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Review

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Innovative Light-Driven Chemical/Catalytic Reactors Towards Contaminants of Emerging Concern Mitigation: A Review

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Abstract

Urban wastewater treatment plants (WWTPs) are among the major sources of contaminants of emerging concern (CECs) release to surface water. This is mainly associated with the low performance of conventional technologies (e.g. activated sludge, sand filtration and UV disinfection processes) for the removal of residual amounts (ng L^{-1} – $\mu\text{g L}^{-1}$) of CECs. In this review, a list of CECs commonly detected in the aquatic environments is presented. Light-driven chemical/catalytic processes for CECs removal, namely UV/oxidant and photocatalysis, are presented with discussion of their process, advantages, drawbacks, and the main attainments. In this context, process intensification has been gaining high relevance for wastewater treatment purposes due to its potential to overcome the main treatment limitations. Accordingly, an overview of advances to overcome the limitations in light-driven chemical/catalytic processes for CECs mitigation was carried out, focusing mainly on the design of novel reactors and devices. Some aspects related to reactor configuration, removal mechanism, devices applied, illumination system, comparison criteria, and catalyst immobilization through implementation of novel reactors designs are also discussed. Regarding the reactor design, several devices exhibit a satisfactory mass transfer due to a large surface-to-volume ratio or enhanced mixing conditions. However, improvements in photon transfer are still the biggest challenge to be overcome. The irradiation of the entire reaction solution and/or catalyst surface has shown to be challenging in many reactor configurations. Nevertheless, the reactor design and treatment process to be applied for CECs removal must be selected according to the site-specific conditions, in order to accomplish CECs mitigation and attain the best reactor performance.

Keywords: Photoreactors, Process intensification, Reactor design, Light induced chemical/catalytic processes.

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1 **1 Introduction**

2 About 71 percent of the Earth's surface is water-covered, however less than 3 percent of this amount
3 can be considered as freshwater [1]. In addition, this limited resource is under threat from the
4 pollution, mainly caused by human factors. Power generation, industrial, agriculture and mining
5 activities among others are some of the contributors to the aquatic compartments contamination,
6 which affects directly life on Earth [2]. Approximately two-thirds of the world's population
7 experiences water shortage for at least one month in a year [3]. Additionally, the World Health
8 Organization (WHO) reported that, in the year of 2017, 2 billion people living in various regions all
9 over the world used drinking-water source contaminated with faeces [4]. In fact, it is estimated that
10 almost 1.8 billion people worldwide might face moderate or severe water scarcity by 2025 [5].
11 Commonly, materials and chemicals used in daily human activities are continuously introduced into
12 the environment. These so-called Contaminants of Emerging Concern (CECs) are one of the main
13 causes of water pollution and, hence, being often related to the risks to human and biota health [6].
14 Therefore, as water safety and quality are fundamental to human development and well-being, the
15 scientific community has been applying great efforts to the development of efficient technologies
16 for water purification.

17 In this context, the conventional treatments applied for water treatment (e.g.
18 coagulation/flocculation and biological reactors), when used individually, became obsolete, as they
19 are not efficient to completely remove CECs [7-9]. On the other hand, advanced oxidation
20 processes (AOPs), based on the production of highly reactive radicals, have emerged as a viable
21 alternative to degrade recalcitrant substances into biodegradable compounds [10]. Among AOPs,
22 light-driven chemical/catalytic processes, especially UV/oxidant and photocatalysis, have been
23 recognized as promising technologies for CECS removal, due to their high efficiency in degrading a
24 wide spectrum of organic chemicals and by-products [10]. However, some drawbacks, namely
25 photon and mass transfer limitations pose as a barrier to their full implementation [11-13]. Here

26 enters the importance of new reactor designs for light-driven chemical/catalytic processes, aiming
27 to minimize photon and mass transfer limitations, reducing device sizes and enhancing their
28 throughput.

29 Mass transfer limitations inherent to light-driven chemical/catalytic processes might be overcome
30 by the reactor engineering. The selection of manufacturing material, reactor geometry and
31 dimensions (length, inner radius and outer radius) among others influences directly on the reactor
32 performance. In conventional tubular photocatalytic reactors, for example, the catalytic surface area
33 per volume of reactor is limited, leading to mass transfer limitations. Therefore, reactors providing
34 greater surface-to-volume ratio, such as microreactors and photocatalytic membrane reactors,
35 appears as a trend for the photocatalysis intensification [14]. In addition to the reactor design, other
36 strategies have been investigated with the aim to intensify light-driven chemical/catalytic processes,
37 such as the coupling of mixing devices in order to promote more intense macromixing dynamics.
38 Another approach is the design of hybrid reactors coupling light-driven chemical/catalytic processes
39 with other technologies. These systems aim to complement the advantages and overcome the
40 challenges of the other, showing great synergistic effects.

41 Nevertheless, one critical issue regarding light-driven chemical/catalytic reactors efficiency is the
42 photon-transfer limitation. The challenges rely on the fact that the light source and internal reactor
43 geometry must allow the irradiation of the entire reaction media and/or catalytic surface area.
44 Regarding the reactor design, parameters such as light source, wavelength, emittance angle and
45 reactor geometry and coupled devices influence the photon transfer in photochemical/photocatalytic
46 reactions. Here, the use of sunlight as energy source appears as an approach to attain a more cost-
47 efficient system. Studies on optimizing photon transfer by the use of optical fibers and LEDs have
48 also been explored; while the use of microscale illumination by LEDs have been shown promising
49 results, major breakthroughs are still lacking by using optical fibers.

50 Academia and industry have shown great advances in the manufacture of innovative light-driven
51 chemical/catalytic reactors; however, many challenges still need to be addressed. Therefore, this

52 review provides an overview of strategies applied for the intensification of light-driven
53 chemical/catalytic reactors, elucidating the recent advances on how to overcome mass and photons
54 transfer limitations focusing on the reactor design.

55 **2 Insights on Contaminants of Emerging Concern (CECs)**

56 *2.1 Presence of CECs in the environment*

57 The occurrence of CECs in the environment has become a matter of very high concern due to the
58 large number of compounds and its recurrent detection in different environmental matrices [15].
59 CECs are defined as naturally occurring, manufactured or manmade chemicals or materials, which
60 are suspected to be present or have been recently detected in diverse environmental compartments
61 and whose characteristics may pose risks to the biota or humans [16, 17]. Among the most
62 commonly CECs found in aquatic ecosystems and wastewater are pharmaceutically active
63 compounds (PhACs), personal care products, synthetic and natural hormones, pesticides, and
64 industrial chemicals (illicit drugs, plasticizers, life-style compounds like caffeine, and other
65 substances) [18, 19]. In most of the cases, these compounds are produced aiming to satisfy the daily
66 society needs, being subsequently introduced into the environment. Their widespread occurrence
67 has been continuously reported at low concentrations ($\text{ng L}^{-1} - \mu\text{g L}^{-1}$) [20].

68 Urban wastewaters are considered a major source of CECs, since conventional technologies used in
69 urban wastewater treatment plants (WWTPs) are not efficient to completely remove them [21].
70 Another via of CECs release to the environment is directly from the skin during swimming or
71 bathing [22]. Additionally, wastewater reuse practices result in the ubiquitous presence of CECs in
72 the agroecosystem and its consequent diffusion into the food-chain [23, 24]. Even at trace
73 concentration, when in contact with living beings, CECs may cause negative effects such as reduced
74 fish reproduction due to endocrine system disruption, decreased abundance of invertebrates due to
75 sublethal toxicity, and proliferation of antibiotic resistant bacteria (ARB) and antibiotic resistant
76 genes (ARG) [25, 26].

77 It is almost impossible to monitor the occurrence of all potentially harmful compounds in the
78 environment as well as the possible sources of contamination. On the other hand, providing data on
79 CECs occurrence is fundamental and serves as a basis for decision makers to define mitigation
80 strategies for a more sustainable water policy. A brief list of CECs commonly detected in the
81 environment is presented in **Table 1**. The compounds are subdivided into 5 classes of contaminants
82 (pharmaceuticals, personal care products, hormones, pesticides, and industrial chemicals) and
83 described according to their detected concentration. All the classes of compounds were detected in
84 the 3 types of water compartment evaluated in this work (groundwater, surface water and
85 wastewater). Within the studies evaluated, pharmaceuticals, personal care products, hormones,
86 pesticides, and industrial chemicals were detected in the range of 0.02-6.9, 0.002-25, 0.0001-1.2,
87 0.014-15.7 and 0.006-66 $\mu\text{g L}^{-1}$, respectively. It is worth noticing that, apart from pesticides, the
88 level of contamination by CECs followed an order according to the aquatic compartment (WW >
89 SW > GW). This aspect is due to the pathway of pollutants into the environment (**Fig. 1**): the main
90 source of pollutants release into aquatic natural environments are the WWTPs, from which the
91 compounds are transported to the rivers and then to groundwater. On the other hand, most studies
92 show the widespread occurrence of pesticides in surface and groundwater, since these pollutants are
93 used for agriculture purposes and may be washed to nearby bodies of surface water or leach to
94 groundwater. The atmosphere is also considered as a source of several volatile CECs. These
95 contaminants are introduced into the atmosphere via emissions during manufacture or incineration
96 processes, as well as via volatilization from surface water or wastewater. Subsequently, these
97 contaminants may enter the aquatic environment through precipitation [27].

98 2.2 Legislation

99 Aiming to overcome the growing water demand and considering the limited availability of fresh
100 water throughout the world, water authorities are developing policy directives to stimulate the use
101 of new tertiary treatment technologies for urban wastewater and to avoid the discharge of hazardous
102 compounds to the aquatic environment. The CECs limits in wastewater discharge remain

103 unregulated; however, some directives and guidelines have been published in the last years [28].
104 According to the newer European Directive 2013/39/EU, monitoring and treatment options for a
105 group of 45 priority substances, in order to fulfill the requirements of human health and
106 environmental protection, is recommended [29]. Additionally, the first watch list of 10
107 substances/groups of substances of environmental concern for European Union monitoring in the
108 field of water policy was launched in the Decision 2015/495 of 20 March 2015 [30]. The substances
109 to be monitored in EU surface waters included three hormones, four pharmaceutical compounds,
110 eight pesticides, a personal care product, and an industrial product. This Decision was updated by
111 the Decision (EU) 2018/840, on 5 June 2018 [31], in which five substances were removed from the
112 watch list (diclofenac, oxadiazon, triallate, 2-ethylhexyl-4-methoxycinnamate and 2,6-di-tert-butyl-
113 4-methylphenol) due to the sufficiently high-quality monitoring data attained; and three new
114 substances were included (amoxicillin, ciprofloxacin and metaflumizone) (**Table 2**). The strategy of
115 these decisions involves the identification of priority substances that pose risks to, or via, European
116 aquatic compartments; development of monitoring and analytical methods; improvement of the
117 information basis for future identification of these compounds; and achievement of good surface
118 water chemical status.

119 Following this protective principle, the Swiss government established legal requirements for
120 reducing the release of micropollutants from urban WWTPs into the aquatic environment [32]. This
121 legislation is based on the consideration that WWTPs are the main sources for contamination of
122 surface waters, thus additional treatment steps must be implemented. The Swiss legislation proposes
123 80% removal for five compounds of a list of twelve (11 pharmaceuticals and 1 biocide). Therefore,
124 the Swiss government expects to reduce contaminants load for downstream water use, protect
125 sensitive waters and protect drinking water resources. In the United States of America, the
126 Environmental Protection Agency (EPA) developed a monitoring program, the Unregulated
127 Contaminant Monitoring Rule (UCMR), to collect data for contaminants that are suspected to be
128 present in drinking water [33]. The EPA is required once every five years to issue a new list of up to

129 30 unregulated contaminants that must be monitored in large and small public water systems. This
130 list includes contaminants such as 17- β -estradiol, 17- α -ethynylestradiol, testosterone, estrone,
131 oxyfluorfen and perfluorooctanoic acid, among others. The UCMR provides scientifically valid data
132 on the occurrence of these contaminants, allowing the development of future water regulatory
133 decisions to protect public health. The National Health and Medical Research Council and the
134 Natural Resource Management Ministerial Council of Australia formulated the Australian Drinking
135 Water Guidelines (ADWG) [34]. The ADWG is used as a benchmark in the Australian legislative
136 and administrative framework to ensure the safety of drinking water by all agencies with
137 responsibilities associated with its supply, including catchment and water resource managers,
138 drinking water suppliers, water regulators and health authorities. Besides to comprise information
139 about a vast array of contaminants that may be present in drinking water, this document also present
140 strategies of drinking water systems management and water monitoring programs.

141 **3 Treatment technologies**

142 Several treatment options for water and wastewater contaminated with CECs have been applied
143 over the years, including adsorption, electrochemical oxidation, membrane filtration. Besides that,
144 advanced oxidation processes, namely UV/oxidant and photocatalysis, appear as emerging
145 technologies receiving huge attention by researchers. This section contains a brief overview of these
146 techniques. Their advantages and drawbacks are also summarized in **Table 3**.

147 *3.1 UV/Oxidant processes*

148 Among the several processes for water treatment, AOPs which ensure complete CECs oxidation are
149 of particular interest. UV/Oxidant processes involve the generation of free reactive radicals ($\text{HO}\bullet$)
150 in relatively high steady-state concentrations in order to efficiently oxidize organic contaminants.
151 These processes imply simple reactions such as the UV photolysis of H_2O_2 , O_3 and other
152 photoactive oxidants.

153 Due to the easy operation, no undesired sludge generation, and high potential for removal of
154 organic contaminants and inactivation of ARB and ARG, UVC/H₂O₂ photochemical process has
155 been widely applied [35, 36]. UVC/H₂O₂ system is based in the hydrogen peroxide homolytic
156 cleavage by UVC irradiation, resulting in highly reactive species (HO•), able to oxidize a wide
157 range of contaminants from water (Eq. 1) [37]. The efficiency of UVC/H₂O₂ oxidation is largely
158 influenced by the effluent matrix composition, wastewater UVC transmittance, photoreactor
159 geometry, hydrodynamic regime, H₂O₂ and UV dose, among others. Nevertheless, due to the low
160 values of H₂O₂ molar absorption coefficient at 254 nm, high hydrogen peroxide or UV dose are
161 necessary to promote the contact between oxidant and light; and attain an efficient performance
162 [38].



164 Most of the investigations using UVC/H₂O₂ process have been focused on the removal of target
165 compounds spiked in synthetic matrices at laboratory scale [39-42]. However, recently, the
166 effectiveness of this technology on trace organic contaminants removal from WWTPs effluents has
167 been also investigated at pilot-scale, achieving average removal values up to 90% [35].

168 Photolytic ozonation (the use of ozone in conjunction with UV light) has been also suggested as an
169 alternative for removing a variety of contaminants from water. Ozone absorption spectrum provides
170 a greater absorption cross section at 254 nm than hydrogen peroxide [43]. In this system, CECs are
171 generally oxidized via two reaction mechanisms: (i) directly by ozone molecules and/or (ii)
172 indirectly by secondary oxidators, such as free hydroxyl radicals (HO•), generated by the
173 disintegration of ozone molecule at alkaline pH conditions, in the presence of catalyst or UVC light
174 (Eqs. 2 and 3) [44].



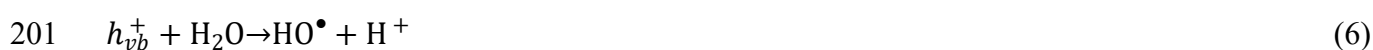
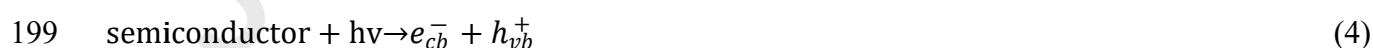
177 The main drawback for the wide application of photolytic ozonation as a tertiary wastewater
178 treatment is the potential of toxic by-products formation (deriving from CECs or wastewater

179 matrix) [45]. Therefore, a deep study of the wastewater matrix composition must be done prior to
 180 the implementation of the photolytic ozonation process (in order to guarantee the maximum process
 181 efficiency), as well as after treatment (in order to guarantee the quality of the treated water).
 182 Additionally, a polishing post-treatment step with a biological active sand filter is recommended,
 183 aiming the biodegradable by-products removal [46].

184 Photochemical processes using different types of oxidant, instead of H₂O₂, such as
 185 peroxymonosulfate, persulfate and periodate have been widely reported in the literature [47-55].
 186 Besides the production of hydroxyl radicals, this photochemical processes are known for the
 187 generation of other highly reactive radical intermediates such as iodyl (IO₃•), periodyl (IO₄•), and
 188 sulfate (SO₄•).

189 3.2 Photocatalysis

190 Catalysis is an important process for both the production and degradation of the wide range of
 191 chemicals [56, 57]. Photocatalysis consists on the photo-excitation of a semiconductor, by the
 192 absorption of photons with energy equal or greater than the photocatalyst bandgap, generating an
 193 electron/hole pair (Eq. 4). Electrons and holes may either recombine or participate in reduction and
 194 oxidation reactions, respectively. CECs can be oxidized directly by the holes (Eq. 5) or indirectly by
 195 reactive oxygen species generated on the catalyst surface (Eqs. 6, 7 and 8) [10, 58]. Titanium
 196 dioxide (Evonik P25-TiO₂) has effectively become a standard as photocatalyst due to its chemical
 197 stability, low cost and high photocatalytic activity [10]. Other semiconductors, including ZnO, ZnS,
 198 WO₃, CdS, Fe₂O₃, and SnO₂ can also be used.



204 Several parameters plays an important role on photocatalysis: (i) solution pH - catalyst particles
205 charge is affected by the solution pH and, consequently, its interaction with pollutants species [59];
206 (ii) photonic flow – reaction rate is directly proportional to photonic flow until reaching a point
207 where it remains constant [60]; (iii) catalyst loading – reaction rate increases with the increment on
208 catalyst loading until a certain value that depends on the reactor configuration and reaction matrix.
209 However, a further increase in photocatalyst load may lead to a decrease in the reaction rate due to
210 light attenuation effects [61]; (iv) presence/absence of dissolved oxygen – electron/hole
211 recombination can be attenuated in the presence of dissolved oxygen; and (v) solution temperature –
212 reactants/pollutants adsorption on the catalyst surface and dissolved oxygen concentration is
213 affected by the solution temperature [60].

214 Photocatalytic processes involve the dispersion of large amounts of catalyst in the water (slurry
215 conditions), being difficult to recover [62]. In addition, nanomaterials, notably TiO_2 , can be
216 considered harmful to human health as well as to the environment due to the very small particle size
217 (<50 nm) [63]. The use of catalyst thin films immobilized in inert supports (heterogeneous
218 photocatalytic processes) by chemical/physical vapor deposition [64, 65], spraying [66] or dip
219 coating [67] eliminates the need for a subsequent filtration/precipitation step and allows the reuse of
220 the catalyst until its stability/activity is maintained. Various types of inert supports have been
221 applied, as for example glass beads [68], stainless steel [69], monolithic structures [69], etc. On the
222 other hand, heterogeneous photocatalytic processes have as limiting step the mass transfer of
223 pollutants/reagents between the liquid phase and the catalyst surface, as well as the limitation of
224 photon transfer. Once the catalyst is activated by incident light, the photocatalytic
225 oxidation/reduction of pollutants can be divided into six stages: (1) diffusion of the
226 pollutant(s)/reagent (s) (O_2 , H_2O_2) from the solution to the surface of the catalyst (external
227 diffusion); (2) diffusion of the pollutant(s)/reagent(s) in the pores of the catalyst film (internal
228 diffusion); (3) adsorption of the pollutant(s)/reagent(s) (O_2 , H_2O_2) in the active centers of the
229 catalyst particles; (4) reaction on the catalyst surface; (5) desorption of the oxidation/reduction by-

230 products from the catalyst surface, renewing the photocatalytic sites; (6) by-products diffusion from
231 the surface of the catalyst into the solution [70].

232 During the last years, CECs removal by photocatalysis has been the study subject of many research
233 groups, although the real industrial application of this technology is yet limited [71-74].

234 Additionally, one of the main advantages of this technology is the possibility to use the sunlight as
235 energy source (solar-driven photocatalysis) [10]. However, the narrow overlap of the solar spectrum
236 with the absorption spectrum of many catalysts [e.g. TiO_2 (<5%)], and the high recombination rate
237 of electron/hole pair are the major drawbacks of this technology [75].

238 **Table 4** shows some studies regarding the degradation of diclofenac (DFC), an anti-inflammatory
239 of great concern [29], by the above described technologies. Additionally, the determination of the
240 electrical energy per order (E_{EO}) is also presented. The procedure for calculating E_{EO} was already
241 described by Bolton, et al. [76]. Since a significant part of photoreactor operational costs is
242 associated with electrical consumption, E_{EO} shows to be an important tool. This parameter is
243 defined as the electrical energy (kWh) required to reduce the contaminant concentration by one
244 order of magnitude in a standardized volume of polluted water (1 m^3) [77]. It is worth mentioning
245 that the presented data just gives an overview of pollutant removal processes. Removal efficiencies
246 are highly dependent on factors such as treated volume, reaction time, light power and
247 oxidant/catalyst amount. As a final point, it is not possible to predict the best treatment process for
248 CECs removal from water matrices. This is mainly attributed to the lack of international guidelines
249 with standardized procedures for correct comparison of technologies performance, such as
250 wastewater characteristics (DOC, UV transmittance, list of CECs, $\Sigma[\text{CECs}]$), target removal
251 efficiency and benchmark parameters. Beyond that, the selection of the best technology to be
252 applied must be done singularly for each specific treatment case.

253 Besides the treatment techniques previously presented, there are many other AOPs technologies that
254 may be applied for CECs removal in order to comply with stringent discharge/reuse requirements.

255 However, it is worth noticing that this work focuses mainly on light-driven chemical/catalytic
256 reactors applying UV/oxidant and/or photocatalytic processes, including also hybrid systems.

257 **4 Process intensification**

258 Process intensification (PI) is the novel approach to chemical process designs that goes beyond
259 “traditional” chemical engineering. These innovative approaches take advantage of reaction units
260 that minimize heat, mass and momentum transfer [78]. PI has several benefits such as: reduce size
261 of equipment and reagents inventory, enhance safety, reduce environmental impact and energy
262 costs, enhance corporate image (environment-friendly), enable large-scale processes by numbering-
263 up rather than scaling-up, among other advantages [78, 79]. It is hard to define exactly the term
264 “process intensification”. However, the most general definition was proposed by Stankiewicz and
265 Moulijn [80] as “Any chemical engineering development that leads to a substantially smaller,
266 cleaner and more energy efficient technology”.

267 The light induced emerging technologies described previously, with potential application in various
268 disciplines, have been receiving an impressive amount of exposure in the literature. However,
269 industrial implementation remains limited due to scale up problems, issues related to the design of
270 photoreactors, photon and mass transfer limitations. Here enters the importance of the process
271 intensification to achieve a cost-effective technology. In this topic, it is presented an overview of
272 advances to overcome the limitations in light-driven chemical/catalytic processes, focusing mainly
273 on the design and application of novel reactors and devices.

274 *4.1 Tubular reactors*

275 Among the tubular reactors, the configurations most used in light-assisted processes for water and
276 wastewater treatment consists on a: i) cylindrical shell equipped with one or several inner
277 cylindrical sleeves filled with UV lamps (annular reactor); ii) cylindrical shell, where the fluid
278 flows, coupled with one or several UV lamps placed outside of the tube [81]. It is worth mentioning
279 that the selection of the reactor shell or sleeve materials must take into account the position and UV

280 spectrum of the light source. Additionally, self-absorption by the UV lamps and reflection
281 phenomena may lead to a significant loss of light. The efficiency of light-driven chemical/catalytic
282 processes is also largely influenced by the reactor hydrodynamics regime, which must dictate the
283 UV fluence within the reactor as well as the contact between reagents/pollutants and the emitted
284 UV photons [82]. These two points are significantly enhanced when operating photoreactors under
285 turbulent flow regimes, which induce a more intense macromixing dynamics inside the reactor.
286 Consequently, a more homogeneous UV radiation distribution is also attained. On the other hand,
287 the use of laminar flow regime instead of turbulent reduces the friction between fluid and catalyst
288 surface, preventing catalyst detachment from the support, and the energy for liquid pump operation
289 is diminished, saving costs. Several commercial photoreactors integrate different mixing systems to
290 improve the degree of mixing inside the reactor. The use of static mixers during the treatment of
291 several micropollutants in an effluent from a WWTP with UV/H₂O₂ process was studied by De la
292 Cruz, et al. [83]. The authors placed the static mixers at the entrance of a reactor in order to
293 guarantee turbulent flux inside of it, achieving 95% of removal efficiency at the most economical
294 setting ($Q = 14 \text{ m}^3 \text{ h}^{-1}$, $[\text{H}_2\text{O}_2]_0 = 50 \text{ mg L}^{-1}$). Beyond that, Díez, et al. [84] tested stainless steel
295 static mixers as catalyst (TiO₂ or Fe₂O₃) support for the degradation of oxytetracycline. A
296 borosilicate tube filled with the static mixer, located above a parabolic reflector, was used as
297 photoreactor prototype. Light was provided by a sunlight simulator. The entire catalyst surface was
298 receiving front side illumination, improving the illumination efficiency. The static mixer provided a
299 good degree of mixing even using a laminar regime. An interesting approach for improving mixing
300 conditions was reported by Sher, et al. [85] through the simple insertion of baffles into the reaction
301 system. Flow behavior of the systems (from none to 4 baffles) was analyzed by electrical resistance
302 tomography (ERT). This tool demonstrates great potential to be used as modelling and diagnostic
303 tool of mixing conditions. When using 4 baffles, less dead zones and consequently proper mixing
304 was observed. The mixing and irradiation conditions can also be improved through the usage of
305 rotating reactors. Several authors have been investigating the use of this type of reactor for

306 contaminants removal purposes [86-89]. Rotating reactors contain one or several rotating elements
307 with the purpose to enhance mixing of the bulk and increase the mass transfer rates [89]. The
308 rotation movement may also result in thin liquid films on the rotating tube, improving the
309 illumination efficiency [87]. A rotating tubular reactor system composed of a cylindrical-shape
310 reactor and a rotating body, including nanotubular TiO₂ (NTT) on Ti meshes, was evaluated by
311 Kim, et al. [90] for the photocatalytic degradation of endocrine disrupting compounds (EDCs)
312 (bisphenol A, 17 β -estradiol, and 17 α -ethynyl estradiol) under solar irradiation. The rotating-reactor
313 was compared with a conventional flat reactor at lab ($V_{\text{reactor}} = 0.3$ L) and pilot-scale ($V_{\text{reactor}} = 10.7$
314 L). At the lab-scale, the rotating reactor showed better performance due to its similar degradation
315 efficiency with a smaller reaction area (area with light and NTT) compared with the flat reactor: 28
316 cm² and 100 cm² respectively. The superior performance of the rotating-reactor was also proved at
317 the pilot-scale setup: the reactor achieved higher EDCs removals (up to 97%) also with a smaller
318 area (1.2 times) compared with the flat reactor ($[\text{EDCs}]_0 = 2.0$ μM). These results were assigned to
319 the fact that rotating NTT on the Ti mesh inside the reactor improved the mass transfer.

320 Changes on the geometry of tubular reactors have been also receiving a lot of attention in order to
321 overcome mass and photon transfer limitations. In this context, a study focused on the selection of
322 the best piping arrangement for a annular channel reactor was conducted by Moreira, et al. [91].
323 CFD simulations at pilot scale revealed that the proposed innovative reactor with tangential
324 inlet/outlet pipes, FluHelik photoreactor (**Fig. 2**), promoted a helical movement of the fluid around
325 the UV lamp inducing: (i) a longer contact time between fluid particles and UV light, (ii) greater
326 dynamics of macromixing as a result of larger velocity gradients, turbulent intensities and
327 dispersion of residence time distribution values around the peak, and (iii) a more homogeneous UV
328 radiation distribution. In addition, the design of the FluHelik reactor can favor the implementation
329 of various reactors in series, promoting its application at industrial scale. Additionally, a
330 comparison study of the performance of the FluHelik reactor and a conventional Jets reactor
331 (containing four inlet/outlet pipes placed in parallel with the fluid flow direction) during the

332 treatment of several CECs by UVC/H₂O₂ process was performed by Espíndola, et al. [92]. The
333 FluHelik design showed superior performance than conventional Jets photoreactor during the
334 treatment of a model compound, oxytetracycline, due to its unique fluid dynamics and irradiation
335 properties ([OTC]₀ = 20 mg L⁻¹). The feasibility of FluHelik scale-up was proved by: (i) employing
336 several reactors in series, (ii) experiments with a complex matrix with 11 micropollutants (Σ CECs
337 <660 $\mu\text{g L}^{-1}$), and (iii) Fish Embryo Toxicity (FET) Tests to assess the decrease in toxicity of the
338 treated wastewater. Beyond that, other UVC/H₂O₂ photoreactors have already proved to be
339 applicable at pilot-scale for micropollutants removal from wastewater. For instance, a pre-designed
340 UV/H₂O₂ step installed on site at the WWTP Gut Marienhof (Munich, Germany), with capacity of
341 11-35 m³ h⁻¹, attained average removal of organic chemical higher than 90% during the period of
342 evaluation (5 days) [35].

343 Following the geometry of the reactors, the dimensions of the reactor (length, inner radius and outer
344 radius) also play an important role in the process efficiency. The modeling of two different
345 configurations of photochemical UVC/H₂O₂ reactors was performed by Coenen, et al. [93], in order
346 to minimize the mean outlet concentration of an organic pollutant. For the single-lamp annular
347 channel reactor evaluated, an optimal reactor length ($L = 5.4$ m) was found. If the absorption
348 coefficient of the solution to be treated increases, the optimal reactor length increases as well (i.e.
349 the reactor becomes narrower). An optimal radial distance between the centers of the reactor and the
350 lamps of 0.35 m was determined for multi-lamp annular reactor. If the solution absorption
351 coefficient or the number of lamps decreases, the optimal radial distance increases in order to
352 promote a more uniform UV dose throughout the reactor. The treatment of Direct Yellow 86 dye
353 wastewater by the UVC/H₂O₂ process in various continuous annular photoreactors was studied by
354 Shen and Wang [94]. Aiming to intensify the process, eight photoreactors with different dimensions
355 [inner radius (r_i) = 1.5 to 2.5 cm, outer radius (r_o) = 2.5 to 3.5 cm] were employed, resulting in
356 removal efficiencies > 90% ([Direct Yellow 86]₀ = 50 mg L⁻¹). The authors reported a higher dye
357 removal efficiency for a wider radius gap ($r_o - r_i$).

358 An appropriate illumination system plays a role of utmost importance on CECs removal and energy
359 efficiency of photoreactors. Characteristics such as light source, geometry, wavelength and
360 emittance angle must be carefully evaluated to guarantee a homogenous illumination of the entire
361 reactor system and avoid irradiation loss and unnecessary costs. Many efforts have been made to
362 overcome photon transfer limitations through the use of different illumination designs and sources.
363 As an example, Wols, et al. [95] performed a study on the development of new UVC/H₂O₂ reactors
364 for the oxidation of different organic micropollutants, in order to guarantee an efficient illumination
365 system, since one of the drawbacks of the UVC/H₂O₂ process is the energy consumption. The
366 authors varied the UVC fluence rate distribution by applying multiple lamps inside the annular
367 reactor. Different illumination systems composed by 1 to 63 lamps, with the same total amount of
368 energy as the single lamp, were assessed by CFD modeling. As expected, an increment on the
369 number of lamps leads to a more uniform UVC fluence rate distribution, boosting the system
370 efficiency. Our research group also evaluated the influence of the illumination system on the
371 degradation of contaminants by UVC/H₂O₂ process with a annular jets reactor [92]. However,
372 instead of varying the number of lamps and positions, the study verified the effect of the lamp
373 power (4, 6 and 11 W) on the overall removal efficiency of oxytetracycline ([OTC]₀ = 20 mg L⁻¹).
374 The UVC 6 W lamp provided the most suitable intensity for the experimental set-up under study,
375 due to a possible loss of the emitted photons when the 11 W lamp was applied.

376 Although being widely used in water treatments, conventional UVC lamps such as low or medium-
377 pressure mercury lamps have many disadvantages: large size, low impact resistance, relatively short
378 life time (<12,000 h), high sensitivity to temperature variations, low conversion of electrical energy
379 into useful light, and contain trace amounts of mercury (one of the main environmental
380 contaminants) [96, 97]. On the other hand, the design of photoreactors using light-emitting diodes
381 (LEDs), as energy source, for the treatment of CECs has exponentially grown [98-102]. LEDs
382 provides numerous advantages, such as: high energy efficiency, long life time, tunable wavelength,
383 small dimensions, and small-angle emittance providing a more homogeneous spatial illumination

384 [103]. In addition, the use of LEDs makes photoreactor design more flexible. However, the use of
385 LEDs introduces significant changes in the light distribution throughout the reactor, hence the main
386 goal must be to select the most beneficial approach combining reactor design and light sources
387 simultaneously. Martín-Sómer, et al. [104] compared the performance of three UVA systems (a
388 mercury fluorescent lamp, and an 8-LED or 40-LED based system) with different light distribution
389 in terms of photocatalytic oxidation of methanol ($[\text{MeOH}]_0 = 100 \text{ mM}$, $[\text{TiO}_2]_0 = 0.1 \text{ g L}^{-1}$). The
390 theoretical distribution of the light inside the annular photoreactor was modeled in a software Ansys
391 14.5 (Ansys Inc.[®]) to explain the relationship between the reaction rate and light distribution. The
392 results showed a very homogeneous light distribution along the reactor with the UVA lamp and 40-
393 LED system. In the case of the 8-LED, it was observed a highly non-uniform radiation field with
394 regions of the reactor with very high intensities and others remained practically in darkness. On the
395 other hand, for the same electric power consumption, the 40-LED system presented the higher
396 photonic flow inside the reaction medium; and the UVA lamp system showed the lowest electricity
397 to light conversion efficiency, as expected. Regarding the oxidation results, the lower energy
398 efficiency of the fluorescent mercury lamp is partially compensated by its “uniform” emission of
399 light, leading to similar results than the 8-LED system. The higher reaction rates per kWh were
400 achieved with the 40 LED system due to its improvement in light distribution over the reactor and
401 energy efficiency. These results confirmed that despite the advantages of LED, it is imperative to
402 optimize the LEDs position over the reactor, number of LEDs and power, to avoid lighting systems
403 less effective than conventional ones. Additionally, the performance of a novel upgraded Light
404 Emitting Diodes (LED) reactor on the photocatalytic degradation of the surfactant sodium
405 dodecylbenzenesulfonate (SDBS) with a 1 L jacketed annular reactor was studied by Dominguez, et
406 al. [105] and further compared with a Hg lamp reactor. The last one presented the highest SDBS
407 removal efficiency, achieving complete degradation after 360 min ($[\text{SDBS}]_0 = 0.144 \text{ mM}$, $[\text{TiO}_2]_0 =$
408 1 g L^{-1}). However, the upgraded LED reactor showed higher performance in terms of energy
409 efficiency: the electrical energy required to degrade the contaminant, by one order of magnitude

410 (90%) in a fixed water volume ($\text{kWh m}^{-3} \text{ order}^{-1}$), was 12.5 times lower. Beyond that, pulsed light
411 technology has been also considered in order to enhance micropollutants' photochemical
412 degradation. In pulsed UV systems, electrical energy is stored in a capacitor and further released, in
413 short duration pulses, towards the reactor. These pulses contain wider wavelengths range and
414 enhanced penetration capacity than standard UV approaches [106]. This technology has already
415 proven to be effective in inactivating a wide range of pathogens [107]. In the case of
416 micropollutants removal, the instant on/off capability of LEDs can be applied to regulate UV
417 fluence and reduce energy consumption when pollutant concentration or flow rate is reduced [108].
418 In this context, the effect of UV-LED duty cycle (expressed as the percentage of time the LED is
419 powered: 5, 10, 30, 50, 70, and 100% of the time) was evaluated by Duckworth, et al. [109] during
420 the degradation of a model contaminant, methylene blue (MB), by UVC/ H_2O_2 process. Seven
421 pulsed UVC LEDs, placed in the end plate of a cylindrical reactor, were employed in order to
422 guarantee that the LEDs emitting surfaces were in physical contact with the MB solution. At all
423 duty cycles, the contaminant was degraded. However, the normalized first-order degradation rate
424 constants ($k/\text{duty cycle}$) for MB were higher at low duty cycles (5 - 10%). The authors attributed
425 this fact to a more effective hydroxyl radical's generation with short-duration UVC pulses. On the
426 other hand, this same result may be assigned to peroxide limitations, indicating the need for reactor
427 design improvement. The authors also reported MB adsorption onto the LEDs during the
428 experiments, further reducing the optical output. The fouling of optical surfaces is a common
429 phenomenon in UV systems and can be overcome through engineering designs or operational
430 controls. Overall, the available literature points to the feasibility of UVC LEDs/ H_2O_2 as an
431 alternative technology for water treatment at lab-scale [102, 109-112]. Nevertheless, at this time,
432 UVC LEDs/ H_2O_2 technology seems to be economically unfeasible for real water treatment due to
433 the low energy-efficiency of UVC LEDs and its high cost.

434 The use of optical fibers also appears as an alternative to improve the illumination efficiency in
435 photoreactors. Along the optical fiber length, a portion of light is propagated by reflection on the

436 fiber wall and a portion is refracted. It is worth mentioning that optical fibers can be used for light
437 transmission and as a support for the catalyst deposition during photocatalytic processes. Therefore,
438 the refracted light may then be absorbed by the photocatalyst resulting in its activation. The
439 coupling of optical fibers with tubular reactors, in order to enhance the degradation of organic
440 contaminants, has become a hot topic [113-115]. As an example, the use of a hollow optical
441 fiber (HOF), coated with a TiO₂-based composite (composed of Er³⁺:YAlO₃/SiO₂/TiO₂ - EYST), in
442 a cylindrical photoreactor for the photocatalytic oxidation of 4-chlorophenol (4-CP) was
443 investigated by Zhong, et al. [113]. As expected, the EYST-coated HOF showed a higher light-
444 inducing ability at the fiber-coating interface and higher photocatalytic activity when compared
445 with the pure TiO₂-coated HOF. Er³⁺:YAlO₃ doped on the titanium film extends its absorption
446 spectrum to visible light, while the SiO₂ dopant decreases the electron/hole recombination rate.
447 However, low reaction rates were observed (69.8 % 4-CP degradation within 10 h) ([4-CP]₀ = 100
448 mg L⁻¹). Regarding coated optical fibers, although this technology presents advantages in terms of
449 long lifetime and low material costs and energy consumption (since solar light source can be used);
450 several developments must be achieved to overcome its major drawbacks: i) light intensity decrease
451 along the fiber length, ii) charge carriers generation far from the liquid-catalyst interface, and iii)
452 large reactor volume required.

453 4.2 Microreactors

454 Special attention has been given to the design and application of microreactors to overcome mass
455 and photon transfer limitations in photochemical/photocatalytic processes. Microreactors are
456 devices that have as main advantage a large surface-to-volume ratio. Additionally, microreactors
457 presents short molecular diffusion distances (short mixing distances) resulting in a good degree of
458 mixing even at a laminar flow regime. These characteristics results in an efficient illumination in
459 photochemical processes, and an efficient catalyst exposure to radiation and reagent/catalyst contact
460 in photocatalytic reactions [12]. Therefore, microreactors offers higher reaction rates due to their
461 higher spatial homogeneity of irradiance and efficient light penetration through the entire solution

462 [116, 117]. The main drawback of microreactors is its relatively small throughput [118]. However, a
463 higher productivity can be achieved by simple employing numerous devices in parallel (numbering-
464 up). As an example, microreactor numbering-up for photocatalytic degradation of organic dyes and
465 phenol was examined by de Sá, et al. [119]. The photocatalytic efficiency was boosted with the
466 numbering-up approach, from 1 to 6 units, decreasing the treatment time to achieve almost
467 complete dyes removal from 8 to 1 h ($[\text{dyes}]_0 = 1.2 \times 10^{-2}$ mM).

468 In order to enhance the illumination efficiency of photocatalytic processes in microreactors and
469 reduce costs associated with energy consumption to produce UV radiation, the use of solar radiation
470 for the treatment of organic contaminants has also been investigated [120, 121]. However, since the
471 design of microreactors is favorable to its real implementation by numbering-up instead of scaling-
472 up, the use of sunlight would require large land areas, making the process unfeasible. On the other
473 hand, the use of artificial illumination, especially UV-emitting diodes (UV-LEDs) and Hg lamps, is
474 an alternative to overcome this problem. **Table 5** presents the most common light sources utilized in
475 microreactors for photochemical processes. In this context, a novel mili-photoreactor, based on
476 NETmix technology developed by Lopes, et al. [122], has been successfully adapted by our
477 research team for the removal of several pollutants from liquid and gas streams under different
478 radiation sources [11, 42, 123, 124]. The NETmix mili-photoreactor consists of a regular network
479 of chambers and channels with small dimensions (mm) sealed by a borosilicate/quartz slab (**Fig. 3**)
480 [125]. The channels work as plug flow perfect segregation zones and the chambers as perfectly
481 mixing zones, enhancing the degree of mixing, and helping to overcome mass and photon transfer
482 limitations in photochemical processes. However, the internal geometry of this mili-photoreactor
483 may lead to the existence of non-illuminated areas. Therefore, to avoid the wasting of irradiation
484 and to increase the interaction of light and H_2O_2 molecules, Espindola, et al. [42] investigated the
485 use of a multiple UVC lamp design (4, 6 or 11 W) allocated in parallel or perpendicular to the
486 solution movement during the oxytetracycline oxidation by UVC/ H_2O_2 system in the NETmix. The
487 best results were achieved with the lamps of 6 or 11 W positioned in the parallel layout: > 90% of

488 OTC removal within 45 min ($[\text{OTC}]_0 = 20 \text{ mg L}^{-1}$, $[\text{H}_2\text{O}_2]_0 = 100 \text{ mg L}^{-1}$). This fact was attributed
489 to the possible higher spatial homogeneity of illumination throughout the entire reaction volume
490 when using this lamp arrangement. Beyond that, when using Hg lamps, not all photons emitted by
491 the light source reaches the photoreactor, especially due their geometry and angle of emittance.
492 Small-angle emittance UVC-LEDs can be a good alternative, directing all the light towards the
493 reactor window. However, more efforts in order to overcome the drawbacks of the use of UVC-
494 LEDs are needed, namely its high cost and low power, as reported above.

495 Microreactors have also been widely applied for heterogeneous photocatalytic reactions, and several
496 designs have been explored for water purification, such as: planar microreactors [121], NETmix
497 mili-photoreactor [126], micro-capillary reactors [127], single straight microchannel reactors [128],
498 and multi-microchannel reactors [14, 129]. When using catalytic thin-films immobilized in inert
499 supports, two irradiation mechanisms can be found: back-side illumination (BSI) and front-side
500 illumination (FSI). In the BSI mechanism, the catalyst film is irradiated on its backside and the
501 pollutants are adsorbed on the coated surface from the other side. On the other hand, in the FSI
502 mechanism, both catalyst thin film and liquid stream are irradiated on the same side [130].
503 Additionally, the light attenuation when using the BSI or FSI mechanisms is governed mainly by
504 light transmissibility of the coated support or filter effects of the water matrix, respectively.
505 Therefore, predicting the optimal film thickness is an important parameter for the intensification of
506 immobilized photocatalytic reactors. Padoin and Soares [117] proposed a mathematical model for
507 the prediction of the optimal film thickness in microreactors, both for the BSI and FSI mechanisms,
508 as a function of the incident irradiation, the apparent first-order reaction constant, the pollutants
509 effective diffusivity and the light absorption coefficient of the solid phase. Besides that, Satuf, et al.
510 [131] developed a simple method for obtaining intrinsic kinetic parameters of photocatalytic
511 reactions in a microreactor. This method can be used as a practical low-cost approach for the design
512 and optimization of photocatalytic reactors for water treatment. To validate the theoretical
513 approach, the degradation of a water pollutant, the pharmaceutical drug clofibric acid (CA), was

514 assessed in the same system; and again the film thickness proved to play an important role on the
515 photocatalytic efficiency. The model results were compared against experimental data, achieving a
516 notable prediction of the microreactor performance.

517 In this context, Vilar and co-workers [126] also studied the intensification of heterogeneous TiO₂
518 photocatalytic processes, using the NETmix mili-photoreactor, for OTC removal. The mili-
519 photoreactor flat design provided an efficient and more uniform exposure of the photocatalyst thin
520 film to UVA radiation; with an illuminated catalyst coated surface per unit of reactor volume and an
521 optimal film thickness of 333/989 m²_{ill} m⁻³_{reactor} and 0.8/1.4 μm when using the BSI/FSI
522 mechanisms, respectively. A 3.4-fold increase on antibiotic oxidation rate was perceived when
523 comparing the FSI with the BSI mechanisms. This result was assigned mostly due to the higher
524 illuminated catalyst coated surface when using the FSI mechanism, rather than the illumination
525 mechanism itself.

526 **Table 6** presents some photoreactors types and their reported catalyst-coated surface per unit of
527 reactor volume. Gorges, et al. [14] reported a microreactor with an extremely high catalyst area-to-
528 reactor volume ratio, almost 12,000 m²_{ill} m⁻³_{reactor}, associated with the low dimensions of the
529 microreactor channels (with a cross-section of approximately 300 μm × 200 μm). The system was
530 tested for the degradation of 4-chlorophenol (4-CP) under UVA-LEDs illumination, achieving
531 about 40% 4-CP removal in a single-passage at flow rate of 3 μL min⁻¹ ([4-CP]₀ = 0.05mM). The
532 lower the dimensions of the channels, the higher the catalyst area-to-reactor volume; however, the
533 throughput capacity may also decrease. Following this concept, in order to provide a high catalyst
534 surface-to-volume ratio, a novel dual-film optofluidic microreactor was proposed and fabricated by
535 Li, et al. [132]. The optofluidic microreactor is composed of three layers: two fluorine-doped tin
536 oxide glasses coated with highly ordered TiO₂ nanorod arrays (TiO₂ NRA) on both the top and
537 bottom internal wall of the microchamber, and a 200 μm-thick adhesive layer as the spacer and
538 sealant (**Fig. 4**). The TiO₂ NRA structure shows a large surface-to-volume ratio (10,000 m² m⁻³),
539 boosting the mass transfer. The feasibility of this design was investigated towards the photocatalytic

540 degradation of methylene blue (MB) under a UVA 150 W mercury lamp irradiance ($[MB]_0 = 2 \times 10^{-5}$ M) and was further compared with a conventional optofluidic microreactor. The novel optofluidic
541 microreactor design always yielded higher reaction rates (near 2-fold increase) when compared to
542 the conventional one. In the novel optofluidic microreactor, light was harvested at the top
543 photocatalytic film and also at the bottom TiO_2 nanorod arrays film, resulting in a better exposition
544 of active catalytic sites to the light and reactants.

546 A final important aspect to consider when using heterogeneous photocatalytic microreactors is the
547 stability of the photocatalytic film over time, representing important economic repercussions. As an
548 example, Eskandarloo, et al. [129] evaluated the photocatalytic efficiency of an Ag/TiO_2 catalyst
549 bed microreactor toward the removal of terephthalic acid (TPA), as a model organic pollutant,
550 under UV-LEDs light irradiation as well as the reusability of the photocatalyst film. The TiO_2
551 catalyst bed was synthesized using the sol-gel method by pumping titanium n-butoxide/ethanol and
552 water into the microchannels. A silver nitrate solution was pumped into the TiO_2 catalyst bed
553 microchannels in the presence of UV-LEDs irradiation for Ag^+ reduction to silver metal. The
554 Ag/TiO_2 catalyst bed microreactor showed a high photocatalytic removal efficiency (98.8%) and
555 good photocatalytic film stability over five reuse cycles, emphasizing its possible use in real scale
556 applications ($[TPA]_0 = 2.94 \text{ mg L}^{-1}$). Additionally, the long-term stability of a photocatalyst film in
557 a TiO_2 -based microreactor was proved by Krivec, et al. [133]. The film was immobilized on the
558 microreactor inner walls with a two-step synthesis: anodization and subsequent hydrothermal
559 treatment. After 3,600 operational cycles, the microreactor still exhibited 60% of its initial
560 performance for the photocatalytic degradation of caffeine under UVA-LEDs radiation.

561 Overall, the use of microreactors under microscale illumination provides both high illumination
562 efficiency and a large photocatalyst coated surface per unit of reactor volume, receiving great
563 attention from researchers. Nevertheless, improvements on the reactor performance can still be
564 performed, especially regarding the enhancement of the reactor throughput and catalyst illumination
565 efficiency. The illumination system efficiency proved to be influenced by both the light

566 source/arrangement and the reactor design. Reactor productivity appears to be significantly
567 enhanced by both the optimization of operational parameters and the numbering-up approach.
568 Therefore, it is projected that less power-consuming and size reduced illumination sources will be
569 available soon, allowing the design of reactors even smaller and with higher throughput.

570 *4.3 Photocatalytic membrane reactors*

571 Membrane technology has already provided remarkable solutions to some of the key problems of
572 our modern society. Membrane processes fill the requirements of PI due to their potential to replace
573 conventional expensive techniques, to carry out the selective and efficient transport of specific
574 substances, and to enhance the performance of several processes. However, even though
575 membranes technologies represent a mature process nowadays, there is still a wide range of
576 opportunities for process optimization and intensification. The challenges remain in overcome the
577 fouling phenomenon and produce membrane materials with high performance. Fouling is the major
578 problem associated with application of pressure-driven membranes reactors. This phenomenon is
579 caused by adsorption of inorganic/organic material on the membrane surface and/or pore blocking
580 [62], reducing the membrane performance and lifetime, and increasing the operating costs. There
581 are two categories of strategies to reduce the fouling effect: remediation and avoidance.
582 Remediation is commonly performed by chemical cleaning at regular times (carefully evaluated and
583 conducted), high tangential velocities along the membrane and/or by backwashing or backpulsing.
584 Applying a suitable pre-treatment, such as coagulation/precipitation, slow sand filtration,
585 adsorption, or advanced oxidation processes, can be a good solution to prevent membrane fouling.
586 Here enters the importance of hybrid membrane reactors for the effectiveness of the membrane
587 performance. Hybrid systems that couples membrane technologies with photocatalytic processes,
588 denominated as photocatalytic membrane reactors (PMRs), are the most common strategy of
589 process intensification. PMRs typically comprise a quartz or Plexiglas window [134, 135], and light
590 source is placed outside the reactor [134, 135]. The configuration with submerged lamps is less
591 widespread [136, 137]. In PRMs, the photocatalyst can be either deposited onto the membrane

592 (nano-engineered membranes-NEM) or suspended in the reaction water [62]. In both systems, the
593 membrane plays the role of contaminants barrier, permeating only small molecules and water
594 through the pores. Additionally, in the suspended catalyst configuration, the membrane also acts as
595 a barrier for the photocatalyst consequently allowing its possible further reuse; and in the coated-
596 catalyst configuration, the NEM is responsible for the *in-situ* contaminants oxidation/reduction,
597 enhancing the membrane antifouling properties and the quality of the permeate and retentate. It is
598 worth noticing that in slurry systems, the catalyst surface area available for CECs adsorption and
599 oxidation is typically greater than in immobilized systems, which leads to higher contaminants
600 degradation rates; however, these systems also present higher permeate flux declines. The
601 fabrication of NEM can be accomplished with different procedures such as dip-coating [138],
602 magnetron sputtering [139], electrospraying [140] and photocatalyst gas phase deposition [141],
603 among other technics. The antifouling properties of NEMs were emphasized by Moustakas, et al.
604 [142]. In their work, a PMR coupled with a double-side ceramic NEM (with TiO₂ active porous
605 layers on both inner and outer surfaces) and irradiated externally by UVA-Vis lamps and internally
606 by UVA-LEDs was able to operate without any indication of fouling. Other alternatives to
607 overcome the permeate flux deterioration in PMRs have also been reported in the literature. Shon,
608 et al. [143] reduced the fouling effect by letting photocatalyst settle and by filtering the supernatant.
609 Additionally, UV irradiation directly on the membrane surface was employed to clean the
610 membrane and increase the permeate flux. A different approach, coupling sonophotocatalysis with
611 ceramic membrane microfiltration, was performed by Cui, et al. [144]. This association minimized
612 the membrane fouling by the nanoparticles, enhancing the membrane performance.

613 Titanium dioxide (Evonik P25-TiO₂) has effectively become a standard photocatalyst in PMR
614 applications. Espíndola, et al. [145] presented a research study comparing a simple UVC-UF hybrid
615 system with two other ones of same configuration plus oxidant (UVC/H₂O₂-UF) or photocatalyst
616 (UVC/TiO₂-UF) for the removal of the antibiotic oxytetracycline (OTC). The lowest permeate flux
617 and OTC degradation efficiency were observed with the UVC-UF system. On the other hand, the

618 addition of oxidant or catalyst enhanced the degradation of the antibiotic and other organic
619 compounds present in solution, and as consequence reduced the membrane fouling. Sarasidis, et al.
620 [146] claimed that, during the diclofenac degradation in a continuous TiO₂ photocatalytic membrane
621 reactor, negligible membrane fouling in long-term operation of the PMR system was observed due
622 to the automatic periodic membrane backwashing. Conversely, the long term assessment of a
623 submerged membrane photocatalytic reactor, evaluated for the removal of 17 β -estradiol in presence
624 of humic acid, revealed that aged TiO₂ caused higher trans-membrane pressure. As a consequence,
625 the membrane reactor performance decreased with time [147]. Several studies have been also
626 reporting the benefits of supporting Evonik P25-TiO₂ on the membrane material [142, 148-150].
627 However, different catalysts can also be employed according to the specific characteristics of the
628 membrane and contaminant, reactor design, and type of irradiation [151-154]. As an example, Lu,
629 et al. [153] tested a new composite membrane fabricated through the anchoring of coordination
630 complex modified polyoxometalate on ethylenediamine functionalized polyvinylidene fluoride
631 towards tetracycline removal. No significant loss of tetracycline removal efficiency and flux after
632 eight operational cycles were observed, showing a good stability of the composite membrane.
633 Similar results were presented by Ma, et al. [155] using a novel catalytic membrane manufactured
634 by grafting a poly(ionic liquid) onto polypropylene membrane followed by complexing with
635 polyoxometalate for the degradation of a model contaminant, acid orange II (AO7). The
636 photocatalytic activity of the membrane upon AO7 degradation proved to be stable for up to 10
637 cycles. On the other hand, besides attaining high phenol removal efficiencies with a N-doped
638 graphene-based catalytic membrane, applied for persulfate activation and degradation of organic
639 pollutants, Pedrosa, et al. [156] reported a decline in photocatalytic activity after each operation
640 cycle. This effect was assigned to the loss of N-pyridinic groups during the reactions. The catalytic
641 activity deactivation in a catalytic membrane reactor (CMR) was also observed by Osegueda, et al.
642 [157]. The authors proposed the application of a CMR for the oxidation of phenol by the *in-situ*
643 generation of hydrogen peroxide. For that, palladium was uniformly deposited onto the ceramic

644 membrane outer surface by sputtering technique; and a second active phase, transitional metal
645 oxides or homogeneous Fe^{2+} , was used for hydroxyl radical generation. After 3 operational cycles,
646 no activity was observed. This effect was assigned to possible undesired reactions of the small size
647 palladium particles, e.g. palladium hydride formation.

648 Another trend in CECs removal by photocatalytic membrane reactors is the use of forward osmosis
649 membrane. Forward osmosis (FO) is an innovative membrane process with high potential in
650 rejection of a wide range of contaminants. In FO membrane reactors, the operational and energy
651 costs are reduced due to the low or no hydraulic pressure applied. Besides that, FO also provides a
652 better fouling control than high pressure-driven membrane separation processes due to the
653 generation of lower irreversible fouling [158-160]. In this context, Ramezani Darabi, et al. [161]
654 developed a modified FO photocatalytic membrane, by integrating $\text{Fe}_3\text{O}_4/\text{ZnO}$ nanocomposite via
655 the interfacial polymerization technique, for pharmaceutical wastewater treatment. The
656 nanocomposite was applied in both membrane surface and sublayer, improving especially the FO
657 membrane antifouling properties.

658 Depending on the desired irradiation emission range and intensity, different typologies of light
659 sources may be applied in membrane reactors. Microwave [162], ultrasound [163, 164], UV lamps
660 [145, 165, 166], LEDs [167], and solar irradiation [148] have been reported during CECs removal
661 using PMRs. As an example, a novel submerged membrane photoreactor, comprising a reactor
662 irradiated with visible-light LEDs and a submerged hollow fiber MF membrane, for the degradation
663 of carbamazepine was developed by Wang, et al. [167]. In order to obtain a more homogeneous
664 illumination of the solution containing TiO_2 and the contaminant, the photoreactor was wrapped
665 with a Vis-LED flexible strip (4 m) comprising 240 Vis-LED units. Another alternative to achieve
666 an efficient illumination was proposed by Athanasiou, et al. [168] through the use of an upgraded
667 photocatalytic membrane reactor that replaced the expensive UV lamps by using optical fibers. For
668 that, several optical fibers were hosted inside the hole of a one-channel membrane or one optical
669 fiber in each channel of a multichannel membrane. The optical fibers received the concentrated

670 solar radiation in their upper edge and transmitted the light towards the membrane surface. In
671 contrast to ultraviolet light source, Fu and Zhang [162] claimed that microwave irradiation could
672 better penetrate the membrane material and induce reactions on the catalyst-coated surface. In fact,
673 in addition to mitigating the membrane fouling, the system was able to promote a higher
674 degradation of 1,4-dioxane, a model water pollutant, when compared with other processes reported
675 in literature.

676 In view of large scale and continuous applications, a novel pilot scale PMR was fully automated for
677 continuous operation [169]. The PMR-pilot, with a maximum system capacity of 1.2 m³ day⁻¹ of
678 treated water, 52 W of UVC power, and combining suspended TiO₂ photocatalysis with a
679 submerged ultrafiltration hollow fiber membrane was evaluated for degradation of the
680 pharmaceutical diclofenac (DCF). The reactor demonstrated excellent steady-state performance for
681 diclofenac degradation: 100% DCF removal efficiency, whereas 52% TOC removal was recorded
682 ([DCF]₀ = 50 - 630 µg L⁻¹). In addition, due to the effectiveness of the automatic backwashing
683 protocol employed during PMR operation, negligible membrane fouling was observed. These
684 results prove that membrane reactors can be successfully employed at large scale for CECs removal
685 purposes. On the other hand, although many methodologies have been proving to reduce membrane
686 fouling, this phenomenon remain the most important limitation in membrane reactors performance
687 that needs further improvement. Notwithstanding, the trends are following the direction of
688 membrane surface/material modification.

689 4.4 Other reactors and hybrid systems

690 In order to enhance the photon and mass transfer rates and overcome some limitations in light-
691 driven chemical/catalytic processes applied for CECs removal, different approaches of
692 photoreactors and hybrid systems have been investigated. **Fig. 5** shows the schemes of some
693 reactors applied for CECs removal. A novel disruptive tube-in-tube membrane microreactor for the
694 intensification of UVC/H₂O₂ processes was proposed by Vilar, et al. [170] and further evaluated
695 towards oxytetracycline removal. This reactor is composed of an inner ultrafiltration membrane and

696 a quartz outer tube irradiated by four UVC lamps (**Fig. 5a**). The radial addition of oxidant through
697 the whole porous membrane length is the main novelty of this system. The proposed novel reactor
698 attained a promising performance: OTC removal efficiencies of about 36% and 7% in a single-pass
699 mode were achieved using ultrapure and urban wastewater as solution matrices ($[\text{OTC}]_0 = 2 \text{ mg L}^{-1}$,
700 $[\text{H}_2\text{O}_2]_0 = 15.8 \text{ mg L}^{-1}$). The authors claimed that the helical motion of water around the membrane
701 shell-side enhanced the oxidant radial mixing, promoting its more homogeneous distribution in the
702 annular reaction zone of the membrane microreactor. Another new reactor concept, composed of a
703 hydrophobic porous membrane support with hydrophilic photocatalytic microchannels, was
704 proposed by Aran, et al. [171] and its efficiency was evaluated towards the photocatalytic
705 degradation of methylene blue and phenol. The polluted solution flows inside the microchannels
706 where the TiO_2 is immobilized, and the photocatalyst surface is illuminated by UV irradiation (**Fig.**
707 **5b**). O_2 , known for enhancing photocatalytic degradation of organic pollutants, permeates through
708 the membrane porous wall reaching the liquid inside the microchannels. The membrane
709 microreactor presented a good performance: 80% MB removal in a single-pass mode at a flow rate
710 of $10 \mu\text{L min}^{-1}$, and the continuous distribution of O_2 to the reaction zone through the membrane
711 enhanced the removal efficiency to 90%. A different approach of a porous photocatalytic membrane
712 microreactor, by exploiting Dean vortices, was developed by Choudhary and Pushpavanam [172].
713 In the modified design, the microchannel is curved in order to enhance the mixing by generating
714 “Dean Vortices” (helical motion of the fluid). This unique flow promoted a better photocatalyst use
715 and an improved mass transfer coefficient. The addition of pure oxygen in photocatalytic systems
716 was also evaluated by Ramos, et al. [173] using a micro-structured reactor for the oxidation of a
717 simulated wastewater containing phenol. The reactor was developed by using glass micro-spheres
718 as structuration element and catalyst support inside an annular reactor, aiming to maximize the
719 catalytic area and overcome the mass-transport limitations inherent of immobilized catalytic
720 systems (**Fig. 5c**). The authors claimed that the micro-structured reactor is similar to a channel
721 microreactor, with the advantage of ensuring a suitable throughput. Furthermore, the addition of O_2

722 improved 8.6 times the phenol degradation rate. Also aiming to increase the photocatalytic surface-
723 to-volume ratio, Kete, et al. [174] tested a compact monolithic reactor for photocatalytic oxidation
724 and photocatalytic ozonation of several contaminants. Titanium dioxide was supported onto porous
725 Al_2O_3 monoliths and irradiated by UV lamps placed in the interior of the monolithic structure (**Fig.**
726 **5d**). Despite the turbulent flow through the coated-monolithic structure, its open porous three-
727 dimensional network structure offered a good permeability (negligible pressure drop across the
728 structure). In addition, the monoliths proved to be mechanically stable and provided a relatively
729 high surface area per volume of reactor (approximately $17,609 \text{ m}^2 \text{ m}^{-3}$). The synergistic effect of
730 photocatalytic ozonation was significantly expressed in terms of mineralization (77% mineralization
731 after 2 h experiment). An alternative photocatalyst support, sand grains, in a tray photocatalytic
732 reactor was tested by Abdel-Maksoud, et al. [175] for the degradation of phenol as a model CEC. A
733 stainless steel tank equipped with a tray for supporting the TiO_2 coated sand grains mainly
734 composes the reactor. A thin water film flows through the tray (in a recirculating batch mode) being
735 illuminated by either artificial UVA radiation or sunlight (**Fig. 5e**). TiO_2 sand particles immobilized
736 by epoxy coating technique showed high resistance to abrasion. The proposed photoreactor
737 operated in a continuous flow mode provided (i) good light penetration to TiO_2 activation, (ii)
738 continuous oxygen supply via passive oxygenation, (iii) minimization of dead zones, and (iv)
739 efficient mass transfer due to the turbulent flow. A different reactor, the photocatalytic spinning disc
740 reactor (SDR), was studied for the degradation of an organic compound and further compared with
741 a conventional annular reactor [176]. In this reactor configuration, the liquid flows through the
742 center of a supporting disc rotating shaft and exits through an annular gap in the nozzle.
743 Subsequently, the liquid flows through the TiO_2 coated-disc, being illuminated by UV radiation,
744 and returns to a reservoir by gravity (**Fig. 5f**). The SDR presented an average photonic efficiency
745 three times higher than the maximum photonic efficiency achieved in the annular reactor, pointing
746 to a more efficient utilization of the incoming light. As consequence, the maximum reaction rate
747 attained with the SDR was 2 times higher than in the annular reactor.

748 In the context of illumination system, the use of solar photoreactors emerges as an alternative to
749 reduce operational costs [60]. However, variations in solar emittance along the time, solar light
750 scarcity in some areas, among other factors poses as drawbacks of this system. An interesting
751 approach is the use of compound parabolic collectors (CPCs), which enhances the process by using
752 the UV radiation that is directed away from the reactor [177]. The use of two parabola sections
753 facing each other allows simple association to solar reactors as there is no need to move the
754 collector to adapt to the solar orientation changes [178]. Great efforts have been also made in order
755 to expand the catalysts absorption spectrum for the visible region, thus allowing the use of solar
756 radiation and enhancing photons transfer. For that, catalysts such as TiO_2 are usually doped (e.g.
757 with N, Fe, S) or submitted to dye-sensitization [179, 180]. The latter technique is used to expand
758 the active spectral range of photocatalysts by taking advantage of the dyes' ability to absorb visible
759 radiation and conduct electrons to the catalyst [181].

760 It is worth noticing that even presenting high removal efficiencies for CECs, the above mentioned
761 photoreactors/processes alone are not able to degrade some specific micropollutants and the
762 generated by-products. This way, hybrid systems can be proposed to enhance the overall CECs
763 removal. In addition, hybrid systems can also be designed to overcome some drawbacks that a
764 singular process/reactor presents, e.g. a previous adsorption process can minimize the fouling
765 phenomenon in membrane reactors by reducing the foulants loading. In hybrid systems, two or
766 more processes can be coupled in the same reactor unit or can be applied in different units
767 following a specific order. PMRs are the most investigated hybrid systems with different processes
768 (i.e. membrane separation and photocatalysis) coupled in the same reactor, and it was widely
769 described in the previous topic. On the other hand, the combination of membrane technology with
770 another processes such as UV/oxidant [182, 183] for micropollutants removal have been widely
771 reported on literature. Typically, this association aims to decrease the organic loadings on the
772 concentrate streams and/or reduce the membrane fouling. As an example, Umar, et al. [111]
773 executed the treatment of municipal wastewater reverse osmosis concentrates by UVC-LED/ H_2O_2

774 oxidation. The authors reported that while the permeate water obtained from the RO process may be
775 employed for industrial applications, that request high quality water, some pollutants were
776 accumulated in the concentrate stream, and the additional step improved the mitigation of several
777 parameters such as DOC, pollutants concentration, and color.

778 Beyond that, several hybrid systems have been reported in the literature for the removal of CECs. A
779 new hybrid system coupling sonocatalysis and photocatalysis was tested for tetracycline (TC)
780 degradation using TiO₂ decorated on magnetic activated carbon (MAC-T) in combination with
781 ultrasound (US) and ultraviolet (UV) irradiations [184]. The TC degradation rate was significantly
782 improved when using the MAC-T/US/UV system. At optimal conditions, above 93% of removal
783 efficiency was attained with 180 min of reaction ($[TC]_0 = 30 \text{ mg L}^{-1}$). Whereas, the addition of
784 oxidants (hydrogen peroxide, peroxymonosulfate, persulfate and periodate) enhance the TC
785 decontamination rate by increasing remarkably the reactive species generation rate in the system
786 and consequently the oxidation of further contaminants molecules. In this case, complete TC
787 removal was achieved within 60 min treatment. Furthermore, MAC-T showed high reusability and
788 stability, given that both loss of the removal efficiency and Fe leaching were negligible during reuse
789 cycles. Lhotský, et al. [185] applied a UV/H₂O₂ process in combination with simple aeration
790 pretreatment for remediating of groundwater heavily contaminated by recalcitrant pharmaceuticals
791 and monoaromatic hydrocarbons. The results showed that monoaromatics were already efficiently
792 removed by using the aeration step (via volatilization, co-precipitation and biodegradation removal
793 mechanisms) and UV/H₂O₂ proved to be necessary for degradation of the pharmaceuticals. The
794 feasibility of a hybrid adsorption-oxidation process on the removal of sulfonamide antibiotics was
795 tested by Peng, et al. [186]. MIL-101(Cr) was used as the adsorbent (0.15 g L⁻¹) and persulfate (PS)
796 was employed to oxidize the contaminants adsorbed. MIL-101(Cr) proved to effectively adsorb the
797 sulfonamides simultaneously; and PS thermal activation showed to be the most appropriate
798 technique for the oxidation of the target compound, sulfadimethoxine (SDM), when compared with
799 UV activation. When using a PS dosage of 10 mmol L⁻¹ and 60 °C, 97.8% of SDM removal

800 efficiency was attained. Photoelectrocatalytic (PEC) hybrid reactors, combining both electrolytic
801 and photocatalytic processes, have also been widely applied for CECs removal [187-189]. In PEC
802 reactors, a photoactive semiconductor is used as anode and irradiated with light. The generated
803 electrons move to the cathode where they can also react with the dissolved oxygen to form
804 superoxide radicals, enhancing the pollutant's degradation rate [190]. The use of an external bias
805 potential leads to a reduced electron-hole recombination rate, also enhancing the photocatalytic
806 degradation process [191]. Ghasemian, et al. [192] fabricated a PEC reactor through the synthesis of
807 an antimony-doped tin-tungsten oxide (Sn80%-W20%-oxide) anode and evaluated this system
808 towards carbamazepine removal. Authors observed that the contribution of the electrochemical
809 oxidation to the pharmaceutical removal was more significant than that of the photochemical
810 oxidation.

811 **Table 7** summarizes the main photoreactors evaluated in this work. In addition, some recent patents
812 related to light-driven chemical/catalytic processes are also addressed. A description of the systems
813 is presented, focusing on specific/new features that promoted process intensification and their
814 advantages. In **Table 8** a brief comparison of the main results obtained by our research group
815 applying different light-driven chemical/catalytic processes, using different reactors and system
816 configurations, for the oxidation of a model micropollutant, oxytetracycline, is presented. Several
817 important parameters are reported to give a clearer view of the reactor performance and to be easily
818 compared with other systems. Additionally, a recent benchmark used for reactors comparison, the
819 photochemical space time yield (PSTY), was introduced. This value is defined as the water volume
820 treated for each kW of light power per reactor volume per day. The procedure for calculating PSTY
821 was already described by Leblebici, et al. [193]. However, these parameters are used only for
822 reactors comparison purposes; the reactor design and photochemical process to be applied for CECs
823 removal must be selected according to the site-specific conditions (i.e. required effluent quality,
824 cost of electricity, pollutants to be treated, available space, weather conditions, among others), in
825 order to accomplish the micropollutant mitigation and attain the best reactor performance.

826 5 Conclusions

827 In this review paper, the occurrence of contaminants of emerging concern in the environment was
828 discussed and some treatment technologies were appointed. Additionally, an overview of advances
829 to overcome the limitations in light-driven chemical/catalytic processes for CECs mitigation was
830 described, especially in relation to the design and application of novel reactors and devices.

831 Based on the information reported, the following can be concluded:

832 (i) AOPs proved to be efficient treatment processes for CECs removal in order to fulfil the
833 more restrictive requirements of recent directives and guidelines. Now, researchers are
834 focused on intensify these processes; attaining a smaller, cleaner and more energy
835 efficient technology.

836 (ii) The wide diversity of CECs and water matrix composition make optimization essential
837 for each treatment application (oxidant and/or catalyst choice, dosages, selection of
838 membranes, dosing procedures, mixing conditions, etc.). In this context, the use of
839 modelling tools (e.g. CFD) appears as an interesting approach to assess features such as
840 hydrodynamics, residence time distribution and UV radiation intensity distribution
841 inside reactors. Thus, the optimization of design parameters may be performed prior to
842 reactor fabrication.

843 (iii) Photon and mass transfer limitations pose as the main barrier to full implementation of
844 light-driven chemical/catalytic processes towards CECs removal. For that, photoreactor
845 engineering appears as a hot spot to work on in order to overcome these issues.
846 Additionally, the use of novel light sources such as LEDs have been successfully
847 verified, offering more cost-efficient, flexible and customizable irradiation profiles.

848 (iv) Significant advances on intensifying light-driven chemical/catalytic processes are
849 reported regarding the use of innovative reactor designs, such as microreactors and
850 photocatalytic membrane reactors. Although a range of investigations have been carried
851 out in novel photoreactors to date, a lot of work remains in this area, namely the

852 relatively small throughput of microreactors and the fouling phenomenon in membrane
853 reactors.

854 (v) The lack of comparative investigations between reactor design and light-driven
855 chemical/catalytic processes difficult the evaluation of the most appropriate solutions for
856 wastewaters advanced treatment. In any case, the selected approach must take into
857 account the site-specific conditions (i.e. required effluent quality, cost of electricity,
858 pollutants to be treated, available space, weather conditions, among others).

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Figure Captions

Fig. 1. Pathway of pollutants into the environment. Adapted from Sophia A and Lima [194].

Fig. 2. FluHelik reactor (a) sketch designed by ANSYS Design Modeler (reprinted (adapted) from Moreira, et al. [91], Copyright ©, with permission from Elsevier); (b) streamlines calculated from CFD simulations data (reprinted (adapted) from Moreira, et al. [91], Copyright ©, with permission from Elsevier); and (c) pilot-scale photography.

Fig. 3. NETmix mili-photoreactor (a) scheme (reprinted (adapted) from Marinho, et al. [11], Copyright ©, with permission from Elsevier); and (b) photography.

Fig. 4. Scheme of the TiO₂ NRA-based dual-film optofluidic microreactor. Reprinted from Li, et al. [132], Copyright ©, with permission from Elsevier.

Fig. 5. Different reactor designs: (a) tube-in-tube membrane microreactor; (b) porous membrane microreactor; (c) micro-structured reactor; (d) monolith reactor; (e) tray photocatalytic reactor; (f) spinning disc reactor - Adapted from Vilar, et al. [170], Aran, et al. [171], Ramos, et al. [173], Abdel-Maksoud, et al. [175] and Boiarkina, et al. [176].

Fig. 1

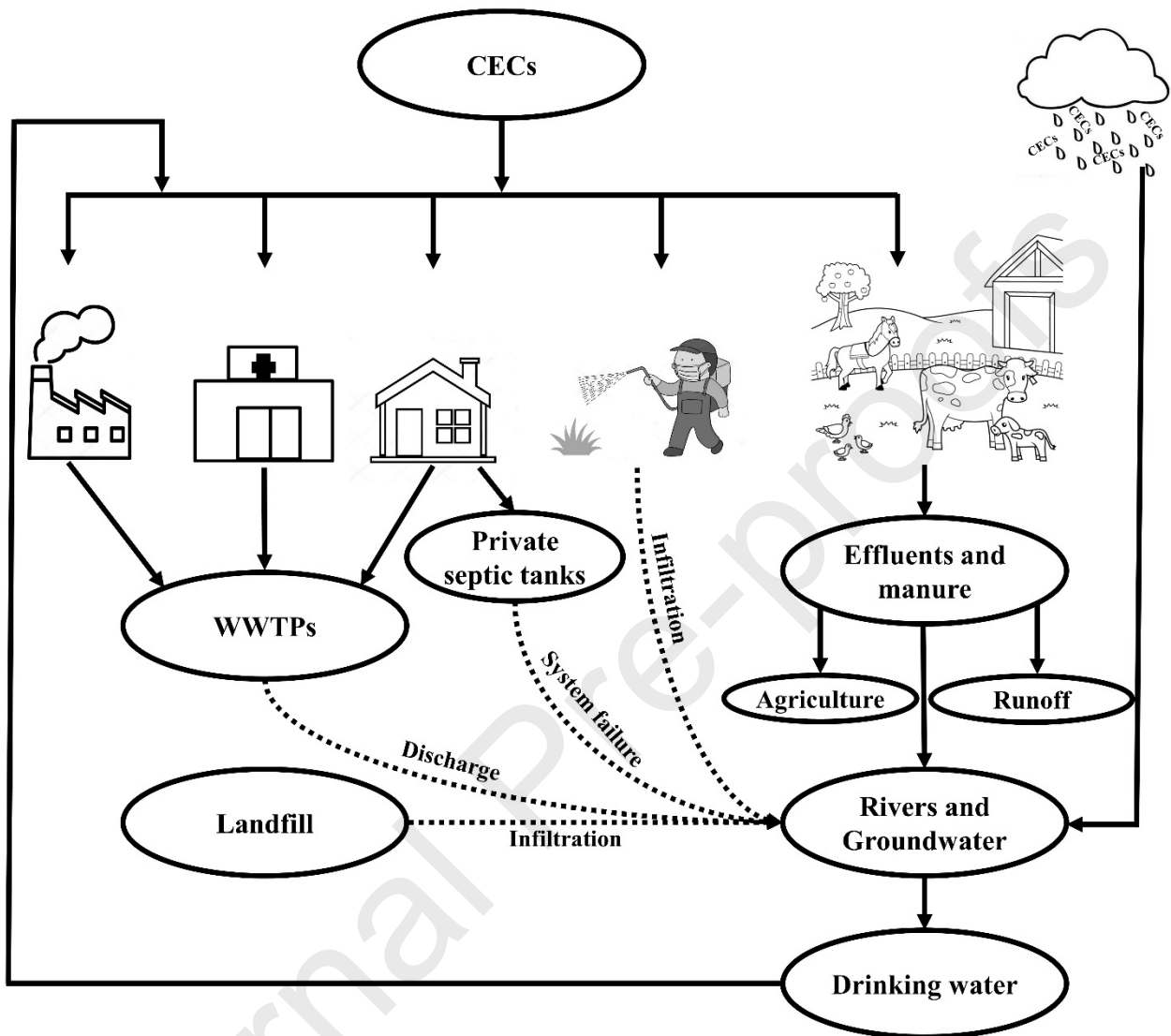


Fig. 2

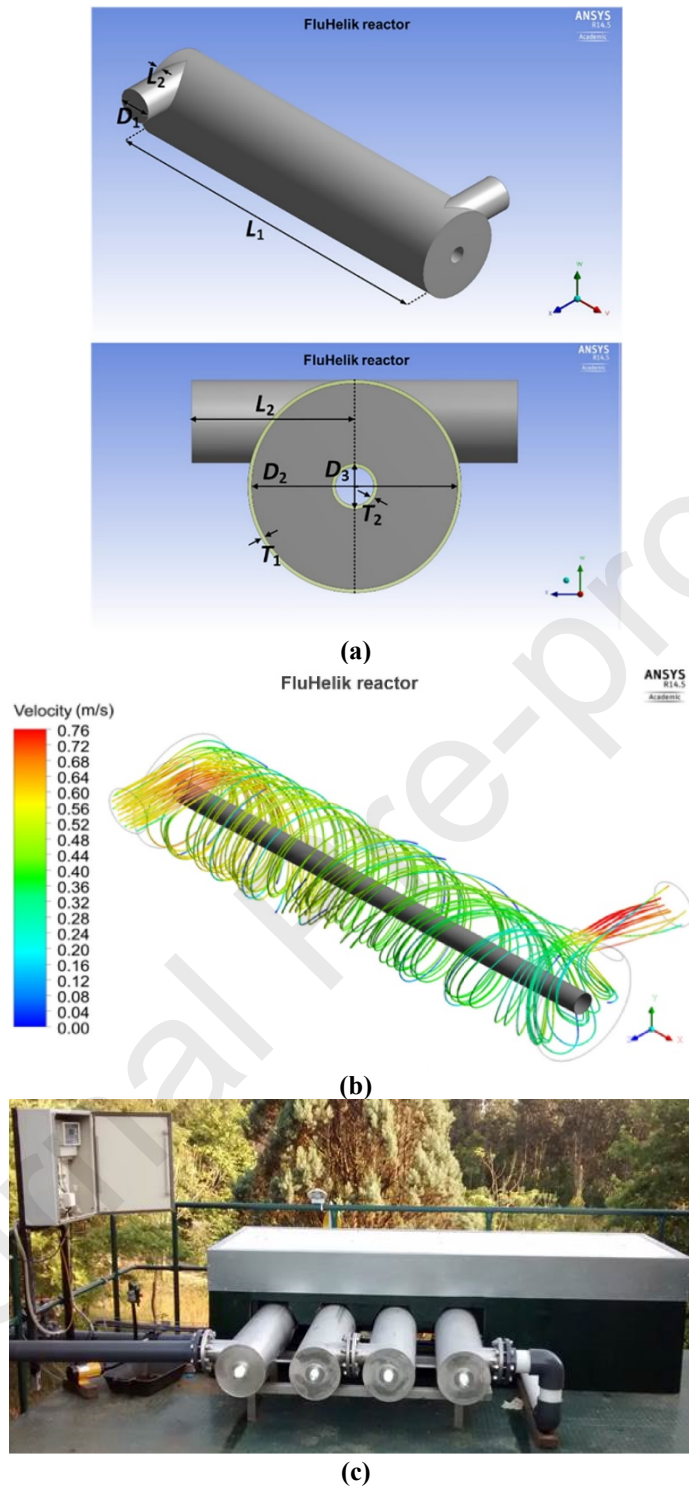
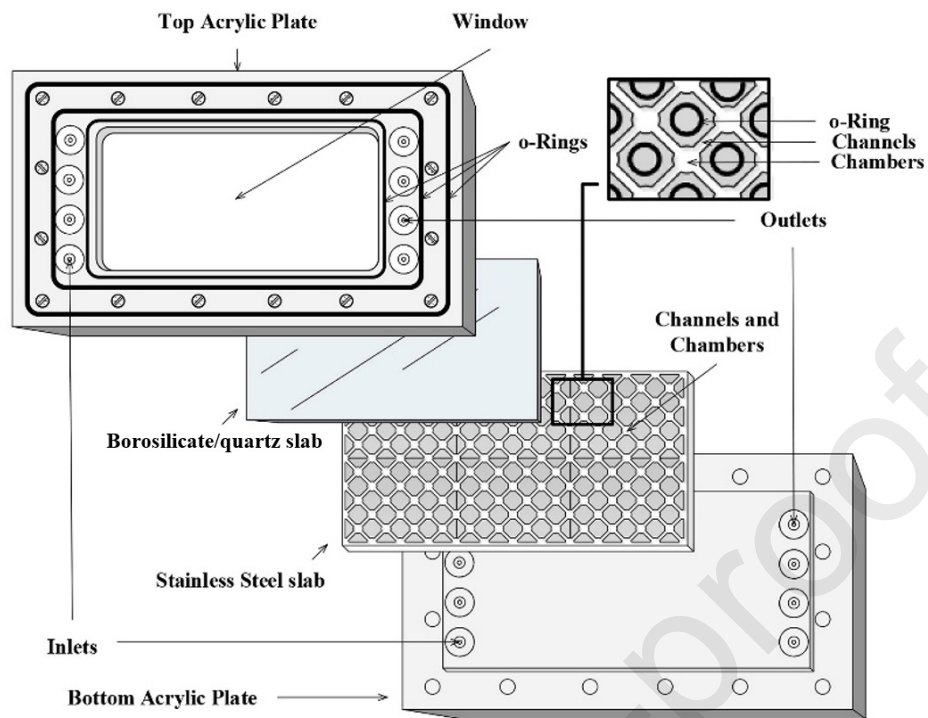
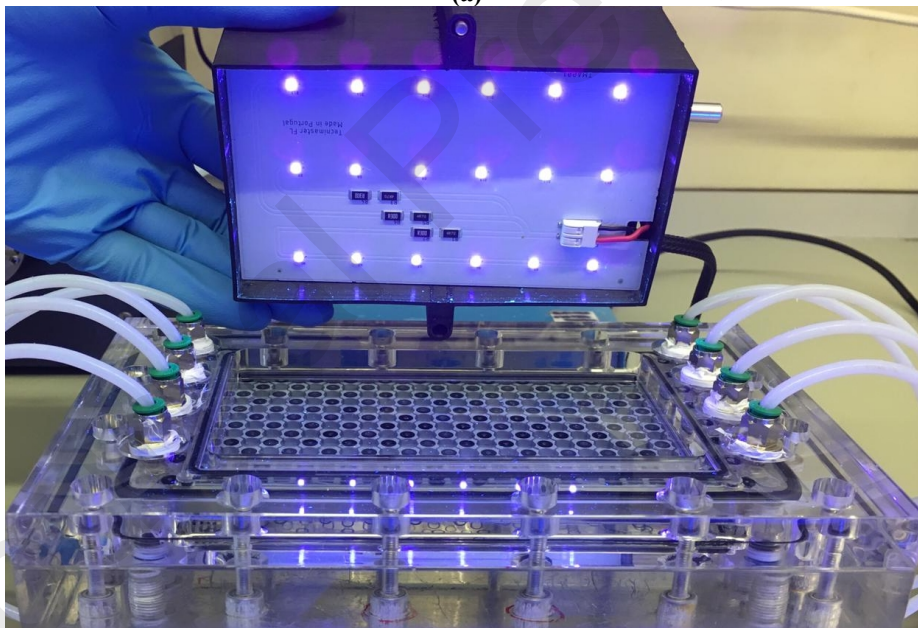


Fig. 3



(a)



(b)

Fig. 4

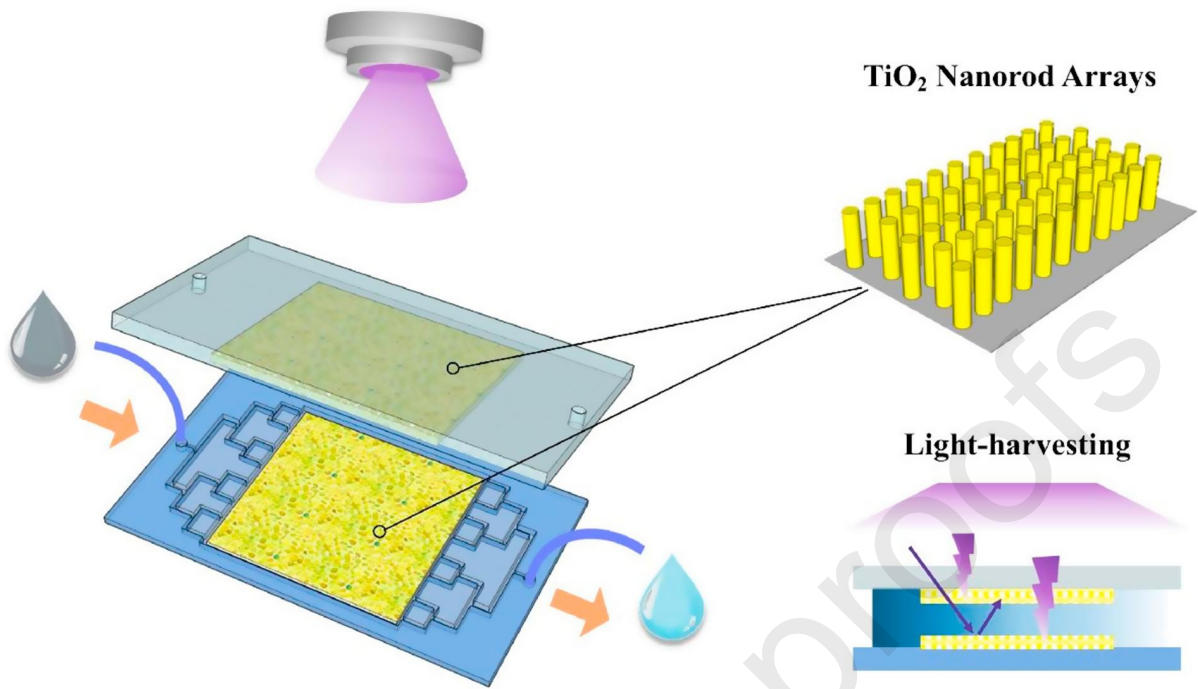


Fig. 5

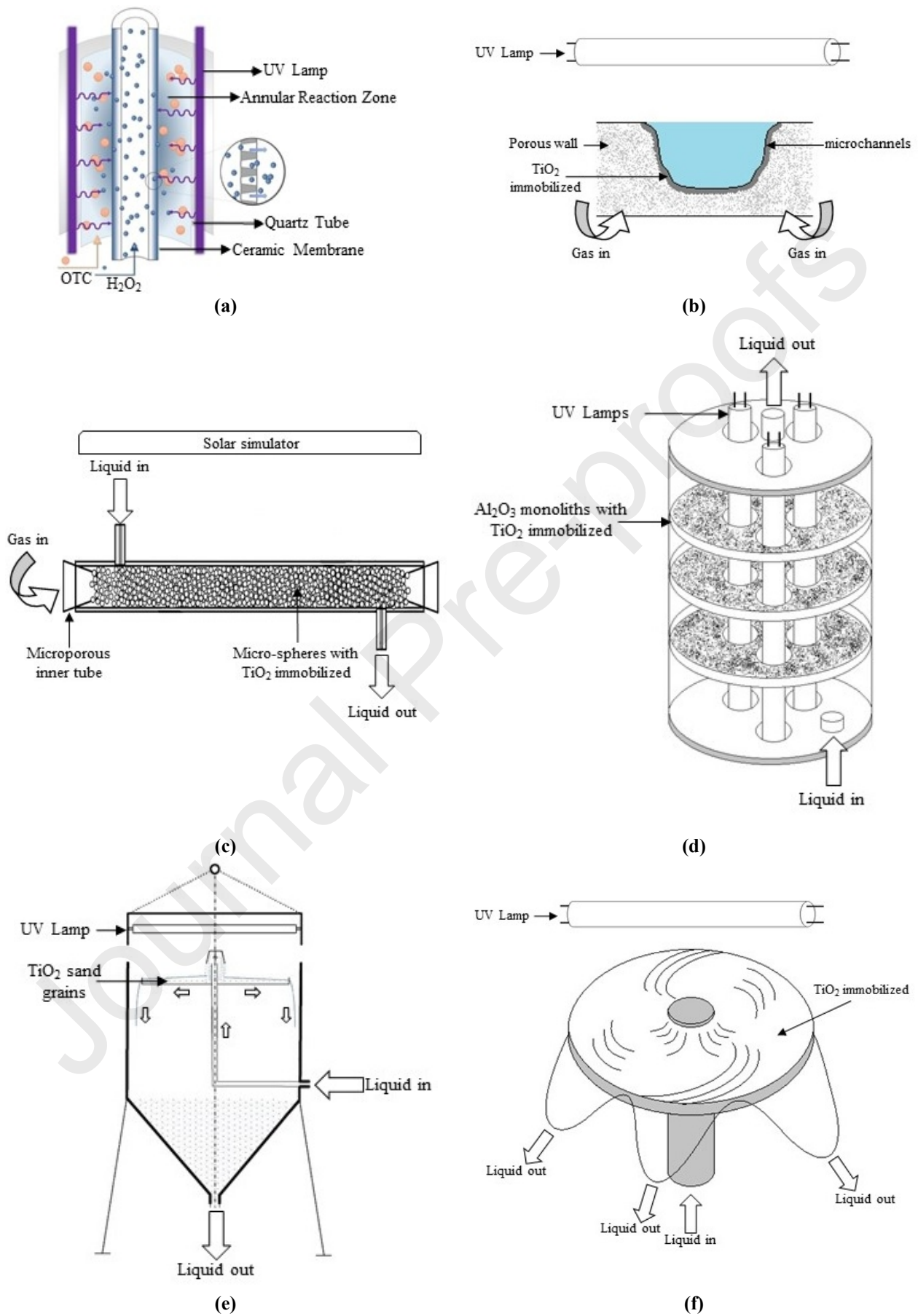


Table 1. Reported data on CECs detection in the environment.

Group	CEC	Molecular formula	Environmental compartment detected	CEC concentration detected ($\mu\text{g L}^{-1}$)	Reference
Pharmaceutical	Azythromycin	$\text{C}_{38}\text{H}_{72}\text{N}_2\text{O}_{12}$	Surface water	0.06-0.1	[195]
			Wastewater	0.66-1.68	[196]
			Wastewater	0.06-2.5	[197]
	Oxytetracycline	$\text{C}_{22}\text{H}_{24}\text{N}_2\text{O}_9$	Surface water	0.02	[198]
			Surface water	0.34	[199]
			Wastewater	0.35	[200]
	Ibuprofen	$\text{C}_{13}\text{H}_{18}\text{O}_2$	Groundwater	0.05	[201]
			Surface water	1.0	[199]
			Wastewater	1.3-2.2	[196]
			Wastewater	4.1	[202]
	Amoxicillin	$\text{C}_{16}\text{H}_{19}\text{N}_3\text{O}_5\text{S}$	Surface water	0.2	[200]
			Surface water	0.3*	[203]
			Wastewater	0.33-0.59	[204]
			Wastewater	6.9	[200]
	Diclofenac	$\text{C}_{14}\text{H}_{11}\text{Cl}_2\text{NO}_2$	Groundwater	0.04*	[205]
Surface water			0.14-0.31	[206]	
Wastewater			0.6	[202]	
Wastewater			0.61-2.43	[196]	
Personal care products	Galaxolide	$\text{C}_{18}\text{H}_{26}\text{O}$	Groundwater	0.043	[205]
			Surface water	0.02-4.8	[207]
			Surface water	0.46	[208]
			Wastewater	1.1-4.0	[209]
			Wastewater	25	[202]
	Tonalide	$\text{C}_{18}\text{H}_{26}\text{O}$	Groundwater	7.5×10^{-3}	[205]
			Surface water	0.1*	[208]
			Surface water	0.95	[207]
			Wastewater	0.2-1.0	[209]
			Wastewater	1.9	[202]
	Triclosan	$\text{C}_{12}\text{H}_7\text{Cl}_3\text{O}_2$	Wastewater	0.04-1.95	[210]
			Groundwater	2×10^{-3}	[211]
			Surface water	1.9×10^{-3} *	[212]
			Surface water	2.3	[199]
	Octocrylene	$\text{C}_{24}\text{H}_{27}\text{NO}_2$	Wastewater	0.18-4.4	[213]
Groundwater			8.4×10^{-3}	[205]	
Surface water			0.05*	[214]	
Celestolide	$\text{C}_{17}\text{H}_{24}\text{O}$	Wastewater	13	[209]	
		Surface water	2.5×10^{-3} *	[208]	

			Wastewater	0.03	[202]
			Wastewater	0.045	[215]
			Wastewater	0.05	[209]
Hormones	Estriol	C ₁₈ H ₂₄ O ₃	Groundwater	0.16 × 10 ⁻³	[216]
			Surface water	1.9 × 10 ⁻³	[216]
			Wastewater	4.9 × 10 ^{-3*}	[217]
	17β-estradiol	C ₁₈ H ₂₄ O ₂	Groundwater	0.1 × 10 ⁻³	[218]
			Surface water	0.01-0.2	[219]
			Surface water	0.2	[199]
			Wastewater	1.1-1.2	[220]
	Estrone	C ₁₈ H ₂₂ O ₂	Groundwater	1.1 × 10 ⁻³	[218]
			Surface water	4.6 × 10 ⁻³	[216]
			Wastewater	0.08	[221]
			Wastewater	0.13	[220]
			Wastewater	0.01-0.18	[210]
	Progesterone	C ₂₁ H ₃₀ O ₂	Groundwater	2.8-4.1 × 10 ⁻³	[222]
			Surface water	1.15 × 10 ⁻³	[223]
			Surface water	1.7-3.5 × 10 ⁻³	[222]
Surface water			0.2	[199]	
Testosterone	C ₁₉ H ₂₈ O ₂	Groundwater	4.3-6 × 10 ⁻³	[222]	
		Surface water	2.8-3.4 × 10 ⁻³	[222]	
		Surface water	0.21	[199]	
Pesticides	Carbofuran	C ₁₂ H ₁₅ NO ₃	Groundwater	0.1	[211]
			Groundwater	10.4	[224]
			Surface water	0.95-1.67	[225]
	Atrazine	C ₈ H ₁₄ ClN ₅	Groundwater	0.03	[226]
			Groundwater	0.06	[227]
			Groundwater	0.06	[205]
			Groundwater	0.2-0.7	[228]
			Surface water	0.1-0.8	[228]
			Surface water	0.06*	[214]
Clomazone	C ₁₂ H ₁₄ ClNO ₂	Groundwater	0.8	[224]	
		Groundwater	2.7-10.8	[228]	
		Surface water	3.2-15.7	[228]	
Iprodione	C ₁₃ H ₁₃ Cl ₂ N ₃ O ₃	Groundwater	0.06	[227]	
		Surface water	11 × 10 ⁻³	[229]	
		Surface water	34 × 10 ^{-3*}	[230]	
Carbendazim	C ₉ H ₉ N ₃ O ₂	Groundwater	1.6	[227]	
		Surface water	0.1-1.8	[214]	
		Surface water	0.2-4.5	[231]	
		Wastewater	0.014-0.078	[232]	

Industrial chemicals	Caffeine	$C_8H_{10}N_4O_2$	Groundwater	6×10^{-3}	[211]
			Groundwater	0.045	[233]
			Surface water	6.0	[199]
			Wastewater	66	[202]
	Cotinine	$C_{10}H_{12}N_2O$	Groundwater	0.012*	[205]
			Groundwater	0.06-0.4	[234]
			Surface water	0.9	[199]
			Wastewater	0.7-2.6	[235]
	Nicotine	$C_{10}H_{14}N_2$	Groundwater	0.041*	[205]
			Groundwater	8.07	[236]
			Wastewater	11.7	[202]
			Wastewater	1.1-14.6	[235]
	bis(2-ethylhexyl) phthalate	$C_{24}H_{38}O_4$	Groundwater	0.39	[227]
			Groundwater	46	[226]
			Surface water	20	[199]
			Wastewater	61	[237]
Cocaine	$C_{17}H_{21}NO_4$	Groundwater	1.2	[236]	
		Wastewater	0.29	[235]	
		Wastewater	0.6-3.7	[238]	

*average value

Table 2. Watch list of substances to be monitored in EU surface waters according to the Decision (EU) 2015/495 and Decision (EU) 2018/840.

Group	Name of substance	Molecular formula	Decision (EU) 2015/495	Decision (EU) 2018/840
Hormones	17 α -ethinylestradiol	C ₂₀ H ₂₄ O ₂	✓	✓
	17 β -estradiol	C ₁₈ H ₂₄ O ₂	✓	✓
	Estrone	C ₁₈ H ₂₂ O ₂	✓	✓
Pharmaceuticals	Amoxicillin	C ₁₆ H ₁₉ N ₃ O ₅ S	-	✓
	Azithromycin	C ₃₈ H ₇₂ N ₂ O ₁₂	✓	✓
	Ciprofloxacin	C ₁₇ H ₁₈ FN ₃ O ₃	-	✓
	Clarithromycin	C ₃₈ H ₆₉ NO ₁₃	✓	✓
	Diclofenac	C ₁₄ H ₁₁ Cl ₂ NO ₂	✓	-
	Erythromycin	C ₃₇ H ₆₇ NO ₁₃	✓	✓
Pesticides	Acetamiprid	C ₁₀ H ₁₁ ClN ₄	✓	✓
	Clothianidin	C ₆ N ₅ H ₈ SO ₂ Cl	✓	✓
	Imidacloprid	C ₉ H ₁₀ ClN ₅ O ₂	✓	✓
	Metaflumizone	C ₂₄ H ₁₆ F ₆ N ₄ O ₂	-	✓
	Methiocarb	C ₁₁ H ₁₅ NO ₂ S	✓	✓
	Oxadiazon	C ₁₅ H ₁₈ Cl ₂ N ₂ O ₃	✓	-
	Thiacloprid	C ₁₀ H ₉ ClN ₄ S	✓	✓
	Thiamethoxam	C ₈ H ₁₀ ClN ₅ O ₃ S	✓	✓
Triallate	C ₁₀ H ₁₆ Cl ₃ NOS	✓	-	
Personal care product	2-ethylhexyl-4-methoxycinnamate	C ₁₈ H ₂₆ O ₃	✓	-
Industrial chemical	2,6-di-tert-butyl-4-methylphenol	C ₁₅ H ₂₄ O	✓	-

Table 3. Advantages and drawbacks for each treatment process.

Treatment	Advantages	Drawbacks
UV/Oxidant	<ul style="list-style-type: none"> • High CECs removal (> 80%) • Easy operation • Effective disinfection • No undesired sludge generation 	<ul style="list-style-type: none"> • Formation of oxidation by-products • High energy and/or oxidant requirements • Control/removal of the oxidant residual concentration on the treated water is needed • Further investigations to evaluate the viability of the process at full scale are needed
Photocatalysis	<ul style="list-style-type: none"> • High CECs removal (> 80%) • Possible use of natural sun light • Effective disinfection 	<ul style="list-style-type: none"> • Formation of oxidation by-products • Low reaction times • Narrow overlap of the solar spectrum with the absorption spectrum of many catalysts (e.g. TiO_2 = < 5% of overlap). • Catalyst separation step is needed for slurry conditions • Catalyst deactivation • Large land area requirements (in the case of using natural sun light)

Table 4. Studies on diclofenac (DCF) removal by different processes.

Treatment process	Operating conditions	CEC abatement (%)	E_{EO} (kW h m ⁻³ order ⁻¹)	Reference
UV/H ₂ O ₂ oxidation	[H ₂ O ₂] ₀ = 20 mg L ⁻¹ 5 UVC lamps (150 W each, λ_{max} = 254 nm) Incident light = 70 W m ⁻² [DCF] ₀ = 0.9 mg L ⁻¹ pH = 6-7 Reaction time = 0.3 h k (min ⁻¹) = 0.23 min ⁻¹ Total volume = 37 L (pilot scale)	99	3.4	[83]
UV/persulfate oxidation	[PS] ₀ = 238 mg L ⁻¹ UVC lamps (75 W, λ_{max} = 254 nm) Incident light = 1 W m ⁻² [DCF] ₀ = 8.9 mg L ⁻¹ pH = 6 Reaction time = 1 h k (min ⁻¹) = 0.03 min ⁻¹ Total volume = 0.1 L (23 ± 1 °C)	85	960	[239]
Heterogeneous photocatalysis (UV/TiO ₂)	[TiO ₂] ₀ = 0.05 g L ⁻¹ UVA lamp (9W, λ = 350-400 nm) Photonic flow = 3.37 × 10 ⁻⁶ einstein s ⁻¹ [DCF] ₀ = 10 mg L ⁻¹ pH = 6 Reaction time = 4 h k (min ⁻¹) = 0.008 min ⁻¹ Total volume = 350 mL (20-25 °C)	85	125	[71]
	[TiO ₂] ₀ = 0.2 g L ⁻¹ Irradiated collector surface = 3.08 m ² Constant solar UV power ≈ 30 W m ⁻² [DCF] ₀ = 50 mg L ⁻¹ pH = no pH adjustment Reaction time = 3.3 h k (min ⁻¹) = 0.02 min ⁻¹ Total volume = 35 L (30-40 °C) (pilot scale)	99-100	4.2	[240]
Heterogeneous photocatalysis (UV/Co ₃ O ₄ /WO ₃)	[Co ₃ O ₄ /WO ₃] ₀ = 0.03 g L ⁻¹ UV lamp (80W, λ = 420 nm) [DCF] ₀ = 15 mg L ⁻¹ pH = 10.7 Reaction time = 3 h k (min ⁻¹) = 0.02 min ⁻¹ Total volume = 0.1 L	99	1273	[241]

Table 5. Most common light sources used in microreactors for photochemical processes (adapted from Su, et al. [242] and Matafonova and Batoev [112]).

Light Source	Emission wavelength (nm)	Comments
Hg Lamps	185 - 600	Relatively short life time, large size, low impact resistance, high sensitivity to temperature variations, low conversion of electrical energy into useful light
Lasers	Discrete wavelengths	High intensity
UV-LEDs	200 - 400	Low-energy input, long life time, expensive, compatible with microreactors
Vis-LEDs	Wide range of wavelengths between 400 - 700 nm	Low-energy input, long life time, cheap, compatible with microreactors
Sunlight	5% UV, 43% Vis and 52% NIR	Variable intensity, large areas requirement, diffuse irradiation

Table 6. Catalyst-coated surface per unit of reactor volume for different photoreactor configurations.

Reactor	Catalyst-coated surface per unit of reactor volume ($\text{m}^2 \text{m}^{-3}$)	Reference
Tubular	27 – 79	[84, 243]
Microreactor	6,780 – 12,000	[14, 133]
Membrane Reactor	24 – 250	[142, 150]
Other Reactors		
- <i>Micro-structured reactor</i>	6,180 – 34,320	[68, 173]
- <i>Monolith reactor</i>	1,538	[244]
- <i>Optofluidic microreactor</i>	10,000	[132]
- <i>Photoelectrocatalytic reactor</i>	0.01	[192]
- <i>Spinning disc reactor</i>	4,000	[176]

Table 7. Summary of main photoreactors presented in this work and patents related to light-driven chemical/catalytic processes.

Reactor type	Reactor/patent	Description of the specific/new features	Advantages	Reference
Tubular reactors	Rotating tubular reactor ^a	The rotating tubular reactor is composed of a cylindrical-shape tube and a rotating body, including nanotubular TiO ₂ (NTT) on Ti meshes. The reactor is irradiated by solar simulator or sun light.	The mass transfer within the photoreactor is improved due to the large catalyst area of the rotating TiO ₂ structure. The system comprises a compact reaction structure (small area required). Reduced energy consumption (use of solar light).	[90]
	FluHelik ^a	FluHelik consists of an annular reactor with tangential inlet/outlet pipes. This geometry promotes a helical movement of the fluid around the UV lamp.	The photoreactor promotes enhanced dynamics of macromixing, a more homogeneous UV radiation distribution and a longer particles/UV light contact time.	[92]
	Photocatalytic reactor with a modular configuration and advanced oxidation process for purifying and disinfecting wastewater from aquaculture (EP1686095A1) ^b	The TiO ₂ -photocatalytic reactor consists of a black polyethylene cylindrical tube. In the inner part, fixed strips of glass sheets covered by TiO ₂ are irradiated by UV lamps.	The cylindrical configuration and reduced size facilitate its construction, transport and installation. No recovery of catalyst from the treated water is necessary (immobilized catalyst).	[245]
Microreactors	Photocatalytic microreactor with immobilized TiO ₂ ^a	The photocatalytic microreactor is composed of 19 channels with a cross-section of approximately 200 μm × 300 μm. The system is equipped with UV-A LEDs.	The reactor poses a significantly high illuminated catalyst surface area per unit of liquid treated inside the reactor (approximately 400 times higher than conventional photocatalytic reactors). The system combines the miniaturization of both reaction size (area required) and illumination source (LEDs). Enhanced mass and photons transfer.	[14]
	Dual-film optofluidic microreactor ^a	The novel microreactor is composed of three layers: two fluorine-doped tin oxide glasses coated with highly ordered TiO ₂ nanorod arrays (TiO ₂ NRA) on both the top and bottom internal wall of the microchamber, and a 200 μm-thick adhesive layer as the spacer and sealant.	The reactor provides a high catalyst surface-to-volume ratio, enhancing the mass transfer. Better exposition of active catalytic sites to the light and reactants (light is harvested at both top and bottom surfaces of the reactor).	[132]
	Network mixer and related mixing process (US8434933B2) ^b	The reactor consists of a regular network of cylindrical chambers interconnected by transport prismatic channels with small dimensions sealed by a borosilicate/quartz slab. The channels work as plug flow perfect segregation zones and the chambers as perfectly mixing zones.	This patent claims to offer a strong and efficient degree of mixing, and, as a result, enhanced mass transfer. Its dimensional character results in a high specific area per volume of reactor.	[122]
Photocatalytic membrane reactors	Photocatalytic membrane reactor with dual active membrane layer ^a	The PMR consists of an ultrafiltration (UF) membrane coated with modified nanostructured titania (m-TiO ₂) on both inner and outer membrane	Membranes with enhanced anti-fouling properties. No need of regeneration or anti-fouling procedures, which makes the process more energy-	[142]

		surfaces. The membrane is irradiated externally by UVA-Vis lamps and internally by UVA-LEDs.	efficient. Low installation and operating costs, since the reactor can operate without any extra device.	
	Multichannel photocatalytic membrane reactor ^a	The PMR consists of a cylindrical tube where a multichannel membrane is housed. The membrane has 44 channels. One optical fiber was hosted inside each channel of the membrane. The optical fibers received the concentrated solar radiation in their upper edge and transmitted the light towards the membrane surface. The radiation system also includes a number of artificial light sources to operate during shade/night.	Low implementation costs due to the replacement of expensive UV lamps by optical fibers. Reduced energy consumption (use of solar light). Autonomy for operation during day and night.	[168]
	Photocatalytic membrane, process for its production and use thereof (EP1555064A1) ^b	The photocatalytic membrane consists of a semiconductor, a photopromoter and a photosensitizer supported by photografting on a microporous support. The photografted layers are irradiated by UV light.	This patent claims to allow continuous solution flow through the microporous membrane, enhancing the reactivity compared with other membranes. In addition, the photografted layers are resistant to UV irradiation.	[246]
Other reactors and hybrid systems	Tube-in-tube membrane microreactor ^a	The novel membrane microreactor is composed of an inner ultrafiltration membrane and a quartz outer tube. The system is irradiated by four UVC lamps. Oxidant is added radially through the entire length of the porous membrane.	The reactor design produces a helical motion of water around the membrane shell-side, enhancing the radial mixing and promoting a more homogeneous oxidant distribution in the annular reaction zone of the membrane reactor.	[170]
	Sono-photocatalysis hybrid system ^a	The hybrid system couples sonocatalysis and photocatalysis using TiO ₂ decorated on magnetic activated carbon (MAC-T) in combination with ultrasound (US) and ultraviolet (UV) irradiations. The reactor consists of a cylindrical quartz vessel under both UV and US irradiation.	Great synergistic effect between MAC@T catalyst and UV and US irradiations. Easy catalyst separation and recovery due to the presence of magnetite nanoparticles loaded on the activated carbon. Catalyst with high surface area and adsorption capacity.	[184]
	Method and apparatus for purification of industrial wastewater with thin film fixed bed TiO ₂ photocatalyst (WO2004058649A1) ^b	This unit consists of a thin photocatalyst film immobilized by spray technic to an inert support (Cuddapah stone). In order to prepare the photocatalytic films, TiO ₂ solution was sprayed on the clean stone. Subsequently, the material was left for drying (no need of additional treatment). This process was repeated until a homogeneous aspect was attained. Effluent flows through the photocatalyst material under solar irradiation.	This patent claims to be an economic approach for water treatment. No need of expensive treatments for catalyst immobilization. No power consumption due to the use of solar light.	[247]
	Apparatus and method for photocatalytic purification and disinfection of water (US6524447B1) ^b	The reactor consists of an open-cell (three dimensionally reticulated and permeable) composed of a rigid substrate integrated with a catalyst. Polluted water flows through the catalyst unit,	This patent claims to offer more intense turbulence inside the reactor. Low electrical energy required due to the use of LEDs.	[248]

		photoactivated by LEDs, where contaminants are removed.		
	Multi-barrier water purification system and method (WO2009044288A2) ^b	The system consists of a closed-loop multi-barrier cross flow-filtration system integrated with AOP. One of the approaches couples a filtration membrane with a honing material. The latter is placed in the polluted water in order to scrub foulants from the membrane. The system includes a UV light source. In some cases, the honing may be provided by turbulent flow inside the reactor. In order to eliminate suspended solids within the loop, a “blowdown” valve can be used. A final barrier (e.g. RO) can also be incorporated into the system to retain inorganic salts, etc.	This patent claims to attain 100% fluid recovery (i.e. zero reject stream). Enhanced performance over the sum of the individual technologies. The multibarrier system allows not only the removal of organic contaminants but also salts, and it is suitable to treat drinking water or reuse water. All stages are conducted in a single unit.	[249]

^a Reactor.

^b Patent.

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Table 8. Comparison of several results attained on oxytetracycline removal from urban wastewaters by different light-driven chemical/catalytic processes using different reactors and system configurations [42, 92, 126, 145, 150].

Parameters at optimized conditions	Different reactors and system configurations							
	Jets	FluHelik	NETmix	NETmix ^a	PMR ^b	Hybrid membrane reactor ^c	PMR ^b	PMR ^d
Oxytetracycline concentration (mg L ⁻¹)	20	20	20	20	5	5	5	5
Radiation source	UVC lamp	UVC lamp	UVC lamp	UVA-LEDs	UVC lamp	UVC lamp	UVA lamp	UVA lamp
Volume treated (L)	1.5	1.5	1.5	1.5	7.0	7.0	5	5
Photonic Flow (J s ⁻¹)	2.0	2.0	1.08	5.25	5.1	5.1	0.53	0.53
Oxidant dose (mg L ⁻¹)	500	500	500	-	-	120	-	-
Photocatalyst loading (mg L ⁻¹)	-	-	.	57 ^e	1,000	-	400	9 ^e
<i>k</i> (min ⁻¹)	0.46	0.49	0.05	0.03	0.33	0.55	0.07	0.007
<i>k</i> (L kJ ⁻¹)	5.8	6.1	1.23	0.15	7.61	12.5	10.5	1.09
ξ (%)	12.4	12.1	2.5	0.2	3.73	5.74	3.5	0.37
Photochemical space time yield (m ³ _{water} m ⁻³ _{reactor} day ⁻¹ kW ⁻¹)	0.50	0.53	0.11	0.01	0.66	1.08	0.91	0.09
E _{EO} (kW h m ⁻³ order ⁻¹)	0.11	0.10	0.55	4.48	0.08	0.05	0.06	0.58

^a Photocatalyst immobilized on the reactor channels and chambers.

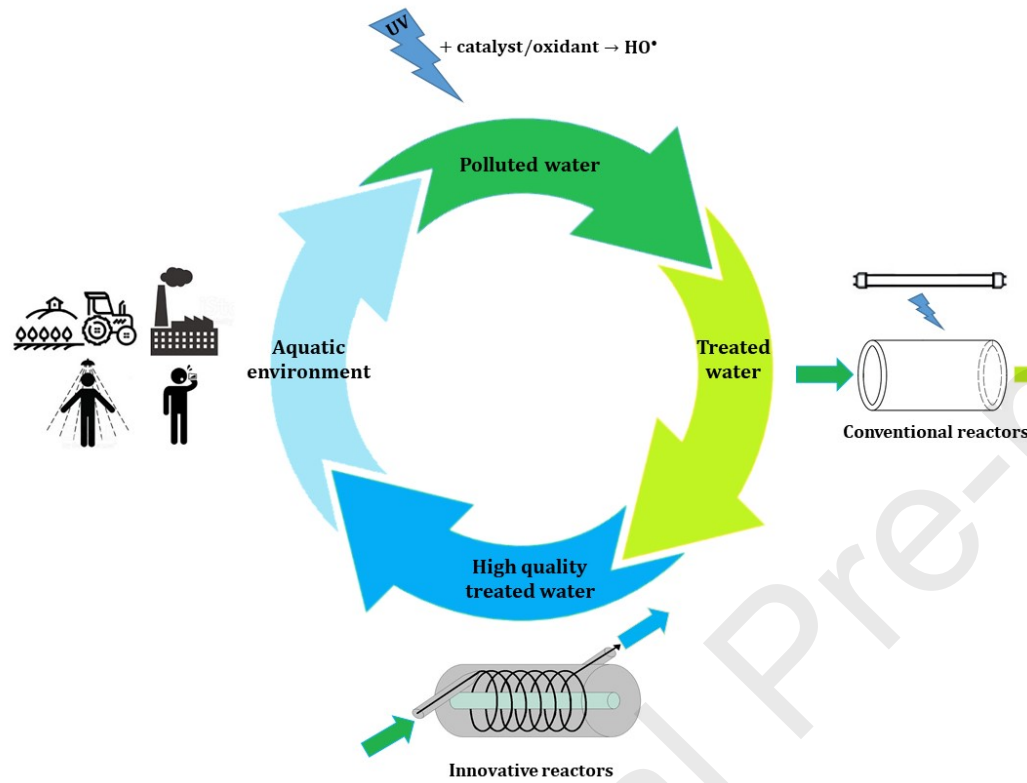
^b Slurry photocatalyst system.

^c Hybrid system coupling membrane separation with H₂O₂/UVC process.

^d Photocatalyst immobilized on the membrane.

^e Defined as the ratio between the amount of catalyst immobilized and the wastewater volume treated.

Graphical Abstract



Highlights

- Light-induced **chemical/catalytic** technologies for effective removal of CECs
- Overview of advances to overcome limitations in light-induced technologies
- **Review on systems with enhanced macromixing dynamics**
- **Review on reactors designs with a high illuminated catalyst surface area**

- Reports on advances in illumination systems

Journal Pre-proofs