Title: Influence of Radiation and TiO_2 Concentration on the Hydroxyl Radicals Generation in a Photocatalytic LED Reactor. Application to dodecylbenzenesulfonate degradation

Author: Sara Dominguez Paula Ribao Maria J.Rivero Inmaculada Ortiz

PII: S0926-3373(14)00606-7
DOI: http://dx.doi.org/doi:10.1016/j.apcatb.2014.09.072
Reference: APCATB 13615

To appear in: *Applied Catalysis B: Environmental*

Received date: 11-7-2014
Revised date: 26-9-2014
Accepted date: 30-9-2014

Please cite this article as: Sara, Influence of Radiation and TiO_2 Concentration on the Hydroxyl Radicals Generation in a Photocatalytic LED Reactor. Application to dodecylbenzenesulfonate degradation., *Applied Catalysis B, Environmental* (2014), http://dx.doi.org/10.1016/j.apcatb.2014.09.072

Highlights

- Photocatalytic degradation of DBS in UV-LED reactor
- Determination of $^{\bullet}$OH generation rate
- Modelling DBS degradation rate as function of $^{\bullet}$OH generation

Graphical abstract

Applied Catalysis B: Environmental

Influence of Radiation and TiO_2 Concentration on the Hydroxyl Radicals Generation in a Photocatalytic LED Reactor. Application to dodecylbenzenesulfonate degradation.

Sara Dominguez, Paula Ribao, Maria J. Rivero and Inmaculada Ortiz*

Department of Chemical and Biomolecular Engineering, ETSIIT, University of Cantabria, Avda. de los Castros, s/n, 39005 Santander, Spain, +34 942201585

(E-mail: *sara.dominguez@unican.es; paula.ribao@unican.es; riveromj@unican.es; inmaculada.ortiz@unican.es*).

ABSTRACT

One of the main issues associated to the development of photocatalysis is the lack of adequate indexes that allow the comparison of the results obtained in different experimental setup designs. The hydroxyl radicals ($^{\bullet}OH$) generation rate is a key factor to determine the overall oxidation rate.

In this work, using a Light Emitting Diodes (LEDs) reactor aimed to maximize light efficiency and minimize energy consumption, the $^{\bullet}OH$ generated have been determined as a function of the radiation and catalyst concentration following an indirect method based on the reaction between $^{\bullet}OH$ and dimethyl sulfoxide (DMSO) to produce formaldehyde.

Finally, the methodology has been applied to analyze the degradation kinetics of the anionic surfactant dodecylbenzenesulfonate (DBS), frequently used in shampoo formulations and detergents for washing machines. We propose a

method based on the indirect determination of $^{\bullet}OH$ radicals generation rate that allows the assessment and comparison of the kinetics of photocatalytic oxidation of pollutants.

Keywords

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

1. Introduction

Increasing water demand and shortage of available water are growing concerns for our society [1]. Since wastewaters constitute one of the largest possible water resources, one attractive option is the possible reuse of onsite wastewater or the effluent of wastewater treatment plants (WWTPs). Conventional water treatments such as chemical oxidation, activated carbon adsorption and biological treatment sometimes seem to be inefficient in degrading some organic compounds [2]-[4].

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

Among these technologies, photocatalysis is an attractive instrument for the removal of organic and inorganic pollutants from water, due to its ambient operating temperature and pressure and absence of secondary pollution. Heterogeneous photocatalysis is a process in which a source of appropriate light and a solid semiconductor material as catalyst are necessary to promote a chemical reaction by means of the generation of electron-hole pairs [6], [7]. Up to now, TiO_2 is the most promising material used as catalyst because it is highly photoreactive, stable with respect to corrosion, inexpensive, nontoxic, biologically and chemically inert and capable of repeated use without considerable loss of catalytic capacity [6]-[9].

Nevertheless, the inherent difficulty to compare the results obtained in the countless experimental setup designs and configurations represents an important issue in the development of photocatalysis that needs further research [10], [11]. Hence, the quantitative determination of the hydroxyl radicals generated in the photocatalytic processes is essential for a better understanding of the results obtained with this technology. However, their high reactivity and short lifetime complicate their direct determination. Therefore, several indirect detection methods related with the introduction of a probe molecule in the medium have been developed [12]-[14].

Some kinetic models considering radiation can be found in literature, but most of them are quite complex and consider the geometry of the reactor [15], [16]. Moreover, they include many parameters that sometimes are difficult to quantify.

To develop an efficient and sustainable photocatalytic process several design parameters must be optimized. A key factor is the energy efficiency. Most of the previously reported photocatalytic studies were carried out using mercury lamps as ultraviolet light source. However, these lamps showed a lack of reliability, durability and efficiency. Light emitting diodes (LEDs) seem to be a promising light source substitute. The main reason is that they are highly efficient converting electricity into light, with little energy burned off into heat and emitting in a specific wavelength. Furthermore, they are considerably cheaper and their useful life is significantly longer than the mercury lamps [17]. Some researchers suggested the feasibility of using LEDs in photocatalytic applications for the removal of environmental pollutants, such as 4-chlorophenol [17], dimethyl sulfide [18], perchloroethylene [19], o-cresol [20], formaldehyde [21], [22] or dyes [23].

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

Previous studies of DBS photocatalytic degradation using TiO_2 showed the viability of the treatment under specific illumination conditions and analyzed the kinetics of the process [27]-[30]. However, they cannot be compared due to the different light applied and a general model considering light and catalyst influence is still an issue.

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

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

2. Experimental

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

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

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

2.1. $^{\bullet}OH$ quantification

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

0.8 L of a 250 mM DMSO solution were mixed with the TiO_2 and kept for 30 min in the dark to reach adsorption equilibrium, then photocatalytic degradation was initiated. At different time intervals, 2 mL of suspension were sampled and filtered through a 0.45 μm syringe filter (Teknokroma). Then 2.5 mL of pH 4.0 H_3PO_4-NaH_2PO_4 buffer solution (Panreac), 0.2 mL of 6 mM DNPH solution dissolved in acetonitrile and 0.3 mL of ultrapure water were added [13]. The mixture was maintained at room temperature for 30 min and analyzed by a Waters 2690 HPLC equipped with a Waters 996 Photodiode Array detector and a XBridge C18 (5 μm, 4,6x250 mm) analytical column. With a flow rate of 0.6 mL/min, the mobile phase used was a mixture of methanol (Panreac) and water (60:40 v/v). The detection wavelength was 355 nm.

2.2. DBS degradation

DBS was obtained from Sigma-Aldrich and the TiO_2 catalyst used was Aeroxide P25 provided by Evonik Industries. 0.8 L of a 0.144 mM DBS solution were mixed with the catalyst and kept for 30 min premixing in the dark to reach adsorption equilibrium before the photocatalytic experiments were started. The suspension was sampled at defined time intervals and filtered through a 0.45 μm syringe filter (Teknokroma) prior to analysis. DBS was analyzed at 223 nm by UV spectrophotometry (Shimadzu, UV-1800).

3. Results and discussion

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

3.1. Light intensity influence

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

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

$$r_{\bullet OHgeneration} = 0.122 \cdot Rad \qquad (1)$$

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

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

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

3.2. Catalyst dosage influence

The catalyst concentration affects the number of active sites available for the photocatalytic process and the light penetration through the catalyst suspension. Fig 4(a) shows the influence of the catalyst dosage between 0.125 mM and 25 mM for a fixed value of radiation. It is observed that the concentration of $^{\bullet}OH$ generated changes linearly with time for a given catalyst concentration. Furthermore, it increases with TiO_2 dosage, due to the rise in the number of active sites accessible for the photocatalytic reaction. However, for TiO_2 concentrations above 12.5 mM the increase in $^{\bullet}OH$ generation is less pronounced because the catalyst excess can lead to an increase in the opacity of the suspension and a decrease in light penetration [33], [34]. This trend is satisfactorily represented (Fig. 4(a)) by the logarithmic correlation shown in Eq. 2 with an average standard deviation of 0.00703 mM (Appendix A).

$$r_{\bullet OH generation} = 5.14 \cdot 10^{-4} \cdot Ln([TiO_2]) + 1.15 \cdot 10^{-3} \qquad (2)$$

Moreover, it is observed that when there is an increase in the concentration of TiO_2, higher DBS removals are achieved, obtaining for 25 mM of TiO_2 that approximately 31 % of the initial concentration of DBS is removed after 180 min (Fig. 4(b)).

3.3 Kinetic modeling

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

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

$$\frac{d\,[^{\bullet}OH]_{generated}}{dt} = k_{[\cdot OH]generated} \cdot [TiO_2]^m \cdot Rad^n \qquad (3)$$

$[^{\bullet}OH]$ is the concentration of $^{\bullet}OH$ generated (in mM), t is the reaction time (in min), $k_{[\bullet OH]generated}$ is the kinetic constant (in mM $^{\bullet}OH \cdot cm^{2n} \cdot min^{-1} \cdot mW^{-n} \cdot$ mM TiO_2^{-m}), $[TiO_2]$ is the catalyst dosage (in mM), m and n are experimental fitted parameters and Rad is the radiation applied (in mW/cm^2).

The kinetic parameters $k_{[\bullet OH]generated}$=0.0396 mM $^{\bullet}OH \cdot cm^{2} \cdot min^{-1} \cdot mW^{-1} \cdot$ mM $TiO_2^{-0.370}$ (T=25 ºC) and m=0.370 and n=1 were obtained from regression of the experimental data to Eq. 3, leading to Eq. 4,

$$\frac{d\,[^{\bullet}OH]_{generated}}{dt} = 0.0396 \cdot [TiO_2]^{0.370} \cdot Rad^{1} \qquad (4)$$

Furthermore, Fig. 5 shows a parity graph between measured and model predicted $^{\bullet}OH$ data. It can be observed than the $^{\bullet}OH$ generation is satisfactorily described by the proposed model, with 68 % of the simulated results falling within the interval $[^{\bullet}OH]_{generated,exp}$ ± 15 % $[^{\bullet}OH]_{generated,exp}$.

Although some authors have proposed kinetic models for the photocatalytic degradation of different compounds by considering the intensity of radiation [35]-[40], no agreement has been reached in terms of a unified kinetic model. Therefore, this work contributes to the state of the art by proposing a kinetic model that considers $^{\bullet}OH$ generated instead of time as the main independent variable.

Next, the rate of DBS removal has been analysed. For a catalyst concentration of 12.5 mM and a solution of 0.144 mM of DBS, experimental data were fitted to a second order kinetic model that takes into account $^{\bullet}OH$ generation as well as DBS concentration. Hence, as the $^{\bullet}OH$ generation depends on radiation and TiO_2 dosage, the kinetic model proposed for the DBS degradation includes both variables (Eq. 5).

$$\frac{-d[DBS]}{dt}=k_{[DBS]}\cdot[^{\bullet}OH]_{generated}\cdot[DBS] \tag{5}$$

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

$$-\frac{d\,[DBS]}{dt}=k_{[DBS]}\cdot k_{[^{\bullet}OH]generated}\cdot[TiO_2]^{0.370}\cdot Rad\cdot t\cdot[DBS] \tag{6}$$

[DBS] is the DBS concentration (in mM), t is the reaction time (in min), $k_{[DBS]}$ is the second order kinetic constant (in mM$\cdot{}^{\bullet}OH^{-1}\cdot min^{-1}$), [$TiO_2$] is the catalyst dosage (in mM), Rad is the radiation (in mW/cm^2) and $[^{\bullet}OH]_{generated}$ is the $^{\bullet}$OH generated (in mM).

$k_{[DBS]}$ takes a value of 0.00402 mM$\cdot{}^{\bullet}OH^{-1}\cdot min^{-1}$ at 25 ºC and $k_{[\bullet OH]generated}$ of 0.0396 mM $^{\bullet}OH\cdot cm^2\cdot min^{-1}\cdot mW^{-1}\cdot$mM $TiO_2^{-0.370}$, therefore the kinetic model can be expressed by Eq. 7.

$$-\frac{d\,[DBS]}{dt}=1.59\cdot10^{-4}\cdot[TiO_2]^{0.370}\cdot Rad\cdot t\cdot[DBS] \tag{7}$$

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

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

4. Conclusions

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

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

Acknowledgements

Financial support from the Spanish Ministry of Economy and Competitiveness and from FEDER funds (projects CTM 2012-33917 and CTQ 2012-31639) are gratefully acknowledged. Sara Dominguez also thanks the FPI postgraduate research grant (BES-2013-064055).

References

[1] J. Blanco, S. Malato, P. Fernández-Ibañez, D. Alarcón, W. Gernjak, M.I. Maldonado, Renew. Sust. Energ. Rev. 13 (2009) 1437-1445.

[2] H. Dimitroula, V.M. Daskalaki, Z. Frontistis, D.I. Kondarides, P.Panagiotopoulou, N.P. Xekoukoulotakis, D. Mantzavinos, Appl. Catal. B-Environ. 117-118 (2012) 283-291.

[3] L. Prieto-Rodriguez, S. Miralles-Cuevas, I. Oller, A. Agüera, G. Li Puma, S. Malato, J. Hazard. Mater. 211-212 (2012) 131-137.

[4] A.V. Wankhade, G.S. Gaikwad, M.G. Dhonde, N.T. Khat, S.R. Thakare, Res. J. Chem. Environ. 17 (2013) 84-94.

[5] C. Comninellis, A. Kapalka, S. Malato, S.A. Parsons, I. Poulios, D. Mantzavinos, J. Chem. Technol. Biotechnol. 83 (2008) 769-776.

[6] J. Kumar, A. Bansal, Mater. Sci. Forum 764 (2013) 130-150.

[7] R.K. Nath, M.F.M. Zain, H.A.A. Kadhum, J. Appl. Sci. Res. 8 (2012) 4147-4155.

[8] D. Friedmann, C. Mendive, D. Bahnemann, Appl. Catal. B-Environ. 99 (2010) 398-406.

[9] M. Pelaez, N.T. Nolan, S.C. Pillai, M.K. Seery, P. Falaras, A.G. Kontos, P.S.M. Dunlop, J.W.J. Hamilton, J.A. Byrne, K. O'Shea, M.H. Entezari, D.D. Dionysiou, Appl. Catal. B-Environ. 125 (2012) 331-349.

[10] H. De Lasa, B. Serrano, M. Salaices, Photocatalytic reaction engineering, Springer, New York, 2005.

[11] I. Grčić, G. Li Puma, Environ. Sci. Technol. 47 (2013) 13702-13711.

[12] J. Kochany, J.R. Bolton, J. Phys. Chem. 95 (1991) 5116-5120.

[13] C. Tai, J.F. Peng, J.F. Liu, G.B. Jiang, H. Zou, Anal. Chim. Acta 527 (2004) 73-80.

[14] S. Yuan, X. Mao, A.N. Alshawabkeh, Environ. Sci. Technol. 46 (2012) 3398-3405.

[15] O.M. Alfano, M.I. Cabrera, A.E. Cassano, J. Catal. 172 (1997), 370-379.

[16] J. Marugán, R. Van Grieken, C. Pablos, M.L. Satuf, A.E. Cassano, O.M. Alfano, Chem. Eng. J. 224 (2013) 39-45.

[17] J.P. Ghosh, C.H. Langford, G. Achari, J. Phys. Chem. A 112 (2008) 10310-10314.

[18] W. Jo, S. Eun, S. Shin, Photochem. Photobiol. 87 (2011) 1016-1023.

[19] D.H. Chen, X. Ye, K. Li, Chem. Eng. Technol. 28 (2005) 95-97.

[20] H. Chen, Y. Ku, A. Irawan, Chemosphere 69 (2007) 184-190.

[21] J.L. Shie, C.H. Lee, C.S. Chiou, C.T. Chang, C.C. Chang, C.Y. Chang, J. Hazard. Mater. 155 (2008) 164-172.

[22] Y. Li, Y. Jiang, S. Peng, F. Jiang, J. Hazard. Mater. 182 (2010) 90-96.

[23] W. Wang, Y. Ku, Water Res. 40 (2006) 2249-2258.

[24] M.E. Suárez-Ojeda, J. Kim, J. Carrera, I.S. Metcalfe, J. Font, J. Hazard. Mater. 144 (2007) 655-662.

[25] J. Rivera-Utrilla, M. Sánchez-Polo, M.I. Bautista-Toledo, J.D. Méndez-Díaz, Chem. Eng. J. 180 (2012) 204-209.

[26] M.I. Bautista-Toledo, J. Rivera-Utrilla, J.D. Méndez-Díaz, M. Sánchez-Polo, F. Carrasco-Marín, J. Colloid Interf. Sci. 418 (2014) 113-119.

[27] H. Hidaka, J. Zhao, E. Pelizzetti, N. Serpone, J. Phys. Chem. 96 (1992) 2226-2230.

[28] T. Zhang, T. Oyama, S. Horikoshi, J. Zhao, N. Serpone, H. Hidaka, Appl. Catal. B-Environ. 42 (2003) 13-24.

[29] R. Zhang, L. Gao, Q. Zhang, Chemosphere 54 (2004) 405-411.

[30] M. Sánchez, M.J. Rivero, I. Ortiz, Appl. Catal. B-Environ. 101 (2011) 515–521.

[31] P.F. Schwarz, N.J. Turro, S.H. Bossmann, A.M. Braun, A.M.A. Abdel Wahaband, H. Dürr, J. Phys. Chem. B 101 (1997) 7127-7134.

[32] Q. Xiang, Y. Jiaguo, P.K. Wong, J. Colloid Interf. Sci. 357 (2011) 163-167.

[33] S. Kaneco, N. Li, K.-k. Itoh, H. Katsumata, T. Suzuki, K. Ohta, Chem. Eng. J. 148 (2009) 50-56.

[34] B. Sun, G. Zhou, C. Shao, B. Jiang, J. Pang, Y. Zhang, Powder Technol. 256 (2014) 118-125.

[35] Y. Meng, X. Huang, Y. Wu, X. Wang, Y. Qian, Environ. Pollut. 117 (2002) 307-313.

[36] M.A. Blesa, B. Sánchez, Eliminación de contaminantes por fotocatálisis heterogénea, CIEMAT, Madrid, 2004.

[37] N. Daneshvar, M. Rabbani, N. Modirshahla, M.A. Behnajady, J. Photochem. Photobiol. A 168 (2004) 39-45.

[38] D.F. Ollis, J. Phys. Chem. B 109 (2005) 2439-2444.

[39] Y. Li, S. Sun, M. Ma, Y. Ouyang, W. Yan, Chem. Eng. J. 142 (2008) 147-155.

[40] Z. Wang, J. Liu, Y. Dai, W. Dong, S. Zhang, J. Chen, Ind. Eng. Chem. Res. 50 (2011) 7977-7984.

[41] H. Yu, K. Zhang, C. Rossi, J. Photochem. Photobiol. A. 88 (2007) 65-73.

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

Fig. 2. Change with time at different radiation intensity of (a) $^{\bullet}OH$ generated and (b) DBS. $[DBS]_0$=0.144 mM, $[TiO_2]_0$=12.5 mM.

Fig. 3. DBS removed vs. $^{\bullet}OH$ generated. $[TiO_2]_0$=12.5 mM.

Fig. 4. Change with time of (a) $^{\bullet}OH$ generated and (b) DBS through the oxidation process at different $[TiO_2]$. $[DBS]_0$=0.144 mM, radiation=0.024 mW/cm^2.

Fig. 5. Fitting of the experimental $^{\bullet}OH$ generation data to the kinetic model proposed by Eq. 4. $[DBS]_0$=0.144 mM, radiation=(0.004-0.024) mW/cm^2, $[TiO_2]$=(0.125-25) mM.

Fig. 6. Fitting of the experimental DBS degradation data to the kinetic model proposed by Eq. 7. $[DBS]_0$=0.144 mM, radiation=(0.004-0.024) mW/cm^2, $[TiO_2]$=(0.125-25) mM.

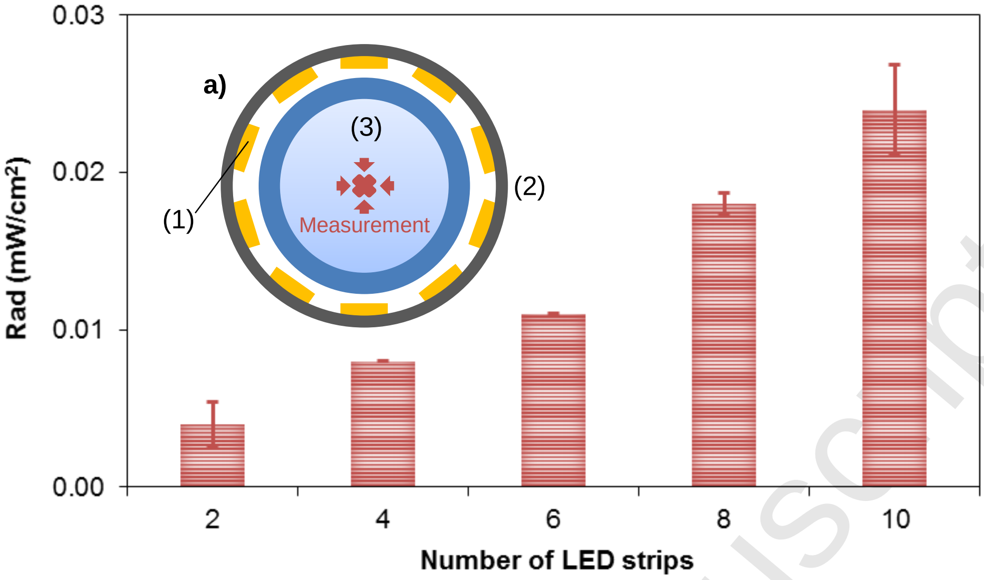

a)
(1)
(2)
(3)
Measurement
0.03
0.02
0.01
0.00
Rad (mW/cm^2)
2
4
6
8
10
Number of LED strips

Figure 2

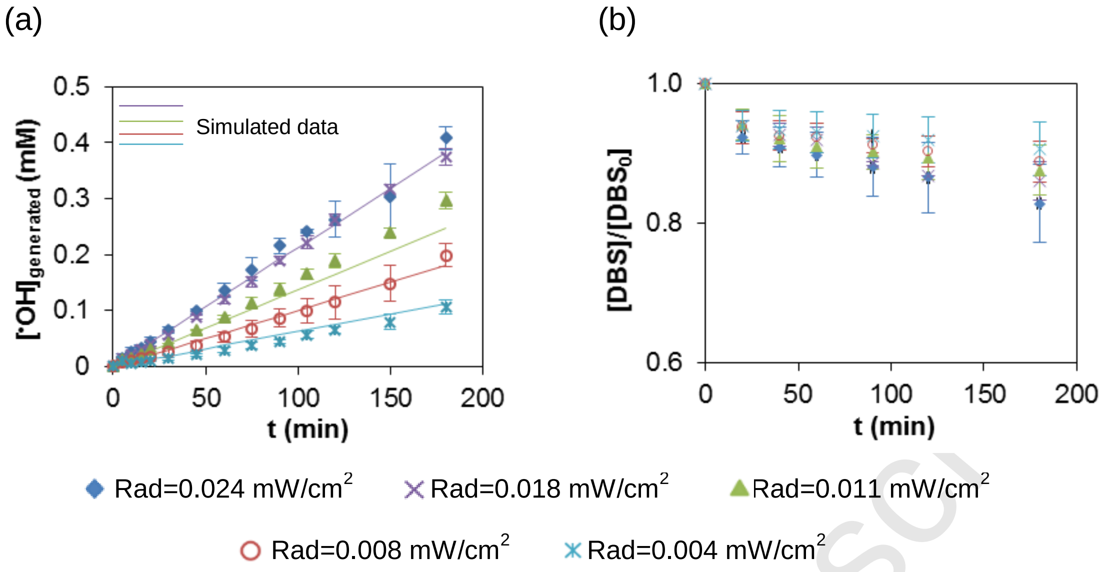

(a)
(b)
[•OH]generated (mM)
0.5
0.4
0.3
0.2
0.1
0
Simulated data
0
50
100
150
200
t (min)
[DBS]/[DBS0]
1.0
0.8
0.6
0
50
100
150
200
t (min)
Rad=0.024 mW/cm2
Rad=0.018 mW/cm2
Rad=0.011 mW/cm2
Rad=0.008 mW/cm2
Rad=0.004 mW/cm2

Figure 3

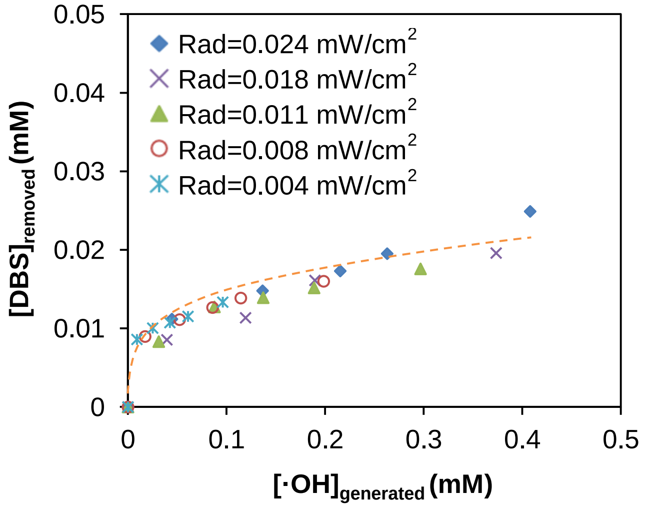

0.05
0.04
0.03
0.02
0.01
0
[DBS]$_{removed}$ (mM)
0
0.1
0.2
0.3
0.4
0.5
[·OH]$_{generated}$ (mM)
Rad=0.024 mW/cm^2
Rad=0.018 mW/cm^2
Rad=0.011 mW/cm^2
Rad=0.008 mW/cm^2
Rad=0.004 mW/cm^2

Figure 4

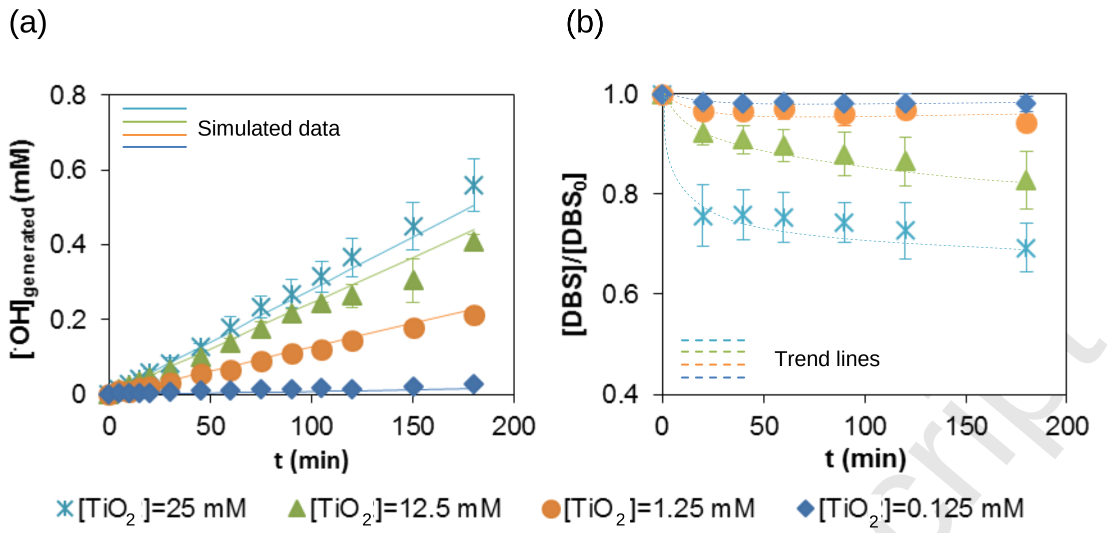
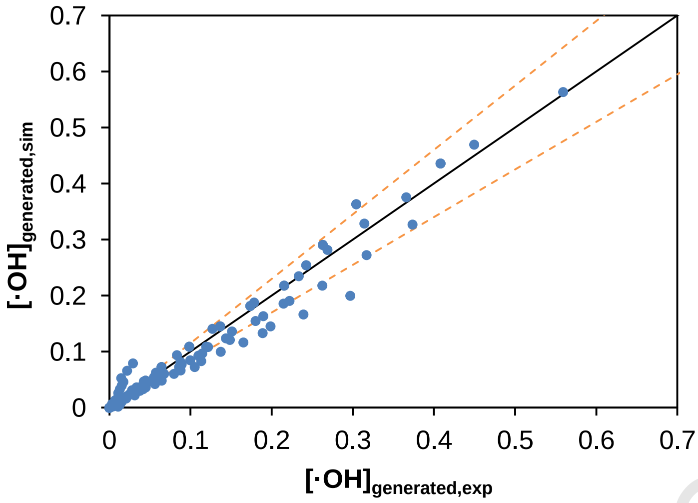
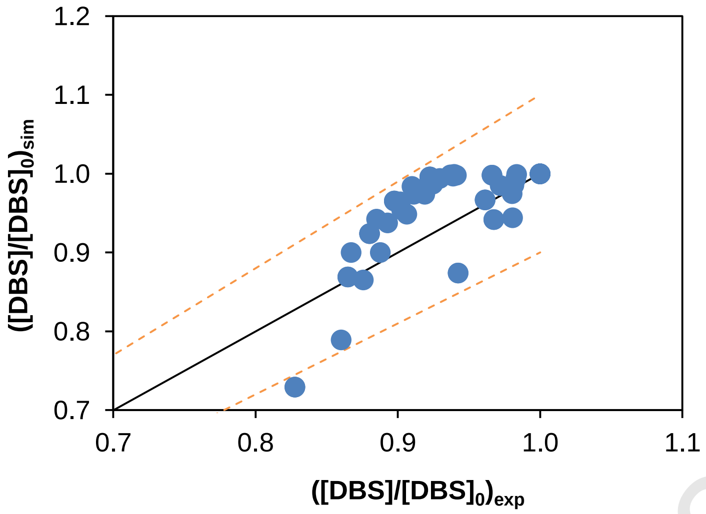
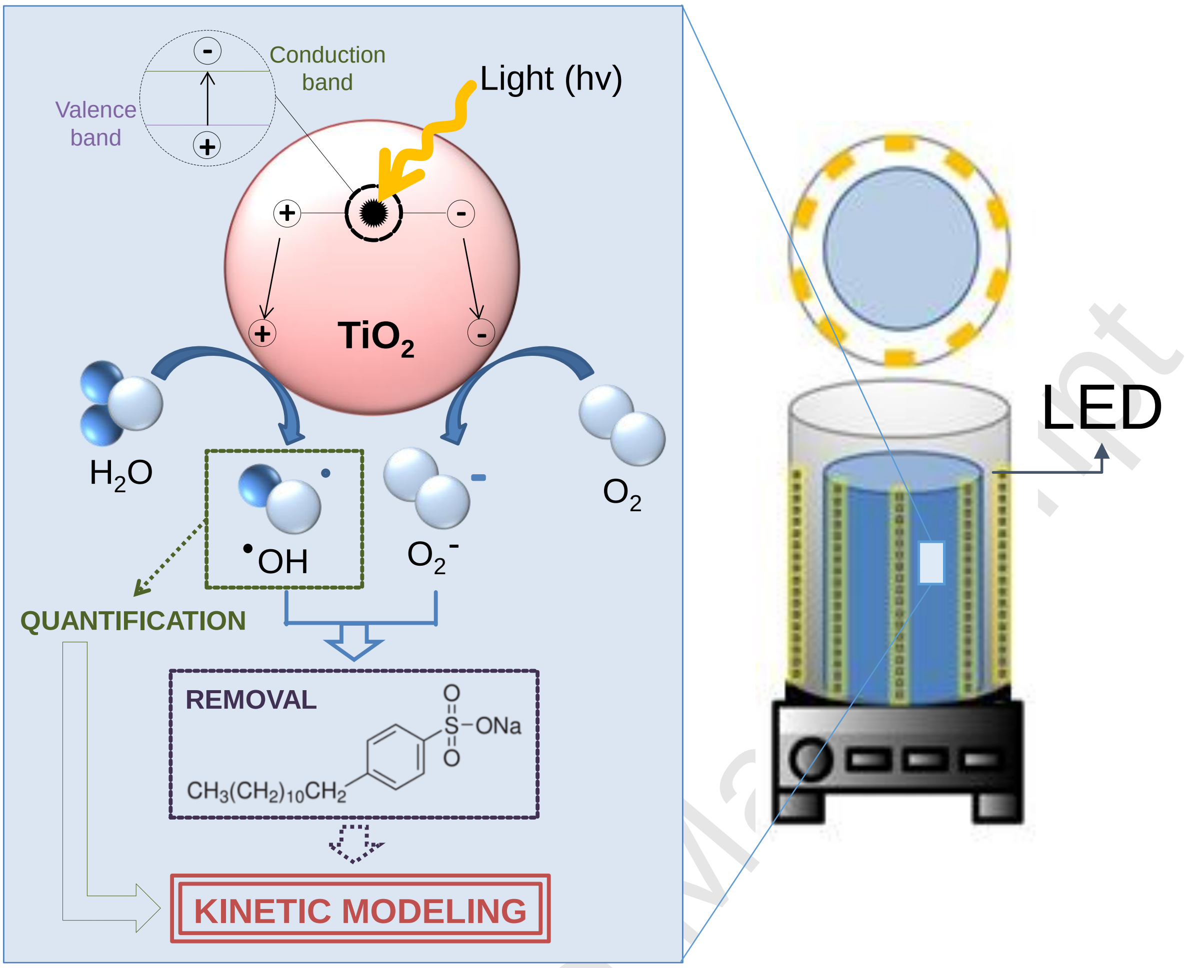

(a)
(b)
0.8
0.6
0.4
0.2
0
[·OH]generated (mM)
Simulated data
0
50
100
150
200
t (min)
1.0
0.8
0.6
0.4
[DBS]/[DBS0]
Trend lines
0
50
100
150
200
t (min)
[TiO2]=25 mM
[TiO2]=12.5 mM
[TiO2]=1.25 mM
[TiO2]=0.125 mM

Figure 5


0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
$[\cdot OH]_{generated,sim}$
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
$[\cdot OH]_{generated,exp}$


1.2
1.1
1.0
0.9
0.8
0.7
0.7
0.8
0.9
1.0
1.1
$([DBS]/[DBS]_0)_{sim}$
$([DBS]/[DBS]_0)_{exp}$


Conduction band
Valence band
Light (hv)
TiO_2
H_2O
$^\bullet OH$
O_2^-
O_2
QUANTIFICATION
REMOVAL
$CH_3(CH_2)_{10}CH_2$
S–ONa
O
O
KINETIC MODELING
LED