems due to radiations - Removal efficiency influenced by pH, temperature, dissolved O_2, and pollutants load	- Research need for safer and cheaper radiation source

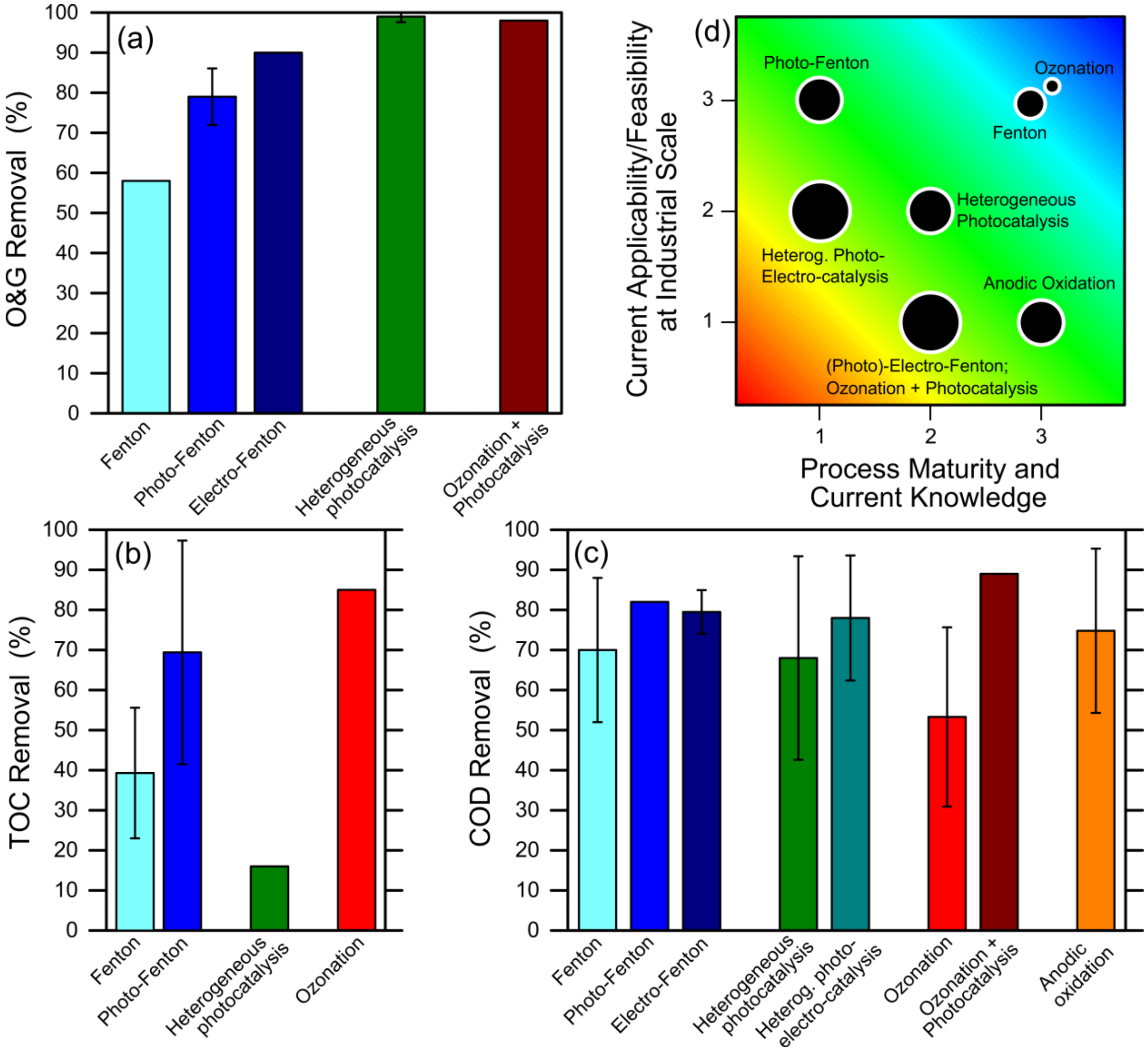


Fig. 4. Evaluation of AOPs in the removal of organic contaminants from produced water effluents. Average removal rate of (a) oil & grease, (b) TOC, and (c) COD of the various AOPs reported in previous studies on PW decontamination (from Table 2). (d) Summary of efficiency, maturity, and real-scale feasibility of the various AOPs in the treatment of PW. Efficiency is evaluated considering the degradation fraction, rate, and the conditions of the tests discussed in the cited literature (and is proportional to the size of the circles). Maturity and feasibility are awarded a score between 1 and 3 based on literature reports and the authors' knowledge of the field. The shade from red to blue represents increasing maturity & feasibility, that is, technology readiness level.

4.5 OVERVIEW OF THE COSTS OF THE MOST COMMON AOPS

In this section, we provide a non-exhaustive economic evaluation of some of the AOPs discussed in this review. The goal of this section is not to offer a complete analysis of the costs of AOPs, which may instead be found in the dedicated literature cited below, but to provide a snapshot of the current magnitude of the investments associated with typical AOPs, as a representative starting point for future cost reductions that should go hand-in-hand with technological development. The above discussion above has pointed out that oxidation performed through an electrochemical process is generally more effective in PW treatment than ozonation ore a Fenton process. The latter, however, is arguably the easiest to implement and one of the cheapest AOPs. An average estimation of the operational costs is 2.4-4.0 €/kg of equivalent O_2 for an electrochemical process, 8.5-10.0 €/kg of equivalent O_2 for ozonation, and 0.7-3.0 €/kg of equivalent O_2 for a Fenton process [154]. The initial investment costs of an electrochemical, an ozonation, and a Fenton process have been estimated, respectively, in the range ~23,000-34,000 €, ~61,000-123,000 €, ~10,000-18,000 € per m^3 of treated wastewater and for the same COD removal rate, namely, 85% [154-156]. The main investment costs of an electrochemical process may be ascribed to the cost of the conductive diamond electrodes (~15,000 €/m^2), while the electrical energy is generally cheap (0.25 €/W). The costs of a Fenton process are mainly related to the reagents (iron, H_2O_2, acids, and bases), and to sludge disposal (~150 €/m^3) [154].

A photocatalytic treatment is also generally more efficient in the removal of organics from PWs, but also more expensive in the current state-of-the-art [157]. The energy costs in photocatalysis range from 0.5 to 8.5 € per m^3 of treated wastewater. However, the UV lamps need periodical replacement (a UV-A lamp generally lasts roughly 2000 h), which may represent up to 65-70 % of the operational cost of a photocatalytic treatment. The reported costs of the catalysts are of secondary importance (30 to 55 % of the operational costs), ranging from 0.6 to 3.4 €/m^3. Also, the investment cost of the treatment is chiefly related to the catalyst support, commonly ranging from 10,000 to 60,000 €/m^3. As of today, the upscale of photocatalytic processes may be challenging on the basis of the high initial investment and the necessary maintenance and replacement of the UV lamps [157, 158]. Therefore, technological development should address these issues together with the improvement in materials efficiency.

Declaration of Competing Interest

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

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Graphical Abstract