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Title: Influence of Radiation and TiO<sub>2</sub> Concentration on the Hydroxyl Radicals Generation in a Photocatalytic LED Reactor. Application to dodecylbenzenesulfonate degradation

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1 Highlights

- 2 • Photocatalytic degradation of DBS in UV-LED reactor

- 3 • Determination of  $\cdot\text{OH}$  generation rate

- 4 • Modelling DBS degradation rate as function of  $\cdot\text{OH}$  generation

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6 Graphical abstract  
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**Applied Catalysis B: Environmental**

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**Influence of Radiation and TiO<sub>2</sub> Concentration on the Hydroxyl Radicals**

9

**Generation in a Photocatalytic LED Reactor. Application to**

10

**dodecylbenzenesulfonate degradation.**

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17

**ABSTRACT**

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One of the main issues associated to the development of photocatalysis is the

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lack of adequate indexes that allow the comparison of the results obtained in

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different experimental setup designs. The hydroxyl radicals ( $\cdot\text{OH}$ ) generation

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rate is a key factor to determine the overall oxidation rate.

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In this work, using a Light Emitting Diodes (LEDs) reactor aimed to maximize

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light efficiency and minimize energy consumption, the  $\cdot\text{OH}$  generated have

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been determined as a function of the radiation and catalyst concentration

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following an indirect method based on the reaction between  $\cdot\text{OH}$  and dimethyl

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sulfoxide (DMSO) to produce formaldehyde.

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Finally, the methodology has been applied to analyze the degradation kinetics

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of the anionic surfactant dodecylbenzenesulfonate (DBS), frequently used in

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shampoo formulations and detergents for washing machines. We propose a

31 method based on the indirect determination of  $\cdot\text{OH}$  radicals generation rate that  
32 allows the assessment and comparison of the kinetics of photocatalytic  
33 oxidation of pollutants.

34

### 35 **Keywords**

36 DBS; hydroxyl radicals; light emitting diode; photocatalysis; kinetic modeling.

37

### 38 **1. Introduction**

39 Increasing water demand and shortage of available water are growing concerns  
40 for our society [1]. Since wastewaters constitute one of the largest possible  
41 water resources, one attractive option is the possible reuse of onsite  
42 wastewater or the effluent of wastewater treatment plants (WWTPs).

43 Conventional water treatments such as chemical oxidation, activated carbon  
44 adsorption and biological treatment sometimes seem to be inefficient in  
45 degrading some organic compounds [2]-[4].

46 Hence, over the last few decades, a group of new technologies called advanced  
47 oxidation processes (AOPs) has been widely reported because of their  
48 effectiveness in the oxidation of organic compounds. AOPs are processes  
49 based on the generation of strongly reactive species such as hydroxyl radicals  
50 ( $\cdot\text{OH}$ ) [4]-[6].

51 Among these technologies, photocatalysis is an attractive instrument for the  
52 removal of organic and inorganic pollutants from water, due to its ambient  
53 operating temperature and pressure and absence of secondary pollution.

54 Heterogeneous photocatalysis is a process in which a source of appropriate  
55 light and a solid semiconductor material as catalyst are necessary to promote a

56 chemical reaction by means of the generation of electron-hole pairs [6], [7].  
57 Up to now,  $\text{TiO}_2$  is the most promising material used as catalyst because it is  
58 highly photoreactive, stable with respect to corrosion, inexpensive, nontoxic,  
59 biologically and chemically inert and capable of repeated use without  
60 considerable loss of catalytic capacity [6]-[9].  
61 Nevertheless, the inherent difficulty to compare the results obtained in the  
62 countless experimental setup designs and configurations represents an  
63 important issue in the development of photocatalysis that needs further  
64 research [10], [11]. Hence, the quantitative determination of the hydroxyl  
65 radicals generated in the photocatalytic processes is essential for a better  
66 understanding of the results obtained with this technology. However, their high  
67 reactivity and short lifetime complicate their direct determination. Therefore,  
68 several indirect detection methods related with the introduction of a probe  
69 molecule in the medium have been developed [12]-[14].  
70 Some kinetic models considering radiation can be found in literature, but most  
71 of them are quite complex and consider the geometry of the reactor [15], [16].  
72 Moreover, they include many parameters that sometimes are difficult to  
73 quantify.  
74 To develop an efficient and sustainable photocatalytic process several design  
75 parameters must be optimized. A key factor is the energy efficiency. Most of the  
76 previously reported photocatalytic studies were carried out using mercury lamps  
77 as ultraviolet light source. However, these lamps showed a lack of reliability,  
78 durability and efficiency. Light emitting diodes (LEDs) seem to be a promising  
79 light source substitute. The main reason is that they are highly efficient  
80 converting electricity into light, with little energy burned off into heat and emitting

81 in a specific wavelength. Furthermore, they are considerably cheaper and their  
82 useful life is significantly longer than the mercury lamps [17]. Some researchers  
83 suggested the feasibility of using LEDs in photocatalytic applications for the  
84 removal of environmental pollutants, such as 4-chlorophenol [17], dimethyl  
85 sulfide [18], perchloroethylene [19], o-cresol [20], formaldehyde [21], [22] or  
86 dyes [23].

87 Surfactants comprise a broad group of chemical compounds synthesized to  
88 exhibit tensioactive properties that make them useful as a key ingredient of  
89 household and industrial detergents and in personal care products. Most  
90 surfactants are only partially biodegradable and they can be found in effluents  
91 of WWTPs [24]. Dodecylbenzenesulfonate (DBS) is an important anionic  
92 surfactant frequently used in shampoo formulations and in detergents for  
93 washing machines that can be easily found in water effluents [25], [26].

94 Previous studies of DBS photocatalytic degradation using  $\text{TiO}_2$  showed the  
95 viability of the treatment under specific illumination conditions and analyzed the  
96 kinetics of the process [27]-[30]. However, they cannot be compared due to the  
97 different light applied and a general model considering light and catalyst  
98 influence is still an issue.

99 The aim of this work is to quantify the  $\cdot\text{OH}$  generated as function of the light  
100 intensity and the catalyst dosage and to correlate this information with the  
101 photocatalytic degradation rate of DBS in a LEDs reactor.

102 Thus, the determination of a new model for the removal of an organic  
103 compound as the DBS correlating to the concentration of contaminant, light  
104 intensity and catalyst content will be shown. This model will play an important  
105 role in the comparison of organic compound removal in different experimental

106 setups and will be essential for an optimal design of the process.

107

## 108 **2. Experimental**

109 The LEDs reactor, depicted in Fig. 1, was constructed according to the authors'  
110 specifications. 180 LEDs (OSA Opto Light Series 400) were employed as  
111 source of light in this work. The emission wavelength was between 375 and 380  
112 nm and the electrical operation conditions were 3.2 V forward voltage and 20  
113 mA forward current for each LED. LEDs were assembled into 10 strips of 18  
114 units providing 0.2 m long illuminating zone and the strips were mounted onto a  
115 dark PVC case (height 41.5 cm, diameter 21 cm) arranged uniformly in the  
116 angular direction. A Pyrex glass reaction vessel of 1 L of capacity (height 25  
117 cm, diameter 7.4 cm) was inside the case. A magnetic stirring plate (Velp  
118 Scientifica) was used to provide proper mixing.

119 To evaluate the influence of light intensity on the  $\cdot\text{OH}$  generation and DBS  
120 degradation, between 2 and 10 LEDs strips were switched on, which  
121 corresponded with values of radiation in a range between 0.004 and 0.024  
122  $\text{mW}/\text{cm}^2$ . All the catalytic experiments were performed in duplicate at room  
123 temperature (25°C), and dissolved oxygen, pH and temperature were measured  
124 in the LEDs reactor with a Crison Multimeter 44.

125 A PCE-UV34 radiation meter (PCE Instruments), with an irradiance  
126 measurement range between 290-390 nm and 0-2  $\text{mW}/\text{cm}^2$  and resolution of  
127 0.001  $\text{mW}/\text{cm}^2$ , was employed to quantify the average radiation intensity. The  
128 measurements were carried out in the center of the empty reactor.

### 129 *2.1. $\cdot\text{OH}$ quantification*



130 The method used in this study for the determination of the  $\cdot\text{OH}$  formation was  
131 initially proposed by Tai et al. [13], and is based on the reaction between  $\cdot\text{OH}$   
132 and dimethyl sulfoxide (DMSO) to produce formaldehyde that reacts with 2,4-  
133 dinitrophenylhydrazine (DNPH) to form the corresponding hydrazone (DNPHo).  
134 Then, quantification of the  $\cdot\text{OH}$  generated is carried out through the  
135 determination of the formaldehyde concentration when the DNPHo is analyzed  
136 by high performance liquid chromatograph (HPLC), assuming that all the  $\cdot\text{OH}$   
137 are consumed by the DMSO. Therefore, this indirect method allows to know the  
138 rate of  $\cdot\text{OH}$  generation, as it is the same as the rate of DMSO transformation  
139 into formaldehyde.

140 0.8 L of a 250 mM DMSO solution were mixed with the  $\text{TiO}_2$  and kept for 30 min  
141 in the dark to reach adsorption equilibrium, then photocatalytic degradation was  
142 initiated. At different time intervals, 2 mL of suspension were sampled and  
143 filtered through a 0.45  $\mu\text{m}$  syringe filter (Teknokroma). Then 2.5 mL of pH 4.0  
144  $\text{H}_3\text{PO}_4\text{-NaH}_2\text{PO}_4$  buffer solution (Panreac), 0.2 mL of 6 mM DNPH solution  
145 dissolved in acetonitrile and 0.3 mL of ultrapure water were added [13]. The  
146 mixture was maintained at room temperature for 30 min and analyzed by a  
147 Waters 2690 HPLC equipped with a Waters 996 Photodiode Array detector and  
148 a XBridge C18 (5  $\mu\text{m}$ , 4,6x250 mm) analytical column. With a flow rate of 0.6  
149 mL/min, the mobile phase used was a mixture of methanol (Panreac) and water  
150 (60:40 v/v). The detection wavelength was 355 nm.

## 151 2.2. DBS degradation

152 DBS was obtained from Sigma-Aldrich and the  $\text{TiO}_2$  catalyst used was Aeroxide  
153 P25 provided by Evonik Industries. 0.8 L of a 0.144 mM DBS solution were

154 mixed with the catalyst and kept for 30 min premixing in the dark to reach  
155 adsorption equilibrium before the photocatalytic experiments were started. The  
156 suspension was sampled at defined time intervals and filtered through a 0.45  
157  $\mu\text{m}$  syringe filter (Teknokroma) prior to analysis. DBS was analyzed at 223 nm  
158 by UV spectrophotometry (Shimadzu, UV-1800).

159

### 160 **3. Results and discussion**

161 Fig. 1 shows the average radiation detected in the center of the reactor. As  
162 expected, a linear relationship between the number of LEDs employed and the  
163 applied light intensity is observed.

#### 164 *3.1. Light intensity influence*

165 The reactor design allows working with five combinations of LEDs strips  
166 switched on to manipulate light intensity.

167 Fig. 2(a) shows the  $\cdot\text{OH}$  generated (equivalent to the concentration of DMSO)  
168 versus the photocatalytic process time. The concentration of radicals generated  
169 increase linearly with reaction time. This behavior has been previously observed  
170 in literature [31]-[32]. Moreover, under the studied conditions the concentration  
171 of  $\cdot\text{OH}$  generated reaches values up to 0.408 mM. For a fixed time,  $\cdot\text{OH}$   
172 generation increases linearly with radiation intensity (Rad), up to a value of  
173  $0.018 \text{ mW/cm}^2$ , and then it remains almost constant. The data of  $\cdot\text{OH}$  generated  
174 were correlated to the radiation intensity and time (data shown in Appendix A).  
175 The experimental values of the  $\cdot\text{OH}$  produced for radiations up to  $0.018$   
176  $\text{mW/cm}^2$  were satisfactorily fitted to Eq. 1, which describes the rate of  $\cdot\text{OH}$   
177 generation, with an average standard deviation of 0.00506 mM (Fig. 2(a)).

$$r_{\cdot\text{OH generation}} = 0.122 \cdot \text{Rad} \quad (1)$$

178  
179 On the other hand, the influence of light intensity on the DBS degradation rate is  
180 depicted in Fig. 2 (b). As expected, when the light intensity increases, higher  
181 DBS removals are achieved for the same operation time; working at 0.024  
182 mW/cm<sup>2</sup> around 17 % of the initial concentration of DBS is removed after 180  
183 min.

184 Removed DBS can be directly correlated to the radiation intensity and therefore  
185 to the  $\cdot\text{OH}$  generated, under the hypothesis that in the experimental conditions  
186 that generated  $\cdot\text{OH}$  only attack the initial compound and not the intermediate  
187 products that could be formed. This hypothesis is confirmed because DOC  
188 values have been quantified and all experimental data are within 5% of the  
189 initial value. Therefore, it is assumed that there is no significant mineralization,  
190 implying that DBS degradation products remain in the oxidation medium at the  
191 same time that DBS disappears and  $\cdot\text{OH}$  are generated.

192 Fig. 3 correlates the concentration of DBS removed at defined operating times  
193 as a function of the concentration of  $\cdot\text{OH}$  that had been generated at the same  
194 time. Data have been taken from Fig. 2 when different radiation intensities were  
195 applied. It is clearly observed that the influence of both variables is lumped in  
196 the concentration of  $\cdot\text{OH}$  generated. Hence, it is concluded that the  
197 concentration of radicals generated is a suitable index to describe the kinetics of  
198 photocatalytic processes.

### 199 3.2. Catalyst dosage influence

200 The catalyst concentration affects the number of active sites available for the  
201 photocatalytic process and the light penetration through the catalyst

202 suspension. Fig 4(a) shows the influence of the catalyst dosage between 0.125  
 203 mM and 25 mM for a fixed value of radiation. It is observed that the  
 204 concentration of  $\cdot\text{OH}$  generated changes linearly with time for a given catalyst  
 205 concentration. Furthermore, it increases with  $\text{TiO}_2$  dosage, due to the rise in the  
 206 number of active sites accessible for the photocatalytic reaction. However, for  
 207  $\text{TiO}_2$  concentrations above 12.5 mM the increase in  $\cdot\text{OH}$  generation is less  
 208 pronounced because the catalyst excess can lead to an increase in the opacity  
 209 of the suspension and a decrease in light penetration [33], [34]. This trend is  
 210 satisfactorily represented (Fig. 4(a)) by the logarithmic correlation shown in Eq.  
 211 2 with an average standard deviation of 0.00703 mM (Appendix A).

$$212 \quad \Gamma_{\cdot\text{OH} \text{ generation}} = 5.14 \cdot 10^{-4} \cdot \ln([\text{TiO}_2]) + 1.15 \cdot 10^{-9} \quad (2)$$

213 Moreover, it is observed that when there is an increase in the concentration of  
 214  $\text{TiO}_2$ , higher DBS removals are achieved, obtaining for 25 mM of  $\text{TiO}_2$  that  
 215 approximately 31 % of the initial concentration of DBS is removed after 180 min  
 216 (Fig. 4(b)).

### 217 3.3 Kinetic modeling

218 The optimal process design relies on the availability of a robust kinetic model  
 219 and parameters. For an energy efficient design, a kinetic model considering  
 220 both catalyst dosage and radiation intensity is desirable.

221 In order to mathematically describe the  $\cdot\text{OH}$  generation kinetics the  
 222 experimental data from Fig. 2(a) and 4(a) were fitted to a model that includes  
 223 the influence of the catalyst dosage and the intensity of the applied radiation  
 224 (Eq. 3).

$$225 \quad \frac{d[\cdot\text{OH}]_{\text{generated}}}{dt} = k_{[\cdot\text{OH}]_{\text{generated}}} \cdot [\text{TiO}_2]^m \cdot \text{Rad}^n \quad (3)$$

226  $[\cdot\text{OH}]$  is the concentration of  $\cdot\text{OH}$  generated (in mM),  $t$  is the reaction time (in  
 227 min),  $k_{[\cdot\text{OH}]_{\text{generated}}}$  is the kinetic constant (in  $\text{mM} \cdot \text{OH} \cdot \text{cm}^{2n} \cdot \text{min}^{-1} \cdot \text{mW}^{-n} \cdot \text{mM TiO}_2^{-m}$ ),  $[\text{TiO}_2]$  is the catalyst dosage (in mM),  $m$  and  $n$  are experimental fitted  
 228 parameters and  $\text{Rad}$  is the radiation applied (in  $\text{mW}/\text{cm}^2$ ).  
 229 The kinetic parameters  $k_{[\cdot\text{OH}]_{\text{generated}}}=0.0396 \text{ mM} \cdot \text{OH} \cdot \text{cm}^2 \cdot \text{min}^{-1} \cdot \text{mW}^{-1} \cdot \text{mM TiO}_2^{-0.370}$   
 230  $^{0.370}$  ( $T=25 \text{ }^\circ\text{C}$ ) and  $m=0.370$  and  $n=1$  were obtained from regression of the  
 231 experimental data to Eq. 3, leading to Eq. 4,

$$232 \frac{d[\cdot\text{OH}]_{\text{generated}}}{dt} = 0.0396 \cdot [\text{TiO}_2]^{0.370} \cdot \text{Rad}^1 \quad (4)$$

233 Furthermore, Fig. 5 shows a parity graph between measured and model  
 234 predicted  $\cdot\text{OH}$  data. It can be observed that the  $\cdot\text{OH}$  generation is satisfactorily  
 235 described by the proposed model, with 68 % of the simulated results falling  
 236 within the interval  $[\cdot\text{OH}]_{\text{generated,exp}} \pm 15 \% [\cdot\text{OH}]_{\text{generated,exp}}$ .  
 237 Although some authors have proposed kinetic models for the photocatalytic  
 238 degradation of different compounds by considering the intensity of radiation  
 239 [35]-[40], no agreement has been reached in terms of a unified kinetic model.  
 240 Therefore, this work contributes to the state of the art by proposing a kinetic  
 241 model that considers  $\cdot\text{OH}$  generated instead of time as the main independent  
 242 variable.

243 Next, the rate of DBS removal has been analysed. For a catalyst concentration  
 244 of 12.5 mM and a solution of 0.144 mM of DBS, experimental data were fitted to  
 245 a second order kinetic model that takes into account  $\cdot\text{OH}$  generation as well as  
 246 DBS concentration. Hence, as the  $\cdot\text{OH}$  generation depends on radiation and  
 247  $\text{TiO}_2$  dosage, the kinetic model proposed for the DBS degradation includes both  
 248 variables (Eq. 5).  
 249

$$250 \quad -\frac{d[\text{DBS}]}{dt} = k_{[\text{DBS}]} \cdot [\text{OH}]_{\text{generated}} \cdot [\text{DBS}] \quad (5)$$

251 Substituting the  $\cdot\text{OH}$  generated by the integrated form of equation 4 leads to Eq.  
252 6 that expresses the degradation rate as a function of the operation variables:

$$253 \quad -\frac{d[\text{DBS}]}{dt} = k_{[\text{DBS}]} \cdot k_{[\text{OH}]_{\text{generated}}} \cdot [\text{TiO}_2]^{0.370} \cdot \text{Rad} \cdot t \cdot [\text{DBS}] \quad (6)$$

254  $[\text{DBS}]$  is the DBS concentration (in mM),  $t$  is the reaction time (in min),  $k_{[\text{DBS}]}$  is  
255 the second order kinetic constant (in  $\text{mM} \cdot \text{OH}^{-1} \cdot \text{min}^{-1}$ ),  $[\text{TiO}_2]$  is the catalyst  
256 dosage (in mM),  $\text{Rad}$  is the radiation (in  $\text{mW}/\text{cm}^2$ ) and  $[\text{OH}]_{\text{generated}}$  is the  $\cdot\text{OH}$   
257 generated (in mM).

258  $k_{[\text{DBS}]}$  takes a value of  $0.00402 \text{ mM} \cdot \text{OH}^{-1} \cdot \text{min}^{-1}$  at  $25^\circ\text{C}$  and  $k_{[\text{OH}]_{\text{generated}}}$  of  
259  $0.0396 \text{ mM} \cdot \text{OH} \cdot \text{cm}^2 \cdot \text{min}^{-1} \cdot \text{mW}^{-1} \cdot \text{mM TiO}_2^{-0.370}$ , therefore the kinetic model can  
260 be expressed by Eq. 7.

$$261 \quad -\frac{d[\text{DBS}]}{dt} = 1.59 \cdot 10^{-4} \cdot [\text{TiO}_2]^{0.370} \cdot \text{Rad} \cdot t \cdot [\text{DBS}] \quad (7)$$

262 A parity graph of simulated versus experimental  $[\text{DBS}]/[\text{DBS}]_0$  data is presented  
263 in Fig. 6. It can be seen that the 98 % of the simulated results fall within the  
264 interval  $([\text{DBS}]/[\text{DBS}]_0)_{\text{exp}} \pm 10 \% ([\text{DBS}]/[\text{DBS}]_0)_{\text{exp}}$ .

265 Photocatalytic reactions generally occur in two regimes within UV light intensity.  
266 For low radiation values below  $1 \text{ mW}/\text{cm}^2$  Daneshvar *et al.* [37] and Wang *et al.*  
267 [40] have found a linear correlation between the reaction rate and radiation.  
268 This behavior is due to the faster consumption of the electron-hole pairs by the  
269 chemical reaction than by their recombination [41]. Therefore, the model  
270 proposed in this work corroborates the existence of this regime. However, for  
271 higher intensities of radiation between  $0.86 \text{ mW}/\text{cm}^2$  and  $60 \text{ mW}/\text{cm}^2$ , Meng *et al.*  
272 [35] and Li *et al.* [39] observed that the reaction rate depends on the square

273 root of the intensity of radiation. In this case, the recombination rate is dominant  
274 [41].

275

#### 276 **4. Conclusions**

277 The feasibility of applying UV-LEDs as light source in the photocatalytic  
278 degradation of DBS has been shown. LEDs seem to be a promising alternative  
279 to solve some of the problems associated to the use of conventional mercury  
280 lamps such as low energy efficiency or short lifetime; thus, allowing an optimal  
281 process design concerning the radiation demand.

282 Furthermore, an indirect method has been used to determine the  $\cdot\text{OH}$   
283 generated, main oxidant specie, in order to establish its correlation with  
284 radiation and concentration of catalyst. This study has been applied to the  
285 photocatalytic degradation of the anionic surfactant DBS. Experimental results  
286 confirmed that the  $\cdot\text{OH}$  generation rate for radiation intensity between 0.004  
287  $\text{mW}/\text{cm}^2$  and 0.024  $\text{mW}/\text{cm}^2$  and catalyst dosage between 0.125 mM and 25  
288 mM is satisfactorily described by a kinetic model that takes into account both  
289 variables. Furthermore, in the studied experimental conditions, DBS removal  
290 has been fitted to a second order kinetic model that includes the influence of the  
291 generated  $\cdot\text{OH}$ .

292

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298

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377 Fig. 1. Radiation distribution in the reactor. a) Schematic diagram of the  
378 transverse section of the LEDs reactor: (1) LEDs strips, (2) PVC case and (3)  
379 reaction vessel.

380

381 Fig. 2. Change with time at different radiation intensity of (a)  $\cdot\text{OH}$  generated and  
382 (b) DBS.  $[\text{DBS}]_0=0.144$  mM,  $[\text{TiO}_2]_0=12.5$  mM.

383

384 Fig. 3. DBS removed vs.  $\cdot\text{OH}$  generated.  $[\text{TiO}_2]_0=12.5$  mM.

385

386 Fig. 4. Change with time of (a)  $\cdot\text{OH}$  generated and (b) DBS through the  
387 oxidation process at different  $[\text{TiO}_2]$ .  $[\text{DBS}]_0=0.144$  mM, radiation= $0.024$   
388  $\text{mW}/\text{cm}^2$ .

389

390 Fig. 5. Fitting of the experimental  $\cdot\text{OH}$  generation data to the kinetic model  
391 proposed by Eq. 4.  $[\text{DBS}]_0=0.144$  mM, radiation=( $0.004$ - $0.024$ )  $\text{mW}/\text{cm}^2$ ,  
392  $[\text{TiO}_2]=(0.125$ - $25)$  mM.

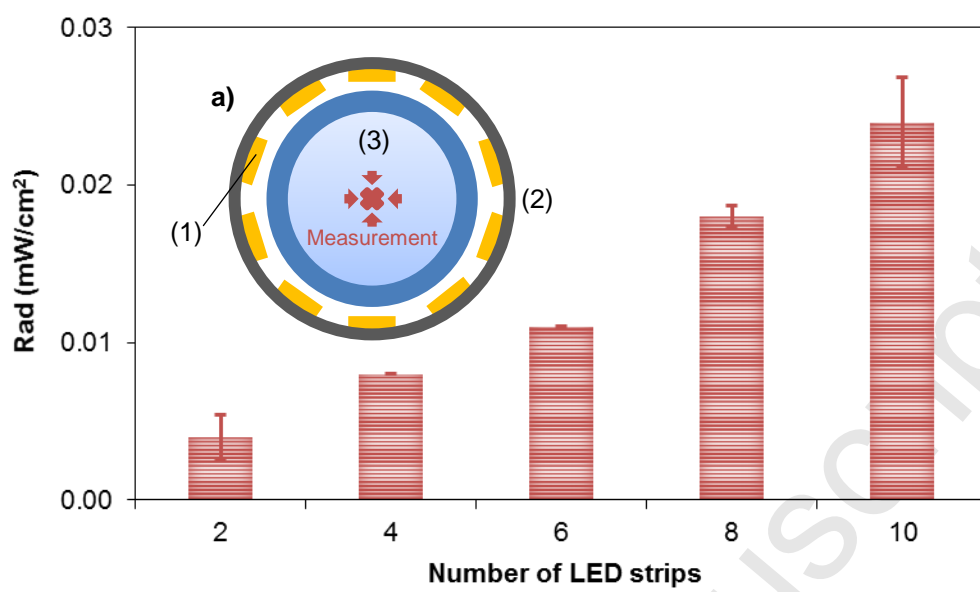
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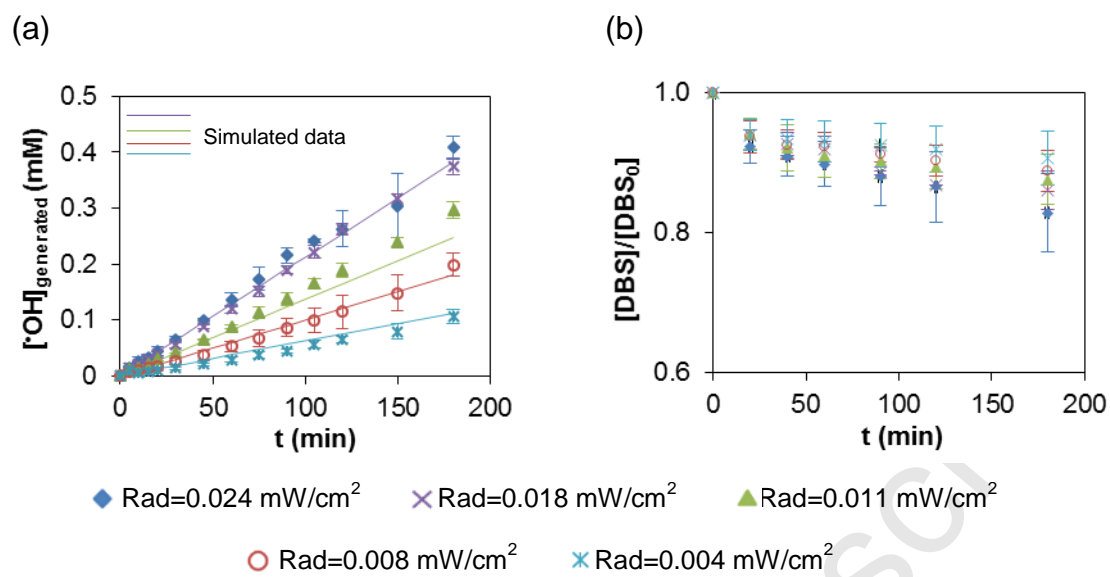
394 Fig. 6. Fitting of the experimental DBS degradation data to the kinetic model  
395 proposed by Eq. 7.  $[\text{DBS}]_0=0.144$  mM, radiation=( $0.004$ - $0.024$ )  $\text{mW}/\text{cm}^2$ ,  
396  $[\text{TiO}_2]=(0.125$ - $25)$  mM.

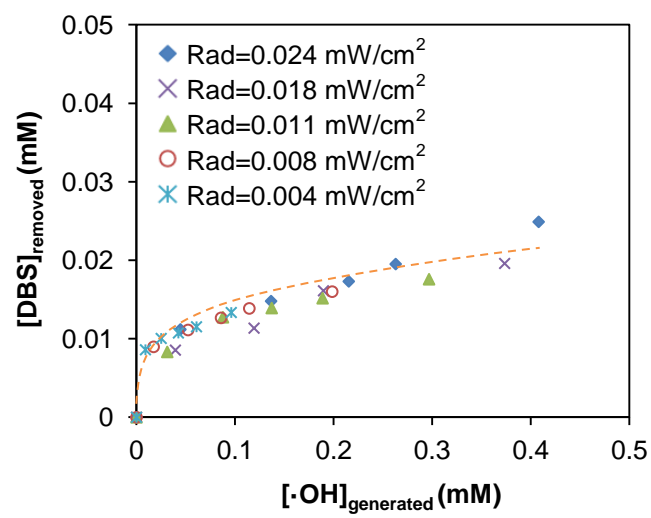
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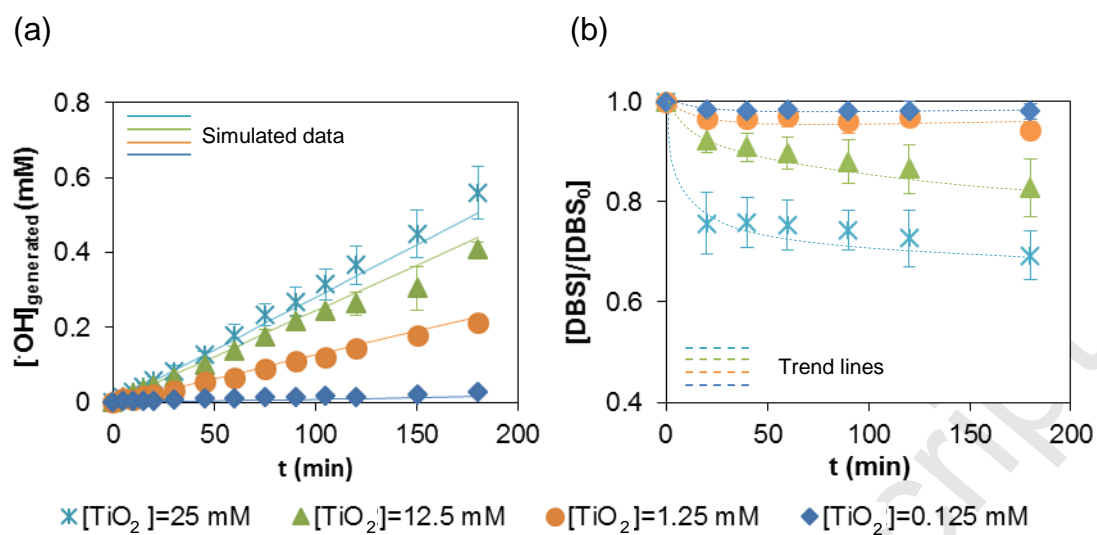
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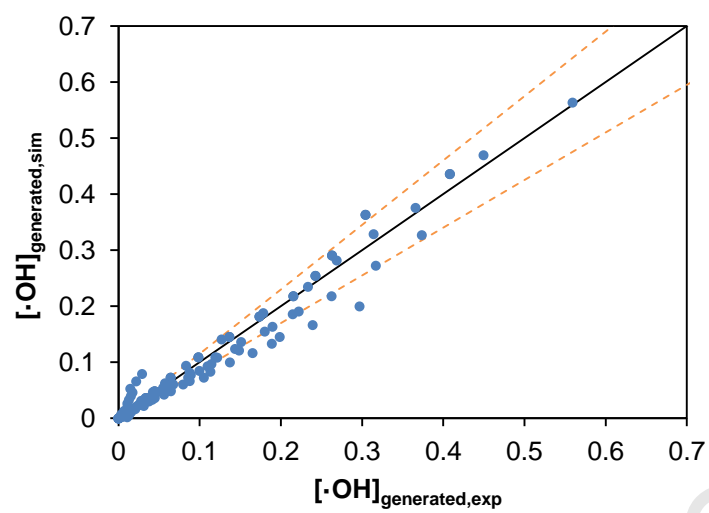




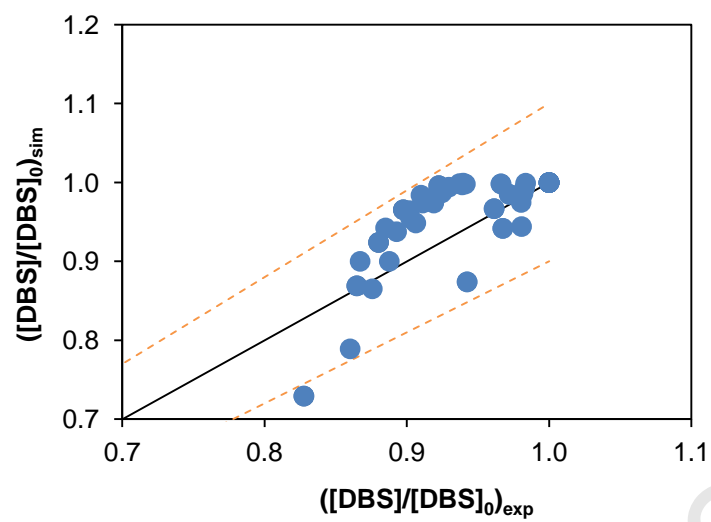
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