

1           **Emerging advanced oxidation processes for water and wastewater treatment**

2                           **– guidance for systematic future research**

3  
4           **Uwe Hübner<sup>a</sup>, Stephanie Spahr<sup>b</sup>, Holger Lutze<sup>c,d,e</sup>, Arne Wieland<sup>f</sup>, Steffen Rüting<sup>f</sup>, Wolfgang**  
5                           **Gernjak<sup>g,h</sup>, Jannis Wenk<sup>i</sup>**

6  
7           <sup>a</sup>Chair of Urban Water Systems Engineering, Technical University of Munich, Am Coulombwall 3,  
8           85748 Garching, Germany

9           <sup>b</sup>Leibniz Institute of Freshwater Ecology and Inland Fisheries (IGB), Müggelseedamm 301, 12587  
10           Berlin, Germany

11           <sup>c</sup>Department of Civil and Environmental Engineering, Institute IWAR, Chair of Environmental  
12           Analytics and Pollutants, Technical University of Darmstadt, Franziska-Braun-Straße 7, 64287  
13           Darmstadt, Germany

14           <sup>d</sup>IWW Water Centre, Moritzstraße 26, 45476 Mülheim an der Ruhr, Germany

15           <sup>e</sup>Centre for Water and Environmental Research (ZWU), Universitätsstraße 5, 45141 Essen,  
16           Germany

17           <sup>f</sup>Xylem Services GmbH, Boschstraße 4-14, 32051 Herford; Germany

18           <sup>g</sup>Catalan Institute for Water Research (ICRA), 17003 Girona, Spain

19           <sup>h</sup>Catalan Institution for Research and Advanced Studies (ICREA), 08010 Barcelona, Spain.

20           <sup>i</sup>University of Bath, Department of Chemical Engineering and Water Innovation & Research Centre  
21           (WIRC@Bath), Bath BA2 7AY, United Kingdom

22  
23           **Keywords: Advanced oxidation processes, experimental design, probe compounds, trace**  
24           **organic chemicals, water treatment**

25           **Abstract**

26           Advanced oxidation processes (AOPs) for water treatment are a growing research field with a large  
27           variety of different concepts and materials being tested at laboratory scale. However, only few

28 concepts have been translated into pilot- and full-scale operation recently. One major concern are  
29 the inconsistent experimental approaches applied across different studies that impede identification,  
30 comparison, and upscaling of the most promising concepts. The aim of this tutorial review is to  
31 streamline future studies on the development of new solutions and materials for advanced oxidation  
32 by providing guidance for comparable and scalable oxidation experiments. We discuss recent  
33 developments in catalytic, ozone-based, radiation-driven, and other mostly physical AOPs, and  
34 outline future perspectives and research needs. Suitable figures-of-merit for comparison and  
35 benchmarking of AOPs are reviewed. Since standardized experimental procedures are not available  
36 for the majority of AOPs, we propose basic rules and key parameters for lab-scale evaluation of new  
37 AOPs including selection of suitable probe compounds, model compounds, and scavengers for the  
38 measurement of (major) reactive species. A two-phased approach to assess new AOP concepts is  
39 proposed, consisting of (i) a feasibility-of-concept study phase with validation of major radical  
40 species and comparison to suitable reference processes and materials, followed by (ii) a  
41 benchmarking phase conducted in the intended water matrix for the process, applying comparable  
42 and scalable parameters such as UV fluence or ozone consumption. Screening for transformation  
43 products should be based on chemical logic and combined with complementary tools (mass balance,  
44 chemical calculations) to advance mechanistic understanding of the process.

45

## 46 **1 Introduction**

47 Advanced oxidation processes (AOPs) are generally defined as processes that use in situ generated  
48 highly reactive radicals for the oxidative degradation of contaminants.<sup>1</sup> The major radical formed in  
49 most AOPs is the hydroxyl radical ( $\cdot\text{OH}$ ).<sup>2</sup> Besides the  $\cdot\text{OH}$ , reactive oxygen species (ROS) including  
50 singlet oxygen and superoxide, radicals derived from persulfate, carbonate or nitrate, other  
51 dissolved inorganic constituents, and solvated electrons may be involved in AOPs and affect  
52 process kinetics, reaction mechanisms, and product formation.<sup>3,4</sup> Sulfate and chlorine radical-  
53 induced oxidations are often also referred to as AOP-like processes.<sup>5</sup> AOPs can be applied during  
54 drinking water and wastewater treatment, water reuse applications, brine and leachate treatment,

55 and groundwater remediation, mostly to degrade organic contaminants but also for reduction of  
56 natural organic matter, disinfection or as pre-treatment to improve performance of downstream  
57 treatment processes.<sup>2,6–14</sup> Radicals for AOPs in water, including  $\cdot\text{OH}$ , can be generated in many  
58 ways, while AOPs can be broadly classified into four categories that include ozone-based, radiation-  
59 driven, catalytic, and other AOPs. The latter encompass a range of different, often high-energy,  
60 physical methods for AOP generation.

61 Given the diversity of AOPs and the wide range of possible applications, research activity and  
62 interest into AOPs has been considerably increasing. Beyond AOPs established at full scale, various  
63 processes have been tested at pilot scale, while other AOPs are being explored and developed at  
64 lab scale (see Figure 1). For instance, research has been conducted on the development of new  
65 materials for catalytic and electrolytic oxidation.<sup>15,16</sup> Similarly, new advanced oxidation processes  
66 such as vacuum UV, plasma treatment as well as new oxidants and radical promoters have been  
67 proposed and investigated.<sup>17–20</sup> Various alternative process combinations, from centralized  
68 treatment approaches to point-of-use-scale, but also reactor designs for catalytic or radiation-driven  
69 AOPs have been developed.<sup>16,21,22</sup> A large array of water contaminants, including so-called  
70 emerging contaminants, has been investigated to a great extent for their degradability by AOPs.<sup>2,23</sup>  
71 Despite several recent reviews on AOPs,<sup>2,5,24–26</sup> it can be challenging for individual researchers to  
72 obtain a comprehensive insight and to keep track with the most recent developments in AOP  
73 research, given the large number of studies published. One needs to be critical when it comes to  
74 the prospective applicability of newly developed AOPs.<sup>27,28</sup> The suitability of many novel AOPs for  
75 water treatment is debatable e.g., due to the utilization of materials with concerning toxicity or lack  
76 of long-term stability.<sup>29–31</sup> AOP studies with new materials or new radical generation mechanisms  
77 often lack critical information that would allow a sound evaluation of the efficiency in real water  
78 matrices, including chemical and energy demand. One example are time-based reaction rate  
79 constants of target contaminants only but without further information on energy input, oxidant dose,  
80 or chemical reactivity of the target contaminant. Another issue can be the choice of adequate  
81 reference processes and treatment objectives. For instance, ozonation has been used as reference

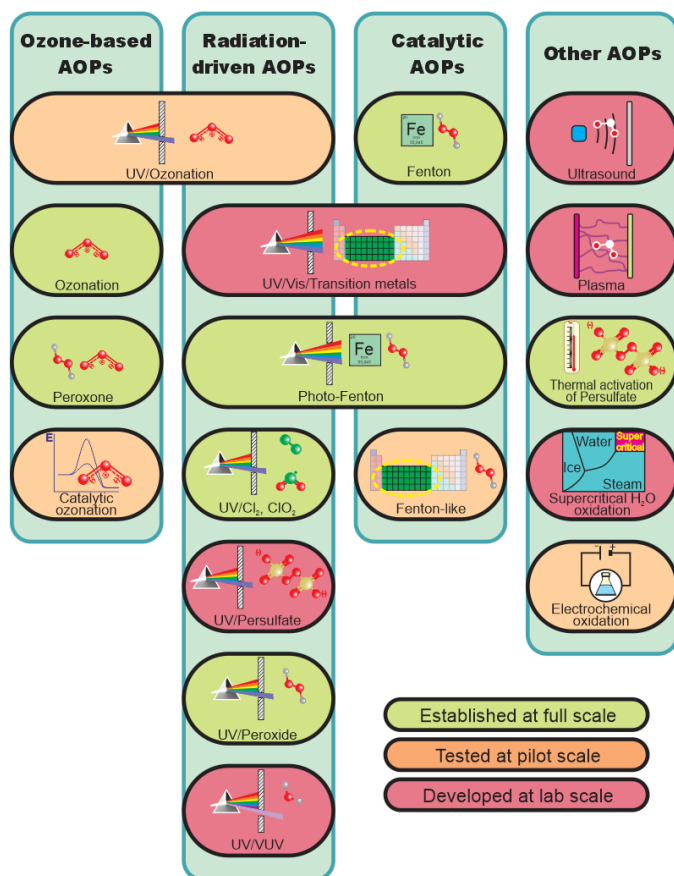
82 process to compare oxidative mineralization efficiency. However, a typical treatment target for  
83 ozonation is partial oxidation of target contaminants, followed by biofiltration, which has a  
84 significantly lower ozone dosage and, thus, energy demand<sup>32,33</sup> and mineralization is not required in  
85 most applications. Many studies combine the assessment of new materials and processes with the  
86 simultaneous investigation of new emerging contaminants, screening for transformation products,  
87 and the analysis of possible toxicological effects. While these aspects provide important information  
88 for a detailed understanding and assessment of the process itself, they do not enable an initial  
89 evaluation on the applicability and efficiency of the investigated process at larger scale. To  
90 streamline research efforts, systematic approaches are needed for an objective assessment of new  
91 concepts for oxidation of emerging contaminants.

92 With this tutorial review, we aim to provide guidance for researchers that work on the development  
93 of new solutions and materials for advanced oxidation. We briefly discuss status, potential and future  
94 research needs for emerging AOPs, summarize available concepts to assess and compare different  
95 AOPs, and outline basic rules for conducting oxidation experiments and selecting probe compounds  
96 and scavengers. Finally, we propose a systematic approach for the assessment of novel concepts  
97 and materials for advanced oxidation.

## 98 **2 Status and perspectives for “emerging” oxidation processes**

99 There is an immense variety of different approaches proposed and tested to generate radicals in  
100 water. Figure 1 summarizes various AOPs with indicated degree of application (lab-scale vs. pilot-  
101 and full-scale). Established AOPs operating at full scale comprise mostly UV- and ozone-based  
102 approaches. In addition, Fenton-based processes are widely established for industrial wastewater  
103 treatment. Besides the long history applying ozone and UV irradiation in drinking water treatment,<sup>27</sup>  
104 these most widely applied AOPs typically also provide the highest energy efficiencies among  
105 AOPs.<sup>25</sup> However, less efficient AOPs might still provide suitable solutions for specific applications,  
106 such as groundwater remediation, industrial wastewater treatment, degradation of otherwise  
107 recalcitrant contaminants, or decentralized water treatment applications with relatively small  
108 volumes of water, including specialized applications such as ballast water treatment.<sup>28,34,35</sup> In this

109 section, we briefly address the current state of the art for different AOPs and provide references to  
 110 studies with more detailed mechanistic discussion. We highlight advantages and limitations of  
 111 individual concepts, discuss future research needs, and identify potential areas for application. This  
 112 section will review current advances in catalytic AOPs, novel concepts and materials for ozone-  
 113 based and radiation-driven AOPs, and new alternative solutions for in situ radical generation.



114

115 *Figure 1. Broad overview and classification of different AOPs and AOP-like processes*

116 **2.1 Emerging materials and concepts for catalytic AOPs**

117 In catalytic oxidation, various homogenous and heterogeneous catalysts can be used to generate  
 118 reactive species by activating radical precursors such as hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), sodium  
 119 percarbonate (Na<sub>2</sub>CO<sub>3</sub> x 1.5 H<sub>2</sub>O<sub>2</sub>), peroxydisulfate (S<sub>2</sub>O<sub>8</sub><sup>2-</sup>), and monochloramine (NH<sub>2</sub>Cl) or  
 120 increase radical formation from oxidants such as ozone.<sup>36–39</sup> This section focuses on dark catalytic  
 121 processes, i.e., those without light as radical initiator, while light-induced AOPs are discussed in the  
 122 section on radiation-driven AOPs. The most widely studied and applied homogeneous catalytic

123 oxidation system is the Fenton reaction, in which  $\text{H}_2\text{O}_2$  reacts with dissolved ferrous iron ( $\text{Fe}(\text{II})$ ) to  
124 generate  $\cdot\text{OH}$ .<sup>40</sup> Although the traditional iron-based Fenton reaction is an established method-of-  
125 choice for the treatment of complex industrial wastewaters, critical aspects for its application include  
126 a narrow operation range determined by a maximum catalytic activity at  $\text{pH} = 2.8 - 3.0$ , rapid  
127 consumption of free radicals by excess  $\text{Fe}(\text{II})$ , and costs for iron-containing sludge disposal.<sup>29,40</sup> To  
128 avoid these bottlenecks, the application of chelating agents as well as iron-free Fenton-like systems  
129 have been explored using other transition metal ions (e.g., copper or cobalt), which can activate  
130  $\text{H}_2\text{O}_2$  at near-neutral pH conditions but only work under well-defined reaction conditions with careful  
131 consideration of catalyst toxicity.<sup>29,41,42</sup> A great deal of attention has been paid to both natural and  
132 synthetic solid catalysts such as iron-, manganese-, or cobalt-based materials,<sup>43–45</sup> engineered  
133 nanomaterials,<sup>46,47</sup> metal-free polymers,<sup>48,49</sup> carbonaceous materials,<sup>50,51</sup> layered double  
134 hydroxides,<sup>52</sup> metal-organic frameworks,<sup>53</sup> and single-atom catalysts.<sup>54,55</sup> Many of these materials  
135 possess high catalytic activity at the laboratory bench scale and promise AOP operation under  
136 neutral pH conditions. However, translation of catalytic AOPs into full-scale water treatment has  
137 been slow.<sup>46</sup> To overcome obstacles that prevent catalytic systems from commercialization and  
138 implementation, efforts should be directed not only towards producing standardized, regenerable,  
139 cost-effective, and sustainable catalysts with high physical and chemical stability but especially  
140 towards testing their suitability and long-term performance for well-defined water treatment  
141 applications.<sup>46</sup> These desirable attributes and testing requirements also apply to photocatalysts (see  
142 section on radiation-driven AOPs). Moreover, challenges concerning reactor design need to be  
143 addressed to allow for high contaminant-to-surface mass transfer and contaminant degradation  
144 efficiency, while at the same time minimizing catalyst loss and operational costs.<sup>46</sup> Innovative  
145 catalysts may broaden AOP applications towards enhanced in situ chemical oxidation or  
146 decentralized point-of-use water treatment, and tackle specific treatment goals for the removal of  
147 recalcitrant contaminants.<sup>46</sup>

## 148 **2.2 Recent progress in ozone-based advanced oxidation**

149 In every ozonation process,  $\cdot\text{OH}$  are formed from the reaction of ozone with the water matrix,  
150 especially with organic matter.<sup>56,57</sup> However, since the formation of  $\cdot\text{OH}$  is “uncontrolled”, ozonation  
151 is often not defined as an AOP.  $\cdot\text{OH}$  formation can be enhanced by the addition of  $\text{H}_2\text{O}_2$  (either as  
152 solution or by electrochemical in situ production) in the peroxone process, pH elevation, catalytic  
153 ozonation, or ozone photolysis.<sup>58–63</sup> UV/ $\text{O}_3$  is discussed as a UV-based AOP in the next section.

154 In the peroxone process, ozone reacts fast with the  $\text{H}_2\text{O}_2$  anion ( $\text{HO}_2^-$ ) ( $k = 9.6 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ ) with a  
155 yield of 0.5 mol  $\cdot\text{OH}$  per mol reacted ozone.<sup>58,61</sup> The peroxone process is often applied to mitigate  
156 formation of undesired bromate<sup>64,65</sup> or to quench excess ozone with the advantage of further  $\cdot\text{OH}$   
157 formation.<sup>66</sup> At elevated pH, ozone may react with hydroxide ions to form  $\cdot\text{OH}$ . However, this reaction  
158 is rather slow ( $k = 70 \text{ M}^{-1} \text{ s}^{-1}$ )<sup>67,68</sup> and the costs for adding bases, especially in strongly buffered  
159 waters, as well as increasing risk of bromate formation may limit ozonation at elevated pH towards  
160 a narrow range of source and wastewaters.<sup>69</sup>

161 Homogeneous and heterogenous catalysis in ozonation is based on the decomposition of ozone by  
162 transition metal ions or solid metal oxide catalysts (mostly iron- and manganese-based materials),  
163 and activated carbon or other carbon-based materials.<sup>62,70,71</sup> In heterogeneous catalytic ozonation,  
164 pollutant removal can be achieved via interfacial reactions at the catalyst surface after sorption of  
165 ozone (gaseous or dissolved) and/or the pollutant, and in the aqueous phase through  $\cdot\text{OH}$ , which is  
166 generated from ozone decomposition at the catalyst surface.<sup>70,72</sup> The process may have an  
167 advantage over homogenous catalysis because no additional metal ions need to be dosed and  
168 subsequently removed. However, it may have mass-transfer limitations as  $\cdot\text{OH}$  are formed at the  
169 catalyst surface. Knowledge about the driving mechanisms for catalytic ozonation is still limited. For  
170 example, different catalytic activity has been reported for various types of  $\text{MnO}_2$ , with some types  
171 leading to ozone decay without significant  $\cdot\text{OH}$  formation.<sup>62,73</sup> Different mechanisms have been  
172 proposed for catalytic ozonation with activated carbon-based materials,<sup>70</sup> with some studies  
173 indicating that radical formation may be related to finite reactions with functional groups of the carbon  
174 leading to a slow consumption of the “catalyst”.<sup>74</sup> A direct comparison of different study results is

175 often hampered by the use of various experimental procedures with different mass transfers  
176 (gaseous ozone vs. injection of ozone stock solution), different design and duration of the  
177 experiments, and different active catalyst surface areas. Research on catalytic ozonation should  
178 therefore follow standardized experimental procedures (see section 5) that enable the assessment  
179 of benefits for radical generation compared to sole ozonation (which already contributes to  
180 considerable radical generation), as well as mid- to long-term stability of the catalytic process.

### 181 **2.3 New solutions in radiation-driven AOPs**

182 In radiation-driven AOPs, the energy of electromagnetic radiation is utilized to form radicals.<sup>75,76</sup> The  
183 applied wavelengths range from > 170 (VUV) to 700 nm (visible light).<sup>77</sup> UV water treatment has  
184 been applied for several decades for water disinfection using mercury (Hg) lamps. Solar radiation  
185 and other lamp technologies exist with a small market share. Recently, light emitting diodes (LEDs)  
186 have quickly evolved in the UV range and show promise to increasingly replace Hg-containing  
187 irradiation sources (see below).

188 **Homogeneous AOPs.** Analogous to dark catalytic AOPs, radiation-driven AOPs can be  
189 distinguished into homogeneous and heterogeneous processes applying a similar range of radical  
190 precursors for homogeneous processes including H<sub>2</sub>O<sub>2</sub>, chlorine and chlorine dioxide,  
191 peroxydisulfate (S<sub>2</sub>O<sub>8</sub><sup>2-</sup>), ozone, and the photo-Fenton process. Photolysis and radical generation  
192 mechanisms in these processes are widely established and well-described in literature.<sup>78–83</sup>

193 UV/H<sub>2</sub>O<sub>2</sub> and UV/chlorine are the most widely applied processes.<sup>84–88</sup> The UV/H<sub>2</sub>O<sub>2</sub> process is used  
194 in drinking water treatment and potable reuse schemes to remove trace contaminants that are  
195 difficult to remove otherwise<sup>89</sup> and can be advantageous when ozone-based processes would result  
196 in undesired bromate formation from naturally occurring Br<sup>-</sup>.<sup>65</sup> The energy demand of UV/H<sub>2</sub>O<sub>2</sub> is  
197 higher compared to conventional ozonation and the peroxone process.<sup>90</sup>

198 In full-scale potable reuse schemes, UV/chlorine (HOCl) is increasingly used with and without the  
199 addition of chloramines.<sup>85</sup> Thereby, the photolysis of HOCl results in the formation of ·OH and  
200 chlorine atoms,<sup>91</sup> the photolysis of chloramines gives rise to formation of aminyl radicals and chlorine  
201 atoms.<sup>92</sup> Reactions of these reactive species in water are discussed in more detail elsewhere.<sup>93,94</sup>



202 UV/chlorine is mostly applied as the last treatment step for simultaneous degradation of pollutants  
203 and disinfectant residuals, with limited application in organic-rich and ammonia-containing waters  
204 due to formation of toxic by-products.<sup>95</sup>

205 Sulfate radicals react more substrate specific than  $\cdot\text{OH}$ .<sup>5</sup> Therefore the UV/S<sub>2</sub>O<sub>8</sub><sup>2-</sup> process benefits  
206 from reduced oxidant scavenging by the water matrix, but less reactive compounds are more difficult  
207 to eliminate compared to the UV/H<sub>2</sub>O<sub>2</sub> process.<sup>96</sup> The UV/S<sub>2</sub>O<sub>8</sub><sup>2-</sup> process may provide tailored  
208 solutions towards individual substances or substance groups rather than broadband treatment  
209 envisioned in most AOP applications.<sup>5</sup> Compared to H<sub>2</sub>O<sub>2</sub> [ $\epsilon_{\text{H}_2\text{O}_2, \lambda=254\text{nm}} = 18.6 \text{ M}^{-1} \text{ cm}^{-1}$ ]<sup>97</sup> and S<sub>2</sub>O<sub>8</sub><sup>2-</sup>  
210 [ $\epsilon_{\text{S}_2\text{O}_8^{2-}, \lambda=254\text{nm}} = 22 \text{ M}^{-1} \text{ cm}^{-1}$ ],<sup>98</sup> ozone has a high molar absorption coefficient of  $\epsilon_{\text{O}_3, \lambda=254\text{nm}} = 3300 \text{ M}^{-1}$   
211  $\text{cm}^{-1}$ ,<sup>57</sup> resulting in an efficient photolysis into  $\cdot\text{OH}$ <sup>82</sup> that is 20 times more efficient than H<sub>2</sub>O<sub>2</sub>  
212 photolysis at the same dissolved molar concentration. However, due to the combination of two  
213 energy-intensive processes, namely ozonation and UV irradiation, the UV/O<sub>3</sub> process is typically not  
214 competitive with alternative solutions.

215 The Photo-Fenton process is based on the absorption of light by Fe(III)-HO<sub>2</sub>-complexes ( $\epsilon = (450$   
216  $\text{nm}) \approx 450 \text{ M}^{-1} \text{ cm}^{-1}$ ).<sup>82</sup> Thereby, the complex cleaves into HO<sub>2</sub> $\cdot$  and Fe(II), and Fe(II) reacts with  
217 H<sub>2</sub>O<sub>2</sub> to form  $\cdot\text{OH}$ . The major obstacle of the photo-Fenton process is that Fe(III) precipitates in water  
218 at pH > 5 and, hence Fenton processes need to be operated at acidic conditions, to avoid excessive  
219 iron sludge formation and to improve process efficiency. Review articles on Photo-Fenton, including  
220 solar photo Fenton are available.<sup>99,100</sup> Recent developments are related to using complexing agents  
221 to operate at pH 7 and using less costly reactor concepts.<sup>101,102</sup>

222 **Heterogeneous photocatalytic AOPs.** Research on photocatalysis for degradation of refractory  
223 pollutants has been intense since the discovery of photocatalytic water splitting.<sup>103</sup> Heterogeneous  
224 photocatalysis employs a range of semiconducting catalysts, of which TiO<sub>2</sub> and ZnO are the most  
225 widely researched materials.<sup>31,104</sup> Despite much research on photocatalysis in the last decades,  
226 including large-scale demonstration on the use of solar spectrum UV-A and UV-B radiation,<sup>99</sup>  
227 photocatalysis is rarely applied in water treatment beyond lab and pilot scale.<sup>28</sup> There is an ongoing  
228 quest for new photocatalysts, with a broad variety of synthesis approaches taken, with the aim to

229 either increase quantum efficiency or to expand the useable wavelength range to access a larger  
230 part of the electromagnetic spectrum.<sup>99</sup> Limitations and barriers for industrial uptake of  
231 photocatalysis comprise low energy efficiency, including low quantum efficiency of photocatalysts,  
232 complex reactor design, catalyst immobilization and process integration. In a critical analysis of the  
233 technology and market prospects of photocatalysis, Loeb et al. (2019) suggest to overcome the  
234 barriers to implementation of photocatalysis by focusing on niche applications and emphasizing the  
235 unique advantages of photocatalysis over competing technologies.<sup>28</sup> One example is the ability to  
236 generate reductive conditions to treat oxyanions (e.g., nitrate) or certain heavy metals such as  
237 chromate or arsenate. The ability to work largely chemical-free can be a valuable competitive  
238 advantage for small-scale and remote applications. One such promising example relevant to  
239 achieving the United Nations Sustainable Development Goals is the photocatalytic enhancement of  
240 solar disinfection (SODIS).<sup>105</sup>

241 **Lamp technology.** New UV radiation sources in water treatment have been tested, primarily for  
242 disinfection and photocatalysis in the UV-A range.<sup>106</sup> UV-light emitting diodes or UV-LEDs are  
243 radiation sources based on semiconductors such as gallium nitride (GaN), indium nitride (InN), and  
244 aluminum nitride (AlN). So far, it has been possible to produce LEDs with an emission wavelength  
245 as short as 210 nm.<sup>107</sup> The acquisition costs of UV LEDs with wavelengths < 300 nm are currently  
246 still high, while the service life, the radiant power, and energy efficiency are limited compared to  
247 visible spectrum LEDs.<sup>107</sup> The small size and control of individual LEDs enables an innovative  
248 reactor design and a larger range of applications.<sup>108,109</sup> UV LED development is a fast-paced  
249 research field, and it is likely that UV LED will soon become the lamp option of choice for many  
250 applications, not least because of anticipated regulatory pressures regarding the use of mercury.  
251 For a comprehensive outlook on the development of UV emitters based on LED technology see  
252 Amano et al. (2020).<sup>110</sup>

253 Alternative lamp technologies have been explored to generate vacuum UV (VUV) radiation (i.e.,  
254 <200 nm) that can be used to photochemically split water into ·OH and solvated electrons.<sup>111</sup> Lamps  
255 employed for AOP development include Xe Excimer lamps at 172 nm emission and, more recently,

256 LP-Hg arcs at 185 nm emission, with the latter having a photon conversion efficiency of 4-8% for  
257 the electricity invested.<sup>112</sup> The main challenges to implement the VUV process relate to the low  
258 penetration depth of VUV into water and possible by-product formation by inorganic ions. At 185 nm,  
259 the decadic absorption coefficient of pure water is  $1.8 \text{ cm}^{-1}$  ( $\epsilon_{\text{H}_2\text{O},\lambda=185\text{nm}} = 0.032 \text{ M}^{-1} \text{ cm}^{-1}$ )<sup>113</sup> meaning  
260 that almost 90% of the photons are absorbed in the first 5 mm of the optical pathlength. Therefore,  
261 the treatment of large volumes of water requires the development of reactor concepts that go beyond  
262 thin-film reactors and enable efficient use of 185 nm photons (and ideally also exploit 254 nm  
263 photons) without excessive pumping energy or reactor construction costs. Note that in most water  
264 matrices, other than reverse osmosis permeate, penetration depth will be substantially lower due to  
265 the competing light absorption of common inorganic anions, specifically chloride.<sup>114</sup> VUV absorption  
266 by chloride in real water matrices raises similar concerns as the UV/chlorine process regarding the  
267 formation of halogenated oxidation byproducts. Analogously, in waters with high nitrate  
268 concentrations, nitrate photolysis may generate potentially harmful nitrogenous oxidation  
269 byproducts.<sup>115,116</sup> This is an aspect that has not yet been thoroughly investigated for the VUV process.

## 270 **2.4 Other AOPs**

271 Here, “other AOPs” include a broad and diverse range of approaches to generate radicals in water  
272 for treatment applications. Apart from heat-activated persulfate activation, these approaches largely  
273 are more energy intensive treatment solutions compared to the other three groups of AOPs (i.e.,  
274 ozone-based, radiation-driven and catalytic AOPs, Figure 1).<sup>25</sup> Despite comparably high energy  
275 demand, these processes may have unique features (e.g., chemical-free operation) that make them  
276 attractive for specific niche applications (e.g., in small and decentralized systems). In addition,  
277 ultrasound, plasma treatment, supercritical water oxidation, and electrochemical oxidation have  
278 been discussed for the removal of highly refractory poly- and perfluoroalkyl substances (PFAS).<sup>117–</sup>  
279 <sup>120</sup> However, PFAS are highly persistent to  $\cdot\text{OH}$  attack and breakdown is related to different  
280 mechanisms, e.g., pyrolysis during ultrasound treatment,<sup>121</sup> or direct electron transfer at anode  
281 surface.<sup>118</sup>

282 Application of ultrasound in water with frequencies of 20-1,000 kHz generates oscillating gas  
283 bubbles. During the growth of these bubbles, expansion gas is drawn inside the bubble. Subsequent  
284 collapse of the bubbles leads to locally high temperatures ( $> 4,000$  K) at the microscale.<sup>122</sup> The  
285 resulting pyrolysis of water vapour inside the bubbles yields  $\cdot\text{OH}$  and  $\text{H}\cdot$  radicals, which do not readily  
286 recombine due to the high temperature.<sup>82</sup> Hence,  $\cdot\text{OH}$  diffuse outside the bubble and accumulate at  
287 the bubble surface. The local accumulation of reactive species results in comparably high energy  
288 demand for contaminant removal.<sup>25</sup> To the best of our knowledge, this process has never been  
289 tested at pilot or full scale.

290 Plasma is a gas-like state of matter in which a significant portion of molecules or atoms are ionized.  
291 This makes plasma highly conductive and a potential initiator of reduction and oxidation reactions.  
292 Plasma has been frequently proposed for water treatment.<sup>123</sup> Hot thermal or equilibrium plasma  
293 states occur at high temperatures, for example in lightnings or plasma arcs, where the ionized  
294 plasma gas molecules eject electrons. Substantial energy input is required for hot plasma formation  
295 and such plasmas are therefore unsuitable for engineering energy-efficient water treatment. Non-  
296 thermal non-equilibrium or cold plasma consists of positively charged molecule ions at ambient  
297 temperature and highly energized electrons.<sup>124</sup> Ionization is induced by strong electric fields such as  
298 dielectric barrier or corona discharge, rather than thermal energy input. Potentially, this leads to a  
299 much-improved ratio of reactive species generated to energy invested compared to hot plasma.

300 The cascading effects of accelerated electrons impacting on carrier gas molecules and water matrix  
301 compounds leads to a plethora of reactive species that include  $\cdot\text{OH}$ , reactive oxygen species (ROS),  
302 but also nitrogen-containing radicals and related species such as different peroxides. Furthermore,  
303 the relaxation of excited states may generate photons across the UV range.<sup>125</sup> All these species can  
304 be involved in the degradation of a pollutant<sup>126</sup> but the contribution of each reactive species is highly  
305 substance and system specific.

306 Regarding the engineering challenges of the process, it is clear that similar to e.g., electrochemical  
307 processes, the active reaction volume, i.e., where plasma contacts with water to be treated, is  
308 small.<sup>125</sup> Consequently, efficient reactor engineering is key to ensure adequate mass transfer and

309 to develop practicable solutions.<sup>127</sup> Another hardware-related challenge is the development of  
310 economic and efficient plasma generation systems tailored to specific needs of water treatment.  
311 Thermal activation of persulfate has been used for in situ chemical oxidation to remediate  
312 contaminated groundwater and soil.<sup>83</sup> Due to the small bond dissociation energy of the peroxide  
313 bond ( $120 \text{ KJ mol}^{-1}$ ).<sup>128</sup> even moderate temperatures ( $> 40 \text{ }^\circ\text{C}$ ) suffice to cleave persulfate into  
314 sulfate radicals.<sup>129</sup> It has also been shown that slow reactions with high activation energies can  
315 become more important/feasible at the elevated temperatures of thermal activation of persulfate.<sup>130</sup>  
316 A disadvantage of using persulfate is a strong drop in pH and strong radical scavenging effects in  
317 the concomitant presence of chloride and bicarbonate.<sup>93</sup>  
318 Supercritical water oxidation (SCWO) has been shown to be applicable for the degradation of  
319 various wastes in laboratory scale and full scale.<sup>131</sup> However, applications other than demonstration  
320 sites are very rare or hardly exist so far. The reason is that alternative treatment options such as  
321 incineration and dumping are less complex.<sup>131</sup> In supercritical water oxidation, the water under  
322 treatment is heated and pressurized to reach the critical state (temperature range  $400\text{-}650^\circ\text{C}$  at  
323 supercritical pressures).<sup>131</sup> In the super critical state, water becomes mixable with nonpolar  
324 compounds, while polar and ionic compounds may still remain soluble.<sup>132</sup> However, inorganic  
325 compounds such as salts can precipitate and be treated as solid waste. In this way, it has been  
326 possible, e.g., to separate radioactive elements from bulky non-flammable material of artificial  
327 nuclear power plant wastes in bench-scale experiments, which may reduce the volume needed for  
328 radioactive waste storage.<sup>133</sup> Under conditions of SCWO the oxidation process is favoured by high  
329 (gas phase) diffusion rates combined with high liquid phase collision rates. Oxygen is typically used  
330 as oxidant and as a source of oxygen,  $\text{H}_2\text{O}_2$  can be used, which decomposes into oxygen upon its  
331 thermal decomposition.<sup>131</sup>  
332 In electrochemical advanced oxidation processes,  $\cdot\text{OH}$  are directly generated from water oxidation  
333 at the electrode surface.<sup>30</sup> Among numerous used electrode materials, boron-doped diamond (BDD)  
334 and mixed metal oxides (MMO) are mostly applied for the removal of organic compounds in water  
335 treatment.<sup>134</sup> BDD electrodes are mainly applied at smaller scale for water treatment, e.g., for the

336 removal of chemical oxygen demand (COD) in industrial wastewaters or the disinfection of ballast  
337 water.<sup>135,136</sup> Due to the efficient conversion of electrical energy into  $\cdot\text{OH}$  and secondary oxidants  
338 ( $\text{H}_2\text{O}_2$ ,  $\text{O}_3$ ) and the chemical-free operation, electrical AOPs are often considered as  
339 environmentally-friendly treatment solutions.<sup>137</sup> However, additional energy is required to facilitate  
340 transfer of contaminants to reactive species generated at the electrode surface. In addition, chloride  
341 is oxidized to active chlorine, which can be rapidly oxidized to chlorate and perchlorate.<sup>136</sup> Current  
342 research is focused on new electrode design to optimize mass transfer and concepts to mitigate by-  
343 product formation.<sup>134,138</sup>

### 344 **3 Comparison and benchmarking of AOPs**

345 One of the first concepts for figures-of-merit for comparing AOPs was proposed by Bolton et al.  
346 (1996) and subsequently published as an IUPAC Technical Report.<sup>139,140</sup> Given that ultimately most  
347 AOPs are electrically driven, the concept employs electric energy required to decrease the  
348 concentration of a target contaminant by 90%, i.e., by one order of magnitude. The electric energy  
349 per order (EEO) concept applies to AOP systems with dilute (low) concentration of contaminants  
350 and therefore most water treatment applications. There are variations of the concept for systems  
351 with high contaminant concentration using electric energy per mass (EEM) and for solar-driven  
352 systems using solar collector area instead of electric energy.<sup>140</sup> For light-induced AOPs, the EEO  
353 concept has been further elaborated to use fluence-based rate constants depending on fundamental  
354 photochemical probe compound characteristics i.e., quantum yield and molar absorption coefficients,  
355 for both single wavelengths and polychromatic light.<sup>141,142</sup> The EEO concept has been extensively  
356 applied on most AOPs, including ozonation and peroxone,<sup>13,63,90</sup> electro-chemical,<sup>136,143</sup> ultrasound-  
357 based,<sup>144</sup> and both homogeneous and heterogeneous UV-based AOPs.<sup>90,145,146</sup> Thereby, the EEO  
358 concept has proven useful for the initial assessment and comparability of the energy efficiency  
359 across different AOPs. However, within each class of AOP, additional relevant experimental and  
360 water quality parameters are required to allow for appropriate comparison between different target  
361 compounds, water matrices, and reactors. For example, UV/ $\text{H}_2\text{O}_2$  requires reporting of probe  
362 compound concentration, molar absorption coefficients, second-order reaction rate constants

363 with  $\cdot\text{OH}$  ( $k_{\text{OH}}$ ), observed reaction rate constants ( $k_{\text{obs}}$ ), and direct phototransformation rates. In  
364 addition, the water matrix pH, light absorbance, and  $\cdot\text{OH}$  scavenging rates by non-target compounds,  
365 e.g., natural organic matter should be reported.<sup>147</sup> To extrapolate upscaling from bench to pilot and  
366 full scale, changes in reactor fluid dynamics, mixing and mass transfer, light distribution, including  
367 transmittance and path lengths need to be considered.<sup>147</sup> The variance of literature data within  
368 individual AOPs indicates the difficulty to compare processes at different scale and in different water  
369 matrices.<sup>25</sup>

370 In addition, the electrical energy dose (EED) of a treatment process can be determined. The EED is  
371 defined as “electrical energy (kWh) consumed per unit volume [...] of water treated”.<sup>89</sup> For example,  
372 for a given UV-AOP it is the UV-reactor’s energy demand divided by the flow rate for a specific  
373 treatment target or for a defined percentage lamp ballast power (regulating supplied voltage and  
374 current). This factor is independent from the water matrix and allows a direct comparison of different  
375 treatment processes. However, it requires a precise definition of the system boundaries to allow a  
376 direct comparison of different processes. Scaling effects need to be considered, because large-  
377 scale systems are often more efficient than lab-scale processes.<sup>89</sup> While the EED and EEO have  
378 their eligibility as sound factors benchmarking the power efficiencies of different AOP-systems, they  
379 are lacking qualification as AOP design parameters. This is because of the difference in energy  
380 efficiencies of different AOP systems. For example, two given AOP systems, A and B, may achieve  
381 the same treatment target. However, due to different equipment properties such as differences in  
382 the efficiency of ozone generation, UV light distribution, or different hydraulic conditions inside each  
383 reactor, both EED and EEO of A and B may differ. Therefore, at the same EED or EEO, system B  
384 might under- or overachieve the treatment target in comparison to system A.

385 In the UV-AOP business for instance, the market is currently shifting away from use of EED and  
386 EEO as design parameters for micropollutant abatement towards the Reduction Equivalent Dose  
387 (RED), similar to the RED defined by the Ultraviolet Disinfection Guidance Manual UVDGM for  
388 pathogen reduction<sup>148</sup> (personal conversation, Xylem). As rule of thumb, disinfection requires less  
389 than 10% of energy demand compared to micropollutant reduction to achieve the same RED value.

#### 390 **4 Selection of suitable probe compounds, model compounds and scavengers**

391 Chemical probe compounds, including scavengers and quenchers, serve a central role as diagnostic  
392 tools in AOP research.<sup>3</sup> Probe compounds are selective, typically low molecular weight, molecules  
393 that allow kinetic and mechanistic investigation of an AOP. Scavengers are compounds that react  
394 with or trap reactive species. Quenchers deactivate excited states by energy transfer, electron  
395 transfer, or a chemical mechanism.<sup>149</sup> However, they are used for very similar objectives and  
396 therefore jointly named scavengers in the following. AOP literature does not always clearly  
397 distinguish between probe, indicator, and model compounds. Here, we define model compounds as  
398 actual contaminants or representatives that occur in a specific treatment scenario. The term indicator  
399 is synonymous and not used in this paper. In contrast, probe compounds also include compounds  
400 that are rarely encountered in water treatment and are only used for diagnostic purposes.

401 Ultimately, both probe and model compounds (if selected based on similar criteria than probe  
402 compounds) can be used to gain information on the efficiency of AOPs and to determine reactive  
403 species concentration and process performance, including under full-scale conditions.<sup>150,151</sup> There  
404 is a wide range of probe compounds available for reactive species in water. Recent reviews have  
405 summarized probe compounds used to detect reactive oxygen species in aqueous environments<sup>152</sup>,  
406 during photocatalysis<sup>153</sup> or in UV-based advanced reduction processes,<sup>154</sup> to assess the  
407 photochemical activity of dissolved organic matter,<sup>155</sup> and the contribution of reactive nitrogen  
408 species to compound transformation.<sup>156</sup> Here, we briefly discuss the requirements for suitable probe  
409 compounds and provide a few examples for frequently employed compounds for the most relevant  
410 reactive species in AOPs.

411 The use of probe compounds in AOP research is imposed by the difficulty to measure reactive  
412 species directly given their short lifetime. The half-life ( $t_{1/2}$ ) of reactive species produced in AOPs  
413 and AOP-like processes in pure water is typically in the range of microseconds ( $\mu\text{s}$ ) as for  $\cdot\text{OH}$  and  
414  $\text{SO}_4^{\cdot-}$ , to milliseconds (ms) for less reactive species such as carbonate radicals and superoxide  
415 radicals.<sup>152,157</sup> Non-radical oxidants such as ozone and  $\text{H}_2\text{O}_2$  are more stable with half-lives in the  
416 range of minutes to hours.<sup>158,159</sup> In real water matrices, the lifetimes of most reactive species may



417 be much shorter due to the presence of reactants, including scavengers (see below). Generally,  
418 short-lived reactive species in water can be measured and characterized directly by laser flash  
419 photolysis and pulse radiolysis hyphenated with fast UV-vis spectroscopy, and by electron spin  
420 resonance after scavenging with a spin trap, which has resulted in comprehensive datasets of  
421 reaction rates for radicals in aqueous solutions.<sup>75,76</sup> However, these methods require expensive,  
422 non-portable specialized instrumentation and considerable expertise with limited availability to most  
423 researchers.

424 There are several requirements for a suitable probe compound in AOP research. A probe compound  
425 should react fast and selectively with the reactive species of interest with a known second-order  
426 reaction rate constant. The reaction of the probe compound with the reactive species should be  
427 specific and well-defined, preferably with a known reaction mechanism. A probe compound should  
428 not physically interact with the system under investigation, for example via adsorption onto solids in  
429 heterogeneous processes or electrodes in electrochemical AOPs. Ideally, probe compounds should  
430 react only via one clearly defined transformation pathway. This is especially important in combined  
431 AOPs with more than one significant reactive species. Particularly, ozone- or UV-based AOPs  
432 require the selection of probe compounds that are insensitive to ozone and photolysis, respectively.  
433 To elucidate and distinguish between different radical sources (e.g., HOCl, H<sub>2</sub>O<sub>2</sub>, and persulfate in  
434 UV-based AOPs), a suite of probe or model compounds may be required that exhibit a wide-ranging  
435 selectivity toward the relevant individual oxidants present.<sup>160–162</sup> Similarly, the study of complex  
436 systems involving the formation of secondary and tertiary radicals may require a combination of  
437 probe compounds and selective scavengers.<sup>94,160</sup> An exemplary procedure for a sulfate radical-  
438 based process in the presence of chloride is provided by Lutze et al. (2015).<sup>93</sup>  
439 Preferably, probe compounds should be inexpensive, non-toxic, non-carcinogenic, and readily  
440 dissolvable in water at a desired concentration without the need for co-solvents. To determine  
441 oxidant exposures, probe compounds are used at low concentrations to not significantly lower the  
442 concentration of reactive species by acting as scavengers themselves. Probe compounds or  
443 reaction products should be straightforward to measure with available analytical equipment. UV/Vis-

444 spectrophotometry has been often the analytical method of choice for initial assessment of AOPs  
445 due to its accessibility and availability of portable devices. As a non-separating analytical method,  
446 UV/Vis has disadvantages due to possible signal interference with reaction products and water  
447 matrix components, especially when working with dyes.<sup>163</sup> Other analytical techniques typically  
448 employed for probe compounds in AOP research include fluorescence spectroscopy, HPLC-UV/Vis  
449 or HPLC/MS, and to a lesser extent ion chromatography.

450 The  $\cdot\text{OH}$  is the reactive species of highest interest for most AOPs. Treatment concepts based on  $\cdot\text{OH}$   
451 can be adequately evaluated through spectrophotometric monitoring of the removal of  
452 chromophores, often dyes such as rhodamine B, methylene blue, and fluorescein. For a summary  
453 of different approaches for UV/H<sub>2</sub>O<sub>2</sub>, including assessment of an external standard calibration  
454 method using methylene blue, see Wang et al. (2020).<sup>163</sup> Typical probe compounds for  $\cdot\text{OH}$  that can  
455 be readily measured via HPLC include *para*-chlorobenzoic acid (*p*CBA), *para*-nitrobenzoic (*p*NBA)  
456 acid, and atrazine.<sup>90,93,164,165</sup> For UV-only probe compounds, including actinometry, see section 5.2  
457 for fluence rate determination.

458 It is important to distinguish between the various scavengers present in real water matrices, such  
459 as organic matter and inorganic ionic species, which have significant effects on AOP treatment  
460 performance,<sup>166–170</sup> and those employed for diagnostic purposes. Diagnostic scavengers can be  
461 used to indicate and quantify the presence of radicals, non-radical reactive species, and excited  
462 states in AOPs by suppressing reactions. In principle, any suitable probe compound can serve as a  
463 scavenger, but in contrast to its role as a probe, it must be added in sufficiently high concentration  
464 to outcompete the radical reactions with the matrix constituents. To adjust the dosing of the  
465 scavenger, the reaction rate constants of the reactive species of interest with all matrix components  
466 and with the scavenger must be known. As a rule of thumb, a scavenger should trap more than 95%  
467 of the reactive species, which can be determined by competition kinetics calculations as described  
468 before.<sup>171</sup> Typical scavengers for  $\cdot\text{OH}$  include *tert*-butanol and dimethyl sulfoxide (DMSO).<sup>172</sup> The  
469 reaction of  $\cdot\text{OH}$  with *tert*-butanol and DMSO leads to the formation of formaldehyde (yield  $\approx$  25%)  
470 and methanesulfinic/methanesulfonic acid (yield of the sum of each  $\approx$  98%), respectively.<sup>172</sup>

471 Quantification of these transformation products allows calculation of the  $\cdot\text{OH}$  formed.<sup>172</sup> While a large  
472 variety of substances can be used to scavenge different reactive species,<sup>173</sup> many scavengers are  
473 non-specific and do not unequivocally indicate the presence of a single reactive species only. In  
474 such cases, in addition to matrix reactions, reaction rate constants with all relevant reactive species  
475 should be considered to avoid misinterpretation of the results. Working at relatively high  
476 concentrations, often in the millimolar range, poses additional challenges. Scavenger reactions may  
477 lead to the formation of secondary reactive species or the formation of unexpected products that  
478 may affect reaction mechanisms, pathways, and kinetics.<sup>174</sup> The use of scavengers, thus, requires  
479 appropriate control experiments to assess the reactivity of the scavenger with the oxidants, target  
480 compounds, and matrix. For heterogenous AOPs, reconsideration of solubility and adsorption of  
481 scavengers onto materials may be required to assess the impact on dissolved and surface-bound  
482 reactive species.

## 483 **5 Basic rules for oxidation experiments**

484 Knowledge transfer from many recent AOP studies is limited because experiments were operated  
485 with set-ups that are not adequately characterized or comparable. Requirements regarding the  
486 experimental design and operation depend on the objective of the study. Initial feasibility tests to  
487 confirm the formation of reactive species or the removal of selected probe compounds can be  
488 conducted in pure or synthetic water matrices using non-standardized experimental set-ups in the  
489 laboratory (see section 6.1 for details). In contrast, for a sophisticated comparison of costs and  
490 energy demand, lab-scale experiments should provide comparable and scalable information from  
491 standardized experimental set-ups. Ideally, these experiments are conducted in real waters to  
492 account for the strong impact of the water matrix on process efficiency (see section 6.2). So far,  
493 standard experimental procedures have been described only for UV-based processes,<sup>175</sup> and such  
494 equipment may not be accessible for researchers or may be unsuitable especially for newly  
495 developed treatment concepts. This section provides recommendations for the systematic selection  
496 of experimental procedures, when standardized set-ups are undefined, unavailable or unsuitable for  
497 the process at study.

## 498 **5.1 General aspects**

499 Requirements for experimental set-ups of AOPs are highly process specific and discussed  
500 separately in the following sections. As already briefly outlined in the section on comparison and  
501 benchmarking, the water matrix needs to be well-defined, and possible matrix effects on the  
502 oxidation process reported.

503 Broadly, the matrix has three impacts. First, the matrix can compete with radical precursors, e.g.,  
504 absorbing photons (inner filter effect) or consuming ozone.<sup>57,176</sup> In some cases, this can generate  
505 secondary reactive species.<sup>57,177</sup> Second, matrix components can scavenge radicals terminating  
506 radical chain reactions in non-productive ways towards treatment targets.<sup>176</sup> Third, upon scavenging  
507 of highly reactive radicals, less reactive and longer-lived radical species such as carbonate radicals,  
508 superoxide, or dichloride anion radicals can be produced.<sup>4</sup> Depending on their respective reactivity  
509 with a target compound and their tendency to accumulate at higher concentrations due to their  
510 persistence compared to other radical species, such secondary reactive species can contribute  
511 significantly to the degradation of a target compound.<sup>178</sup> Probe compounds (see section 4) can be  
512 used to estimate the contribution of different radicals. Depending on the target application, matrix  
513 components that contribute to scavenging may include organic matter (typically measured as  
514 dissolved or total organic carbon, DOC/TOC), inorganic carbon or alkalinity, and nitrogen species  
515 (nitrate, nitrite, ammonia). In addition, process-specific reporting of additional water quality  
516 parameters affecting the radical generation might be needed (see details in sections 5.2-5.5).  
517 Similarly, the pH must be recorded and reported at least before and after, and if possible during the  
518 experiment, as it can affect acid-base-equilibria and reactivity of matrix and target contaminants.<sup>179–</sup>  
519 <sup>181</sup> In experiments with synthetic waters, buffer effects should be considered as for example  
520 carbonate and phosphate buffers may scavenge radicals, form secondary radicals or interact with  
521 catalysts.<sup>72,182,183</sup> Furthermore, concentrations of any added chemicals need to be listed.

## 522 **5.2 UV-based processes**

523 **Fluence-based evaluation.** As outlined in the previous section on benchmarking, scale and  
524 geometry importantly affect EEO and EED. That situation is generally exacerbated for laboratory-

525 scale set-ups, which are rarely designed for optimal energy efficiency. At laboratory scale, it is  
526 preferable to focus on directly evaluating the photochemical processes only, i.e., direct photolysis of  
527 contaminants and photolysis of radical precursor species such as H<sub>2</sub>O<sub>2</sub>. This is done by using set-  
528 ups that allow assessing photochemical reactions as function of the fluence rate<sup>149</sup> in the reactor as  
529 basis for comparing photochemical studies.

530 The fluence rate allows to model the fundamental reactions i.e., radical formation rate, direct  
531 photolysis and it can be used to determine fundamental photochemical characteristics such as  
532 quantum yields of photochemical reactions. These fluence-based parameters such as reaction rates  
533 can be translated in time-based parameters by simple calculations with the apparent fluence rate at  
534 hand when needed.<sup>90</sup>

535 **Light source and its impact on process evaluation.** The choice of light source is usually  
536 intrinsically related to the goal of the study, but the experimenter needs to be aware that the choice  
537 of photon source will impact the process evaluation procedure. There are quasi-monochromatic light  
538 sources (e.g., low-pressure Hg lamps, excimer lamps, and LEDs with a slightly broader emission  
539 peak) and polychromatic light sources (e.g., medium- and high-pressure mercury lamps, Xenon arc  
540 lamps, or sunlight). Fundamental photochemical properties such as molar absorption coefficients  
541 and quantum yields of photochemical reactions depend on wavelength. How this can be addressed  
542 has been extensively discussed for UV disinfection processes.<sup>184</sup> The same approach has been  
543 transferred also to AOPs.<sup>185</sup>

544 **Fluence rate determination.** There are several methodologies to measure the photon flux. These  
545 can rely on different principles, which affects how the information obtained can be used to determine  
546 fluence rate. First, there are numerous chemical actinometers, most of which have been  
547 conveniently described in an IUPAC Technical Report,<sup>186</sup> some of which have been reviewed  
548 recently.<sup>187</sup> Among them we can distinguish opaque actinometers, e.g., the iodide/ iodate  
549 actinometer frequently used to determine 254 nm radiation<sup>188,189</sup> and non-opaque actinometers such  
550 as the uridine actinometer, also used to determine 254 nm radiation.<sup>187</sup> The first type essentially  
551 determines the incident fluence rate (full absorption after contacting the reactor, no penetration of

552 light into the reactor) yielding a value for irradiance, whereas with the second type allows photons  
553 to fully move through the reactor (vanishing absorption). By that means an average fluence rate of  
554 photons available for photochemical reactions is measured. It should be noted that actinometers  
555 provide information different from biosimetry. The latter is suited to identify deficient mixing and  
556 radiation fields in reactors leading to a broadened distribution of applied UV dose.<sup>190</sup> This is an  
557 aspect particularly important in disinfection, where several orders of magnitude of microorganism  
558 inactivation are typically envisaged. For AOPs it tends to be of lesser relevance, except perhaps in  
559 processes prone to mass transfer limitations. Finally, radiometers and spectroradiometers are  
560 commonly applied to measure by means of an electronic device, calibrated against an absolute  
561 standard, the photon flux at a chosen location in the experimental set-up.<sup>175</sup>

562 When choosing the way to measure fluence-rate, the experimenter must be aware that using opaque  
563 actinometers and radiometer measurements may require a complex mathematical post-processing  
564 to obtain a reliable fluence-rate (depending on the geometry of the photochemical reactor). This  
565 issue can be circumvented by using a simplified geometry such as a quasi-collimated beam  
566 apparatus (see below). Also, using polychromatic light sources can complicate the use of  
567 actinometers for this purpose, although wavelength-dependent quantum yields have been reported  
568 for several commonly used actinometers.<sup>187</sup>

569 Finally, on a very practical level, it is recommended to implement a combined approach of radiometry  
570 and actinometry in the laboratory, whereby on a routine-basis radiometry is used to determine  
571 irradiance and chemical actinometry is used periodically to verify that the calibration of the  
572 radiometer is still accurate and does not show drifts.

573 **Advantages and disadvantages of different laboratory set-ups.** From a chemical engineering  
574 point of view, we can distinguish batch experiments in continuously stirred tank reactors (CSTR)  
575 and experiments in flow-through reactors. Among CSTRs, the most referred to and most  
576 standardized approach is the quasi-collimated beam apparatus (qCB).<sup>175</sup> In flow-through reactors,  
577 we can distinguish single-pass and multiple-pass systems, i.e., where treated fluid is fed back to a  
578 feed tank and recycled multiple times through the photoreactor.

579 A qCB consists of a (i) light source, (ii) an optical system that eliminates non-parallel radiation and  
580 (iii) a shallow, typically round photoreactor whose surface is homogeneously illuminated with the  
581 resulting parallel rays. Guidance on system design and acceptable deviations from ideality (therefore  
582 quasi-collimated beam) have been reported<sup>175</sup> and recently complemented with additional guidance  
583 on evaluation.<sup>184</sup> The key advantage of this geometry is that due to its simplicity the pathlength of  
584 photons and its attenuation by absorption through the treated solution is well-defined. Hence all  
585 chemical actinometers as well as radiometry are suitable to determine fluence rate without complex  
586 mathematical processing. qCB systems have been extensively used in research using mercury  
587 lamps but with modern LEDs with comparably higher power outputs, it is straightforward to construct  
588 a qCB with multiple LEDs to satisfy qCB design criteria (e.g., APRIA Systems<sup>191</sup>).

589 Other CSTRs include similar photoreactors, in its simplest form a beaker, exposed to light, often  
590 used when working with solar light or solar simulators only. In such geometries, measuring fluence  
591 rates accurately is more challenging due to the complex direction and optical pathlength of rays  
592 through the treated solution. Actinometers that directly estimate fluence rate or biosimetry are  
593 preferable rather than opaque actinometers and radiometers to avoid the complex post-processing  
594 to obtain fluence rate from the actinometry result.<sup>175</sup> Radiation evaluation methods and processes  
595 for matching wavelength-dependent responses apply in analogy to action spectra for different  
596 pathogens and irradiation sources in disinfection.<sup>192</sup>

597 The second type of photoreactor are flow-through systems, either single pass or multi-pass,  
598 including plug-flow reactors. Radiation input into such systems is characterized by biosimetry  
599 (often provided by the manufacturer) or actinometry (often conducted in the research laboratory).

600 When using such systems measured fluence rates and radiation distribution are not transferable  
601 across optically different solutions e.g., clear water vs. wastewater. Actinometry must be conducted  
602 separately for each solution. Similarly, when using radiometry or opaque chemical actinometers  
603 geometric complexities and hydraulic flow fields need to be considered. For multi-pass systems,  
604 choice of sampling points, recirculation velocity, feed tank volume, and mixing is important to obtain

605 meaningful results. Such considerations are especially important for upscaling to pilot systems, for  
606 more details see.<sup>99</sup>

### 607 **5.3 Ozone-based processes**

608 **Ozone consumption and mass transfer.** Transfer of results from lab-scale ozonation requires  
609 characterization of injected or reacted (consumed) ozone, because mass transfer in lab-scale  
610 experiments is not comparable to larger-scale operations. While pilot- and full-scale ozone injection  
611 systems typically provide mass transfer of >95% gaseous ozone into solution, mass transfer in lab-  
612 scale reactors can be highly variable.<sup>72</sup> Standardized concepts to determine transfer efficiency of a  
613 reactor (e.g.  $k_L a$ ) do not provide a reliable characterization for ozonation because the high reactivity  
614 of ozone affects its transfer efficiency into water.<sup>72</sup> Observed better removal of contaminants with  
615 ozone-based AOPs compared to ozone alone may be a result of enhanced mass transfer (and  
616 ozone consumption) in inefficient lab reactors and not only related to improved treatment efficiency.  
617 To generate transferable data from lab- and pilot-scale ozonation, consumed ozone should be  
618 reported as a reliable figure of merit.<sup>193</sup> In batch ozonation experiments, monitoring of ozone decay  
619 over time can provide helpful complementary information. This section discusses major aspects for  
620 experiments with ozone-based AOPs. A detailed manual for ozonation experiments is provided by  
621 Gottschalk (2010).<sup>72</sup>

622 **Determination of radical formation efficiency.** In a pure water at neutral pH, ozone is slowly  
623 decomposed by water ( $\text{OH}^-$ ,  $k = 70 \text{ M}^{-1}\text{s}^{-1}$ ) giving rise to the formation of  $\cdot\text{OH}$ .<sup>67</sup> In more complex  
624 matrices such as secondary effluents, elevated ozone decay through reactions with organic matter  
625 also leads to considerable  $\cdot\text{OH}$  formation.<sup>194</sup> Active enhancement of radical formation in ozone-  
626 based AOPs can therefore have two objectives: i) to accelerate ozone decomposition kinetics into  
627 radicals by “quenching” (often residual) ozone with a radical promoter, and/or ii) to enhance overall  
628 radical generation compared to conventional ozonation. In complex water matrices, the benefits of  
629 the AOP are often limited due to the competing reactions of organic matter with ozone that already  
630 generate considerable amounts of  $\cdot\text{OH}$ .<sup>177</sup> The  $\cdot\text{OH}$  yield in the tested AOP should therefore always  
631 be assessed in comparison to conventional ozonation. In experiments with gaseous ozone,



632 researchers also need to account for potential bias caused by effects on mass transfer (see previous  
633 discussion).

634 The  $R_{CT}$ -concept by Elovitz and von Gunten (1999),<sup>195</sup> which defines the  $R_{CT}$  as the ratio  
635 between  $\cdot OH$  exposure and ozone exposure, has often been applied to assess efficiency of ozone-  
636 based AOPs. However, this concept was not designed for this purpose and  $R_{CT}$  values should be  
637 evaluated carefully because enhanced kinetics compared to conventional ozonation primarily  
638 reduce ozone exposure in the denominator.<sup>196</sup> It is therefore recommended to compare radical yields  
639 (or exposures) from ozonation and the tested AOP as a function of the consumed ozone as for  
640 example described in Hübner et al. (2015).<sup>177</sup>

641 **Advantages and disadvantages of different lab set-ups.** Like UV-based processes, lab-scale  
642 ozonation systems can be distinguished into CSTRs (with injection of gaseous ozone (semi-batch  
643 experiments) or as a concentrated ozone solution (batch experiments)), and continuously operating  
644 systems.

645 For most experiments with ozone, batch experiments with an ozone stock solution generated in  
646 ultrapure water and injected into the water sample are recommended as the easiest and best  
647 characterized approach. Concentration of the stock solution can be controlled by adjustment of  
648 ozone gas concentration, pressure, and temperature,<sup>197,198</sup> and easily measured photometrically  
649 prior to injection.<sup>199</sup> Consumed ozone is then determined as the difference between the diluted stock  
650 solution and the residual at the end of the experiments. Previous comparison experiments confirmed  
651 good agreement between contaminant oxidation in CSTR batch experiments and experimental set-  
652 ups using gas/liquid mass transfer in the sample.<sup>193</sup>

653 For experiments with gaseous ozone, a full ozone mass balance including continuous monitoring of  
654 gas flow, in-gas and off-gas ozone, and residual ozone in the water is needed to determine the  
655 consumed ozone. Lab-scale experiments are mostly operated in semi-batch mode (gaseous ozone  
656 injected into a batch reactor). For an accurate determination of consumed ozone in such  
657 experiments, it is important to include all residual ozone in off-gas pipes into the mass balance.<sup>72,193</sup>

658 A time-resolved sampling from such experiments is not recommended because the consumed  
659 ozone at different times (often referred to as “transferred ozone dose”) is not accurately described.  
660 Lab-scale experiments are typically not conducted at continuous water flow, since even the smallest  
661 commercially available ozone generators (2-4 g O<sub>3</sub>/h) would induce considerable water flow rates  
662 (or ozone doses). Electrochemical ozone generation can provide a suitable solution for continuous  
663 operation of ozonation at lab scale.<sup>33</sup> As an alternative approach, gaseous ozone can be injected  
664 into a side stream to generate a concentrated solution, which is then continuously mixed into the  
665 sample.<sup>200</sup> Continuous flow operation might be required for some applications, e.g., mid- to long-  
666 term stability testing of catalytic ozone decomposition or the continuous feeding into a post-treatment  
667 step.

668 **Set-up modifications and important aspects for ozone-based advanced oxidation.** Procedures  
669 for testing ozone-based AOPs depend on the objectives and conditions of the target application. In  
670 most studies, radical promoters or catalysts are dosed before ozonation. However, for some  
671 applications, parallel or later dosing might be more beneficial, e.g., to reduce competition with ozone-  
672 reactive water constituents or to utilize the efficiency of direct ozone reactions (e.g., for disinfection)  
673 before rapid decomposition during the AOP.

674 For heterogeneous catalytic ozonation, the reactor design should be carefully selected. In addition  
675 to the basic rules for catalytic AOPs (see section 5.4), the experimenter needs to account for ozone-  
676 related characteristics of the process including the potentially different interaction of gaseous and  
677 dissolved ozone with the catalyst and the ozone decay into <sup>•</sup>OH without catalyst. Reference  
678 experiments at identical conditions are needed to test effects of ozone alone (ideally with a non-  
679 catalytic reference material) as well as sorption of probe compounds onto the catalyst. Different  
680 probe compounds may be used to account for various affinity to the catalyst. Moreover, the  
681 experiments should provide information on the stability of catalytic activity, because <sup>•</sup>OH can also  
682 be generated by finite reactions, e.g., from the reaction of ozone with activated carbon.<sup>74</sup>

## 683 **5.4 Catalytic AOPs**

684 **Characterization of the dissolved compounds and the catalyst.** In contrast to established  
685 ozone- or UV-based processes, experimental protocols for catalytic AOPs are much less  
686 standardized,<sup>201</sup> which complicates the comparability between different studies and oxidation  
687 processes. In this case, the experimenter must carefully select and report a suitable set-up so that  
688 the research outcomes are not only repeatable but also transferrable.

689 Catalytic AOPs require consideration and thorough characterization of (i) the homogeneous  
690 (dissolved) and / or heterogeneous (solid) catalyst, and (ii) the water quality. While most  
691 homogeneous catalysts are straightforward to describe, the characterization of heterogeneous  
692 catalysts can be a research task in itself, requiring the use of sophisticated analytical techniques to  
693 determine, e.g., catalyst loading density for supported catalysts, particle size, surface area to volume  
694 ratio, surface charge, and other relevant quantities. In addition, the synthesis of the catalyst must  
695 be reported in detail. It must be taken into account that the properties of the catalyst may change in  
696 the application environment compared to the conditions during material characterization. For  
697 instance, the solution pH can change the surface charge of heterogeneous catalysts and affect their  
698 reactivity.<sup>72</sup> Water quality measurements should include the parameters listed in section 5.1.

699 **Process evaluation.** For catalytic reactions, catalytic activity can be normalized by combining  
700 observed kinetics with applied catalyst concentration to determine kinetics-related metrics such as  
701 turnover frequency,<sup>202</sup> which denotes the number of reactions per catalytic reaction center or,  
702 alternatively, per catalyst mass or surface area. Note that the turnover frequency is sometimes used  
703 interchangeably with the turnover number, which describes the maximum number of reactions  
704 before catalytic activity is lost.<sup>202</sup> However, the applicability of this concept to catalytic oxidation is  
705 not trivial because the turnover in catalytic processes in theory describes the catalytic reaction, i.e.,  
706 the generation of short-lived radicals in an AOP. The actually measured reaction of these radicals  
707 with a contaminant is affected by many parameters including the mixing efficiency, contaminant  
708 characteristics and reactivity, which do not depend on catalyst activity. In addition, catalytic oxidation  
709 often involves different reactive species and mechanisms.

710 Experimenters must carefully report the experimental conditions, e.g., stirring velocity, temperature,  
711 and the chemical and catalyst concentrations used. Ideally, results are presented as kinetic rate  
712 constants at various chemical and catalyst doses. If the reaction follows pseudo-first order (i.e., rate  
713 constants correlate linearly with catalyst and chemical concentrations), normalized rate constants  
714 might be used as a suitable figure of merit for comparison. However, it should be noted that the  
715 selection of probe compounds can have a significant impact on the results. In addition to compound  
716 removal, the process evaluation should also include consumption, stability, life cycle, regeneration  
717 potential, and toxicity of the catalyst.

718 **Advantages and disadvantages of different lab set-ups.** Since the evaluation of catalytic  
719 systems is inherently nontrivial, we recommend batch experiments in CSTRs for initial feasibility  
720 testing of new catalyst materials. This is because CSTRs allow for straightforward control of the  
721 experimental environment and exclusion of mass transfer limitations for most catalytic systems. To  
722 directly compare the performance of new catalyst materials with that of established materials,  
723 contaminant or probe compound degradation kinetics with both catalysts should be determined  
724 using exactly the same experimental set-up (see section 6.1). The experimental set-ups or probe  
725 compounds can also be selected based on previous studies with promising catalysts to facilitate  
726 comparison. To elucidate the formation of different reactive radical species, an adequate system of  
727 probe compounds and radical scavengers can be employed, as described in section 4. Given the  
728 complexity of a catalytic system, control experiments are required for the reactions of the probe  
729 compounds with the oxidant and catalyst separately, including possible physical interactions with  
730 the catalyst.

731 To generate scalable data for benchmarking of a catalytic AOP, the experimental design should  
732 consider the engineering of the entire process, including approaches for optimized mass transfer  
733 and subsequent catalyst separation. Continuously operated flow-through or flow-by reactors can  
734 provide information on process performance and mid- to long-term stability of the process and  
735 catalyst in different water matrices. In addition, process engineering may involve novel concepts  
736 where the innovation is a novel catalyst (support) geometry itself, e.g., (photo)catalytic membranes

737 and foams,<sup>203,204</sup> or immobilized catalysts in filters.<sup>16</sup> However, the experimenter needs to consider  
738 process-related parameters such as the applicable transmembrane flow velocity or backwashing of  
739 filters in addition to evaluation of mid- to long-term performance of the process. Furthermore, control  
740 experiments are essential to characterize the removal of probe compounds in the process without  
741 catalyst or oxidant, e.g., to account for removal by sorption. Furthermore, mass transfer-related  
742 parameters (such as surface area of catalyst, hydrophilicity) which control e.g., contacting of ozone  
743 with the heterogenous catalyst, require thorough characterization and reporting.

## 744 **5.5 Other AOPs**

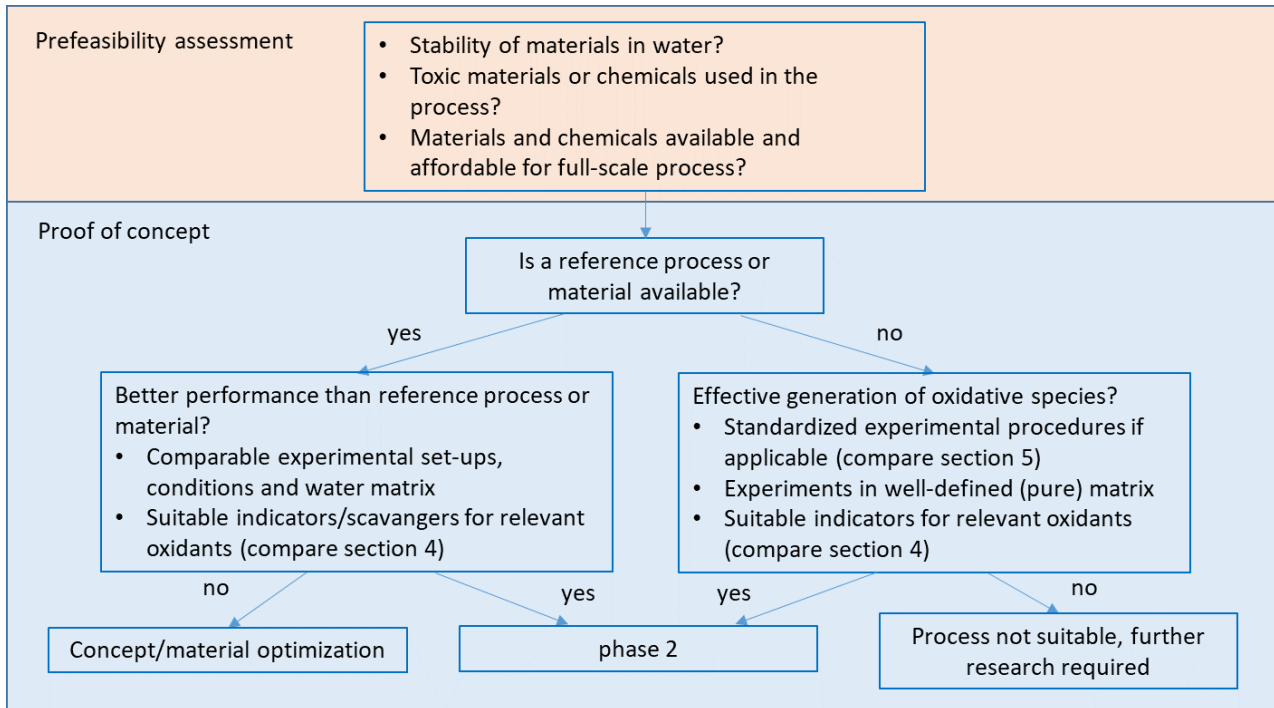
745 The diverse range of other AOPs is challenging to evaluate because standardized set-ups and  
746 suitable figures-of-merit are mostly not available and different treatment efficiency is observed with  
747 different lab reactors. For example, for plasma treatment, energy yield, which was defined as mass  
748 of pollutant degraded (grams) per unit of electrical energy invested (kWh) at a given percentage of  
749 degradation, was differing by up to five orders of magnitude among studied experimental systems.<sup>127</sup>  
750 Also results from sonolysis using slightly different reactor design at the same experimental  
751 conditions were not comparable.<sup>205</sup> Reactor concepts for pilot- and full-scale operation are often not  
752 available, which further limits upscaling of costs and energy efficiencies to realistic treatment  
753 scenarios. In addition, mass transfer will play an essential role in practical application and hence,  
754 experimental set-ups will have to cope with this situation and with the related difficulties in reporting  
755 accurately. For instance, contaminant removal by electrochemical oxidation can be improved by  
756 increasing turbulent flow at the electrode, but this will also increase energy demand for pumping. As  
757 advised previously for other processes, describing the reactor characteristics as well as the process  
758 conditions including the hydraulic conditions becomes even more critical for these processes. Ideally,  
759 this includes relevant parameters for the energy efficiency of the set-up (e.g., the calorimetric  
760 efficiency of transducers used for sonochemical treatment). A detailed review of this diverse set of  
761 processes goes beyond the scope of this manuscript and we kindly refer to review papers outlining  
762 reactor concepts for electrochemical oxidation,<sup>136</sup> plasma,<sup>127</sup> and cavitation processes.<sup>206</sup>

763 **6 Implications for future research: Assessment of new concepts and materials for**  
764 **advanced oxidation**

765 Research on AOPs can be separated into two major research tasks: i) the development and  
766 assessment of new concepts and materials for advanced oxidation and ii) the selection of suitable  
767 oxidation processes for specific treatment targets. This section presents a systematic approach for  
768 feasibility testing (Figure 2) and benchmarking of new concepts for advanced oxidation in water  
769 treatment (Figure 3), which approximately corresponds to a technology readiness level (TRL) of 5,  
770 defined as a validated process in a relevant environment.<sup>207</sup> Subsequent pilot- and full-scale  
771 implementation is briefly discussed, including a corresponding approach for systematically selecting  
772 a suitable process for specific treatment targets (Figure 4). Finally, we outline scientific approaches  
773 to elucidate oxidation mechanisms and assess the potential formation of currently unknown by-  
774 products.

775 **6.1 Phase 1 – Feasibility study**

776 In phase 1, the general feasibility of a concept is evaluated based on theoretical considerations and  
777 preliminary, (non-)standardized bench-scale experiments. The feasibility study elucidates the  
778 suitability of applied materials and chemicals for water treatment and the potential of the new  
779 concept for contaminant elimination. In addition, this phase provides initial information for the cost  
780 and energy evaluation in phase 2. In some cases (e.g., the synthesis of new catalytic materials),  
781 lab-scale experiments may already provide direct comparison to established (reference) materials  
782 or concepts.



783

784 *Figure 2. Phase 1 - Assessing the feasibility of new developments in advanced oxidation (after*  
 785 *positive evaluation the new concept will be benchmarked against established AOPs in Phase 2)*

786 **Prefeasibility assessment.** It is recommended to consider the fundamental applicability of a new  
 787 process on a theoretical basis. These considerations include (i) stability and functionality of the new  
 788 material or process under water treatment conditions, (ii) potential toxicity or risks of materials and  
 789 their components, and (iii) availability and costs of required chemicals and materials. The major  
 790 conditions to be considered in water treatment include pH, salinity, temperature, and matrix  
 791 constituents. These treatment conditions have a wide span depending on the target application (e.g.,  
 792 municipal and industrial wastewater, seawater, or drinking water). A new process must be robust  
 793 and materials must be durable or self-renewing under the prevailing conditions. For example, metal-  
 794 based electrodes may corrode in waters with high salinity. New materials may increase the toxicity  
 795 of water, e.g., by leaching heavy metals, which may require precautionary measures. Cobalt, for  
 796 instance, is a potent catalyst to initiate sulfate radical formation. However, cobalt is a toxic heavy  
 797 metal that should only be used after immobilization on a surface.<sup>208</sup> In general, researchers should  
 798 ensure that the applied materials are approved for the intended application (e.g., drinking water  
 799 directives).

800 The availability of chemicals and materials and the envisaged scale of application are important  
801 points to consider. For example, new iron-based materials may not be constrained by shortage of  
802 resources, but complex catalysts may have these limitations.<sup>130,209</sup> Another example is ultrasound  
803 treatment, which is often tested in an artificial argon atmosphere, which would incur high costs in  
804 full-scale applications.<sup>210</sup> Robust materials that are nontoxic and not resource-limited can be used  
805 at large scale (e.g., for municipal wastewater treatment). More sophisticated catalysts, which require  
806 rare earth metals, for example, may be tailored to specific applications such as small-scale industrial  
807 wastewater treatment. Fundamental research on new materials in the context of water treatment is  
808 a highly important research field that should not be restricted by any boundary conditions. However,  
809 the recommended prefeasibility considerations are crucial and should be addressed prior to  
810 suggesting a new water treatment process.

811 **Proof of concept.** Initial laboratory-scale experiments test the suitability of the process for  
812 contaminant removal in well-defined (pure) water systems. The experiments should follow the basic  
813 rules for oxidation experiments as described in section 5. If a suitable reference material or treatment  
814 concept can be identified, the proof-of-concept study should demonstrate at least similar preferably  
815 better performance of the new development (i.e., more efficient pollutant degradation or less by-  
816 product formation) in comparison to the reference process or material. An ideal reference material  
817 or process would closely mimic the set-up and reaction conditions of the proposed new water  
818 treatment process. Note that a detailed comparison to benchmark AOPs regarding energy  
819 efficiencies and other relevant aspects is highly case specific (involving target contaminants and  
820 water matrix) and, therefore, proposed at a later stage of the evaluation scheme (phase 2). At this  
821 stage, experiments should be designed to provide a first estimate on process feasibility.

822 A direct comparison to a reference is often possible in case new materials are designed for a certain  
823 advanced oxidation. For example, new catalysts can often be directly compared to already  
824 established materials using the same experimental set-up. In this case, simple probe compounds  
825 (see section 4) can be used for a first assessment, but it is important that researchers ensure direct  
826 comparability of experimental results, e.g., by using normalized surface areas and similar reaction



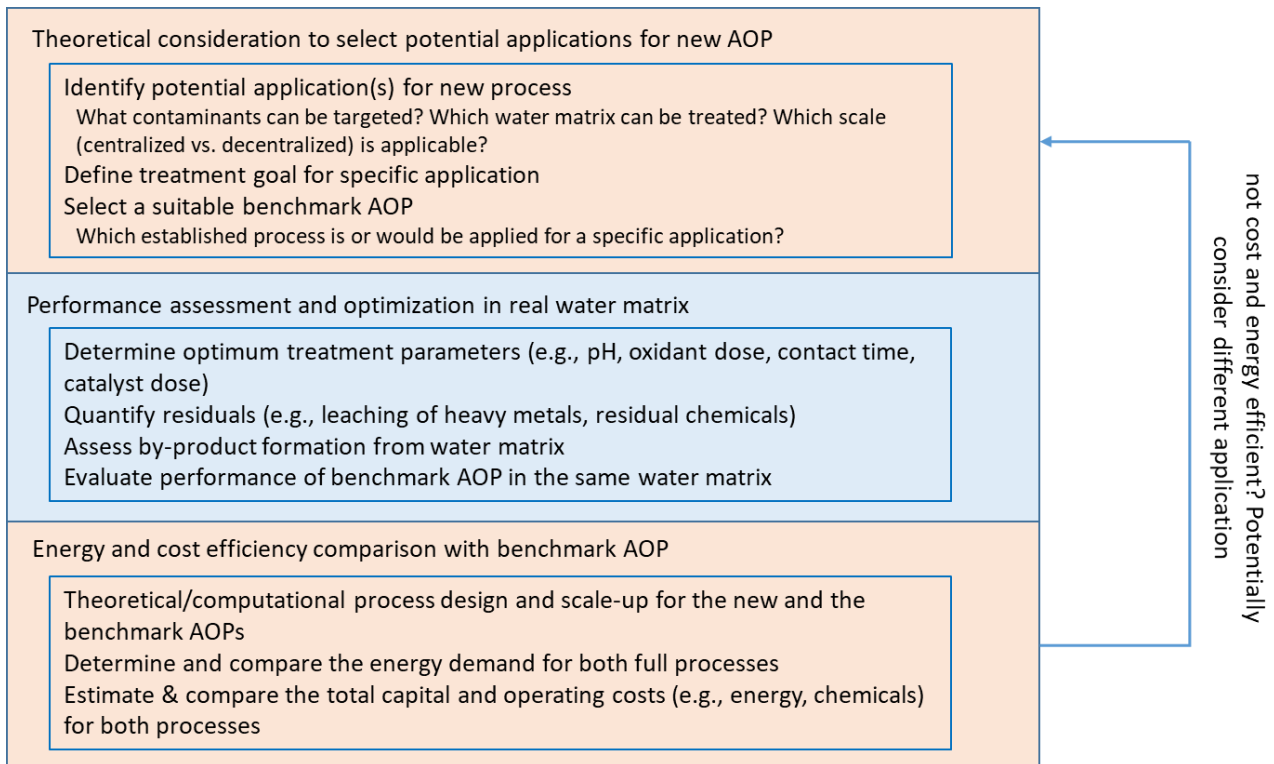
827 conditions (e.g., pH and temperature) compared to the reference process. For some new processes  
828 and reactor designs, direct comparison is also possible with well-studied experimental set-ups  
829 described in section 5, e.g., for ozone- and UV-based AOPs. In such cases, transferable and up-  
830 scalable parameters (i.e., UV fluence rate, reacted ozone) are important for comparison. However,  
831 it has to be noted that ideal reference materials might not be available in all cases.

832 If a direct comparison to a reference process or material is not possible, initial feasibility tests should  
833 be conducted to i) confirm that the process has an “oxidation strength”, ii) identify major reactive  
834 species involved in the process, and iii) provide first information on process and material stability.  
835 Experiments should be designed to provide the required information for considerations in phase 2.  
836 Although different analytical approaches may be used to validate the presence of individual radical  
837 species, relevant exposures of these radicals should be verified experimentally with selected probe  
838 compounds. In this case, a broader selection of probe compounds with different affinity to sorption,  
839 photolysis, ozone, and different radical species can provide a better assessment of process  
840 feasibility and involved mechanisms (compare section 4). The details for the feasibility tests are  
841 determined by the existing knowledge about the process at study. In some cases (e.g., the  
842 combination of UV-LEDs with H<sub>2</sub>O<sub>2</sub>), a general feasibility study may not be needed because the  
843 reaction mechanism and major oxidants are already well-known. In such cases, the evaluation of  
844 the process would start directly with phase 2.

## 845 **6.2 Phase 2 – Benchmarking new concepts for advanced oxidation**

846 Individual AOPs have specific advantages and disadvantages depending on target contaminants,  
847 water matrix, and process scale. Lab-scale experiments to benchmark new AOP solutions should  
848 be conducted in real water matrices in direct comparison to an established AOP to account for  
849 matrix-specific efficiencies. Thereby, the new process has to be compared with the established or  
850 already applied AOP (benchmark AOP) under comparable reaction conditions (same water matrix,  
851 pH, etc). Unlike the reference process in phase 1, which is selected based on mechanistic similarity,  
852 the benchmark AOP should provide the most suitable solution for the selected application.

853 Therefore, the identification of suitable applications for a new AOP is a key step that has often been  
854 paid little attention in past studies. Here, we propose benchmarking new AOPs in a three-step  
855 procedure that includes theoretical considerations to select potential applications, lab-scale  
856 performance assessment in a real water matrix, and cost and energy comparison with a benchmark  
857 AOP (Figure 3).



858  
859 *Figure 3. Phase 2 - Benchmarking new concepts for advanced oxidation*

860 **Theoretical consideration to select potential applications for new AOP.** Before conducting the  
861 experiments to assess and optimize treatment efficiency in the selected water matrix, theoretical  
862 considerations are needed to identify the most suitable application for an AOP. Researchers should  
863 carefully evaluate the available information on the process at study (i.e., data from feasibility tests,  
864 literature data) and translate it into the definition of potential applications. Current water research  
865 has a strong focus on the removal of trace organic chemicals from secondary effluents, but many  
866 AOPs are unsuitable for this application due to high energy demands (e.g., ultrasound, see section  
867 2), potential by-product formation (e.g., electrochemical oxidation), or the required pH range (Fenton  
868 reaction). Unique features of these oxidative processes can still make them attractive for

869 applications in different water matrices (industrial wastewater, mine water, drinking water, and water  
870 reuse), for different contaminants (e.g., individual chemicals from specific industries), and treatment  
871 targets (e.g., removal of COD instead of individual compounds). Alternatively, they may be more  
872 relevant for decentralized and small-scale systems, as they potentially offset higher costs by  
873 avoiding the need for storage and dosing of chemicals or the removal of residuals.<sup>16</sup> Criteria for the  
874 identification of suitable applications include substrate-specificity of the major reactive species,  
875 expected matrix effects on the generation and scavenging of radicals, potential by-product formation  
876 in the respective water matrix, as well as requirements for space, labor (for operation and  
877 maintenance), and infrastructure (chemicals, electricity). Example discussions on the identification  
878 of potential niche applications can be found in reviews on photocatalytic oxidation,<sup>28</sup> ballast water  
879 treatment,<sup>35</sup> and activation of persulfates.<sup>5</sup>

880 In addition, a specific treatment goal needs to be defined for the selected application. This goal may  
881 include percent elimination of a chemical or list of chemicals, but also the removal of alternative  
882 parameters such as TOC or COD. Treatment targets can be based on established concepts for  
883 comparison as discussed in section 3 (e.g., 90% elimination following the EEO concept), regulatory  
884 requirements, or case-specific requirements (e.g., in industrial applications).

885 Finally, a suitable benchmark AOP needs to be identified for the selected application. Researchers  
886 should answer the following questions: Is a state-of-the-art process already applied? If not, which  
887 established processes would likely be used for the defined treatment targets? As an example,  $\cdot\text{OH}$ -  
888 based processes would not be applied for the oxidation of compounds with electron-rich functional  
889 groups (e.g., phenols, anilines, amines), where more specific oxidants such as ozone (or potentially  
890 sulfate radicals) are more efficient. Similarly, ozonation alone is not an adequate benchmark for  
891 mineralization of a target chemical or COD removal, because the reaction typically stops after few  
892 individual transformation reactions.

893 **Performance assessment and optimization in real water matrix.** Based on the selected  
894 treatment targets for the new process, studies to evaluate the treatment efficiency should be  
895 operated in a real water matrix with environmentally relevant concentration of target pollutants

896 and/or probe compounds. Lab-scale experiments should be designed according to the principles  
897 described in section 5 to generate results that are scalable and comparable to the benchmark AOP.  
898 They should (i) provide information on optimum treatment parameters for the performance of the  
899 process (e.g., pH, oxidant dose, contact time, catalyst dose), (ii) indicate toxic residuals, (iii) quantify  
900 residual chemicals, and (iv) assess by-product formation. In some cases, additional mechanistic  
901 studies might be needed to characterize and optimize the process. In most cases, we would not  
902 expect a systematic analysis of transformation products or a screening for toxicological effects at  
903 this point (see discussion in section 6.4 for details). The performance of the benchmark AOP needs  
904 to be tested in the same water matrix to ensure comparability of both processes.

905 **Energy and cost efficiency comparison with benchmark AOP.** Because energy consumption  
906 data from lab-scale experiments (i.e., energy consumption of the laboratory apparatus) are barely  
907 scalable, we recommend using theoretical approaches to upscale both experimentally tested AOPs  
908 (AOP under study and benchmark AOP) to a representative full-scale operation. For standard  
909 processes such as ozonation or UV/H<sub>2</sub>O<sub>2</sub>, manufacturers can often provide energy and cost  
910 estimations based on system dimensions, UV transmittance of the treated water and scalable results  
911 from experiments (i.e., required UV fluence rates or ozone consumption). Some processes might be  
912 upscaled by implementation of individual modules (e.g., additional electrodes). However, for some  
913 innovative AOPs, upscaling of lab-scale results might not be straightforward because pilot- and full-  
914 scale applications are not (yet) established (e.g., high frequency ultrasound reactors). Process  
915 scale-up is an integral part of chemical engineering to anticipate the performance of a certain  
916 process at large scale based on available preliminary lab- or pilot-scale data, and to raise the  
917 analyzed process to a similar scale as other commercially available solutions. Traditional scale-up  
918 by construction of a pilot-scale plant is expensive and time consuming. Alternative approaches using  
919 predictive models and building information modeling based on laboratory data are increasingly used  
920 for planning and designing water treatment modules, a scale-up framework for chemical processes  
921 was recently proposed by Piccinno et al. (2016).<sup>211</sup> At scale, a comparison of efficacy and efficiency  
922 to the benchmark AOP can provide an initial assessment of the competitiveness of the new process.

923 In addition, data from upscaling may also be used for decision making, e.g., in a life cycle  
924 assessment inventory<sup>212</sup> or a triple bottom line (TBL, social, environmental, economic)  
925 assessment.<sup>213</sup>

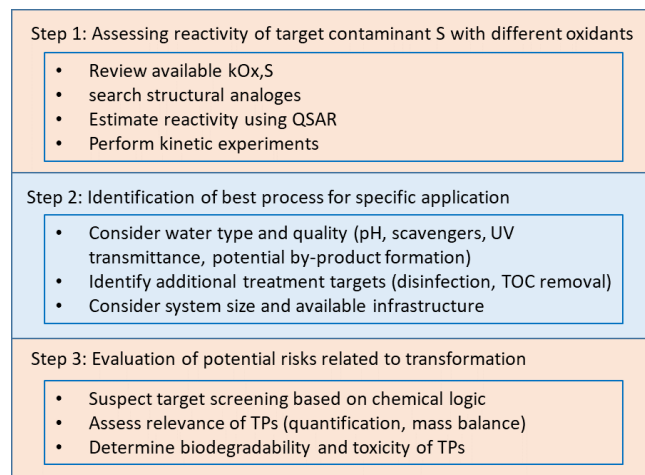
926 The cost and energy evaluation needs to consider the entire process including the dosing of  
927 chemicals and subsequent removal and treatment of residuals. In some AOPs, major energy  
928 consumption is not only related to the process of radical generation (ozonation, UV-light, or plasma),  
929 but also includes energy demand needed to run the desired hydraulics, for example to generate  
930 turbulent flow in electrolytic and catalytic AOPs.

### 931 **6.3 Implementation of new AOPs**

932 **Pilot-scale testing.** The functionality of a new treatment process under real conditions is typically  
933 tested at pilot scale. Even though laboratory experiments are conducted in real water matrices, some  
934 aspects such as the longevity of new treatment materials, the influence of changes in the water  
935 matrix, the effects of combining with other treatment processes, and unforeseen effects can only be  
936 revealed in pilot tests. The latter are ideally carried out directly at the planned site of operation. In  
937 case the pilot testing disproves the applicability of a new material or process, the concept of the new  
938 AOP must be revised. Considering the undesired effects revealed in the pilot tests, solutions can be  
939 developed through revisiting and revising the investigations in detail in phase 2. Successful pilot  
940 testing paves the way for full-scale application of new AOPs, which ideally complement the spectrum  
941 of well-characterized and ready-for-use AOPs to provide optimal treatment solutions for a wide  
942 spectrum of pollutants and scales.

943 **Selection of suitable oxidation processes for specific treatment targets.** New AOP concepts  
944 will be of particular interest in meeting new treatment targets triggered by revised regulatory  
945 requirements for specific chemicals and chemical classes, e.g., the recent regulations for poly- and  
946 perfluoroalkyl substances in drinking water.<sup>214</sup> Moreover, the discovery of an ever-increasing  
947 number of new contaminants, such as persistent, mobile, and potentially toxic organic chemicals,  
948 will increase the need for novel and efficient mitigation processes.<sup>215</sup> The selection of a suitable  
949 oxidation process for a specific treatment target depends on the reactivity of the target

950 contaminant(s), but also on the composition of the water matrix, treatment scale, and other treatment  
951 objectives (e.g., disinfection). Based on these considerations, we propose a three-step approach to  
952 systematically identify a suitable AOP for a defined application (Figure 4).



953

954 *Figure 4. Systematic approach for the selection of a suitable oxidation process for mitigation of a*  
955 *contaminant S.*

956 In a first step, the reactivity of the target contaminant S with different oxidants (e.g., ozone,  $\cdot\text{OH}$ , or  
957 sulfate radicals) should be systematically evaluated, starting with a literature search for reaction rate  
958 constants and additional information on the fate of the contaminants in oxidative or photochemical  
959 processes. For compounds with unknown reactivity, reactivity could be estimated based on  
960 structural analogues<sup>216</sup> or using in-silico tools based on quantitative structure-activity  
961 relationships,<sup>217</sup> Simple lab-scale kinetic experiments<sup>164</sup> can be performed to complement existing  
962 knowledge. In case the chemicals cannot be removed effectively by oxidation, alternative solutions  
963 to oxidation need to be considered.

964 Second, the best-suited oxidative treatment for the prevailing conditions should be selected, taking  
965 into account information on water quality, process dimensions, and available infrastructure. Although  
966 different processes are often based on the same reactive species (e.g.,  $\cdot\text{OH}$ ), the activity of water  
967 matrix parameters as oxidant scavengers, promoters of radical chain reactions or precursors for by-  
968 product formation may strongly affect the applicability of individual processes.<sup>167</sup> Additional  
969 treatment targets and potential process benefits should also be identified, such as the activity of the

970 oxidants as disinfectants or the formation of biodegradable products that may favor the combination  
971 of oxidation with biological processes.

972 A third step should address potential risks associated with the transformation of the target  
973 contaminant. Especially in waters with high pollutant concentrations (e.g., industrial wastewaters),  
974 significant amounts of potentially toxic transformation products may form. The identification of  
975 relevant transformation products should follow a systematic approach including available knowledge  
976 on transformation reactions of different oxidants from literature,<sup>218</sup> and in-silico chemistry.<sup>219</sup> Ideally,  
977 product screenings should be accompanied by mass-balances to assess the relevance of detected  
978 transformation products formed from the target pollutant. Alternatively, effect-directed analysis can  
979 be used as a powerful approach to first determine the toxicity of the overall chemical mixture in a  
980 sample, and then unravel individual toxicants through a combination of bioanalytical tools,  
981 fractionation steps, and chemical analyses.<sup>220</sup> In both cases, relevance of effects for the aquatic  
982 environment should be assessed carefully, as toxic effects as well as transformation products are  
983 often removed in subsequent biological treatment steps.<sup>221</sup>

#### 984 **6.4 Scientific approaches for mechanistic investigation and extended risk assessment**

985 Experiments described in sections 6.1 - 6.3 are not designed to provide a detailed mechanistic  
986 understanding of the process at study. Nevertheless, there are several examples of detailed  
987 mechanistic information being useful to determine potentials for process optimization, identify and  
988 manage risks, and develop corrective actions. One example is the development of bromate  
989 mitigation strategies in ozonation processes (e.g., by addition of H<sub>2</sub>O<sub>2</sub>) based on fundamental  
990 investigations on the formation mechanisms.<sup>69,222</sup> Other examples in advanced oxidation include the  
991 characterization of nitrite as a scavenger or the identification of NDMA precursors and formation  
992 pathways.<sup>223</sup>

993 Due to the very different approaches to develop new AOPs, studies on the understanding of main  
994 reactions in a new oxidative process are diverse and case specific. Experiments may address the  
995 whole range and variety of formed reactive species, the reactive sites in heterogeneous processes,  
996 transformation mechanisms for individual pairs of oxidant and contaminant, but also nonspecific

997 toxicity and specific mixture effects caused by complex mixtures of products formed in waters treated  
998 with AOPs. Experimental approaches often combine various tools such as the use of (multiple)  
999 probe compounds and scavengers, (see section 4), quantum chemical calculation, and the analysis  
1000 of transformation products using high-resolution mass spectrometry (HRMS). Good example studies  
1001 include the characterization of the heterogenous catalytic persulfate process by Zhang et al.  
1002 (2022),<sup>224</sup> and the peroxone process by Merényi et al. (2010).<sup>61</sup> Potential risks related to the  
1003 formation of unknown by-products may be addressed through bioanalytical tools<sup>221</sup> or non-target  
1004 screening methods for previously unknown and unregulated by-products.<sup>225</sup>  
1005 HRMS can be a powerful method-of-choice to identify transformation products when it is combined  
1006 with mechanistic considerations to corroborate reaction pathways. The analysis of known  
1007 transformation products can help to identify relevant reactive species and formation pathways,<sup>226</sup>  
1008 and substantiate or falsify results from identification of reactive species. In addition, screening for  
1009 unknown products can assist to elucidate relevant transformation pathways.<sup>227,228</sup> It should be noted  
1010 that these studies should be conducted according to a systematic experimental design that is based  
1011 on existing knowledge (e.g., transformation mechanisms involving  $\cdot\text{OH}$  and different functional  
1012 groups are well-described) and provides transferable knowledge.  
1013 Quantum chemical calculation is an important tool to obtain a first estimate on conceivable reaction  
1014 mechanisms and transformation products facilitating actual product identification using HRMS <sup>219</sup>.  
1015 Further insights on the potential of these in-silico tools for mechanistic evaluation of oxidative  
1016 processes and example applications are provided in literature.<sup>61,67,219,224</sup>  
1017 Bioassays with suitable endpoints can be applied for indicating mixture toxicity effects after water  
1018 treatment,<sup>228</sup> identifying unknown toxic chemicals through effect-directed analysis,<sup>220</sup> and  
1019 monitoring certain classes of chemicals.<sup>229</sup> For instance, the estrogen receptor alpha (ER- $\alpha$ ) is  
1020 activated in the presence of endocrine disruptors,<sup>230</sup> which can be expressed as estradiol equivalent  
1021 concentrations. However, similar targeted approaches to monitor induced effects from oxidative  
1022 processes are not available. Könemann et al. (2018) identified most suitable bioassays to detect



1023 adverse effects generated during ozonation of secondary effluents, but these effects have never  
1024 been attributed to specific unknown transformation products and oxidation by-products.<sup>230</sup>

## 1025 **7 Acknowledgment**

1026 This study was initiated from the Technical Committee “Oxidative Processes” within the German  
1027 Water Chemistry Society. We gratefully thank Emil Bein and Nebojša Ilić for their feedback and input  
1028 in different subsections and Nenad Stojanovic for his tremendous help with illustration of Figure 1.

## 1029 **8 References**

1030 (1) Comninellis, C.; Kapalka, A.; Malato, S.; Parsons, S. A.; Poulios, I.; Mantzavinos, D. Advanced  
1031 oxidation processes for water treatment: Advances and trends for R&D. *Journal of Chemical*  
1032 *Technology & Biotechnology* **2008**, *83* (6), 769–776. DOI: 10.1002/jctb.1873.

1033 (2) Oturan, M. A.; Aaron, J.-J. Advanced Oxidation Processes in Water/Wastewater Treatment:  
1034 Principles and Applications. A Review. *Critical Reviews in Environmental Science and Technology*  
1035 **2014**, *44* (23), 2577–2641. DOI: 10.1080/10643389.2013.829765.

1036 (3) Wang, J.; Wang, S. Reactive species in advanced oxidation processes: Formation,  
1037 identification and reaction mechanism. *Chemical Engineering Journal* **2020**, *401*, 126158. DOI:  
1038 10.1016/j.cej.2020.126158.

1039 (4) Wang, J.; Wang, S. Effect of inorganic anions on the performance of advanced oxidation  
1040 processes for degradation of organic contaminants. *Chemical Engineering Journal* **2021**, *411*,  
1041 128392. DOI: 10.1016/j.cej.2020.128392.

1042 (5) Lee, J.; Gunten, U. von; Kim, J.-H. Persulfate-Based Advanced Oxidation: Critical Assessment  
1043 of Opportunities and Roadblocks. *Environmental science & technology* **2020**, *54* (6), 3064–3081.  
1044 DOI: 10.1021/acs.est.9b07082. Published Online: Feb. 27, 2020.

1045 (6) Ao, X.-W.; Eloranta, J.; Huang, C.-H.; Santoro, D.; Sun, W.-J.; Lu, Z.-D.; Li, C. Peracetic acid-  
1046 based advanced oxidation processes for decontamination and disinfection of water: A review.  
1047 *Water Res.* **2021**, *188*, 116479. DOI: 10.1016/j.watres.2020.116479. Published Online: Sep. 30,  
1048 2020.

- 1049 (7) Ayoub, K.; van Hullebusch, E. D.; Cassir, M.; Bermond, A. Application of advanced oxidation  
1050 processes for TNT removal: A review. *Journal of Hazardous Materials* **2010**, *178* (1-3), 10–28.  
1051 DOI: 10.1016/j.jhazmat.2010.02.042. Published Online: Feb. 18, 2010.
- 1052 (8) Chen, W.; Gu, Z.; Wen, P.; Li, Q. Degradation of refractory organic contaminants in membrane  
1053 concentrates from landfill leachate by a combined coagulation-ozonation process. *Chemosphere*  
1054 **2019**, *217*, 411–422. DOI: 10.1016/j.chemosphere.2018.11.002. Published Online: Nov. 5, 2018.
- 1055 (9) Gassie, L. W.; Englehardt, J. D. Advanced oxidation and disinfection processes for onsite net-  
1056 zero greywater reuse: A review. *Water Res.* **2017**, *125*, 384–399. DOI:  
1057 10.1016/j.watres.2017.08.062. Published Online: Aug. 30, 2017.
- 1058 (10) Giannakis, S.; Lin, K.-Y. A.; Ghanbari, F. A review of the recent advances on the treatment of  
1059 industrial wastewaters by Sulfate Radical-based Advanced Oxidation Processes (SR-AOPs).  
1060 *Chemical Engineering Journal* **2021**, *406*, 127083. DOI: 10.1016/j.cej.2020.127083.
- 1061 (11) Matilainen, A.; Sillanpää, M. Removal of natural organic matter from drinking water by  
1062 advanced oxidation processes. *Chemosphere* **2010**, *80* (4), 351–365. DOI:  
1063 10.1016/j.chemosphere.2010.04.067. Published Online: May. 21, 2010.
- 1064 (12) Oller, I.; Malato, S.; Sánchez-Pérez, J. A. Combination of Advanced Oxidation Processes  
1065 and biological treatments for wastewater decontamination--a review. *The Science of the total*  
1066 *environment* **2011**, *409* (20), 4141–4166. DOI: 10.1016/j.scitotenv.2010.08.061. Published Online:  
1067 Oct. 16, 2010.
- 1068 (13) Pisarenko, A. N.; Stanford, B. D.; Yan, D.; Gerrity, D.; Snyder, S. A. Effects of ozone and  
1069 ozone/peroxide on trace organic contaminants and NDMA in drinking water and water reuse  
1070 applications. *Water Res.* **2012**, *46* (2), 316–326. DOI: 10.1016/j.watres.2011.10.021. Published  
1071 Online: Oct. 25, 2011.
- 1072 (14) Sillanpää, M.; Ncibi, M. C.; Matilainen, A. Advanced oxidation processes for the removal of  
1073 natural organic matter from drinking water sources: A comprehensive review. *Journal of*  
1074 *environmental management* **2018**, *208*, 56–76. DOI: 10.1016/j.jenvman.2017.12.009. Published  
1075 Online: Dec. 14, 2017.

- 1076 (15) El Kateb, M.; Trellu, C.; Darwich, A.; Rivallin, M.; Bechelany, M.; Nagarajan, S.; Lacour, S.;  
1077 Bellakhal, N.; Lesage, G.; Héran, M.; Cretin, M. Electrochemical advanced oxidation processes  
1078 using novel electrode materials for mineralization and biodegradability enhancement of  
1079 nanofiltration concentrate of landfill leachates. *Water Res.* **2019**, *162*, 446–455. DOI:  
1080 10.1016/j.watres.2019.07.005. Published Online: Jul. 5, 2019.
- 1081 (16) Xu, J.; Zheng, X.; Feng, Z.; Lu, Z.; Zhang, Z.; Huang, W.; Li, Y.; Vuckovic, D.; Li, Y.; Dai, S.;  
1082 Chen, G.; Wang, K.; Wang, H.; Chen, J. K.; Mitch, W.; Cui, Y. Organic wastewater treatment by a  
1083 single-atom catalyst and electrolytically produced H<sub>2</sub>O<sub>2</sub>. *Nat Sustain* **2021**, *4*, 233–241. DOI:  
1084 10.1038/s41893-020-00635-w. Published Online: Nov. 9, 2020.
- 1085 (17) Ansari, M.; Sharifian, M.; Ehrampoush, M. H.; Mahvi, A. H.; Salmani, M. H.; Fallahzadeh, H.  
1086 Dielectric barrier discharge plasma with photocatalysts as a hybrid emerging technology for  
1087 degradation of synthetic organic compounds in aqueous environments: A critical review.  
1088 *Chemosphere* **2021**, *263*, 128065. DOI: 10.1016/j.chemosphere.2020.128065. Published Online:  
1089 Aug. 23, 2020.
- 1090 (18) Lee, M.-Y.; Wang, W.-L.; Du, Y.; Hu, H.-Y.; Huang, N.; Xu, Z.-B.; Wu, Q.-Y.; Ye, B.  
1091 Enhancement effect among a UV, persulfate, and copper (UV/PS/Cu<sup>2+</sup>) system on the  
1092 degradation of nonoxidizing biocide: The kinetics, radical species, and degradation pathway.  
1093 *Chemical Engineering Journal* **2020**, *382*, 122312. DOI: 10.1016/j.cej.2019.122312.
- 1094 (19) Li, M.; Li, W.; Wen, D.; Bolton, J. R.; Blatchley, E. R.; Qiang, Z. Micropollutant Degradation  
1095 by the UV/H<sub>2</sub>O<sub>2</sub> Process: Kinetic Comparison among Various Radiation Sources. *Environmental*  
1096 *science & technology* **2019**, *53* (9), 5241–5248. DOI: 10.1021/acs.est.8b06557. Published Online:  
1097 Apr. 12, 2019.
- 1098 (20) Tian, F.-X.; Ye, W.-K.; Xu, B.; Hu, X.-J.; Ma, S.-X.; Lai, F.; Gao, Y.-Q.; Xing, H.-B.; Xia, W.-  
1099 H.; Wang, B. Comparison of UV-induced AOPs (UV/Cl<sub>2</sub>, UV/NH<sub>2</sub>Cl, UV/ClO<sub>2</sub> and UV/H<sub>2</sub>O<sub>2</sub>) in  
1100 the degradation of iopamidol: Kinetics, energy requirements and DBPs-related toxicity in  
1101 sequential disinfection processes. *Chemical Engineering Journal* **2020**, *398*, 125570. DOI:  
1102 10.1016/j.cej.2020.125570. Published Online: May. 30, 2020.

- 1103 (21) Scheideler, J.; Lekkerkerker-Teunissen, K.; Knol, T.; Ried, A.; Verberk, J.; van Dijk, H.  
1104 Combination of O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> and UV for multiple barrier micropollutant treatment and bromate  
1105 formation control - an economic attractive option. *Water Practice and Technology* **2011**, 6 (4). DOI:  
1106 10.2166/wpt.2011.0063.
- 1107 (22) Wang, W.-L.; Wu, Q.-Y.; Li, Z.-M.; Lu, Y.; Du, Y.; Wang, T.; Huang, N.; Hu, H.-Y. Light-  
1108 emitting diodes as an emerging UV source for UV/chlorine oxidation: Carbamazepine degradation  
1109 and toxicity changes. *Chemical Engineering Journal* **2017**, 310, 148–156. DOI:  
1110 10.1016/j.cej.2016.10.097.
- 1111 (23) Rodriguez-Narvaez, O. M.; Peralta-Hernandez, J. M.; Goonetilleke, A.; Bandala, E. R.  
1112 Treatment technologies for emerging contaminants in water: A review. *Chemical Engineering*  
1113 *Journal* **2017**, 323, 361–380. DOI: 10.1016/j.cej.2017.04.106.
- 1114 (24) Cheng, M.; Zeng, G.; Huang, D.; Lai, C.; Xu, P.; Zhang, C.; Liu, Y. Hydroxyl radicals based  
1115 advanced oxidation processes (AOPs) for remediation of soils contaminated with organic  
1116 compounds: A review. *Chemical Engineering Journal* **2016**, 284, 582–598. DOI:  
1117 10.1016/j.cej.2015.09.001.
- 1118 (25) Miklos, D. B.; Remy, C.; Jekel, M.; Linden, K. G.; Drewes, J. E.; Hübner, U. Evaluation of  
1119 advanced oxidation processes for water and wastewater treatment - A critical review. *Water Res.*  
1120 **2018**, 139, 118–131. DOI: 10.1016/j.watres.2018.03.042. Published Online: Mar. 22, 2018.
- 1121 (26) Ribeiro, A. R.; Nunes, O. C.; Pereira, M. F. R.; Silva, A. M. T. An overview on the advanced  
1122 oxidation processes applied for the treatment of water pollutants defined in the recently launched  
1123 Directive 2013/39/EU. *Environment international* **2015**, 75, 33–51. DOI:  
1124 10.1016/j.envint.2014.10.027. Published Online: Nov. 15, 2014.
- 1125 (27) Gunten, U. von. Oxidation Processes in Water Treatment: Are We on Track? *Environmental*  
1126 *science & technology* **2018**, 52 (9), 5062–5075. DOI: 10.1021/acs.est.8b00586. Published Online:  
1127 Apr. 19, 2018.
- 1128 (28) Loeb, S. K.; Alvarez, P. J. J.; Brame, J. A.; Cates, E. L.; Choi, W.; Crittenden, J.; Dionysiou,  
1129 D. D.; Li, Q.; Li-Puma, G.; Quan, X.; Sedlak, D. L.; David Waite, T.; Westerhoff, P.; Kim, J.-H. The

- 1130 Technology Horizon for Photocatalytic Water Treatment: Sunrise or Sunset? *Environmental*  
1131 *science & technology* **2019**, 53 (6), 2937–2947. DOI: 10.1021/acs.est.8b05041. Published Online:  
1132 Dec. 21, 2018.
- 1133 (29) Bokare, A. D.; Choi, W. Review of iron-free Fenton-like systems for activating H<sub>2</sub>O<sub>2</sub> in  
1134 advanced oxidation processes. *Journal of Hazardous Materials* **2014**, 275, 121–135. DOI:  
1135 10.1016/j.jhazmat.2014.04.054. Published Online: May. 2, 2014.
- 1136 (30) Chaplin, B. P. Critical review of electrochemical advanced oxidation processes for water  
1137 treatment applications. *Environmental Science. Processes & Impacts* **2014**, 16 (6), 1182–1203.  
1138 DOI: 10.1039/c3em00679d.
- 1139 (31) Lee, K. M.; Lai, C. W.; Ngai, K. S.; Juan, J. C. Recent developments of zinc oxide based  
1140 photocatalyst in water treatment technology: A review. *Water Res.* **2016**, 88, 428–448. DOI:  
1141 10.1016/j.watres.2015.09.045. Published Online: Oct. 28, 2015.
- 1142 (32) Lim, S.; Shi, J. L.; Gunten, U. von; McCurry, D. L. Ozonation of organic compounds in water  
1143 and wastewater: A critical review. *Water Res.* **2022**, 213, 118053. DOI:  
1144 10.1016/j.watres.2022.118053. Published Online: Jan. 10, 2022.
- 1145 (33) Zoumpouli, G. A.; Scheurer, M.; Brauch, H.-J.; Kasprzyk-Hordern, B.; Wenk, J.; Happel, O.  
1146 COMBI, continuous ozonation merged with biofiltration to study oxidative and microbial  
1147 transformation of trace organic contaminants. *Environ. Sci.: Water Res. Technol.* **2019**, 5 (3), 552–  
1148 563. DOI: 10.1039/C8EW00855H.
- 1149 (34) Wang, J.; Wang, S. Activation of persulfate (PS) and peroxymonosulfate (PMS) and  
1150 application for the degradation of emerging contaminants. *Chemical Engineering Journal* **2018**,  
1151 334, 1502–1517. DOI: 10.1016/j.cej.2017.11.059.
- 1152 (35) Werschkun, B.; Banerji, S.; Basurko, O. C.; David, M.; Fuhr, F.; Gollasch, S.; Grummt, T.;  
1153 Haarich, M.; Jha, A. N.; Kacan, S.; Kehrer, A.; Linders, J.; Mesbahi, E.; Pughiuc, D.; Richardson,  
1154 S. D.; Schwarz-Schulz, B.; Shah, A.; Theobald, N.; Gunten, U. von; Wieck, S.; Höfer, T. Emerging  
1155 risks from ballast water treatment: the run-up to the International Ballast Water Management

1156 Convention. *Chemosphere* **2014**, *112*, 256–266. DOI: 10.1016/j.chemosphere.2014.03.135.

1157 Published Online: May. 16, 2014.

1158 (36) Chen, N.; Lee, D.; Kang, H.; Cha, D.; Lee, J.; Lee, C. Catalytic persulfate activation for  
1159 oxidation of organic pollutants: A critical review on mechanisms and controversies. *Journal of*  
1160 *Environmental Chemical Engineering* **2022**, *10* (3), 107654. DOI: 10.1016/j.jece.2022.107654.

1161 (37) Kasprzyk-Hordern, B.; Ziółek, M.; Nawrocki, J. Catalytic ozonation and methods of enhancing  
1162 molecular ozone reactions in water treatment. *Applied Catalysis B: Environmental* **2003**, *46* (4),  
1163 639–669. DOI: 10.1016/S0926-3373(03)00326-6.

1164 (38) Liu, X.; He, S.; Yang, Y.; Yao, B.; Tang, Y.; Luo, L.; Zhi, D.; Wan, Z.; Wang, L.; Zhou, Y. A  
1165 review on percarbonate-based advanced oxidation processes for remediation of organic  
1166 compounds in water. *Environmental research* **2021**, *200*, 111371. DOI:  
1167 10.1016/j.envres.2021.111371. Published Online: May. 31, 2021.

1168 (39) Wang, Z.; Sun, P.; Li, Y.; Meng, T.; Li, Z.; Zhang, X.; Zhang, R.; Jia, H.; Yao, H. Reactive  
1169 Nitrogen Species Mediated Degradation of Estrogenic Disrupting Chemicals by  
1170 Biochar/Monochloramine in Buffered Water and Synthetic Hydrolyzed Urine. *Environmental*  
1171 *science & technology* **2019**, *53* (21), 12688–12696. DOI: 10.1021/acs.est.9b04704. Published  
1172 Online: Oct. 24, 2019.

1173 (40) Bautista, P.; Mohedano, A. F.; Casas, J. A.; Zazo, J. A.; Rodriguez, J. J. An overview of the  
1174 application of Fenton oxidation to industrial wastewaters treatment. *J. Chem. Technol. Biotechnol.*  
1175 **2008**, *83* (10), 1323–1338. DOI: 10.1002/jctb.1988.

1176 (41) Goldstein, S.; Meyerstein, D.; Czapski, G. The Fenton reagents. *Free Radical Biology and*  
1177 *Medicine* **1993**, *15* (4), 435–445. DOI: 10.1016/0891-5849(93)90043-T.

1178 (42) Zhang, Y.; Zhou, M. A critical review of the application of chelating agents to enable Fenton  
1179 and Fenton-like reactions at high pH values. *Journal of Hazardous Materials* **2019**, *362*, 436–450.  
1180 DOI: 10.1016/j.jhazmat.2018.09.035. Published Online: Sep. 14, 2018.

- 1181 (43) Hu, P.; Long, M. Cobalt-catalyzed sulfate radical-based advanced oxidation: A review on  
1182 heterogeneous catalysts and applications. *Applied Catalysis B: Environmental* **2016**, *181*, 103–  
1183 117. DOI: 10.1016/j.apcatb.2015.07.024.
- 1184 (44) Huang, J.; Zhang, H. Mn-based catalysts for sulfate radical-based advanced oxidation  
1185 processes: A review. *Environment international* **2019**, *133* (Pt A), 105141. DOI:  
1186 10.1016/j.envint.2019.105141. Published Online: Sep. 11, 2019.
- 1187 (45) Luo, H.; Zeng, Y.; He, D.; Pan, X. Application of iron-based materials in heterogeneous  
1188 advanced oxidation processes for wastewater treatment: A review. *Chemical Engineering Journal*  
1189 **2021**, *407*, 127191. DOI: 10.1016/j.cej.2020.127191.
- 1190 (46) Hodges, B. C.; Cates, E. L.; Kim, J.-H. Challenges and prospects of advanced oxidation  
1191 water treatment processes using catalytic nanomaterials. *Nature nanotechnology* **2018**, *13* (8),  
1192 642–650. DOI: 10.1038/s41565-018-0216-x. Published Online: Aug. 6, 2018.
- 1193 (47) Sun, M.; Chu, C.; Geng, F.; Lu, X.; Qu, J.; Crittenden, J.; Elimelech, M.; Kim, J.-H.  
1194 Reinventing Fenton Chemistry: Iron Oxochloride Nanosheet for pH-Insensitive H<sub>2</sub>O<sub>2</sub> Activation.  
1195 *Environ. Sci. Technol. Lett.* **2018**, *5* (3), 186–191. DOI: 10.1021/acs.estlett.8b00065.
- 1196 (48) Han, M.; Duan, X.; Cao, G.; Zhu, S.; Ho, S.-H. Graphitic nitride-catalyzed advanced oxidation  
1197 processes (AOPs) for landfill leachate treatment: A mini review. *Process safety and environmental*  
1198 *protection : transactions of the Institution of Chemical Engineers, Part B* **2020**, *139*, 230–240. DOI:  
1199 10.1016/j.psep.2020.04.046. Published Online: May. 5, 2020.
- 1200 (49) Yang, Y.; Li, X.; Zhou, C.; Xiong, W.; Zeng, G.; Huang, D.; Zhang, C.; Wang, W.; Song, B.;  
1201 Tang, X.; Li, X.; Guo, H. Recent advances in application of graphitic carbon nitride-based catalysts  
1202 for degrading organic contaminants in water through advanced oxidation processes beyond  
1203 photocatalysis: A critical review. *Water Res.* **2020**, *184*, 116200. DOI:  
1204 10.1016/j.watres.2020.116200. Published Online: Jul. 18, 2020.
- 1205 (50) Duan, X.; Sun, H.; Wang, S. Metal-Free Carbocatalysis in Advanced Oxidation Reactions.  
1206 *Accounts of chemical research* **2018**, *51* (3), 678–687. DOI: 10.1021/acs.accounts.7b00535.  
1207 Published Online: Mar. 1, 2018.

- 1208 (51) Zhao, Y.; Yuan, X.; Li, X.; Jiang, L.; Wang, H. Burgeoning prospects of biochar and its  
1209 composite in persulfate-advanced oxidation process. *Journal of Hazardous Materials* **2021**, *409*,  
1210 124893. DOI: 10.1016/j.jhazmat.2020.124893. Published Online: Jan. 5, 2021.
- 1211 (52) Xie, Z.-H.; Zhou, H.-Y.; He, C.-S.; Pan, Z.-C.; Yao, G.; Lai, B. Synthesis, application and  
1212 catalytic performance of layered double hydroxide based catalysts in advanced oxidation  
1213 processes for wastewater decontamination: A review. *Chemical Engineering Journal* **2021**, *414*,  
1214 128713. DOI: 10.1016/j.cej.2021.128713.
- 1215 (53) Du, X.; Zhou, M. Strategies to enhance catalytic performance of metal–organic frameworks in  
1216 sulfate radical-based advanced oxidation processes for organic pollutants removal. *Chemical*  
1217 *Engineering Journal* **2021**, *403*, 126346. DOI: 10.1016/j.cej.2020.126346.
- 1218 (54) Huang, B.; Wu, Z.; Zhou, H.; Li, J.; Zhou, C.; Xiong, Z.; Pan, Z.; Yao, G.; Lai, B. Recent  
1219 advances in single-atom catalysts for advanced oxidation processes in water purification. *Journal*  
1220 *of Hazardous Materials* **2021**, *412*, 125253. DOI: 10.1016/j.jhazmat.2021.125253. Published  
1221 Online: Jan. 29, 2021.
- 1222 (55) Shang, Y.; Xu, X.; Gao, B.; Wang, S.; Duan, X. Single-atom catalysis in advanced oxidation  
1223 processes for environmental remediation. *Chemical Society reviews* **2021**, *50* (8), 5281–5322.  
1224 DOI: 10.1039/d0cs01032d.
- 1225 (56) Pocostales, J. P.; Sein, M. M.; Knolle, W.; Sonntag, C. von; Schmidt, T. C. Degradation of  
1226 ozone-refractory organic phosphates in wastewater by ozone and ozone/hydrogen peroxide  
1227 (peroxone): the role of ozone consumption by dissolved organic matter. *Environmental science &*  
1228 *technology* **2010**, *44* (21), 8248–8253. DOI: 10.1021/es1018288.
- 1229 (57) Sonntag, C. von; Gunten, U. von. *Chemistry of ozone in water and wastewater*  
1230 *treatment: From basic principles to applications*; IWA Publishing, 2012. DOI:  
1231 10.2166/9781780400839.
- 1232 (58) Fischbacher, A.; Sonntag, J. von; Sonntag, C. von; Schmidt, T. C. The (•)OH radical yield in  
1233 the H<sub>2</sub>O<sub>2</sub> + O<sub>3</sub> (peroxone) reaction. *Environmental science & technology* **2013**, *47* (17), 9959–  
1234 9964. DOI: 10.1021/es402305r. Published Online: Aug. 21, 2013.



1235 (59) Lamsal, R.; Walsh, M. E.; Gagnon, G. A. Comparison of advanced oxidation processes for  
1236 the removal of natural organic matter. *Water Res.* **2011**, *45* (10), 3263–3269. DOI:  
1237 10.1016/j.watres.2011.03.038. Published Online: Mar. 29, 2011.

1238 (60) Lucas, M. S.; Peres, J. A.; Li Puma, G. Treatment of winery wastewater by ozone-based  
1239 advanced oxidation processes (O<sub>3</sub>, O<sub>3</sub>/UV and O<sub>3</sub>/UV/H<sub>2</sub>O<sub>2</sub>) in a pilot-scale bubble column  
1240 reactor and process economics. *Separation and Purification Technology* **2010**, *72* (3), 235–241.  
1241 DOI: 10.1016/j.seppur.2010.01.016.

1242 (61) Merényi, G.; Lind, J.; Naumov, S.; Sonntag, C. von. Reaction of ozone with hydrogen  
1243 peroxide (peroxone process): a revision of current mechanistic concepts based on thermokinetic  
1244 and quantum-chemical considerations. *Environ. Sci. Technol.* **2010**, *44* (9), 3505–3507. DOI:  
1245 10.1021/es100277d.

1246 (62) Wang, J.; Chen, H. Catalytic ozonation for water and wastewater treatment: Recent  
1247 advances and perspective. *The Science of the total environment* **2020**, *704*, 135249. DOI:  
1248 10.1016/j.scitotenv.2019.135249. Published Online: Nov. 22, 2019.

1249 (63) Yao, W.; Ur Rehman, S. W.; Wang, H.; Yang, H.; Yu, G.; Wang, Y. Pilot-scale evaluation of  
1250 micropollutant abatements by conventional ozonation, UV/O<sub>3</sub>, and an electro-peroxone process.  
1251 *Water Res.* **2018**, *138*, 106–117. DOI: 10.1016/j.watres.2018.03.044. Published Online: Mar. 16,  
1252 2018.

1253 (64) Gunten, U. von; Oliveras, Y. Kinetics of the reaction between hydrogen peroxide and  
1254 hypobromous acid: Implication on water treatment and natural systems. *Water Res.* **1997**, *31* (4),  
1255 900–906. DOI: 10.1016/S0043-1354(96)00368-5.

1256 (65) Gunten, U. von; Oliveras, Y. Advanced Oxidation of Bromide-Containing Waters: Bromate  
1257 Formation Mechanisms. *Environmental science & technology* **1998**, *32* (1), 63–70. DOI:  
1258 10.1021/es970477j.

1259 (66) Gunten, U. von. Ozonation of drinking water: Part I. Oxidation kinetics and product formation.  
1260 *Water Res.* **2003**, *37* (7), 1443–1467. DOI: 10.1016/S0043-1354(02)00457-8.

- 1261 (67) Merényi, G.; Lind, J.; Naumov, S.; Sonntag, C. von. The reaction of ozone with the hydroxide  
1262 ion: Mechanistic considerations based on thermokinetic and quantum chemical calculations and  
1263 the role of HO<sub>4</sub><sup>-</sup> in superoxide dismutation. *Chemistry (Weinheim an der Bergstrasse, Germany)*  
1264 **2010**, 16 (4), 1372–1377. DOI: 10.1002/chem.200802539.
- 1265 (68) Staehelin, J.; Hoigne, J. Decomposition of ozone in water: rate of initiation by hydroxide ions  
1266 and hydrogen peroxide. *Environmental science & technology* **1982**, 16 (10), 676–681. DOI:  
1267 10.1021/es00104a009.
- 1268 (69) Gunten, U. von. Ozonation of drinking water: Part II. Disinfection and by-product formation in  
1269 presence of bromide, iodide or chlorine. *Water Res.* **2003**, 37 (7), 1469–1487. DOI:  
1270 10.1016/S0043-1354(02)00458-X.
- 1271 (70) Rekhate, C. V.; Srivastava, J. K. Recent advances in ozone-based advanced oxidation  
1272 processes for treatment of wastewater- A review. *Chemical Engineering Journal Advances* **2020**,  
1273 3, 100031. DOI: 10.1016/j.ceja.2020.100031.
- 1274 (71) Yan, L.; Bing, J.; Wu, H. The behavior of ozone on different iron oxides surface sites in water.  
1275 *Scientific reports* **2019**, 9 (1), 14752. DOI: 10.1038/s41598-019-50910-w. Published Online: Oct.  
1276 14, 2019.
- 1277 (72) Gottschalk, C. *Ozonation of Water and Waste Water: A Practical Guide to Understanding*  
1278 *Ozone and Its Applications*, 2nd ed.; John Wiley & Sons Incorporated, 2010.
- 1279 (73) Nawaz, F.; Cao, H.; Xie, Y.; Xiao, J.; Chen, Y.; Ghazi, Z. A. Selection of active phase of  
1280 MnO<sub>2</sub> for catalytic ozonation of 4-nitrophenol. *Chemosphere* **2017**, 168, 1457–1466. DOI:  
1281 10.1016/j.chemosphere.2016.11.138. Published Online: Dec. 4, 2016.
- 1282 (74) Sánchez-Polo, M.; Gunten, U. von; Rivera-Utrilla, J. Efficiency of activated carbon to  
1283 transform ozone into <sup>\*</sup>OH radicals: influence of operational parameters. *Water Res.* **2005**, 39 (14),  
1284 3189–3198. DOI: 10.1016/j.watres.2005.05.026.
- 1285 (75) Buxton, G. V.; Greenstock, C. L.; Helman, W. P.; Ross, A. B. Critical Review of rate  
1286 constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals (<sup>\*</sup>OH/<sup>\*</sup>O – in

- 1287 Aqueous Solution. *Journal of Physical and Chemical Reference Data* **1988**, 17 (2), 513–886. DOI:  
1288 10.1063/1.555805.
- 1289 (76) Neta, P.; Huie, R. E.; Ross, A. B. Rate Constants for Reactions of Inorganic Radicals in  
1290 Aqueous Solution. *Journal of Physical and Chemical Reference Data* **1988**, 17 (3), 1027–1284.  
1291 DOI: 10.1063/1.555808.
- 1292 (77) Brezonik, P. L.; Arnold, W. A. *Water chemistry: An introduction to the chemistry of natural and*  
1293 *engineered aquatic systems*; Oxford University Press, 2011.
- 1294 (78) Bulman, D. M.; Mezyk, S. P.; Remucal, C. K. The Impact of pH and Irradiation Wavelength  
1295 on the Production of Reactive Oxidants during Chlorine Photolysis. *Environmental science &*  
1296 *technology* **2019**, 53 (8), 4450–4459. DOI: 10.1021/acs.est.8b07225. Published Online: Mar. 27,  
1297 2019.
- 1298 (79) Chuang, Y.-H.; Chen, S.; Chinn, C. J.; Mitch, W. A. Comparing the UV/Monochloramine and  
1299 UV/Free Chlorine Advanced Oxidation Processes (AOPs) to the UV/Hydrogen Peroxide AOP  
1300 Under Scenarios Relevant to Potable Reuse. *Environmental science & technology* **2017**, 51 (23),  
1301 13859–13868. DOI: 10.1021/acs.est.7b03570. Published Online: Nov. 22, 2017.
- 1302 (80) Garoma, T.; Gurol, M. D. Degradation of tert-butyl alcohol in dilute aqueous solution by an  
1303 O<sub>3</sub>/UV process. *Environ. Sci. Technol.* **2004**, 38 (19), 5246–5252. DOI: 10.1021/es0353210.
- 1304 (81) Goldstein, S.; Aschengrau, D.; Diamant, Y.; Rabani, J. Photolysis of aqueous H<sub>2</sub>O<sub>2</sub>:  
1305 quantum yield and applications for polychromatic UV actinometry in photoreactors. *Environ. Sci.*  
1306 *Technol.* **2007**, 41 (21), 7486–7490. DOI: 10.1021/es071379t.
- 1307 (82) Sonntag, C. von. Advanced oxidation processes: Mechanistic aspects. *Water Science and*  
1308 *Technology* **2008**, 58 (5), 1015–1021. DOI: 10.2166/wst.2008.467.
- 1309 (83) Wacławek, S.; Lutze, H. V.; Grübel, K.; Padil, V. V.; Černík, M.; Dionysiou, D. Chemistry of  
1310 persulfates in water and wastewater treatment: A review. *Chemical Engineering Journal* **2017**, 330,  
1311 44–62. DOI: 10.1016/j.cej.2017.07.132.
- 1312 (84) Kruithof, J. C.; Kamp, P. C.; Belosevic, M.; Stefan, M. UV/H<sub>2</sub>O<sub>2</sub> retrofit of PWN's water  
1313 treatment plant Andijk for primary disinfection and organic contaminant control. In *2nd IWA*

- 1314 *Leading-Edge Conference on Water and Wastewater Treatment Technologies*; Water and  
1315 environmental management series; IWA Publ, 2004; pp 53–65.
- 1316 (85) Kwon, M.; Royce, A.; Gong, Y.; Ishida, K. P.; Stefan, M. I. UV/chlorine vs. UV/H<sub>2</sub>O<sub>2</sub> for  
1317 water reuse at Orange County Water District, CA: a pilot study. *Environ. Sci.: Water Res. Technol.*  
1318 **2020**, 6 (9), 2416–2431. DOI: 10.1039/D0EW00316F.
- 1319 (86) Swaim, P.; Royce, A.; Smith, T.; Maloney, T.; Ehlen, D.; Carter, B. Effectiveness of UV  
1320 Advanced Oxidation for Destruction of Micro-Pollutants. *Ozone: Science & Engineering* **2008**, 30  
1321 (1), 34–42. DOI: 10.1080/01919510701753390.
- 1322 (87) Wang, D.; Bolton, J. R.; Andrews, S. A.; Hofmann, R. UV/chlorine control of drinking water  
1323 taste and odour at pilot and full-scale. *Chemosphere* **2015**, 136, 239–244. DOI:  
1324 10.1016/j.chemosphere.2015.05.049. Published Online: May. 26, 2015.
- 1325 (88) Wang, C.; Moore, N.; Bircher, K.; Andrews, S.; Hofmann, R. Full-scale comparison of  
1326 UV/H<sub>2</sub>O<sub>2</sub> and UV/Cl<sub>2</sub> advanced oxidation: The degradation of micropollutant surrogates and the  
1327 formation of disinfection byproducts. *Water Res.* **2019**, 161, 448–458. DOI:  
1328 10.1016/j.watres.2019.06.033. Published Online: Jun. 13, 2019.
- 1329 (89) Collins, J.; Bolton, J. R. *Advanced oxidation handbook*, First edition; American Water Works  
1330 Association, 2016.
- 1331 (90) Katsoyiannis, I. A.; Canonica, S.; Gunten, U. von. Efficiency and energy requirements for the  
1332 transformation of organic micropollutants by ozone, O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> and UV/H<sub>2</sub>O<sub>2</sub>. *Water Res.* **2011**, 45  
1333 (13), 3811–3822. DOI: 10.1016/j.watres.2011.04.038. Published Online: May. 7, 2011.
- 1334 (91) Khajouei, G.; Finklea, H. O.; Lin, L.-S. UV/chlorine advanced oxidation processes for  
1335 degradation of contaminants in water and wastewater: A comprehensive review. *Journal of*  
1336 *Environmental Chemical Engineering* **2022**, 10 (3), 107508. DOI: 10.1016/j.jece.2022.107508.
- 1337 (92) Li, W.; Patton, S.; Gleason, J. M.; Mezyk, S. P.; Ishida, K. P.; Liu, H. UV Photolysis of  
1338 Chloramine and Persulfate for 1,4-Dioxane Removal in Reverse-Osmosis Permeate for Potable  
1339 Water Reuse. *Environmental science & technology* **2018**, 52 (11), 6417–6425. DOI:  
1340 10.1021/acs.est.7b06042. Published Online: May. 7, 2018.

- 1341 (93) Lutze, H. V.; Kerlin, N.; Schmidt, T. C. Sulfate radical-based water treatment in presence of  
1342 chloride: formation of chlorate, inter-conversion of sulfate radicals into hydroxyl radicals and  
1343 influence of bicarbonate. *Water Research* **2015**, *72*, 349–360. DOI: 10.1016/j.watres.2014.10.006.
- 1344 (94) McElroy, W. J. A laser photolysis study of the reaction of sulfate(1-) with chloride and the  
1345 subsequent decay of chlorine(1-) in aqueous solution. *J. Phys. Chem.* **1990**, *94* (6), 2435–2441.  
1346 DOI: 10.1021/j100369a044.
- 1347 (95) Guo, K.; Wu, Z.; Chen, C.; Fang, J. UV/Chlorine Process: An Efficient Advanced Oxidation  
1348 Process with Multiple Radicals and Functions in Water Treatment. *Accounts of chemical research*  
1349 **2022**, *55* (3), 286–297. DOI: 10.1021/acs.accounts.1c00269. Published Online: Jan. 13, 2022.
- 1350 (96) Nihemaiti, M.; Miklos, D. B.; Hübner, U.; Linden, K. G.; Drewes, J. E.; Croué, J.-P. Removal  
1351 of trace organic chemicals in wastewater effluent by UV/H<sub>2</sub>O<sub>2</sub> and UV/PDS. *Water Res.* **2018**,  
1352 *145*, 487–497. DOI: 10.1016/j.watres.2018.08.052. Published Online: Aug. 27, 2018.
- 1353 (97) Stefan, M. I.; Hoy, A. R.; Bolton, J. R. Kinetics and Mechanism of the Degradation and  
1354 Mineralization of Acetone in Dilute Aqueous Solution Sensitized by the UV Photolysis of Hydrogen  
1355 Peroxide. *Environmental science & technology* **1996**, *30* (7), 2382–2390. DOI: 10.1021/es950866i.
- 1356 (98) Heidt, L. J. The Photolysis of Persulfate. *The Journal of Chemical Physics* **1942**, *10* (5), 297–  
1357 302. DOI: 10.1063/1.1723724.
- 1358 (99) Malato, S.; Fernández-Ibáñez, P.; Maldonado, M. I.; Blanco, J.; Gernjak, W. Decontamination  
1359 and disinfection of water by solar photocatalysis: Recent overview and trends. *Catalysis Today*  
1360 **2009**, *147* (1), 1–59. DOI: 10.1016/j.cattod.2009.06.018.
- 1361 (100) Spasiano, D.; Marotta, R.; Malato, S.; Fernandez-Ibañez, P.; Di Somma, I. Solar  
1362 photocatalysis: Materials, reactors, some commercial, and pre-industrialized applications. A  
1363 comprehensive approach. *Applied Catalysis B: Environmental* **2015**, *170-171*, 90–123. DOI:  
1364 10.1016/j.apcatb.2014.12.050.
- 1365 (101) Cabrera-Reina, A.; Miralles-Cuevas, S.; Sánchez Pérez, J. A.; Salazar, R. Application of  
1366 solar photo-Fenton in raceway pond reactors: A review. *The Science of the total environment*  
1367 **2021**, *800*, 149653. DOI: 10.1016/j.scitotenv.2021.149653. Published Online: Aug. 14, 2021.

- 1368 (102) Clarizia, L.; Russo, D.; Di Somma, I.; Marotta, R.; Andreatti, R. Homogeneous photo-  
1369 Fenton processes at near neutral pH: A review. *Applied Catalysis B: Environmental* **2017**, *209*,  
1370 358–371. DOI: 10.1016/j.apcatb.2017.03.011.
- 1371 (103) Fujishima, A.; Honda, K. Electrochemical photolysis of water at a semiconductor electrode.  
1372 *Nature* **1972**, *238* (5358), 37–38. DOI: 10.1038/238037a0.
- 1373 (104) Chong, M. N.; Jin, B.; Chow, C. W. K.; Saint, C. Recent developments in photocatalytic  
1374 water treatment technology: a review. *Water Res.* **2010**, *44* (10), 2997–3027. DOI:  
1375 10.1016/j.watres.2010.02.039. Published Online: Mar. 18, 2010.
- 1376 (105) Cowie, B. E.; Porley, V.; Robertson, N. Solar Disinfection (SODIS) Provides a Much  
1377 Underexploited Opportunity for Researchers in Photocatalytic Water Treatment (PWT). *ACS Catal.*  
1378 **2020**, *10* (20), 11779–11782. DOI: 10.1021/acscatal.0c03325.
- 1379 (106) Hinds, L. M.; O'Donnell, C. P.; Akhter, M.; Tiwari, B. K. Principles and mechanisms of  
1380 ultraviolet light emitting diode technology for food industry applications. *Innovative Food Science &*  
1381 *Emerging Technologies* **2019**, *56*, 102153. DOI: 10.1016/j.ifset.2019.04.006.
- 1382 (107) Kneissl, M.; Seong, T.-Y.; Han, J.; Amano, H. The emergence and prospects of deep-  
1383 ultraviolet light-emitting diode technologies. *Nat. Photonics* **2019**, *13* (4), 233–244. DOI:  
1384 10.1038/s41566-019-0359-9.
- 1385 (108) Autin, O.; Romelot, C.; Rust, L.; Hart, J.; Jarvis, P.; MacAdam, J.; Parsons, S. A.; Jefferson,  
1386 B. Evaluation of a UV-light emitting diodes unit for the removal of micropollutants in water for low  
1387 energy advanced oxidation processes. *Chemosphere* **2013**, *92* (6), 745–751. DOI:  
1388 10.1016/j.chemosphere.2013.04.028. Published Online: May. 10, 2013.
- 1389 (109) Song, K.; Mohseni, M.; Taghipour, F. Application of ultraviolet light-emitting diodes (UV-  
1390 LEDs) for water disinfection: A review. *Water Res.* **2016**, *94*, 341–349. DOI:  
1391 10.1016/j.watres.2016.03.003. Published Online: Mar. 2, 2016.
- 1392 (110) Amano, H.; Collazo, R.; Santi, C. de; Einfeldt, S.; Funato, M.; Glaab, J.; Hagedorn, S.;  
1393 Hirano, A.; Hirayama, H.; Ishii, R.; Kashima, Y.; Kawakami, Y.; Kirste, R.; Kneissl, M.; Martin, R.;  
1394 Mehnke, F.; Meneghini, M.; Ougazzaden, A.; Parbrook, P. J.; Rajan, S.; Reddy, P.; Römer, F.;

- 1395 Ruschel, J.; Sarkar, B.; Scholz, F.; Schowalter, L. J.; Shields, P.; Sitar, Z.; Sulmoni, L.; Wang, T.;
- 1396 Wernicke, T.; Weyers, M.; Witzigmann, B.; Wu, Y.-R.; Wunderer, T.; Zhang, Y. The 2020 UV
- 1397 emitter roadmap. *J. Phys. D: Appl. Phys.* **2020**, *53* (50), 503001. DOI: 10.1088/1361-6463/aba64c.
- 1398 (111) Legrini, O.; Oliveros, E.; Braun, A. M. Photochemical processes for water treatment. *Chem.*
- 1399 *Rev.* **1993**, *93* (2), 671–698. DOI: 10.1021/cr00018a003.
- 1400 (112) Imoberdorf, G.; Mohseni, M. Modeling and experimental evaluation of vacuum-UV
- 1401 photoreactors for water treatment. *Chemical Engineering Science* **2011**, *66* (6), 1159–1167. DOI:
- 1402 10.1016/j.ces.2010.12.020.
- 1403 (113) Weeks, J. L.; Meaburn, G. M. A. C.; Gordon, S. Absorption Coefficients of Liquid Water and
- 1404 Aqueous Solutions in the Far Ultraviolet. *Radiation Research* **1963**, *19* (3), 559. DOI:
- 1405 10.2307/3571475.
- 1406 (114) Furatian, L.; Mohseni, M. Influence of major anions on the 185 nm advanced oxidation
- 1407 process - Sulphate, bicarbonate, and chloride. *Chemosphere* **2018**, *201*, 503–510. DOI:
- 1408 10.1016/j.chemosphere.2018.02.160. Published Online: Mar. 1, 2018.
- 1409 (115) Lyon, B. A.; Milsk, R. Y.; DeAngelo, A. B.; Simmons, J. E.; Moyer, M. P.; Weinberg, H. S.
- 1410 Integrated chemical and toxicological investigation of UV-chlorine/chloramine drinking water
- 1411 treatment. *Environmental science & technology* **2014**, *48* (12), 6743–6753. DOI:
- 1412 10.1021/es501412n. Published Online: Jun. 4, 2014.
- 1413 (116) Martijn, B. J.; van Rompay, A. R.; Penders, E. J. M.; Alharbi, Y.; Baggelaar, P. K.; Kruithof,
- 1414 J. C.; Rietjens, I. M. C. M. Development of a 4-NQO toxic equivalency factor (TEF) approach to
- 1415 enable a preliminary risk assessment of unknown genotoxic compounds detected by the Ames II
- 1416 test in UV/H<sub>2</sub>O<sub>2</sub> water treatment samples. *Chemosphere* **2016**, *144*, 338–345. DOI:
- 1417 10.1016/j.chemosphere.2015.08.070. Published Online: Sep. 14, 2015.
- 1418 (117) Pinkard, B. R.; Shetty, S.; Stritzinger, D.; Bellona, C.; Novosselov, I. V. Destruction of
- 1419 perfluorooctanesulfonate (PFOS) in a batch supercritical water oxidation reactor. *Chemosphere*
- 1420 **2021**, *279*, 130834. DOI: 10.1016/j.chemosphere.2021.130834. Published Online: May. 18, 2021.

- 1421 (118) Radjenovic, J.; Duinslaeger, N.; Avval, S. S.; Chaplin, B. P. Facing the Challenge of Poly-  
1422 and Perfluoroalkyl Substances in Water: Is Electrochemical Oxidation the Answer? *Environmental*  
1423 *science & technology* **2020**, *54* (23), 14815–14829. DOI: 10.1021/acs.est.0c06212. Published  
1424 Online: Nov. 15, 2020.
- 1425 (119) Topolovec, B.; Škoro, N.; Puač, N.; Petrovic, M. Pathways of organic micropollutants  
1426 degradation in atmospheric pressure plasma processing - A review. *Chemosphere* **2022**, *294*,  
1427 133606. DOI: 10.1016/j.chemosphere.2022.133606. Published Online: Jan. 13, 2022.
- 1428 (120) Vecitis, C. D.; Park, H.; Cheng, J.; Mader, B. T.; Hoffmann, M. R. Treatment technologies  
1429 for aqueous perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA). *Front. Environ. Sci.*  
1430 *Eng. China* **2009**, *3* (2), 129–151. DOI: 10.1007/s11783-009-0022-7.
- 1431 (121) Vecitis, C. D.; Park, H.; Cheng, J.; Mader, B. T.; Hoffmann, M. R. Kinetics and mechanism  
1432 of the sonolytic conversion of the aqueous perfluorinated surfactants, perfluorooctanoate (PFOA),  
1433 and perfluorooctane sulfonate (PFOS) into inorganic products. *The journal of physical chemistry. A*  
1434 **2008**, *112* (18), 4261–4270. DOI: 10.1021/jp801081y.
- 1435 (122) Rae, J.; Ashokkumar, M.; Eulaerts, O.; Sonntag, C. von; Reisse, J.; Grieser, F. Estimation  
1436 of ultrasound induced cavitation bubble temperatures in aqueous solutions. *Ultrasonics*  
1437 *sonochemistry* **2005**, *12* (5), 325–329. DOI: 10.1016/j.ultsonch.2004.06.007.
- 1438 (123) Kumar, A.; Škoro, N.; Gernjak, W.; Puač, N. Cold atmospheric plasma technology for  
1439 removal of organic micropollutants from wastewater—a review. *Eur. Phys. J. D* **2021**, *75* (11). DOI:  
1440 10.1140/epjd/s10053-021-00283-5.
- 1441 (124) Lieberman, M. A. *Principles of plasma discharges and materials processing*, 2nd ed.; Wiley-  
1442 Interscience, 2005. DOI: 10.1002/0471724254.
- 1443 (125) Bruggeman, P. J.; Kushner, M. J.; Locke, B. R.; Gardeniers, J. G. E.; Graham, W. G.;  
1444 Graves, D. B.; Hofman-Caris, R. C. H. M.; Maric, D.; Reid, J. P.; Ceriani, E.; Fernandez Rivas, D.;  
1445 Foster, J. E.; Garrick, S. C.; Gorbanev, Y.; Hamaguchi, S.; Iza, F.; Jablonowski, H.; Klimova, E.;  
1446 Kolb, J.; Krcma, F.; Lukes, P.; Machala, Z.; Marinov, I.; Mariotti, D.; Mededovic Thagard, S.;  
1447 Minakata, D.; Neyts, E. C.; Pawlat, J.; Petrovic, Z. L.; Pflieger, R.; Reuter, S.; Schram, D. C.;



- 1448 Schröter, S.; Shiraiwa, M.; Tarabová, B.; Tsai, P. A.; Verlet, J. R. R.; Woedtke, T. von; Wilson, K.  
1449 R.; Yasui, K.; Zvereva, G. Plasma–liquid interactions: a review and roadmap. *Plasma Sources Sci.*  
1450 *Technol.* **2016**, *25* (5), 53002. DOI: 10.1088/0963-0252/25/5/053002.
- 1451 (126) Zeghioud, H.; Nguyen-Tri, P.; Khezami, L.; Amrane, A.; Assadi, A. A. Review on discharge  
1452 Plasma for water treatment: mechanism, reactor geometries, active species and combined  
1453 processes. *Journal of Water Process Engineering* **2020**, *38*, 101664. DOI:  
1454 10.1016/j.jwpe.2020.101664.
- 1455 (127) Malik, M. A. Water Purification by Plasmas: Which Reactors are Most Energy Efficient?  
1456 *Plasma Chem Plasma Process* **2010**, *30* (1), 21–31. DOI: 10.1007/s11090-009-9202-2.
- 1457 (128) Sonntag, C. von. *Free-Radical-Induced DNA Damage and Its Repair. A Chemical*  
1458 *Perspective*; SpringerLink Bücher; Springer Berlin Heidelberg, 2006. DOI: 10.1007/3-540-30592-0.
- 1459 (129) Liang, C.; Bruell, C. J. Thermally Activated Persulfate Oxidation of Trichloroethylene:  
1460 Experimental Investigation of Reaction Orders. *Ind. Eng. Chem. Res.* **2008**, *47* (9), 2912–2918.  
1461 DOI: 10.1021/ie070820l.
- 1462 (130) Kim, C.; Ahn, J.-Y.; Kim, T. Y.; Shin, W. S.; Hwang, I. Activation of Persulfate by Nanosized  
1463 Zero-Valent Iron (NZVI): Mechanisms and Transformation Products of NZVI. *Environmental*  
1464 *science & technology* **2018**, *52* (6), 3625–3633. DOI: 10.1021/acs.est.7b05847. Published Online:  
1465 Feb. 28, 2018.
- 1466 (131) Brunner, G. Near and supercritical water. Part II: Oxidative processes. *The Journal of*  
1467 *Supercritical Fluids* **2009**, *47* (3), 382–390. DOI: 10.1016/j.supflu.2008.09.001.
- 1468 (132) Weingärtner, H.; Franck, E. U. Supercritical water as a solvent. *Angewandte Chemie*  
1469 *(International ed. in English)* **2005**, *44* (18), 2672–2692. DOI: 10.1002/anie.200462468.
- 1470 (133) Sugiyama, W.; Yamamura, T.; Park, K. C.; Tomiyasu, H.; Satoh, I.; Shiokawa, Y.; Okada,  
1471 H.; Sugita, Y. Recovery of radioactivity as solids from nonflammable organic low-level radioactive  
1472 wastes using supercritical water mixed with RuO<sub>2</sub>. *The Journal of Supercritical Fluids* **2005**, *35* (3),  
1473 240–246. DOI: 10.1016/j.supflu.2005.02.003.

- 1474 (134) Shestakova, M.; Sillanpää, M. Electrode materials used for electrochemical oxidation of  
1475 organic compounds in wastewater. *Rev Environ Sci Biotechnol* **2017**, *16* (2), 223–238. DOI:  
1476 10.1007/s11157-017-9426-1.
- 1477 (135) Moreno-Andrés, J.; Ambauen, N.; Vadstein, O.; Hallé, C.; Acevedo-Merino, A.; Nebot, E.;  
1478 Meyn, T. Inactivation of marine heterotrophic bacteria in ballast water by an Electrochemical  
1479 Advanced Oxidation Process. *Water Res.* **2018**, *140*, 377–386. DOI:  
1480 10.1016/j.watres.2018.04.061. Published Online: May. 3, 2018.
- 1481 (136) Radjenovic, J.; Sedlak, D. L. Challenges and Opportunities for Electrochemical Processes  
1482 as Next-Generation Technologies for the Treatment of Contaminated Water. *Environmental*  
1483 *science & technology* **2015**, *49* (19), 11292–11302. DOI: 10.1021/acs.est.5b02414. Published  
1484 Online: Sep. 25, 2015.
- 1485 (137) Tröster, I.; Schäfer, L.; Fryda, M.; Matthée, T. Electrochemical advanced oxidation process  
1486 using DiaChem®electrodes. *Water Science and Technology* **2004**, *49* (4), 207–212. DOI:  
1487 10.2166/wst.2004.0264.
- 1488 (138) Yang, Y. Recent advances in the electrochemical oxidation water treatment: Spotlight on  
1489 byproduct control. *Front. Environ. Sci. Eng.* **2020**, *14* (5). DOI: 10.1007/s11783-020-1264-7.
- 1490 (139) Bolton, J. R.; Bircher, K. G.; Tumas, W.; Tolman, C. A. Figures-of merit for the technical  
1491 development and application of advanced oxidation processes. *Journal of Advanced Oxidation*  
1492 *Technologies* **1996**, *1*, 13–17. DOI: 10.1515/jaots-1996-0104.
- 1493 (140) Bolton, J. R.; Bircher, K. G.; Tumas, W.; Tolman, C. A. Figures-of-merit for the technical  
1494 development and application of advanced oxidation technologies for both electric- and solar-driven  
1495 systems (IUPAC Technical Report). *Pure and Applied Chemistry* **2001**, *73* (4), 627–637. DOI:  
1496 10.1351/pac200173040627.
- 1497 (141) Bolton, J. R.; Stefan, M. I. Fundamental photochemical approach to the concepts of fluence  
1498 (UV dose) and electrical energy efficiency in photochemical degradation reactions. *Res. Chem.*  
1499 *Intermed.* **2002**, *28* (7-9), 857–870. DOI: 10.1163/15685670260469474.

1500 (142) Stefan, M. I.; Bolton, J. R. Fundamental approach to the fluence-based kinetic and electrical  
1501 energy efficiency parameters in photochemical degradation reactions: polychromatic light. *Journal*  
1502 *of Environmental Engineering and Science* **2005**, *4* (Supplement 1), S13-S18. DOI: 10.1139/s04-  
1503 026.

1504 (143) Lanzarini-Lopes, M.; Garcia-Segura, S.; Hristovski, K.; Westerhoff, P. Electrical energy per  
1505 order and current efficiency for electrochemical oxidation of p-chlorobenzoic acid with boron-doped  
1506 diamond anode. *Chemosphere* **2017**, *188*, 304–311. DOI: 10.1016/j.chemosphere.2017.08.145.  
1507 Published Online: Aug. 30, 2017.

1508 (144) Mahamuni, N. N.; Adewuyi, Y. G. Advanced oxidation processes (AOPs) involving  
1509 ultrasound for waste water treatment: a review with emphasis on cost estimation. *Ultrasonics*  
1510 *sonochemistry* **2010**, *17* (6), 990–1003. DOI: 10.1016/j.ultsonch.2009.09.005. Published Online:  
1511 Sep. 29, 2009.

1512 (145) Saien, J.; Ojaghloo, Z.; Soleymani, A. R.; Rasoulifard, M. H. Homogeneous and  
1513 heterogeneous AOPs for rapid degradation of Triton X-100 in aqueous media via UV light, nano  
1514 titania hydrogen peroxide and potassium persulfate. *Chemical Engineering Journal* **2011**, *167* (1),  
1515 172–182. DOI: 10.1016/j.cej.2010.12.017. Published Online: Dec. 13, 2010.

1516 (146) Zhang, Y.; Wang, H.; Li, Y.; Wang, B.; Huang, J.; Deng, S.; Yu, G.; Wang, Y. Removal of  
1517 micropollutants by an electrochemically driven UV/chlorine process for decentralized water  
1518 treatment. *Water Res.* **2020**, *183*, 116115. DOI: 10.1016/j.watres.2020.116115. Published Online:  
1519 Jul. 1, 2020.

1520 (147) Keen, O.; Bolton, J.; Litter, M.; Bircher, K.; Oppenländer, T. Standard reporting of Electrical  
1521 Energy per Order (EEO ) for UV/H<sub>2</sub>O<sub>2</sub> reactors (IUPAC Technical Report). *Pure and Applied*  
1522 *Chemistry* **2018**, *90* (9), 1487–1499. DOI: 10.1515/pac-2017-0603.

1523 (148) Schmelling, D.; Cotton, C.; Owen, D.; Mackey, E.; Wright, H.; Linden, K. G.; Malley, J. P.  
1524 *Ultraviolet disinfection guidance manual for the final long term 2 enhanced surface water treatment*  
1525 *rule*.

- 1526 (149) IUPAC. *The IUPAC Compendium of Chemical Terminology*; International Union of Pure and  
1527 Applied Chemistry (IUPAC), 2019. DOI: 10.1351/goldbook.
- 1528 (150) Lee, Y.; Kovalova, L.; McArdell, C. S.; Gunten, U. von. Prediction of micropollutant  
1529 elimination during ozonation of a hospital wastewater effluent. *Water Res.* **2014**, *64*, 134–148.  
1530 DOI: 10.1016/j.watres.2014.06.027. Published Online: Jun. 27, 2014.
- 1531 (151) Wünsch, R.; Mayer, C.; Plattner, J.; Eugster, F.; Wülser, R.; Gebhardt, J.; Hübner, U.;  
1532 Canonica, S.; Wintgens, T.; Gunten, U. von. Micropollutants as internal probe compounds to  
1533 assess UV fluence and hydroxyl radical exposure in UV/H<sub>2</sub>O<sub>2</sub> treatment. *Water Res.* **2021**, *195*,  
1534 116940. DOI: 10.1016/j.watres.2021.116940. Published Online: Feb. 18, 2021.
- 1535 (152) Burns, J. M.; Cooper, W. J.; Ferry, J. L.; King, D. W.; DiMento, B. P.; McNeill, K.; Miller, C.  
1536 J.; Miller, W. L.; Peake, B. M.; Rusak, S. A.; Rose, A. L.; Waite, T. D. Methods for reactive oxygen  
1537 species (ROS) detection in aqueous environments. *Aquat Sci* **2012**, *74* (4), 683–734. DOI:  
1538 10.1007/s00027-012-0251-x.
- 1539 (153) Nosaka, Y.; Nosaka, A. Y. Generation and Detection of Reactive Oxygen Species in  
1540 Photocatalysis. *Chem. Rev.* **2017**, *117* (17), 11302–11336. DOI: 10.1021/acs.chemrev.7b00161.  
1541 Published Online: Aug. 4, 2017.
- 1542 (154) Fennell, B. D.; Mezyk, S. P.; McKay, G. Critical Review of UV-Advanced Reduction  
1543 Processes for the Treatment of Chemical Contaminants in Water. *ACS Environ. Au* **2022**, *2* (3),  
1544 178–205. DOI: 10.1021/acsenvironau.1c00042.
- 1545 (155) Rosario-Ortiz, F. L.; Canonica, S. Probe Compounds to Assess the Photochemical Activity  
1546 of Dissolved Organic Matter. *Environmental science & technology* **2016**, *50* (23), 12532–12547.  
1547 DOI: 10.1021/acs.est.6b02776. Published Online: Nov. 9, 2016.
- 1548 (156) Scholes, R. C. Emerging investigator series: contributions of reactive nitrogen species to  
1549 transformations of organic compounds in water: a critical review. *Environmental Science*.  
1550 *Processes & Impacts* **2022**, *24* (6), 851–869. DOI: 10.1039/D2EM00102K. Published Online: Jun.  
1551 22, 2022.

- 1552 (157) Zhou, L.; Sleiman, M.; Ferronato, C.; Chovelon, J.-M.; Richard, C. Reactivity of sulfate  
1553 radicals with natural organic matters. *Environ Chem Lett* **2017**, *15* (4), 733–737. DOI:  
1554 10.1007/s10311-017-0646-y.
- 1555 (158) Gardoni, D.; Vailati, A.; Canziani, R. Decay of Ozone in Water: A Review. *Ozone: Science &*  
1556 *Engineering* **2012**, *34* (4), 233–242. DOI: 10.1080/01919512.2012.686354.
- 1557 (159) Hoigné, J.; Bader, H. Characterization Of Water Quality Criteria for Ozonation Processes.  
1558 Part II: Lifetime of Added Ozone. *Ozone: Science & Engineering* **1994**, *16* (2), 121–134. DOI:  
1559 10.1080/01919519408552417.
- 1560 (160) Guo, Y.; Zhang, Y.; Yu, G.; Wang, Y. Revisiting the role of reactive oxygen species for  
1561 pollutant abatement during catalytic ozonation: The probe approach versus the scavenger  
1562 approach. *Applied Catalysis B: Environmental* **2021**, *280*, 119418. DOI:  
1563 10.1016/j.apcatb.2020.119418.
- 1564 (161) Guo, Y.; Long, J.; Huang, J.; Yu, G.; Wang, Y. Can the commonly used quenching method  
1565 really evaluate the role of reactive oxygen species in pollutant abatement during catalytic  
1566 ozonation? *Water Res.* **2022**, *215*, 118275. DOI: 10.1016/j.watres.2022.118275. Published Online:  
1567 Mar. 10, 2022.
- 1568 (162) Zeng, T.; Arnold, W. A. Pesticide photolysis in prairie potholes: probing photosensitized  
1569 processes. *Environmental science & technology* **2013**, *47* (13), 6735–6745. DOI:  
1570 10.1021/es3030808. Published Online: Nov. 29, 2012.
- 1571 (163) Wang, C.; Rosenfeldt, E.; Li, Y.; Hofmann, R. External Standard Calibration Method To  
1572 Measure the Hydroxyl Radical Scavenging Capacity of Water Samples. *Environmental science &*  
1573 *technology* **2020**, *54* (3), 1929–1937. DOI: 10.1021/acs.est.9b06273. Published Online: Jan. 10,  
1574 2020.
- 1575 (164) Huber, M. M.; Canonica, S.; Park, G.-Y.; Gunten, U. von. Oxidation of pharmaceuticals  
1576 during ozonation and advanced oxidation processes. *Environ. Sci. Technol.* **2003**, *37* (5), 1016–  
1577 1024. DOI: 10.1021/es025896h.

- 1578 (165) Wenk, J.; Gunten, U. von; Canonica, S. Effect of dissolved organic matter on the  
1579 transformation of contaminants induced by excited triplet states and the hydroxyl radical.  
1580 *Environmental science & technology* **2011**, *45* (4), 1334–1340. DOI: 10.1021/es102212t.  
1581 Published Online: Jan. 27, 2011.
- 1582 (166) Keen, O. S.; McKay, G.; Mezyk, S. P.; Linden, K. G.; Rosario-Ortiz, F. L. Identifying the  
1583 factors that influence the reactivity of effluent organic matter with hydroxyl radicals. *Water Res.*  
1584 **2014**, *50*, 408–419. DOI: 10.1016/j.watres.2013.10.049. Published Online: Nov. 1, 2013.
- 1585 (167) Lado Ribeiro, A. R.; Moreira, N. F.; Li Puma, G.; Silva, A. M. Impact of water matrix on the  
1586 removal of micropollutants by advanced oxidation technologies. *Chemical Engineering Journal*  
1587 **2019**, *363*, 155–173. DOI: 10.1016/j.cej.2019.01.080.
- 1588 (168) Nöthe, T.; Fahlenkamp, H.; Sonntag, C. von. Ozonation of wastewater: rate of ozone  
1589 consumption and hydroxyl radical yield. *Environ. Sci. Technol.* **2009**, *43* (15), 5990–5995. DOI:  
1590 10.1021/es900825f.
- 1591 (169) Vione, D.; Falletti, G.; Maurino, V.; Minero, C.; Pelizzetti, E.; Malandrino, M.; Ajassa, R.;  
1592 Olariu, R.-I.; Arsene, C. Sources and sinks of hydroxyl radicals upon irradiation of natural water  
1593 samples. *Environ. Sci. Technol.* **2006**, *40* (12), 3775–3781. DOI: 10.1021/es052206b.
- 1594 (170) Zhang, K.; Parker, K. M. Halogen Radical Oxidants in Natural and Engineered Aquatic  
1595 Systems. *Environmental science & technology* **2018**, *52* (17), 9579–9594. DOI:  
1596 10.1021/acs.est.8b02219. Published Online: Aug. 23, 2018.
- 1597 (171) Willach, S.; Lutze, H. V.; Eckey, K.; Löppenber, K.; Lüling, M.; Terhalle, J.; Wolbert, J.-B.;  
1598 Jochmann, M. A.; Karst, U.; Schmidt, T. C. Degradation of sulfamethoxazole using ozone and  
1599 chlorine dioxide - Compound-specific stable isotope analysis, transformation product analysis and  
1600 mechanistic aspects. *Water Res.* **2017**, *122*, 280–289. DOI: 10.1016/j.watres.2017.06.001.  
1601 Published Online: Jun. 3, 2017.
- 1602 (172) Flyunt, R.; Leitzke, A.; Mark, G.; Mvula, E.; Reisz, E.; Schick, R.; Sonntag, C. von.  
1603 Determination of  $\cdot\text{OH}$ ,  $\text{O}_2^{\cdot-}$ , and Hydroperoxide Yields in Ozone Reactions in Aqueous Solution.  
1604 *J. Phys. Chem. B* **2003**, *107* (30), 7242–7253. DOI: 10.1021/jp022455b.

1605 (173) Wang, L.; Lan, X.; Peng, W.; Wang, Z. Uncertainty and misinterpretation over identification,  
1606 quantification and transformation of reactive species generated in catalytic oxidation processes: A  
1607 review. *Journal of Hazardous Materials* **2021**, *408*, 124436. DOI: 10.1016/j.jhazmat.2020.124436.  
1608 Published Online: Nov. 2, 2020.

1609 (174) Zhou, Y.; Jiang, J.; Gao, Y.; Ma, J.; Pang, S.-Y.; Li, J.; Lu, X.-T.; Yuan, L.-P. Activation of  
1610 Peroxymonosulfate by Benzoquinone: A Novel Nonradical Oxidation Process. *Environmental*  
1611 *science & technology* **2015**, *49* (21), 12941–12950. DOI: 10.1021/acs.est.5b03595. Published  
1612 Online: Oct. 23, 2015.

1613 (175) Bolton, J. R.; Linden, K. G. Standardization of Methods for Fluence (UV Dose)  
1614 Determination in Bench-Scale UV Experiments. *Journal of Environmental Engineering* **2003**, *129*  
1615 (3), 209–215. DOI: 10.1061/(ASCE)0733-9372(2003)129:3(209).

1616 (176) Ulliman, S. L.; Miklos, D. B.; Hübner, U.; Drewes, J. E.; Linden, K. G. Improving UV/H<sub>2</sub>O<sub>2</sub>  
1617 performance following tertiary treatment of municipal wastewater. *Environ. Sci.: Water Res.*  
1618 *Technol.* **2018**, *4* (9), 1321–1330. DOI: 10.1039/C8EW00233A.

1619 (177) Hübner, U.; Zucker, I.; Jekel, M. Options and limitations of hydrogen peroxide addition to  
1620 enhance radical formation during ozonation of secondary effluents. *Journal of Water Reuse and*  
1621 *Desalination* **2015**, *5* (1), 8. DOI: 10.2166/wrd.2014.036.

1622 (178) Zhou, Y.; Chen, C.; Guo, K.; Wu, Z.; Wang, L.; Hua, Z.; Fang, J. Kinetics and pathways of  
1623 the degradation of PPCPs by carbonate radicals in advanced oxidation processes. *Water Res.*  
1624 **2020**, *185*, 116231. DOI: 10.1016/j.watres.2020.116231. Published Online: Jul. 24, 2020.

1625 (179) Canonica, S.; Meunier, L.; Gunten, U. von. Phototransformation of selected  
1626 pharmaceuticals during UV treatment of drinking water. *Water Res.* **2008**, *42* (1-2), 121–128. DOI:  
1627 10.1016/j.watres.2007.07.026. Published Online: Jul. 26, 2007.

1628 (180) Prasse, C.; Wenk, J.; Jasper, J. T.; Ternes, T. A.; Sedlak, D. L. Co-occurrence of  
1629 Photochemical and Microbiological Transformation Processes in Open-Water Unit Process  
1630 Wetlands. *Environmental science & technology* **2015**, *49* (24), 14136–14145. DOI:  
1631 10.1021/acs.est.5b03783. Published Online: Nov. 12, 2015.

- 1632 (181) Wenk, J.; Graf, C.; Aeschbacher, M.; Sander, M.; Canonica, S. Effect of Solution pH on the  
1633 Dual Role of Dissolved Organic Matter in Sensitized Pollutant Photooxidation. *Environmental*  
1634 *science & technology* **2021**, *55* (22), 15110–15122. DOI: 10.1021/acs.est.1c03301. Published  
1635 Online: Oct. 29, 2021.
- 1636 (182) Canonica, S.; Kohn, T.; Mac, M.; Real, F. J.; Wirz, J.; Gunten, U. von. Photosensitizer  
1637 method to determine rate constants for the reaction of carbonate radical with organic compounds.  
1638 *Environ. Sci. Technol.* **2005**, *39* (23), 9182–9188. DOI: 10.1021/es051236b.
- 1639 (183) Maruthamuthu, P.; Neta, P. Phosphate radicals. Spectra, acid-base equilibria, and  
1640 reactions with inorganic compounds. *J. Phys. Chem.* **1978**, *82* (6), 710–713. DOI:  
1641 10.1021/j100495a019.
- 1642 (184) Bolton, J. R.; Mayor-Smith, I.; Linden, K. G. Rethinking the Concepts of Fluence (UV Dose)  
1643 and Fluence Rate: The Importance of Photon-based Units - A Systemic Review. *Photochemistry*  
1644 *and photobiology* **2015**, *91* (6), 1252–1262. DOI: 10.1111/php.12512. Published Online: Sep. 24,  
1645 2015.
- 1646 (185) Velo-Gala, I.; Farré, M. J.; Radjenovic, J.; Gernjak, W. N -Nitrosodimethylamine (NDMA)  
1647 Degradation by the Ultraviolet/Peroxodisulfate Process. *Environ. Sci. Technol. Lett.* **2019**, *6* (2),  
1648 106–111. DOI: 10.1021/acs.estlett.8b00667.
- 1649 (186) Kuhn, H. J.; Braslavsky, S. E.; Schmidt, R. Chemical actinometry (IUPAC Technical  
1650 Report). *Pure and Applied Chemistry* **2004**, *76* (12), 2105–2146. DOI: 10.1351/pac200476122105.
- 1651 (187) Rabani, J.; Mamane, H.; Pousty, D.; Bolton, J. R. Practical Chemical Actinometry-A Review.  
1652 *Photochemistry and photobiology* **2021**, *97* (5), 873–902. DOI: 10.1111/php.13429. Published  
1653 Online: Jul. 27, 2021.
- 1654 (188) Rahn, R. O. Potassium Iodide as a Chemical Actinometer for 254 nm Radiation: Use of  
1655 Iodate as an Electron Scavenger. *Photochemistry and photobiology* **1997**, *66* (4), 450–455. DOI:  
1656 10.1111/j.1751-1097.1997.tb03172.x.
- 1657 (189) Rahn, R. O.; Stefan, M. I.; Bolton, J. R.; Goren, E.; Shaw, P.-S.; Lykke, K. R. Quantum Yield  
1658 of the Iodide–Iodate Chemical Actinometer: Dependence on Wavelength and Concentration¶.



- 1659 *Photochemistry and photobiology* **2003**, 78 (2), 146. DOI: 10.1562/0031-
- 1660 8655(2003)078%3C0146:qyotic%3E2.0.co;2.
- 1661 (190) Wols, B. A.; Hofman-Caris, C.; Harmsen, D. J.; Beerendonk, E. F.; van Dijk, J. C.; Chan, P.-
- 1662 S.; Blatchley, E. R. Comparison of CFD, Biodosimetry and Lagrangian Actinometry to Assess UV
- 1663 Reactor Performance. *Ozone: Science & Engineering* **2012**, 34 (2), 81–91. DOI:
- 1664 10.1080/01919512.2012.651398.
- 1665 (191) APRIA Systems. *Collimated beam reactor*. [https://photochemistry.apriasystems.es/](https://photochemistry.apriasystems.es/products-collimated-beam/)
- 1666 [products-collimated-beam/](https://photochemistry.apriasystems.es/products-collimated-beam/) (accessed 2022-09-07).
- 1667 (192) Bolton, J. R.; Cotton, C. E. *The ultraviolet disinfection handbook*, 1st ed.; American Water
- 1668 Works Association, 2008.
- 1669 (193) Hübner, U.; Keller, S.; Jekel, M. Evaluation of the prediction of trace organic compound
- 1670 removal during ozonation of secondary effluents using tracer substances and second order rate
- 1671 kinetics. *Water Res.* **2013**, 47 (17), 6467–6474. DOI: 10.1016/j.watres.2013.08.025. Published
- 1672 Online: Sep. 4, 2013.
- 1673 (194) Buffle, M.-O.; von Gunten, U. Phenols and Amine Induced HO • Generation During the
- 1674 Initial Phase of Natural Water Ozonation. *Environ. Sci. Technol.* **2006**, 40 (9), 3057–3063. DOI:
- 1675 10.1021/es052020c.
- 1676 (195) Elovitz, M. S.; von Gunten, U. Hydroxyl Radical/Ozone Ratios During Ozonation Processes.
- 1677 I. The R ct Concept. *Ozone: Science & Engineering* **1999**, 21 (3), 239–260. DOI:
- 1678 10.1080/01919519908547239.
- 1679 (196) Wang, Y.; Yu, G. Challenges and pitfalls in the investigation of the catalytic ozonation
- 1680 mechanism: A critical review. *Journal of Hazardous Materials* **2022**, 436, 129157. DOI:
- 1681 10.1016/j.jhazmat.2022.129157. Published Online: May. 17, 2022.
- 1682 (197) Atkins, P. W.; Paula, J. de. *Atkins' physical chemistry*, Tenth edition; Oxford University
- 1683 Press, 2014.
- 1684 (198) Zietzschmann, F.; Stapf, M.; Sperlich, A.; Ruhl, A. S.; Mieke, U.; Gnirß, R.; Jekel, M.
- 1685 *TestTools – Entwicklung und Validierung von schnellen Testmethoden zum Spurenstoffverhalten*

- 1686 *in technischen und natürlichen Barrieren des urbanen Wasserkreislaufs*; Universitätsverlag der TU  
1687 Berlin, 2018. DOI: 10.14279/depositonce-7524.
- 1688 (199) Bader, H.; Hoigné, J. Determination of ozone in water by the indigo method. *Water Res.*  
1689 **1981**, *15* (4), 449–456. DOI: 10.1016/0043-1354(81)90054-3.
- 1690 (200) Ying, Z.; Yechezkel, Y.; Huo, M.; Hübner, U.; Zucker, I. Ozone Consumption by Soils: A  
1691 Critical Factor in In Situ Ozonation Processes. *ACS EST Water* **2021**, *1* (11), 2403–2411. DOI:  
1692 10.1021/acsestwater.1c00236.
- 1693 (201) Bligaard, T.; Bullock, R. M.; Campbell, C. T.; Chen, J. G.; Gates, B. C.; Gorte, R. J.; Jones,  
1694 C. W.; Jones, W. D.; Kitchin, J. R.; Scott, S. L. Toward Benchmarking in Catalysis Science: Best  
1695 Practices, Challenges, and Opportunities. *ACS Catal.* **2016**, *6* (4), 2590–2602. DOI:  
1696 10.1021/acscatal.6b00183.
- 1697 (202) Kozuch, S.; Martin, J. M. L. “Turning Over” Definitions in Catalytic Cycles. *ACS Catal.* **2012**,  
1698 *2* (12), 2787–2794. DOI: 10.1021/cs3005264.
- 1699 (203) Tasso Guaraldo, T.; Wenk, J.; Mattia, D. Photocatalytic ZnO Foams for Micropollutant  
1700 Degradation. *Adv. Sustainable Syst.* **2021**, *5* (5), 2000208. DOI: 10.1002/adsu.202000208.
- 1701 (204) Warren, Z.; Guaraldo, T. T.; Wenk, J.; Mattia, D. Synthesis of photocatalytic pore size-tuned  
1702 ZnO molecular foams. *J. Mater. Chem. A* **2022**, *10* (21), 11542–11552. DOI:  
1703 10.1039/D2TA02038F.
- 1704 (205) Hung, H.-M.; Hoffmann, M. R. Kinetics and Mechanism of the Sonolytic Degradation of  
1705 Chlorinated Hydrocarbons: Frequency Effects. *J. Phys. Chem. A* **1999**, *103* (15), 2734–2739. DOI:  
1706 10.1021/jp9845930.
- 1707 (206) Gałgól, M.; Przyjazny, A.; Boczkaj, G. Wastewater treatment by means of advanced  
1708 oxidation processes based on cavitation – A review. *Chemical Engineering Journal* **2018**, *338*,  
1709 599–627. DOI: 10.1016/j.cej.2018.01.049.
- 1710 (207) Armstrong, K. Emerging Industrial Applications. In *Carbon Dioxide Utilisation*; Elsevier,  
1711 2015; pp 237–251. DOI: 10.1016/B978-0-444-62746-9.00013-X.

- 1712 (208) Anipsitakis, G. P.; Stathatos, E.; Dionysiou, D. D. Heterogeneous activation of oxone using  
1713 Co<sub>3</sub>O<sub>4</sub>. *J. Phys. Chem. B* **2005**, *109* (27), 13052–13055. DOI: 10.1021/jp052166y.
- 1714 (209) Yang, Q.; Niu, X.; Zhu, Y.; Cui, Y.; Chao, Y.; Liang, P.; Zhang, C.; Wang, S. Modulating  
1715 anion defect in La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>0.8</sub>Fe<sub>0.2</sub>O<sub>3-δ</sub> for enhanced catalytic performance on  
1716 peroxymonosulfate activation: Importance of hydrated electrons and metal-oxygen covalency.  
1717 *Journal of Hazardous Materials* **2022**, *432*, 128686. DOI: 10.1016/j.jhazmat.2022.128686.  
1718 Published Online: Mar. 12, 2022.
- 1719 (210) Sidnell, T.; Wood, R. J.; Hurst, J.; Lee, J.; Bussemaker, M. J. Sonolysis of per- and poly  
1720 fluoroalkyl substances (PFAS): A meta-analysis. *Ultrasonics sonochemistry* **2022**, *87*, 105944.  
1721 DOI: 10.1016/j.ultsonch.2022.105944. Published Online: Feb. 7, 2022.
- 1722 (211) Piccinno, F.; Hischer, R.; Seeger, S.; Som, C. From laboratory to industrial scale: a scale-  
1723 up framework for chemical processes in life cycle assessment studies. *Journal of Cleaner*  
1724 *Production* **2016**, *135*, 1085–1097. DOI: 10.1016/j.jclepro.2016.06.164.
- 1725 (212) Mery, Y.; Tiruta-Barna, L.; Benetto, E.; Baudin, I. An integrated “process modelling-life cycle  
1726 assessment” tool for the assessment and design of water treatment processes. *Int J Life Cycle*  
1727 *Assess* **2013**, *18* (5), 1062–1070. DOI: 10.1007/s11367-012-0541-5.
- 1728 (213) Schimmoller, L. J.; Kealy, M. J.; Foster, S. K. Triple bottom line costs for multiple potable  
1729 reuse treatment schemes. *Environ. Sci.: Water Res. Technol.* **2015**, *1* (5), 644–658. DOI:  
1730 10.1039/C5EW00044K.
- 1731 (214) *Directive (EU) 2020/2184 of the European Parliament and of the Council of 16 December*  
1732 *2020 on the quality of water intended for human consumption (recast):DWD, 2020.*
- 1733 (215) Schulze, S.; Zahn, D.; Montes, R.; Rodil, R.; Quintana, J. B.; Knepper, T. P.; Reemtsma, T.;  
1734 Berger, U. Occurrence of emerging persistent and mobile organic contaminants in European water  
1735 samples. *Water Res.* **2019**, *153*, 80–90. DOI: 10.1016/j.watres.2019.01.008. Published Online:  
1736 Jan. 18, 2019.

- 1737 (216) Lee, Y.; Gunten, U. von. Quantitative structure-activity relationships (QSARs) for the  
1738 transformation of organic micropollutants during oxidative water treatment. *Water Res.* **2012**, *46*  
1739 (19), 6177–6195. DOI: 10.1016/j.watres.2012.06.006. Published Online: Jun. 16, 2012.
- 1740 (217) Lee, M.; Blum, L. C.; Schmid, E.; Fenner, K.; Gunten, U. von. A computer-based prediction  
1741 platform for the reaction of ozone with organic compounds in aqueous solution: kinetics and  
1742 mechanisms. *Environ. Sci. Process. Impacts* **2017**, *19* (3), 465–476. DOI: 10.1039/C6EM00584E.
- 1743 (218) Lee, Y.; Gunten, U. von. Advances in predicting organic contaminant abatement during  
1744 ozonation of municipal wastewater effluent: reaction kinetics, transformation products, and  
1745 changes of biological effects. *Environ. Sci.: Water Res. Technol.* **2016**, *2* (3), 421–442. DOI:  
1746 10.1039/c6ew00025h.
- 1747 (219) Tentscher, P. R.; Lee, M.; Gunten, U. von. Micropollutant Oxidation Studied by Quantum  
1748 Chemical Computations: Methodology and Applications to Thermodynamics, Kinetics, and  
1749 Reaction Mechanisms. *Accounts of chemical research* **2019**, *52* (3), 605–614. DOI:  
1750 10.1021/acs.accounts.8b00610. Published Online: Mar. 4, 2019.
- 1751 (220) Brack, W.; Ait-Aissa, S.; Burgess, R. M.; Busch, W.; Creusot, N.; Di Paolo, C.; Escher, B. I.;  
1752 Mark Hewitt, L.; Hilscherova, K.; Hollender, J.; Hollert, H.; Jonker, W.; Kool, J.; Lamoree, M.;  
1753 Muschket, M.; Neumann, S.; Rostkowski, P.; Ruttkies, C.; Schollee, J.; Schymanski, E. L.;  
1754 Schulze, T.; Seiler, T.-B.; Tindall, A. J.; Aragão Umbuzeiro, G. de; Vrana, B.; Krauss, M. Effect-  
1755 directed analysis supporting monitoring of aquatic environments--An in-depth overview. *The*  
1756 *Science of the total environment* **2016**, *544*, 1073–1118. DOI: 10.1016/j.scitotenv.2015.11.102.  
1757 Published Online: Jan. 11, 2016.
- 1758 (221) Völker, J.; Stapf, M.; Miehe, U.; Wagner, M. Systematic Review of Toxicity Removal by  
1759 Advanced Wastewater Treatment Technologies via Ozonation and Activated Carbon.  
1760 *Environmental science & technology* **2019**, *53* (13), 7215–7233. DOI: 10.1021/acs.est.9b00570.  
1761 Published Online: Jun. 17, 2019.
- 1762 (222) Heeb, M. B.; Criquet, J.; Zimmermann-Steffens, S. G.; Gunten, U. von. Oxidative treatment  
1763 of bromide-containing waters: formation of bromine and its reactions with inorganic and organic

- 1764 compounds--a critical review. *Water Res.* **2014**, *48*, 15–42. DOI: 10.1016/j.watres.2013.08.030.  
1765 Published Online: Sep. 4, 2013.
- 1766 (223) Spahr, S.; Cirpka, O. A.; Gunten, U. von; Hofstetter, T. B. Formation of N-  
1767 Nitrosodimethylamine during Chloramination of Secondary and Tertiary Amines: Role of Molecular  
1768 Oxygen and Radical Intermediates. *Environmental science & technology* **2017**, *51* (1), 280–290.  
1769 DOI: 10.1021/acs.est.6b04780. Published Online: Dec. 13, 2016.
- 1770 (224) Zhang, Y.-J.; Huang, G.-X.; Winter, L. R.; Chen, J.-J.; Tian, L.; Mei, S.-C.; Zhang, Z.; Chen,  
1771 F.; Guo, Z.-Y.; Ji, R.; You, Y.-Z.; Li, W.-W.; Liu, X.-W.; Yu, H.-Q.; Elimelech, M. Simultaneous  
1772 nanocatalytic surface activation of pollutants and oxidants for highly efficient water  
1773 decontamination. *Nature communications* **2022**, *13* (1), 3005. DOI: 10.1038/s41467-022-30560-9.  
1774 Published Online: May. 30, 2022.
- 1775 (225) Lavonen, E. E.; Gonsior, M.; Tranvik, L. J.; Schmitt-Kopplin, P.; Köhler, S. J. Selective  
1776 chlorination of natural organic matter: identification of previously unknown disinfection byproducts.  
1777 *Environmental science & technology* **2013**, *47* (5), 2264–2271. DOI: 10.1021/es304669p.  
1778 Published Online: Feb. 18, 2013.
- 1779 (226) Spahr, S.; Gunten, U. von; Hofstetter, T. B. Carbon, Hydrogen, and Nitrogen Isotope  
1780 Fractionation Trends in N-Nitrosodimethylamine Reflect the Formation Pathway during  
1781 Chloramination of Tertiary Amines. *Environmental science & technology* **2017**, *51* (22), 13170–  
1782 13179. DOI: 10.1021/acs.est.7b03919. Published Online: Nov. 6, 2017.
- 1783 (227) Bletsou, A. A.; Jeon, J.; Hollender, J.; Archontaki, E.; Thomaidis, N. S. Targeted and non-  
1784 targeted liquid chromatography-mass spectrometric workflows for identification of transformation  
1785 products of emerging pollutants in the aquatic environment. *TrAC Trends in Analytical Chemistry*  
1786 **2015**, *66*, 32–44. DOI: 10.1016/j.trac.2014.11.009.
- 1787 (228) Prasse, C.; Stalter, D.; Schulte-Oehlmann, U.; Oehlmann, J.; Ternes, T. A. Spoilt for choice:  
1788 A critical review on the chemical and biological assessment of current wastewater treatment  
1789 technologies. *Water Res.* **2015**, *87*, 237–270. DOI: 10.1016/j.watres.2015.09.023. Published  
1790 Online: Sep. 14, 2015.

- 1791 (229) Escher, B. I.; Lawrence, M.; Macova, M.; Mueller, J. F.; Poussade, Y.; Robillot, C.; Roux, A.;  
1792 Gernjak, W. Evaluation of contaminant removal of reverse osmosis and advanced oxidation in full-  
1793 scale operation by combining passive sampling with chemical analysis and bioanalytical tools.  
1794 *Environmental science & technology* **2011**, *45* (12), 5387–5394. DOI: 10.1021/es201153k.  
1795 Published Online: May. 25, 2011.
- 1796 (230) Könemann, S.; Kase, R.; Simon, E.; Swart, K.; Buchinger, S.; Schlüsener, M.; Hollert, H.;  
1797 Escher, B. I.; Werner, I.; Aït-Aïssa, S.; Vermeirssen, E.; Dulio, V.; Valsecchi, S.; Polesello, S.;  
1798 Behnisch, P.; Javurkova, B.; Perceval, O.; Di Paolo, C.; Olbrich, D.; Sychrova, E.; Schlichting, R.;  
1799 Leborgne, L.; Clara, M.; Scheffknecht, C.; Marneffe, Y.; Chalon, C.; Tušil, P.; Soldà, P.; Danwitz,  
1800 B. von; Schwaiger, J.; San Martín Becares, M. I.; Bersani, F.; Hilscherová, K.; Reifferscheid, G.;  
1801 Ternes, T.; Carere, M. Effect-based and chemical analytical methods to monitor estrogens under  
1802 the European Water Framework Directive. *TrAC Trends in Analytical Chemistry* **2018**, *102*, 225–  
1803 235. DOI: 10.1016/j.trac.2018.02.008.