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1 **Photo-Electrochemical Reactors for Treatment of Water**
2 **and Wastewater**

3
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14 **REVIEW PAPER**

15 ***ENVIRONMENTAL CHEMISTRY LETTERS***

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32 **Abstract**

33 To address the increasing global water demand in parallel to water scarcity, especially
34 exacerbated by the climate change, the “Water Reuse” option is more and more considered. It
35 consists of the reuse of water for different sectors with different water quality requirement such
36 as industry, agriculture and even for human consumption. The biotechnologies currently
37 implemented are usually cheaper but are not sufficient to completely remove biorecalcitrant
38 pollution. Advanced oxidation technologies for wastewater treatment have gained significant
39 interests the last few years as an answer to this issue by producing very strong oxidizing agent
40 such as hydroxyl radical ($\cdot\text{OH}$) in mild conditions. Electrochemical advanced oxidation
41 processes have attracted particular attention for water treatment through the continuous and *in*
42 *situ* electro-catalytic generation of strong oxidizing species under mild conditions with the
43 possibility to avoid the external addition of chemicals. The synergy between photochemical
44 systems and electrolysis has more recently seen increasing interest considering benefits from
45 using solar light as a free energy source. However, there is a lack of literature review on the
46 reactions and engineering aspects of the photo-electrochemical reactors that play a paramount
47 role on the overall process efficiency.

48 In this context, we reviewed the trends of photo-electrochemical reactors through two major
49 points. Firstly, the reactions involved were presented along with the possible synergetic
50 mechanisms. Under maximal conditions, eight $\cdot\text{OH}$ production sites could be identified when
51 implementing photoelectro-Fenton combined with photoanodic oxidation and photocatalysis or
52 photoelectrocatalysis. Several factors affect the occurrence of these reactions such as the
53 solution pH, the applied wavelength, and the competition between reactions requiring the same
54 reagent. Secondly, the different reactor design developed in response to the catalytic
55 phenomena are discussed. Different configurations have been considered: sequential or hybrid
56 reactors, divided or undivided cells, flow-cell or stirred tank reactor and light source
57 positioning, i.e. external or immersed, vertical or horizontal, on the top or bottom or on the side
58 of reactor. To obtain maximal synergy and maximum quantum yields, the distance between the
59 light source and the electrode needs to be minimized. Hybrid reactors in undivided flow-cells
60 are practically preferred for the lower footprint area, the possibility to regenerate iron catalysts
61 and the enhancement of mass transfer compared with stirred tank reactor. Moreover, the
62 interelectrode gap can be easily controlled in flow-cell, which permits optimisation of the

63 penetration depth when the light is applied through the reactor. These insights give some keys
64 for future development of photo-electrochemical technologies.

65

66 **Keywords** Advanced oxidation • Anodic oxidation • Electrocatalysis • Electro-Fenton •
67 Photocatalysis • Photo-electrochemical processes • Reactor design • Wastewater

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92 **1. Introduction**

93 The release of hazardous micropollutants such as pesticides, pharmaceuticals and personal care
94 products at the outlet of wastewater treatment plants into the water bodies is a problem of major
95 concern (UNESCO 2017). These contaminants can be potentially toxic for the environment and
96 human health even at very low concentrations (pg/L to µg/L) (Luo et al. 2014; Cizmas et al.
97 2015).

98 The biological processes involved in conventional treatment plants are not suitable enough to
99 remove completely these biorecalcitrant compounds (Besnault and Martin 2011). Therefore,
100 advanced physical-chemical technologies have been proposed to answer this issue and among
101 them advanced oxidation processes have gained interest (Shi et al. 2020). They all rely on the
102 generation of very strong oxidizing agents such as hydroxyl radicals ($\cdot\text{OH}$) having a high
103 standard potential ($E^\circ(\cdot\text{OH}/\text{H}_2\text{O})$) that is equal to 2.80 V versus the standard hydrogen
104 electrode, noted in V for the sake of simplicity in all the chapter (Glaze et al. 1987; Oturan and
105 Aaron 2014; Stefan 2017). $\cdot\text{OH}$ radical is a reactive oxygen species that has a very short lifetime
106 in the range of nanoseconds, which avoids its persistence into the environment (Gligorovski et
107 al. 2015). $\cdot\text{OH}$ radical is also known for its almost non-selectivity due to its four reaction modes,
108 i.e. hydrogen atom abstraction, electrophilic addition to unsaturated bonds, electron transfer
109 and the ipso-substitution with perhalogenocarbon compounds, which permit the oxidation of a
110 broad spectrum of compounds (Dorfman and Adams 1973; Von Sonntag 2008; Mousset et al.
111 2018a). $\cdot\text{OH}$ reaction is particularly fast with C=C double bonds that are present in molecular
112 structure of many organic micropollutants, with oxidation rate constants ranging from 10^8 to
113 $10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$ (Mousset et al., 2016a).

114 Among advanced oxidation processes there are the traditional chemical ones that involve either
115 (i) an oxidant such as hydrogen peroxide (H_2O_2) and a catalyst such as ferrous ion (Fe^{2+}), known
116 as Fenton or Fenton-like processes, or (ii) photons produced by light irradiation photolysing an
117 oxidant like H_2O_2 (Oturan and Aaron 2014). These processes present some drawbacks such as
118 the need to continuously add reagents such as H_2O_2 (Oturan and Aaron 2014) or have
119 applicability at a limited pH range. At the end of the nineties, the electrochemical-based
120 advanced oxidation processes have been proposed as an alternative for producing *in situ* and
121 continuously the oxidant species during the electrolysis, the electron being the main reagent
122 involved (Brillas et al. 2009; Panizza and Cerisola 2009; Vasudevan and Oturan 2014; Sirés et
123 al. 2014; Martínez-Huitle et al. 2015; Moreira et al. 2017). These characteristics make

124 electrochemical advanced oxidation processes gaining great interest in the scientific
125 community since degradation and mineralisation yields can reached higher than 99% for a wide
126 range of organic pollutant and organic load represented by a chemical oxygen demand below
127 100 g-O₂ L⁻¹ (Lahkimi et al. 2007; Alcántara et al. 2009; Mousset et al. 2013, 2014a, b; Sirés
128 et al. 2014; dos Santos et al. 2015, 2017; Shukla and Oturan 2015; Ganzenko et al. 2018).
129 More recently, photo-assisted electrochemical processes have been proposed in order to make
130 use of renewable energy in response to the sustainable development objectives (Garcia-Segura
131 et al. 2013; Garza-Campos et al. 2014; Ramirez et al. 2015; Mousset et al. 2017a). Photo-
132 electrochemical processes have been applied for the treatment of biorefractory pollutants as
133 reviewed recently (dos Santos and Scialdone 2018). Dyes are presents in textile effluents and
134 they could be treated for discoloration and mineralisation (Martínez-Huitle and Brillas 2009;
135 Zhao et al. 2010; Zhou et al. 2010; Xu et al. 2013; Brillas and Martínez-Huitle 2015). Pesticides
136 released in wastewater (Fang et al. 2012; Almazán-Sánchez et al. 2017) have also been removed
137 by photo-electrochemical processes. Pharmaceuticals detected as micropollutants in municipal
138 wastewater treatment plants outflow or in hospital wastewaters could be degraded and
139 mineralized (Zhao et al. 2009; Feng et al. 2013). Water disinfection is another promising
140 application of such processes by inactivating pathogenic microorganisms such as bacteria like
141 *Candida parapsilosis* and *Escherichia coli* (Liu et al. 2014; dos Santos and Scialdone 2018).
142 Interestingly, synergy in reactions can be obtained in photo-electrochemical combinations,
143 especially in hybrid reactors. In fact, the reactor design represents an essential engineering
144 aspects in photoprocesses efficiency. This is the reason why it is proposed to discuss those
145 facets in the following sections.

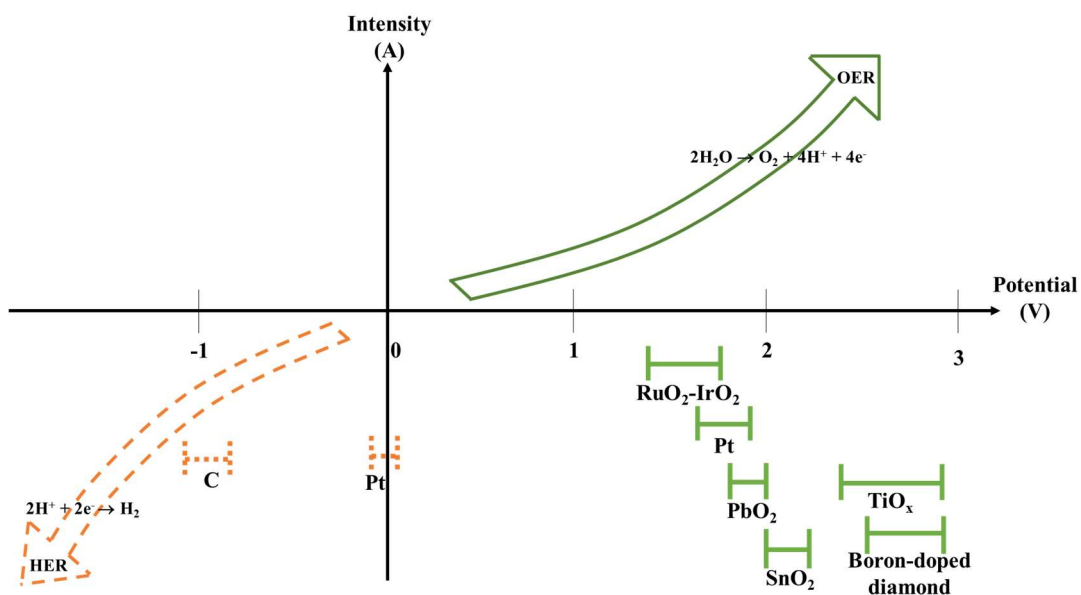
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147 **2. Influence of catalytic oxidation**

148 **2.1. Selection of electrode materials for electrocatalytic oxidation**

149 In electrochemical processes, electrode materials play a major role in the removal efficiency
150 (Mousset et al., 2016c, 2016d; Mousset et al., 2017b; Oturan et al., 2012; Panizza and Martinez-
151 Huitle, 2013; Yu et al., 2015; Zhou et al., 2014). According to their properties they will act as
152 catalyst to promote or not the oxidation of organic and inorganic compounds. There are two
153 ways of oxidation, either by direct electron exchange through redox reactions with electroactive
154 species, i.e. the so-called direct oxidation, or the indirect oxidation by electrogenerating
155 oxidizing species at the electrode materials surface (Sirés et al. 2014). The first mode occurs

156 less frequently due to its more specific oxidation behavior, since many organic pollutants are
 157 not electroactive. The indirect oxidation mode is generally considered as the main degradation
 158 and mineralisation mechanisms for electrochemical treatment of wastewater. Both anode and
 159 cathode can play a role in this oxidation process, according to their overvoltage values – also
 160 known as overpotential values – for oxygen evolution and hydrogen evolution, respectively
 161 (Figure 1) (Panizza and Cerisola 2009; Comninellis and Chen 2010; Mousset and Zhou 2017).
 162 The anode materials can be divided into two categories: (i) the active anodes that have a low
 163 overvoltage for O₂ evolution usually considered below 1.9 V; this is the case of dimensionally
 164 stable anode (DSA[®]) like RuO₂-IrO₂ with 1.4-1.7 V and platinum (Pt) in the range of 1.6-1.9
 165 V, (ii) the non-active anodes that have a high O₂ evolution overvoltage usually considered
 166 higher than 1.9 V; this is the case of lead dioxide (PbO₂) with 1.8-2.0 V, tin oxide (SnO₂) with
 167 2.0-2.2 V, sub-stoichiometric titanium oxide (Ti_xO_{2x-1} (4 ≤ x ≤ 9)) referred as TiO_x (x < 2) in
 168 this chapter (2.4-2.8 V), and boron-doped diamond with 2.2-2.8 V (Panizza and Cerisola 2009;
 169 Comninellis and Chen 2010). The oxidation involving at active anode materials is referred to
 170 electro-oxidation in this book chapter. In contrast to the active anodes, high O₂ overvoltage
 171 materials favor the generation of physisorbed •OH radicals at their surface by water (H₂O)
 172 oxidation (Panizza and Cerisola 2009). This weak sorption makes •OH radical available for
 173 matrix oxidation through the following reactions (Eqs. 1a-1b) at the anode (M) surface material
 174 (Panizza and Cerisola 2009):

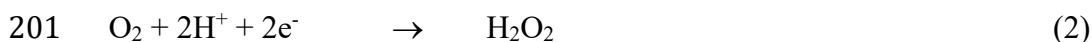


177

178 **Figure 1.** Overvoltage for hydrogen evolution at cathode (dashed line) and oxygen evolution at anode
179 (full line) materials. OER occurs at the highest potentials using boron-doped diamond and TiO_x
180 anodes, which makes them having a high oxidation power. HER occurs at low potential with carbon-
181 based cathodes, which permit the electro-generation of H₂O₂ at their surface. Abbreviations: HER:
182 hydrogen evolution reaction, OER: oxygen evolution reaction.
183

184 The non-active anodes are preferentially employed due to their benefit that can be obtained
185 from the •OH production and the subsequent high organic pollutant removal efficiency in an
186 advanced electro-oxidation technology, that will be referred as anodic oxidation in this chapter.
187 PbO₂ is a cheap material but has been put aside to avoid the possible release of toxic Pb²⁺ ions,
188 though more recent studies highlight the development of more stable PbO₂-based anode
189 (Panizza and Cerisola 2009; Aquino et al. 2014). Boron-doped diamond is the most widely used
190 anode material in advanced electro-oxidation treatment for its high efficiency and good stability
191 and resistance (Comminellis and Chen 2010; Brillas and Martinez-Huitle 2011). However, its
192 relatively high cost makes its application limited to quite small treatment plants. TiO_x (x < 2)
193 is gaining interest for its lower cost and its flexibility (Ganiyu et al. 2016, 2017). Though SnO₂
194 materials have currently a low stability for wastewater treatment application (Panizza and
195 Cerisola 2009), its transparency makes it very interesting for hybrid photoelectrochemical
196 processes (Mousset et al. 2017a) as discussed in sub-section 3.4.

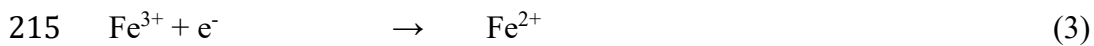
197 The cathode materials can also participate in the oxidation mechanism according to their
198 hydrogen (H₂) evolution overvoltage properties (Figure 1). A high H₂ overvoltage can promote
199 the electrogeneration of hydrogen peroxide (H₂O₂) through the two-electron O₂ reduction
200 reaction (Brillas et al. 2009):



202
203 Platinum (Pt) is chemically inert in the electrochemical advanced oxidation processes'
204 operating conditions and is useful for mechanism understanding studies. Though it has been
205 widely employed at laboratory scale, Pt material is not only expensive but also not efficient to
206 produce H₂O₂ (Sopaj 2013). Stainless steel is comparatively a cheap metal material, but the
207 amount of electrogenerated H₂O₂ is still very low (Sopaj 2013; Mousset et al. 2018a).

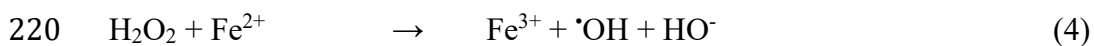
208 Carbon materials have been preferentially studied in the electrochemical advanced oxidation
209 processes area for their high H₂ overvoltage as well as high stability, high flexibility and low
210 cost (Brillas et al. 2009; Chaplin 2014). Graphite represents an abundant natural form of carbon

211 and is therefore a cheap carbon material. However, its low specific surface area does not permit
212 significant level of H₂O₂ concentration (Mousset et al. 2016d). The three-dimensional structure
213 of felt form of carbon-based cathode has been widely investigated for its high specific surface
214 area that allows the fast reduction of Fe³⁺ into Fe²⁺ (Eq. 3) (Sirés et al. 2007).



216

217 This regeneration reaction permits the continuous production of •OH radicals through Fenton
218 reaction (Eq. 4) implemented in the so-called homogeneous electro-Fenton process when Fe²⁺
219 is dissolved or present initially in solution (Brillas et al. 2009; Mousset et al. 2016b):



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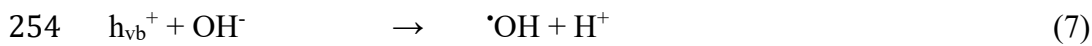
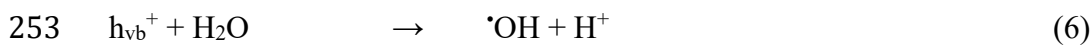
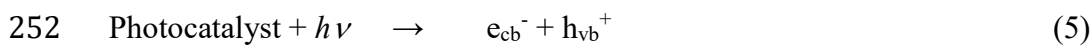
222 Heterogeneous electro-Fenton processes that involve a source of iron, e.g. FeS₂ and Fe₃O₄,
223 coated on the cathode material are emerging (Ganiyu et al. 2018). It avoids the pH adjustment
224 to 3 unlike in homogeneous Fenton-based technology in which the dissolved Fe³⁺ would
225 precipitate in Fe(OH)₃ otherwise. Sacrificial iron or steel anode materials have been widely
226 employed as an alternative source of Fe²⁺ in peroxi-coagulation process (Brillas et al. 1997,
227 2003; Ren et al. 2018; Nidheesh 2018). Peroxi-coagulation consists of the combination of
228 electro-Fenton that electro-generate H₂O₂ at cathode and electro-coagulation to produce Fe²⁺
229 by anodic dissolution.

230 Gas diffusion electrodes using carbon-polytetrafluoroethylene have been also suggested as
231 carbon-based cathode material (Brillas et al. 2009). The O₂ flows through the thin and the
232 porous carbon material, which enhances the O₂ transfer towards the cathode and therefore the
233 yield of H₂O₂ electrogeneration (Sirés et al. 2007; Brillas et al. 2009; Martínez-Huitle et al.
234 2015). One drawback of gas diffusion electrodes cathodes is their low specific surface area that
235 limits the rate of Fe²⁺ regeneration as compared to three dimensional carbon-based materials
236 (Sirés et al. 2007). Some efforts have been made to enhance the specific surface area of carbon
237 materials, including thermal treatment (Le et al. 2016), chemical treatment (Zhou et al. 2014)
238 and graphene-doped modifications (Garcia-Rodriguez et al., 2018; Le et al., 2015a, 2015b;
239 Mousset et al., 2017b, 2016c), with encouraging results for both H₂O₂ electrogeneration and
240 Fe²⁺ regeneration.

241

2.2. Selection of photocatalyst for photocatalytic oxidation

Photocatalysis has been widely developed the last few decades as an alternative to traditional chemical advanced oxidation processes, by benefitting from the light to produce strong oxidizing agents like $\cdot\text{OH}$ radicals using a catalyst (Fujishima et al. 2000; Malato et al. 2009; Lazar et al. 2012; Pelaez et al. 2012; Schneider et al. 2014). This photocatalyst is a semiconductor that possess an energy gap region known as bandgap. Photocatalyst excitation with energy higher (i.e., light irradiation at a specific wavelength) than the bandgap promotes an excited electron into the conduction band (e_{cb}^-) leaving behind a positive vacancy namely as a hole (h_{vb}^+) (Eq. 5) that can then oxidize water (H_2O) (Eq. 6) or hydroxide ion (OH^-) (Eq. 7) to produce $\cdot\text{OH}$ radicals.



Among the numerous photocatalysts that have been tested in literature, titanium dioxide (TiO_2) is the most common material employed. The band gap for its anatase crystal phase is 3.2 eV, meaning that ultraviolet - noted UV in this chapter - radiation bellow 387 nm is required to initiate photocatalysis process. These UV-based photocatalysis are energy-consuming processes. Thus, numerous efforts have been devoted to benefit from the use of free solar light that is composed of 40% of visible light, in wavelength ranging from 400 nm to 800 nm. In this context, several visible light active photocatalysts have been proposed in literature with reduced band gap, including modified TiO_2 (Pelaez et al. 2012; Ding et al. 2012, 2014; Andersen et al. 2014; Barndök et al. 2016; Fagan et al. 2016).

The photocatalysis can be implemented through two ways, either the photocatalyst is in suspension in the effluent to be treated or it is immobilized on a substrate. The first version allows for a higher surface of contact between the catalyst and the photons per unit volume, which can increase the quantum yield (Stefan 2017). However, a further separation stage is required in the treatment since the catalyst has to be recovered before the release of treated wastewater. Therefore, a preliminary catalyst immobilisation step is alternatively considered (Stefan 2017). The catalyst support is then another parameter to take into account for a good coating stability. A further advantage is that conductive substrate could bring synergy when combining electrochemical treatment with heterogeneous photocatalysis as discussed in section 2.3.

275

276 **2.3. Selection of the catalyst support for electrocatalytic and photocatalytic** 277 **oxidation combination**

278 According to the following criteria, different processes can be implemented or not, i.e.
279 electrochemical treatments or not, and/or photochemical processes or not, and/or photo-
280 electrochemical combinations (Table 1):

- 281 (1) presence or not of electrode, involvement or not of high overvoltage electrode
282 (2) presence of light or not, presence of photocatalyst or not, presence of photocatalyst
283 on electrode or not

284 **Table 1.** Implementation of electrolysis, photochemical processes and possible combinations between
285 electrolysis and photochemistry, depending on criteria involved. According to the kind of
286 combination, the processes implemented can vary from a simple photolysis or electro-oxidation to a
287 more complex system combining electrochemical advanced oxidation processes with
288 photoelectrocatalysis.
289

	Absence of light	Light without catalyst	Light with photocatalyst not coated on electrode	Light with photocatalyst coated on electrode
Absence of electrode	∅	Photolysis	Photocatalysis	∅
Absence of high overvoltage electrode	Electro-oxidation	Electro-oxidation/ photolysis	Electro-oxidation/ photocatalysis	Photoelectrocatalysis
High overvoltage electrode	Electro-chemical advanced oxidation processes	Electrochemical advanced oxidation processes/ photolysis	Electrochemical advanced oxidation processes/ photocatalysis	Electrochemical advanced oxidation processes/ photoelectrocatalysis

290

291 The possible combinations highlight a possible increase of electrocatalytic activity
292 accompanying by a possible increase of photocatalytic activity according to the criteria
293 involved. The increase of catalytic activity leads to higher number of $\cdot\text{OH}$ production sites as it
294 has been previously proposed in literature (Brillas et al., 2009; Goldstein et al., 2007; Luo et
295 al., 2015; Mousset et al., 2017a; Sun and Pignatello, 1993), which is summarized in Table 2
296 and displayed in Figure 2.

297 As represented in Table 2 and Figure 2, the electro-oxidation process does not bring any source
298 of $\cdot\text{OH}$ production, since only direct oxidation occurs. When electro-oxidation is combined to

299 photolysis (electro-oxidation/photolysis), there is no $\cdot\text{OH}$ production as well, since only
300 photosensitive pollutants are degraded by photolysis. In electro-oxidation/photocatalysis the
301 $\cdot\text{OH}$ production site is coming from the photocatalysis itself as explained in sub-section 2.2.
302 Similarly, photoelectrocatalysis lead to the generation of one $\cdot\text{OH}$ site. Still, a difference of
303 oxidation efficiency can be observed between photocatalysis and photoelectrocatalysis
304 processes. An important waste reaction occurs during the photocatalysis mechanism, which
305 consists on the electron/hole pair recombination (Eq. 8) (Schneider et al. 2014):

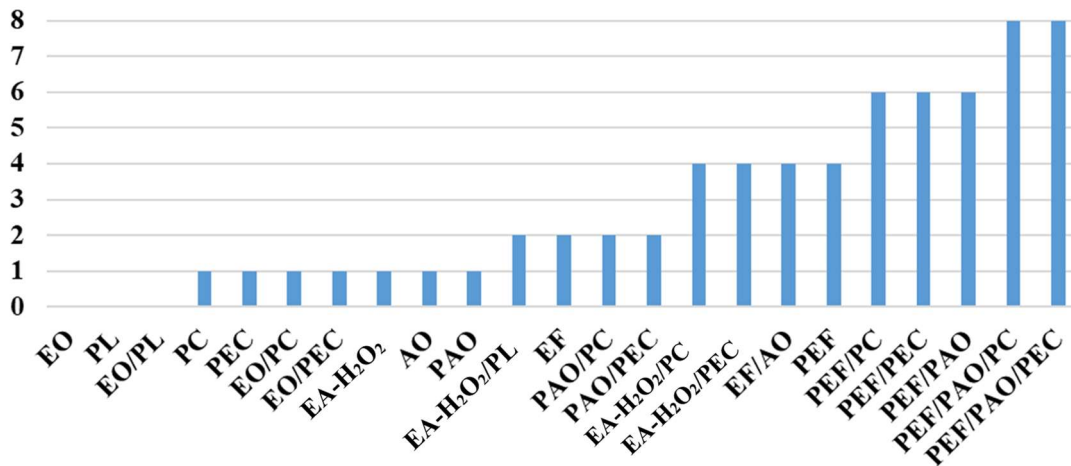


307

308
309 **Table 2.** Number of $\cdot\text{OH}$ production sites according to the kind of combination between electrolysis
310 and photochemical processes. There is no $\cdot\text{OH}$ production in electro-oxidation system combined with
311 photolysis. Implementing photocatalysis or photoelectrocatalysis results in increasing the number of
312 $\cdot\text{OH}$ production site by one. The number of $\cdot\text{OH}$ production site drastically increases when
313 electrochemical advanced oxidation processes such as anodic oxidation and/or electro-Fenton are
314 involved. Their combination with photolysis or photocatalysis/photoelectrocatalysis increases even
315 higher the number of $\cdot\text{OH}$ production site due to synergy. Abbreviations: AO: anodic oxidation, EA-
316 H_2O_2 : H_2O_2 electro-activation, EO: electro-oxidation, $\text{H}_2\text{O}_2\text{-O}_2^{\cdot-}$: H_2O_2 reaction with $\text{O}_2^{\cdot-}$, PL:
317 photolysis, PC: photocatalysis, PEC: photoelectrocatalysis.

Electrochemical process	Photochemical process		
	Photolysis (0 × $\cdot\text{OH}$)	Photocatalysis (1 × $\cdot\text{OH}$)	Photoelectrocatalysis (1 × $\cdot\text{OH}$)
Electro-oxidation (0 × $\cdot\text{OH}$)	$(0 \times \cdot\text{OH})_{\text{PL}}$ + $(0 \times \cdot\text{OH})_{\text{EO}}$ = 0 × $\cdot\text{OH}$	$(1 \times \cdot\text{OH})_{\text{PC}}$ + $(0 \times \cdot\text{OH})_{\text{EO}}$ = 1 × $\cdot\text{OH}$	$(1 \times \cdot\text{OH})_{\text{PC}}$ + $(0 \times \cdot\text{OH})_{\text{EO}}$ = 1 × $\cdot\text{OH}$
H_2O_2 electro-activation (1 × $\cdot\text{OH}$)	$(0 \times \cdot\text{OH})_{\text{PL}}$ + $(1 \times \cdot\text{OH})_{\text{EA-H}_2\text{O}_2}$ + $(1 \times \cdot\text{OH})_{\text{synergyPL/EA-H}_2\text{O}_2}$ = 2 × $\cdot\text{OH}$	$(1 \times \cdot\text{OH})_{\text{PC}}$ + $(1 \times \cdot\text{OH})_{\text{EA-H}_2\text{O}_2}$ + $(1 \times \cdot\text{OH})_{\text{synergyPL/EA-H}_2\text{O}_2}$ + $(1 \times \cdot\text{OH})_{\text{H}_2\text{O}_2\text{-O}_2^{\cdot-}}$ = 4 × $\cdot\text{OH}$	$(1 \times \cdot\text{OH})_{\text{PC}}$ + $(1 \times \cdot\text{OH})_{\text{EA-H}_2\text{O}_2}$ + $(1 \times \cdot\text{OH})_{\text{synergyPL/EA-H}_2\text{O}_2}$ + $(1 \times \cdot\text{OH})_{\text{H}_2\text{O}_2\text{-O}_2^{\cdot-}}$ = 4 × $\cdot\text{OH}$
Anodic oxidation (1 × $\cdot\text{OH}$)	$(0 \times \cdot\text{OH})_{\text{PL}}$ + $(1 \times \cdot\text{OH})_{\text{AO}}$ = 1 × $\cdot\text{OH}$	$(1 \times \cdot\text{OH})_{\text{PC}}$ + $(1 \times \cdot\text{OH})_{\text{AO}}$ = 2 × $\cdot\text{OH}$	$(1 \times \cdot\text{OH})_{\text{PC}}$ + $(1 \times \cdot\text{OH})_{\text{AO}}$ = 2 × $\cdot\text{OH}$
Electro-Fenton (2 × $\cdot\text{OH}$)	$(0 \times \cdot\text{OH})_{\text{PL}}$ + $(1 \times \cdot\text{OH})_{\text{EF}}$ + $(1 \times \cdot\text{OH})_{\text{EA-H}_2\text{O}_2}$ + $(1 \times \cdot\text{OH})_{\text{synergyPL/EA-H}_2\text{O}_2}$ + $(1 \times \cdot\text{OH})_{\text{synergyPL/EF}}$ = 4 × $\cdot\text{OH}$	$(1 \times \cdot\text{OH})_{\text{PC}}$ + $(1 \times \cdot\text{OH})_{\text{EF}}$ + $(1 \times \cdot\text{OH})_{\text{EA-H}_2\text{O}_2}$ + $(1 \times \cdot\text{OH})_{\text{synergyPL/EA-H}_2\text{O}_2}$ + $(1 \times \cdot\text{OH})_{\text{synergyPL/EF}}$ + $(1 \times \cdot\text{OH})_{\text{H}_2\text{O}_2\text{-O}_2^{\cdot-}}$ = 6 × $\cdot\text{OH}$	$(1 \times \cdot\text{OH})_{\text{PC}}$ + $(1 \times \cdot\text{OH})_{\text{EF}}$ + $(1 \times \cdot\text{OH})_{\text{EA-H}_2\text{O}_2}$ + $(1 \times \cdot\text{OH})_{\text{synergyPL/EA-H}_2\text{O}_2}$ + $(1 \times \cdot\text{OH})_{\text{synergyPL/EF}}$ + $(1 \times \cdot\text{OH})_{\text{H}_2\text{O}_2\text{-O}_2^{\cdot-}}$ = 6 × $\cdot\text{OH}$
Electro-Fenton/anodic oxidation (4 × $\cdot\text{OH}$)	$(0 \times \cdot\text{OH})_{\text{PL}}$ + $(1 \times \cdot\text{OH})_{\text{EF}}$ + $(1 \times \cdot\text{OH})_{\text{AO}}$ + $(1 \times \cdot\text{OH})_{\text{EA-H}_2\text{O}_2}$ + $(1 \times \cdot\text{OH})_{\text{synergyEF/AO-peroxone}}$ + $(1 \times \cdot\text{OH})_{\text{synergyPL/EA-H}_2\text{O}_2}$ + $(1 \times \cdot\text{OH})_{\text{synergyPL/EF}}$ = 6 × $\cdot\text{OH}$	$(1 \times \cdot\text{OH})_{\text{PC}}$ + $(1 \times \cdot\text{OH})_{\text{EF}}$ + $(1 \times \cdot\text{OH})_{\text{AO}}$ + $(1 \times \cdot\text{OH})_{\text{EA-H}_2\text{O}_2}$ + $(1 \times \cdot\text{OH})_{\text{synergyEF/AO-peroxone}}$ + $(1 \times \cdot\text{OH})_{\text{synergyPL/EA-H}_2\text{O}_2}$ + $(1 \times \cdot\text{OH})_{\text{synergyPL/EF}}$ + $(1 \times \cdot\text{OH})_{\text{H}_2\text{O}_2\text{-O}_2^{\cdot-}}$ = 8 × $\cdot\text{OH}$	$(1 \times \cdot\text{OH})_{\text{PC}}$ + $(1 \times \cdot\text{OH})_{\text{EF}}$ + $(1 \times \cdot\text{OH})_{\text{AO}}$ + $(1 \times \cdot\text{OH})_{\text{EA-H}_2\text{O}_2}$ + $(1 \times \cdot\text{OH})_{\text{synergyPL/EA-H}_2\text{O}_2}$ + $(1 \times \cdot\text{OH})_{\text{synergyPL/EF}}$ + $(1 \times \cdot\text{OH})_{\text{synergyEF/AO-peroxone}}$ + $(1 \times \cdot\text{OH})_{\text{H}_2\text{O}_2\text{-O}_2^{\cdot-}}$ = 8 × $\cdot\text{OH}$

**Number of $\cdot\text{OH}$
active sites**



319

320 **Figure 2.** Number of $\cdot\text{OH}$ active sites according to the single and combined processes implemented.

321 The combination giving the maximum number of $\cdot\text{OH}$ production site, i.e. eight production sites, is
322 photoelectro-Fenton with photoanodic oxidation and photocatalysis or photoelectrocatalysis.

323 Abbreviations: AO: anodic oxidation, EA-H₂O₂: H₂O₂ electro-activation, EO: electro-oxidation, PAO:

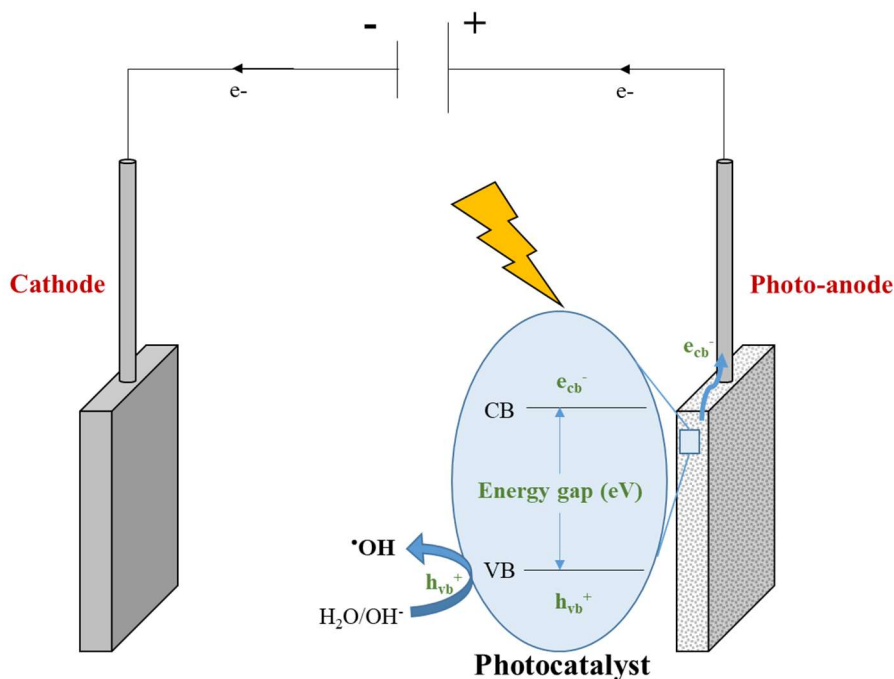
324 photoanodic oxidation, PC: photocatalysis, PEC: photoelectrocatalysis, PEF: photoelectro-Fenton, PL:

325 photolysis.

326

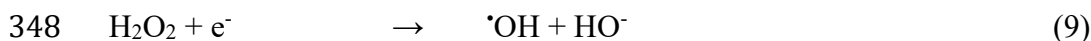
327 In photoelectrocatalysis, the photocatalyst is coated on a conductive material that can be used
328 as an electrode in the electrolysis process (Catanho et al. 2006; Esquivel et al. 2009; Liu et al.
329 2009; Ding et al. 2012; Daskalaki et al. 2013; Garcia-Segura et al. 2013; Zhai et al. 2013;
330 Ramirez et al. 2015; Bessegato et al. 2015). This configuration has the advantage to reduce the
331 charge recombination (Zhai et al. 2013; Bessegato et al. 2015), as depicted in Figure 3. This
332 enhances the degradation and mineralisation efficiency as demonstrated previously by Ding et
333 al. (2012) who noticed a 2.5 times increase of degradation rate with photoelectrocatalysis-based
334 process as compared to photocatalysis technology. This synergistic effect can be ascribed to the
335 transfer of photo-electrons to the cathode that enhance the electro-generation of H₂O₂ for
336 electro-Fenton process while limiting the charge recombination in photocatalysis mechanism
337 (Ding et al. 2012).

338



339
 340 **Figure 3.** Photoelectrocatalysis process combining the electrolysis with a photo-anode. The advantage
 341 of this system compared to photocatalysis is that it limits the charge recombination, i.e. e_{cb}^- and h_{vb}^+ ,
 342 since the electron (e_{cb}^-) is driven to the cathode. Abbreviations: CB: conductive band, e_{cb}^- : electron in
 343 the conduction band, h_{vb}^+ : positive vacancy (hole) in the valence band, VB: valence band.

344
 345 In the presence of the cathodic generation of H_2O_2 , it has recently been demonstrated that $\cdot OH$
 346 radicals could be formed through electro-activation of H_2O_2 with one electron (Eq. 9) (Luo et
 347 al. 2015):

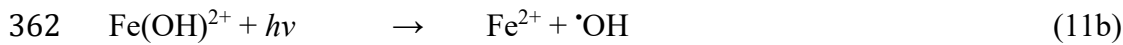


349
 350 When H_2O_2 electro-activation is combined with photocatalysis or photoelectrocatalysis, a
 351 synergy could be observed with the H_2O_2 photolysis under UVC irradiation ($\lambda < 280$ nm) by
 352 homolytic cleavage giving another source of $\cdot OH$ (Eq. 10) (Goldstein et al. 2007):



354
 355 Anodic oxidation process combined with photolysis – referred as photoanodic oxidation in this
 356 chapter – cannot bring another production site of $\cdot OH$ (Table 2). Interestingly, electro-Fenton
 357 can bring synergy in electro-Fenton/photolysis combination, namely photoelectro-Fenton
 358 process, through the UV irradiation of Fe(III)-monohydroxy complex ($Fe(OH)^{2+}$) that

359 represents an additional $\cdot\text{OH}$ production source (Eqs. 11a-11b) (Sun and Pignatello 1993;
360 Brillas et al. 2009):

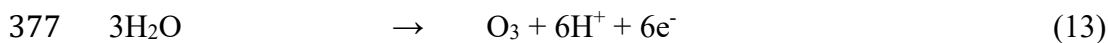


363

364 $\text{Fe}(\text{OH})^{2+}$ is the predominant Fe(III) species at pH around 3 (Faust and Hoigné 1990), which
365 corresponds to the optimal pH for electro-Fenton process (Brillas et al. 2009; Mousset et al.
366 2016e). Therefore, the production rate of $\text{Fe}(\text{OH})^{2+}$ is not negligible and indirectly the $\cdot\text{OH}$
367 production as well. In addition, the UV light allow the regeneration of Fe^{2+} in the meanwhile
368 from Eq. 11b.

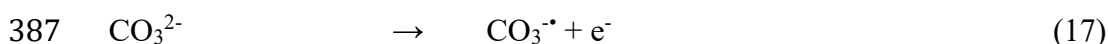
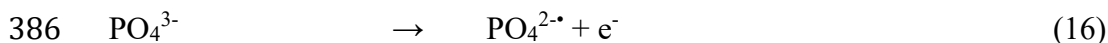
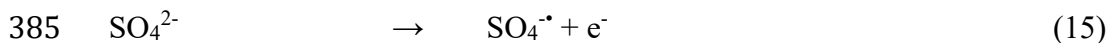
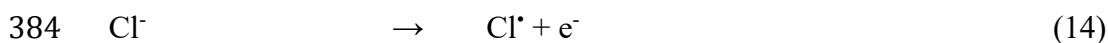
369

370 It is critical to underline that $\cdot\text{OH}$ is not the sole oxidant that can participate in the organic
371 removal efficiency. Mediated oxidation can also occur during the photoelectrochemical
372 processes, by the production of weaker oxidants such as some reactive oxygen species like
373 superoxide anion ($\text{O}_2^{\cdot-}$) (Eq. 12) in photocatalysis and photoelectrocatalysis processes and
374 ozone (O_3) (Eq. 13) with non-active anodes in anodic oxidation technology (Bergmann et al.
375 2009; dos Santos and Scialdone 2018):



378

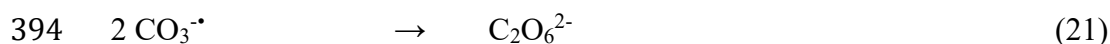
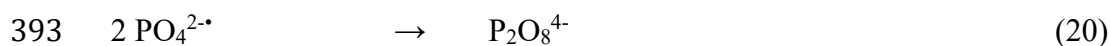
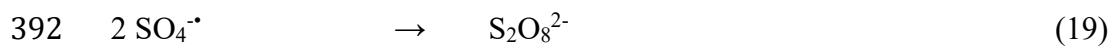
379 Furthermore, depending on the characteristic of the effluent to treat and/or on the supporting
380 electrolyte that is potentially added, the presence of chloride ion (Cl^-), sulfate ion (SO_4^{2-}),
381 phosphate ion (PO_4^{3-}), and carbonate ion (CO_3^{2-}) can lead to the formation of radical species
382 such as Cl^{\cdot} (Eq. 14), $\text{SO}_4^{\cdot-}$ (Eq. 15), $\text{PO}_4^{2\cdot-}$ (Eq. 16), $\text{CO}_3^{\cdot-}$ (Eq. 17), respectively (Sirés et al.
383 2014):



388

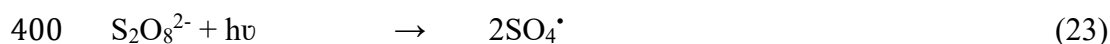
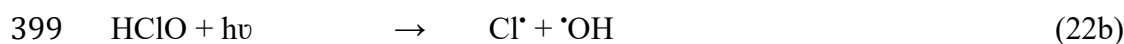
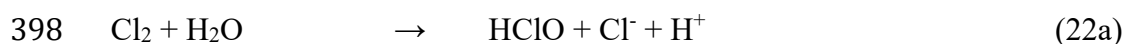
389 More stable oxidants can be generated from these radical species (Cl_2 (Eq. 18), $\text{S}_2\text{O}_8^{2-}$ (Eq. 19),
390 $\text{P}_2\text{O}_8^{4-}$ (Eq. 20), $\text{C}_2\text{O}_6^{2-}$ (Eq. 21)) (Moreira et al. 2017):





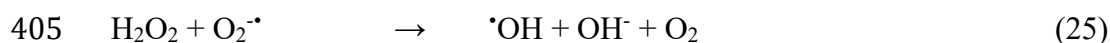
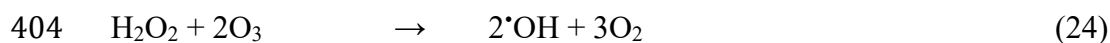
395

396 Under light irradiation, Cl_2 and $\text{S}_2\text{O}_8^{2-}$ can generate Cl^{\cdot} (Eqs. 22a-22b) and $\text{SO}_4^{\cdot-}$ (Eq. 23),
 397 respectively (dos Santos and Scialdone 2018):



401

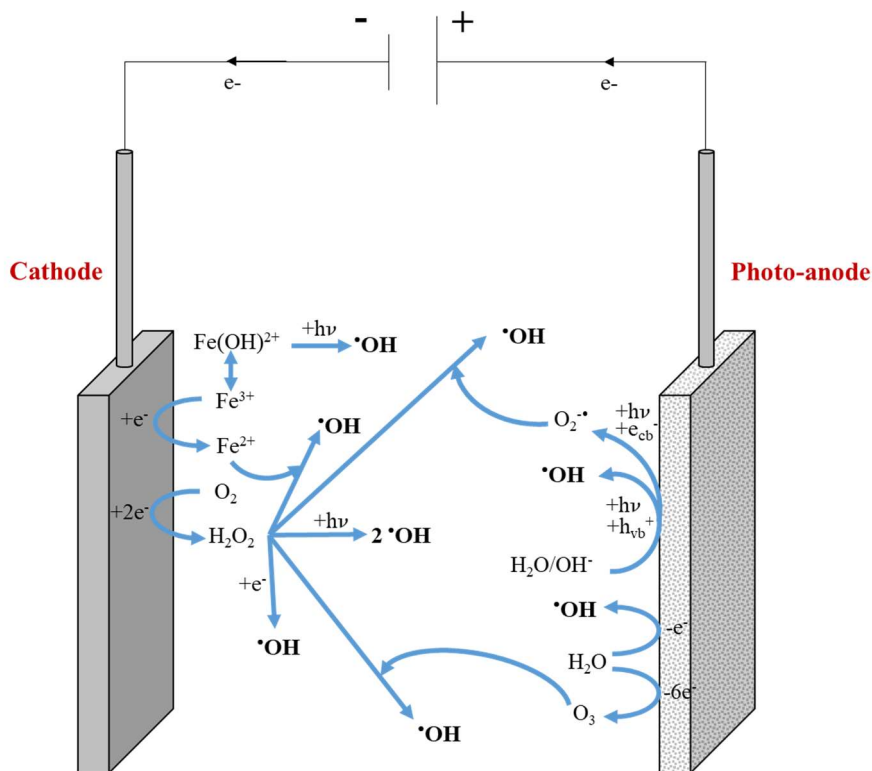
402 This mediated oxidation can also lead to additional production source of $\cdot\text{OH}$ through peroxone
 403 equation (Eq. 24) and H_2O_2 reaction with $\text{O}_2^{\cdot-}$ (Eq. 25) (Brillas et al. 2009; Merényi et al. 2010):



406

407 However, mediated oxidants such as chlorinated ones can lead to toxic inorganic, e.g. chlorate
 408 (ClO_3^-) and perchlorate (ClO_4^-), and organic intermediates such as trihalomethanes (THMs) and
 409 chloroform that accumulate in solution (Araújo et al. 2015; Brito et al. 2015; Mousset et al.
 410 2018b, 2020). It is therefore important to control their concentration and to adapt the operating
 411 conditions in order to limit their formation.

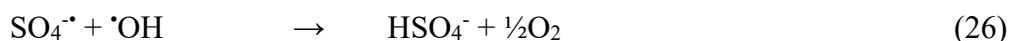
412 Interestingly, the combination that could give theoretically the highest number of $\cdot\text{OH}$
 413 production sites, i.e. 8 production sites, is photoelectro-Fenton with photoanodic oxidation and
 414 photocatalysis or photoelectrocatalysis, i.e. photoelectro-Fenton/photoanodic
 415 oxidation/photocatalysis or photoelectro-Fenton/photoanodic oxidation/photoelectrocatalysis
 416 respectively (Mousset et al. 2017a), as schematically presented in Figure 4.

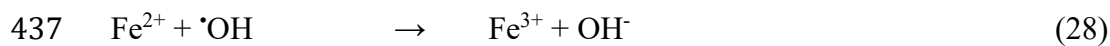


417
 418 **Figure 4.** Different $\cdot\text{OH}$ production sites in the photoelectro-Fenton/photoanodic
 419 oxidation/photoelectrocatalysis process combining electrochemical advanced oxidation processes with
 420 photoelectrocatalysis. There is a maximum of eight $\cdot\text{OH}$ production sites from eight different reactions
 421 involved at the photo-anode, at the cathode and in the bulk solution. It is important to highlight that
 422 the occurrence of these reactions is depending on the solution pH, the applied wavelength, and the
 423 production rate of reagent such as H_2O_2 involved in parallel reactions.

424
 425 It is important to emphasize the fact that a higher number of $\cdot\text{OH}$ production sites does not
 426 systematically mean that the oxidation efficiency will be better. There can be kinetic
 427 competitions with reactions requiring the same reagents to produce $\cdot\text{OH}$ radicals. For instance,
 428 H_2O_2 is involved in Fenton reaction (Eq. 4) but also in H_2O_2 electro-activation (Eq. 9), in H_2O_2
 429 photolysis (Eq. 10), in peroxone equation (Eq. 24) and in reaction with $\text{O}_2\cdot^-$ (Eq. 25), meaning
 430 that the $\cdot\text{OH}$ production yield will not be automatically increased through five production sites
 431 instead of one at constant electrogeneration of H_2O_2 , the rate of H_2O_2 production being the
 432 limiting step (Mousset et al. 2017a).

433 Moreover, some side reactions that consume $\cdot\text{OH}$ can limit its action (dos Santos and Scialdone
 434 2018):





438

439 The reaction between Fe^{2+} and $\cdot\text{OH}$ (Eq. 28) is particularly an important parasitic reactions in
440 Fenton-based processes (Brillas et al. 2009; Mousset et al. 2016a). In addition, the solution pH
441 can interfere in the number of $\cdot\text{OH}$ production sites since the Fenton reaction is optimal at pH
442 3 in homogeneous systems (Brillas et al. 2009). In contrast, $\text{O}_2\cdot^-$ species is predominant at pH
443 higher than 6.8, considering a pKa ($\text{HO}_2\cdot/\text{O}_2\cdot^-$) equal to 4.8, and therefore the generation of $\cdot\text{OH}$
444 through Eq. 25 is optimal at circumneutral pH (Mousset et al. 2018a). Implementing
445 heterogeneous electro-Fenton process in combination to photoelectrocatalysis could solve this
446 issue. The wavelength range of light irradiation also plays a role in the number of $\cdot\text{OH}$
447 production sites. Thus, H_2O_2 photolysis mainly occurs under UVC irradiation ($\lambda < 280$ nm),
448 while photocatalysis and photoelectrocatalysis are often performed using UVA (315 nm $< \lambda <$
449 400 nm) and even visible light irradiation (400 nm $< \lambda < 800$ nm). It should be emphasized that
450 the synergy of combinations between H_2O_2 photolysis and photocatalysis or
451 photoelectrocatalysis, i.e. in H_2O_2 electro-activation/photocatalysis, H_2O_2 electro-
452 activation/photoelectrocatalysis, photoelectro-Fenton/photocatalysis, photoelectro-
453 Fenton/photoelectrocatalysis, photoelectro-Fenton/photoanodic oxidation/photocatalysis,
454 photoelectro-Fenton/photoanodic oxidation/photoelectrocatalysis, cannot occur if the
455 photocatalyst does not absorb light under UVC irradiation and/or for economic reason if the
456 system is operated under solar light. The organic load has an impact on the kinetics of
457 degradation rates but should not hamper the number of $\cdot\text{OH}$ production sites (Garcia-Segura et
458 al. 2014). This is the case only if the turbidity is not impacted by the increase of organic load,
459 otherwise the yields of UV-based reactions will be altered.

460

461

462 The combination of processes along with possible synergy can be optimized via reactor design
463 that need to be adapted according to the reactions involved as discussed in section 3.

464

465 **3. Reactor design**

466 The reactor design is an important parameter to take into account in order to optimize the photo-
467 electrochemical technologies. The existing combinations between electrolysis and

468 photocatalysis or photoelectrocatalysis technologies proposed in literature for wastewater
469 treatment application are presented in Table 3. The influence of criteria studied in literature
470 about the photo-electrochemical reactor design is presented in the following sub-sections 3.2,
471 3.3 and 3.4.
472

Table 3. Processes combination between electrolysis and photocatalysis or photoelectrocatalysis processes proposed in literature for wastewater treatment application. Different reactor designs have been proposed: sequential or hybrid reactors, divided or undivided cells, flow-cell or stirred tank reactor, external or immersed light source, light source positioned on the top or bottom or on the side of reactor, light source placed vertically or horizontally.

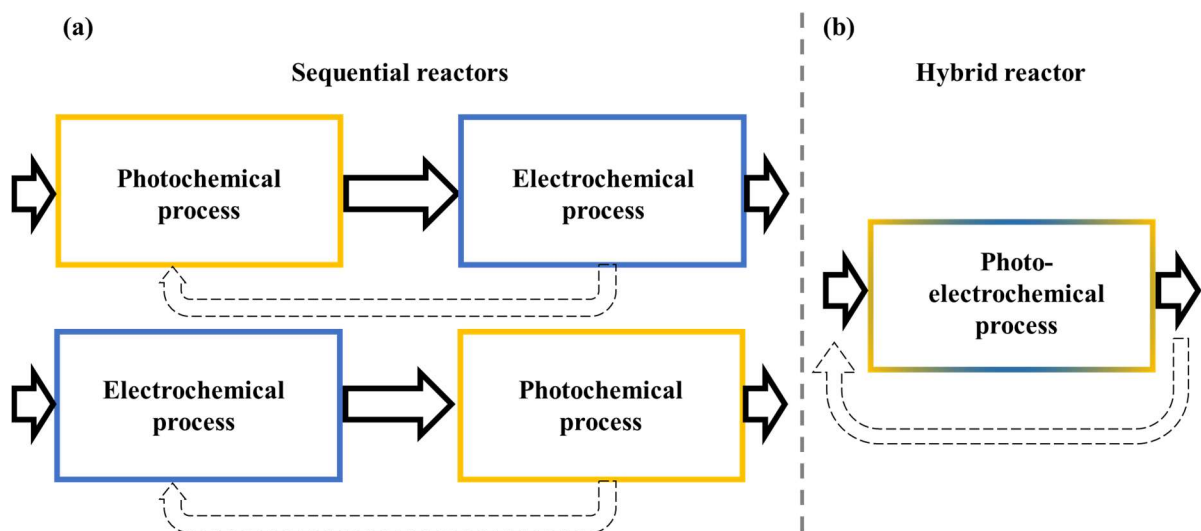
Processes implemented	Reactor configuration	Cathode	Anode	Electrode positioning	Photocatalyst	Kind of light	Light source positioning	Reference
Photoelectro-Fenton/photocatalysis	Undivided cell Cylindrical stirred tank photo-reactor	Boron-doped diamond	Boron-doped diamond	Both parallel and vertical	TiO ₂ immobilized on glass spheres and horizontal nylon mesh	Solar light	Externally, on the top of the reactor	(Garza-Campos et al. 2014)
Photoelectro-Fenton/photocatalysis	Undivided cell Electrochemical flow-cell Sequential reactors (electrolyser→photoreactors) in recirculation	Carbon-polytetrafluoroethylene air diffusion cathode	Pt	Both parallel and vertical	TiO ₂ immobilized on glass spheres	Solar light	Externally, on the top of the reactor	(Garza-Campos et al. 2016)
Photoelectro-Fenton/photocatalysis	Undivided cell Parallelepiped stirred tank photo-reactor	Graphite/Carbon nanotubes	Pt	Both parallel and vertical	TiO ₂ immobilized on glass plates on vertical sides of the reactor	UV light	Immersed vertically in the reactor	(Khataee et al. 2012)
Photoelectro-Fenton/photoanodic oxidation/photocatalysis	Undivided cell Cylindrical glass stirred tank photo-reactor	Carbon felt	Glass/fluorine-doped tin oxide (transparent)	Both parallel and vertical	TiO ₂ immobilized on cylindrical glass reactor	UV light	Externally, on the side of the reactor, close to the cathode	(Mousset et al. 2017a)
Photoelectrocatalysis	Undivided cell Cylindrical stirred tank photo-reactor	Ti/Ru	Boron-doped TiO ₂ nanotubes	Both parallel and vertical	TiO ₂	UV/Visible light	Immersed vertically in the reactor	(Bessegato et al. 2015)
Photoelectrocatalysis	Undivided cell Cylindrical quartz stirred tank photo-reactor	Pt	Carbon cloth/reduced graphene oxide/TiO ₂	Both parallel and vertical	TiO ₂	Visible light	Not specified	(Zhai et al. 2013)
Photoelectrocatalysis	Undivided cell Cylindrical stirred tank photo-reactor	Boron-doped diamond	Indium tin oxide/TiO ₂	Anode: horizontal	TiO ₂	Solar light	Externally, on the top of the reactor	(Daskalaki et al. 2013)

				(at the bottom) Cathode: vertical				
Photoelectrocatalysis	Undivided cell Cylindrical stirred tank photo-reactor	Carbon-polytetrafluoroethylene air diffusion cathode	Stainless steel/TiO ₂	Anode: oblique Cathode: vertical	TiO ₂	Solar light	Externally, on the top of the reactor	(Garcia-Segura et al. 2013)
Photoelectrocatalysis	Undivided cell Photo-electrochemical flow-cell	Ti mesh on a quartz plate (transparent)	Ti/Ru _{0.3} Ti _{0.7} O ₂	Both parallel and vertical	Ti _{0.7} O ₂	UV light	Externally, on the side of the reactor, close to the cathode	(Catanho et al. 2006)
Photoelectro-Fenton/ photoelectrocatalysis	Undivided cell Cylindrical quartz stirred tank photo-reactor	Reticulated vitreous carbon	Ti/TiO ₂	Anode: horizontal (at the bottom) Cathode: vertical	TiO ₂	UV/Visible light	Externally, at the bottom of the reactor	(Xie and Li 2006)
Photoelectro-Fenton/ photoelectrocatalysis	Divided cell Cylindrical quartz stirred tank photo-reactors	Carbon felt	Ti/TiO ₂	Both parallel and vertical	TiO ₂	UV light	Externally, on the side of the anodic compartment	(Ramirez et al. 2015)
Photoelectro-Fenton/ photoelectrocatalysis	Divided cell Cylindrical glass stirred tank photo-reactor	Carbon cloth	Antimony-doped tin oxide/Optical fibre/TiO ₂ (transparent)	Both parallel and vertical	TiO ₂	UV light	Immersed vertically in the reactor	(Esquivel et al. 2009)
Photoelectro-Fenton/photoanodic oxidation/ photoelectrocatalysis	Undivided cell semi-cylindrical quartz stirred tank photo-reactor	Activated carbon fibre/Fe@Fe ₂ O ₃	Glass/fluorine-doped tin oxide/Bi ₂ WO ₆ (transparent)	Both parallel and vertical; anode close to the flat side of the reactor	Bi ₂ WO ₆ (visible light active)	Visible light	Externally, on the flat side of the reactor	(Ding et al. 2012)

453

454 3.1. Sequential versus hybrid reactors

455 There are two possibilities to consider the combination between photochemical and
456 electrochemical processes combination. The first one is a configuration as sequential reactors
457 with a possibility of recirculation of the effluent (Figure 5a). The photochemical process can be
458 either positioned as primary treatment followed by the electrochemical process or in the reverse
459 order. If a continuous system is considered without recirculation, the electrochemical
460 technology has advantages to be placed first because the stable oxidizing species such as H_2O_2
461 formed by the electrode materials can then be photolysed in the photo process and produce $\cdot OH$
462 radicals (Garcia-Segura and Brillas 2014; Garza-Campos et al. 2016). In the same way, the
463 ferro-hydroxy complex formed in the electrolyser can also be photolysed in the subsequent
464 photo-reactor (Garcia-Segura and Brillas 2014; Garza-Campos et al. 2016).
465



466

467 **Figure 5.** Sequential (a) versus hybrid (b) reactors for photochemical and electrochemical processes
468 combination. In a continuous system an electrochemical process followed by a photochemical
469 technology has the advantage to produce $\cdot OH$ from the photolysis of some species such as H_2O_2 and
470 ferro-hydroxy complex produced by electrolysis. A hybrid photo-electrochemical process leads to less
471 footprint area and higher possibility of synergy between photochemical and electrochemical reactions.
472

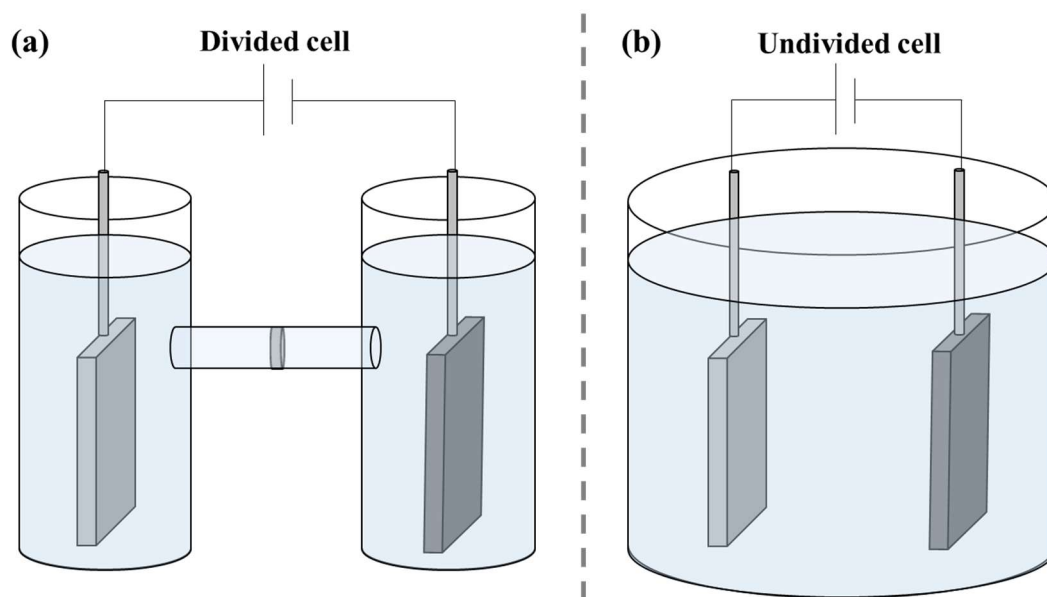
473 In contrast, the hybrid photo-electrochemical process (Figure 5b) offers many other advantages
474 such as the low footprint area, the possibility of synergy between photochemical and
475 electrochemical reactions according to the catalyst support as discussed in section 2.3 and to
476 the hybrid reactor configuration as shown in the following sub-sections 3.2, 3.3 and 3.4. These

477 benefits gained from the hybrid process explain the higher number of studies selecting this
478 configuration (Table 3).

479

480 3.2. Reactor configuration: divided versus undivided cells

481 In electrolysis, there are two possibilities of operation, either in divided cell (Figure 6a) or in
482 undivided cell (Figure 6b). Considering the photo-electrochemical process implementation, the
483 main influence of efficiency comes from the electrochemical reactions. In divided cell, the
484 advantage is that there is the possibility to avoid decomposition of oxidants at anode or cathode
485 which increases the faradic yield (Esquivel et al. 2009; Ramirez et al. 2015). However, some
486 redox reactions cannot be involved in the cell such as ferrous/ferric cycle that is useful for the
487 Fe^{2+} regeneration (Eq. 3) in an electro-Fenton process for example. In contrast, this catalytic
488 behaviour of iron species can be obtained in an undivided cell (Sirés et al. 2007). This latter
489 configuration has been the most studied in photo-electrochemical reactors (Table 3), especially
490 for its easier implementation at industrial scale if a stirred tank reactor is foreseen.



491

492 **Figure 6.** Divided cell (a) versus undivided cell (b) configurations for hybrid photo-electrochemical
493 processes. Divided cell configuration avoids the decomposition of oxidants on the anode or cathode
494 surfaces depending on the species. Practically, undivided cell is more developed and the redox cycle
495 of iron can occur in this condition to implement Fenton reaction.

496

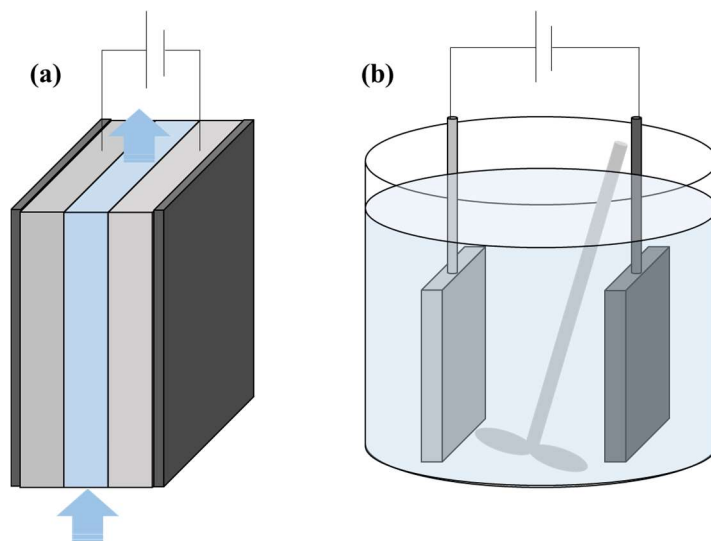
497 **3.3. Operation mode: flow-cell versus stirred tank reactor**

498 There are two main operation modes of photo-electrochemical reactors developed in literature
499 (Figure 7). In the flow cell (Figure 7a), the flux is forced to go between parallel electrodes and
500 the mode can be assimilated to a plug-flow reactor when flushed continuously. Most of the time
501 it is operated in recirculated batch in lab scale studies. In a stirred tank reactor (Figure 7b), the
502 electrodes are placed in parallel in a tank that is mechanically stirred (Ding et al. 2012; Zhai et
503 al. 2013; Garcia-Segura et al. 2014; Bessegato et al. 2015; Mousset et al. 2017a). The effluent
504 can be flushed continuously and can be ascribed to a continuous stirred tank reactor mode when
505 the solution is assumed as perfectly mixed, i.e. the homogeneous concentration in the reactor
506 equal the output stream.

507 A hydrodynamic characterisation has shown that parallel electrodes system in a stirred tank
508 reactor could be modelled as an ideal single continuous stirred tank reactor at high rotational
509 speed of the impeller with impeller Reynolds number higher than 10^4 (Polcaro et al., 2007).
510 The geometry proposed in literature is either parallelepipedal (Khataee et al. 2012) or
511 cylindrical (Ding et al. 2012; Zhai et al. 2013; Garcia-Segura et al. 2014; Bessegato et al. 2015;
512 Mousset et al. 2017a). The latter is the most frequent shape since it limits the stagnant zone in
513 which no mixing occurs. The drawbacks of continuous stirred tank reactor is that the mass
514 transfer rate is lower than in flow cell (Anglada et al. 2010). This is confirmed by the
515 comparison between a cylindrical stirred tank reactor of 0.1 L and a flow-by cell with a reservoir
516 tank of 10 L that was performed by Garcia-Segura et al. (2014). Considering the difference of
517 electrochemical reactor volume in each kind of reactor, the time to reach 50% of
518 chloramphenicol degradation was 26-fold higher in stirred tank reactor than in solar filter-press
519 reactor (Garcia-Segura et al. 2014).

520 Moreover, the electrode distance can be better controlled and easily optimized in flow cells by
521 varying it from a few tens of microns until several centimetres (Scialdone et al. 2010). It leads
522 to better mass transport of targeted compounds towards the electrodes, with mass transport
523 coefficient improved by two to more than ten times (Anglada et al. 2010; Mousset et al. 2019b).
524 A high mass transport is essential to favour heterogeneous catalysis (Mousset et al. 2019a) that
525 is involved at electrode surface in photo-electrochemical processes. Minimized electrode
526 distances also permit the reduction of cell potential and therefore the energy requirement is
527 reduced. The flow cell has also advantage for process scale-up since it can be arranged in series
528 and parallel to increase the removal efficiency and the treatment capacity respectively, while

529 keeping a low footprint compared to continuous stirred tank reactor (Martínez-Huitle et al.
530 2015).



531
532 **Figure 7.** Flow-by cell (a) and stirred tank reactor (b) configurations for hybrid photo-electrochemical
533 processes. The flow-by cell is assimilated to a plug-flow reactor while the stirred tank reactor is
534 associated with the continuous stirred tank reactor model. The flow-by cell increases the mass
535 transfers towards the electrodes compared to the stirred tank reactor, which is an advantage to
536 implement heterogeneous catalysis and photochemical reactions.

537

538 3.4. Light source positioning

539 The light positioning is an important parameter in photochemical processes since the energy
540 delivered by light irradiation decrease with the distance between the light source and the
541 targeted compound in solution. The influence of light irradiation source placed in stirred tank
542 reactor or in flow-cell configurations considering hybrid photo-electrochemical processes is
543 displayed in Figure 8.

544 The light source can be placed externally of the reactor (Figures 8a-8g) and especially at the
545 top of a stirred tank reactor with parallel electrode configuration (Garza-Campos et al. 2014)
546 (Figure 8a) or with one vertical electrode and one horizontal electrode that contain the
547 photocatalyst (Daskalaki et al. 2013) (Figure 8b) in order to improve the contact between the
548 light and photocatalyst. In this latter case, the light can also be shined at the bottom of the stirred
549 tank reactor (Xie and Li 2006) (Figure 8b) through the reactor in order to minimize the distance
550 between the light and the horizontal photo-electrode. It is important to highlight that quartz
551 reactors are preferred instead of glass reactors, since the transmittance of quartz material is very
552 high for a wide range of wavelength, even in UV region (Mousset et al. 2017a).

553 Another possibility is to let shine the light across the side of the stirred tank reactor (Figure 8c)
554 and either enhance the H₂O₂ photolysis by being close to the carbon cathode (Mousset et al.
555 2017a) or improve the photoelectrocatalysis performance using a transparent photo-anode
556 (Mousset et al. 2017a). This latter option has been proposed to be implemented in a semi-
557 cylindrical reactor in which the transparent photo-anode is placed against the flat side (Ding et
558 al. 2012) (Figure 8d) in order to optimize the distance between the light and the photo-anode.
559 This distance is even better optimized in flow-cell systems in which interelectrode distance can
560 be easily reduced as discussed in section 3.3. In this configuration, the light is usually shined
561 through a mesh electrode (Catanho et al. 2006) (Figure 8e) or a transparent electrode (Figure
562 8f) using an external transparent wall.

563 More recently, it has been proposed to make full use of light energy by letting shine the light
564 directly across a transparent anode material (Mousset et al. 2017a) (Figure 8g), named fluorine-
565 doped tin oxide. This customized configuration could be obtained by additive manufacturing,
566 avoiding the use of quartz material that is expensive and fragile. The proposed three
567 dimensional-printed reactor design allowed for 1.87 times increase of efficiency of photo-based
568 processes involved in the reactor as compared to a continuous stirred tank reactor system.
569 Moreover, the use of fluorine-doped tin oxide offers the advantage of being a high O₂
570 overvoltage anode reaching a potential of 2.1 V (Mousset et al. 2017a), which constitutes
571 another source of [•]OH production for electrochemical advanced oxidation processes
572 combination with photocatalysis or photoelectrocatalysis.

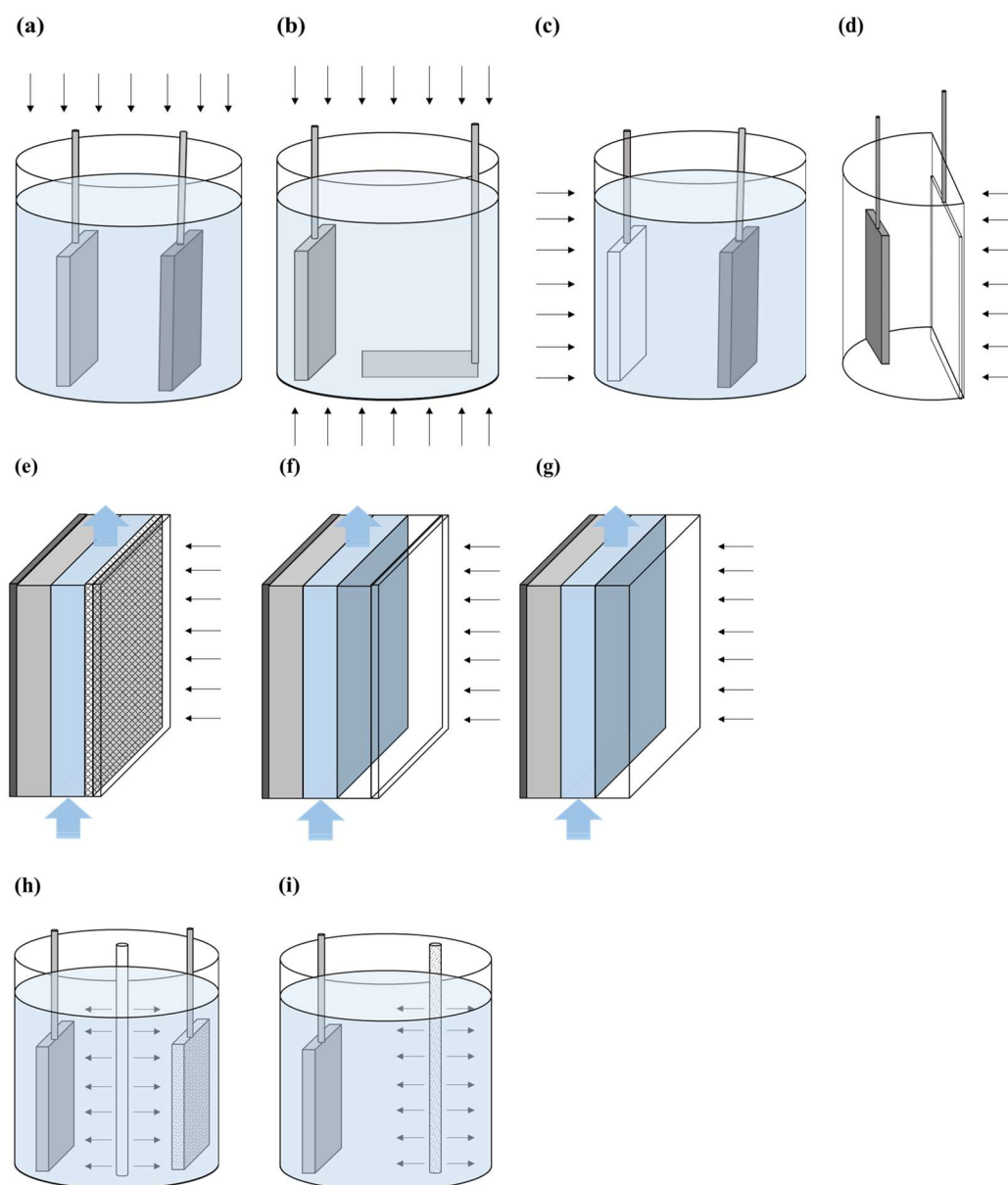
573
574 Immersed light positioning systems have also been considered (Bessegato et al., 2015; Esquivel
575 et al., 2009; Khataee et al., 2012) (Figures 8h, 8i). The source can be placed close to the cathode
576 and the anode in order to favour the photocatalysis mechanism combined with electrolysis
577 (Khataee et al. 2012; Bessegato et al. 2015) (Figure 8h). A second option is to use a source such
578 as optical fibre that is coated with a photocatalyst and employed as a photo-anode connected to
579 a cathode (Esquivel et al. 2009) (Figure 8i). In this latter case, the photoelectrocatalysis is
580 implemented and can be combined to electrochemical advanced oxidation processes
581 technologies for a better pollutant removal efficiency than electrochemical advanced
582 oxidation/photocatalysis processes combination, as discussed in section 2.3.

583 It is necessary to note that when a transparent material is used to involve photocatalysis or
584 photoelectrocatalysis in a light-through electrolytic system, there is an optimal photocatalyst
585 loading. It depends on several factors such as optical properties of the catalyst, e.g. optical

586 thickness and transmittance, and of the transparent substrate material as well as photocatalyst
587 particle size (Hurtado et al., 2015; Motegh et al., 2012; Murakami et al., 2012). For instance, it
588 has been shown that a transmittance of 20%, corresponding to a dose of 0.31 mg cm^{-2} of TiO_2
589 (P-25) coated on a glass/fluorine-doped tin oxide transparent material, was found optimal for a
590 maximum pollutant removal efficiency in a hybrid photo-electrochemical reactor (Mousset et
591 al. 2017a).

592

593 Another important point is that the use of solar light as irradiation source is decisive in the
594 position of electrodes in the reactor and in the reactor design as well. Since the solar light is
595 coming from the top, compound parabolic concentrators oriented towards the sun have been
596 developed to maximize the quantum yield and have been combined with electrolysis cells
597 (Garcia-Segura et al. 2014). Solar light was used as free energy source in photoelectrochemical
598 systems and could successfully reduce the operating costs while keeping very high removal
599 yield as compared to artificial light (El-Ghenymy et al. 2012, 2013; Garcia-Segura and Brillas
600 2014).



601
 602 **Figure 8.** Influence of light irradiation source placed externally of the reactor ((a)-(g)) or immersed
 603 ((h), (i)), in stirred tank reactor ((a)-(d), (h), (i)) and in flow-cell ((e), (f), (g)) configurations
 604 considering hybrid photo-electrochemical processes. If an external source is implemented on the side
 605 or at the bottom of the reactor, the reactor material needs to be suitable for allowing UV radiation to
 606 pass through. Such material is quartz that is very fragile and expensive. When the light is implemented
 607 in a stirred tank reactor, the distance between the light source and the electrode needs to be minimized
 608 for better synergy and maximum quantum yields. Flow-cell allows varying the interelectrode gap from
 609 micro-distance (50-500 μm) to macro-distance (1-5 cm), which can easily permit optimisation of the
 610 penetration depth when light is applied through the cell.

611 **4. Conclusion**

612 Studies on photo-electrochemical reactors applied for advanced oxidation treatment of
613 wastewater are still at early stages though increasing attention is being devoted to this
614 technology. This chapter presented an overview of the possible synergetic combinations
615 between advanced electrochemical treatments and photochemical processes. The effect of
616 reactor design, i.e. sequential versus hybrid photo-reactors, divided versus undivided cells,
617 operation mode, i.e. flow cell versus stirred tank reactors, and light source positioning, on the
618 photo-reactors efficiency has been addressed. The synergy between photoelectrocatalysis and
619 electrochemical advanced oxidation processes seems promising in terms of removal efficiency
620 of organic pollutants.

621 Upon these preliminary results, there is a need to manufacture multifunctional electrode
622 materials possessing optimum properties and configuration for the design/development of
623 heterogeneous photocatalytic reactors with enhanced performance. In parallel, the
624 photocatalysts have to be developed so they can possess long-term activity and improved
625 coating stability, particularly when subjected to electric field.

626 Furthermore, most studies from literature are performed at laboratory scale while most of the
627 effluents tested are synthetic solutions. There is a need to upscale those processes by testing
628 real water matrix solutions. The pH, the temperature, the turbidity, the presence of organic
629 matter as well as the inorganic salts could interfere with the combined process efficiency. A
630 techno-economic study could then be assessed for comparison with commercialized
631 technologies.

632

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