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TÍTULO DEL TRABAJO FIN DE MASTER

Influencia de la radiación y la concentración de TiO_2 en la generación de radicales hidroxilo en un reactor de LEDs fotocatalítico. Aplicación a la degradación de dodecilsulfonato (DBS).

TITLE IN ENGLISH

Influence of Radiation and TiO_2 Concentration on the Hydroxyl Radicals Generation in a Photocatalytic LEDs Reactor. Application to Dodecylbenzenesulfonate (DBS) Degradation.

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INFLUENCE OF THE RADIATION AND TiO_2 CONCENTRATION ON THE HYDROXYL RADICALS GENERATION IN A PHOTOCATALYTIC LED REACTOR. APPLICATION TO DODECYLBENZENESULFONATE (DBS) DEGRADATION.

Paula Ribao Martínez

1. 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. Photocatalytic degradation of pollutants is based on the generation of strongly reactive species such as hydroxyl radicals ($\cdot\text{OH}$) that attack and oxidize the target compound. Therefore, determining the generation rate and concentration of hydroxyl radicals in the reaction medium is the first step to describe their influence on the photocatalytic degradation and to compare the results obtained under different conditions and geometries.

In this work, using a Light Emitting Diodes (LEDs) reactor aimed to maximize the light efficiency and minimize the energy consumption, the $\cdot\text{OH}$ concentration has been determined as a function of the radiation and catalyst concentration following an indirect method.

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.

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

2. INTRODUCTION

Increasing water demand and shortage of available water are growing concerns for our society (Blanco et al., 2009). 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 (Dimitroula et al., 2012; Prieto-Rodriguez et al., 2012; Wankhade et al., 2013).

Hence, over the last few decades, a group of new technologies called advanced oxidation processes (AOPs) has been widely reported because of their highly effectiveness in the oxidation of organic compounds. AOPs are processes based on the generation of strongly reactive species such as hydroxyl radicals ($\bullet\text{OH}$) (Comninellis et al., 2008; Kumar and Bansal, 2013; Wankhade et al., 2013).

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 (Nath et al., 2012; Kumar and Bansal, 2013).

Up to now, TiO₂ 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 (Friedmann et al., 2010; Nath et al., 2012; Pelaez et al., 2012; Kumar and Bansal, 2013).

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 (De Lasa et al. 2005; Grčić and Li Puma, 2013). 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 (Kochany and Bolton, 1991; Tai et al., 2004; Yuan et al., 2012).

Some kinetic models considering radiation can be found in literature, but most of them are quite complex and consider the geometry of the reactor (Alfano et al., 1997; Marugán et al., 2013). 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) seems 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 (Ghosh et al., 2008). Some researchers suggested the feasibility of using LEDs in photocatalytic applications for the removal of environmental pollutants, such as 4-chlorophenol (Gosh et al., 2008), dimethyl sulfide (Jo et al., 2011), perchloroethylene (Chen et al., 2005), o-cresol (Chen et al., 2007), formaldehyde (Shie et al., 2008; Li et al., 2010) or dyes (Wang and Ku, 2006).

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 partially biodegradable and they can be found in effluents of WWTPs (Suárez-Ojeda, et al. 2007). 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 (Rivera-Utrilla et al., 2012; Bautista-Toledo et al., 2014). There are some previous researchers that studied DBS photocatalytic degradation using TiO_2 , showing the viability of the treatment under specific illumination conditions and analyzing the kinetics of the process (Hidaka et al., 1992; Zhang et al., 2003; Zhang et al., 2004; Sánchez et al., 2011). However, they can not 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 $\bullet\text{OH}$ concentration in the reaction medium 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.

3. EXPERIMENTAL

The LEDs reactor 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 arranged uniformly in the angular direction. A Pyrex glass reaction vessel was inside the case and a magnetic stirring plate (Velp Scientifica) was used to provide proper mixing.

To evaluate the influence of light intensity on the $\bullet\text{OH}$ generation and DBS degradation, between 2 and 10 LEDs strips were switched on, which corresponded with values of radiation in a range between 0.005 and 0.026 mW/cm². All the catalytic experiments were performed in duplicate at room temperature (25°C), 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/cm² and resolution of 0.001 mW/cm², was employed to quantify the radiation intensity.

3.1. \cdot OH QUANTIFICATION

The method used in this study for the determination of the \bullet OH formation was initially proposed by Tai et al. (2004), and it 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, the quantification of \bullet OH is carried out through the determination of the formaldehyde concentration when the DNPHo is analyzed by high performance liquid chromatograph (HPLC).

0.8 L of 250 mM of DMSO solution was mixed with the TiO_2 and kept 24 h in the dark to reach adsorption equilibrium, then photocatalytic degradation was initiated. At different time intervals, 2 mL of suspension was 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 (Tai et al., 2004). 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.

3.2. DBS DEGRADATION

DBS was obtained from Sigma-Aldrich and the TiO₂ catalyst used was Aeroxide P25 provided by Evonik Industries. 0.80 L of 0.144 mM of DBS solution were mixed with the catalyst and kept 30 min premixing in the dark before the photocatalytic experiments were started to reach adsorption equilibrium. 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).

4. RESULTS AND DISCUSSION

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

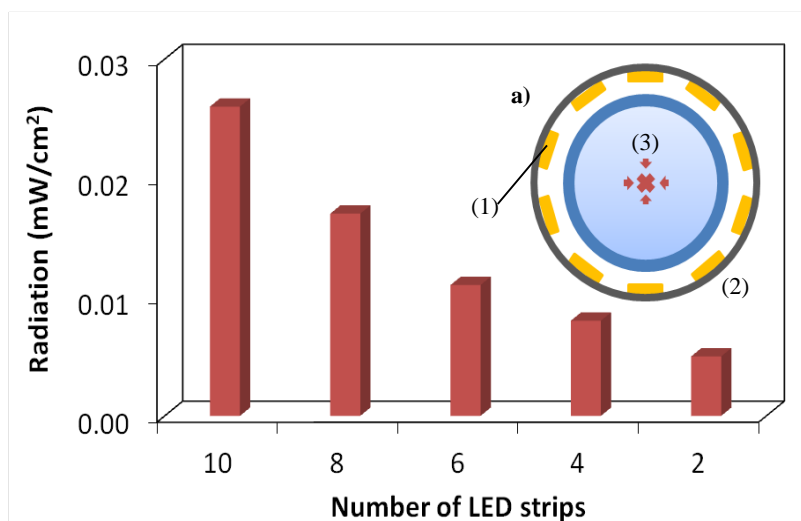


Fig. 1. Radiation distribution in the reactor. A) Schematic diagram of the transverse section of the LEDs reactor: (1) LEDs strips, (2) PVC case and (3) reaction vessel.

4.1. LIGHT INTENSITY INFLUENCE

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

Fig. 2(a) shows the $\cdot\text{OH}$ generation rate on the irradiated TiO_2 over the photocatalytic process time. The $\cdot\text{OH}$ concentration is proportional to the reaction time. This behavior has been previously observed (Schwarz *et al.*, 1997; Xiang *et al.*, 2011). Moreover, under the studied conditions the amount of $\cdot\text{OH}$ generated reaches values up to 0.408 mM. For a fixed time, the concentration of $\cdot\text{OH}$ in the medium increases with radiation intensity in a linear way, up to a value of 0.017 mW/cm², and then it

remains almost constant. The data of $\cdot\text{OH}$ concentration were correlated to the radiation intensity and time (data shown in Appendix A). Eq. 1 satisfactorily fits to the experimental values of the concentration of $\cdot\text{OH}$ for radiations up to 0.017 mW/cm^2 , with an average standard deviation of 0.00506 mM (Fig. 2(a)).

$$[\cdot\text{OH}] = 0.125 \cdot \text{Radiation} \cdot t \quad [1]$$

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 at the same operation time; working at 0.026 mW/cm^2 around 17 % of the initial concentration of DBS is removed after 180 min.

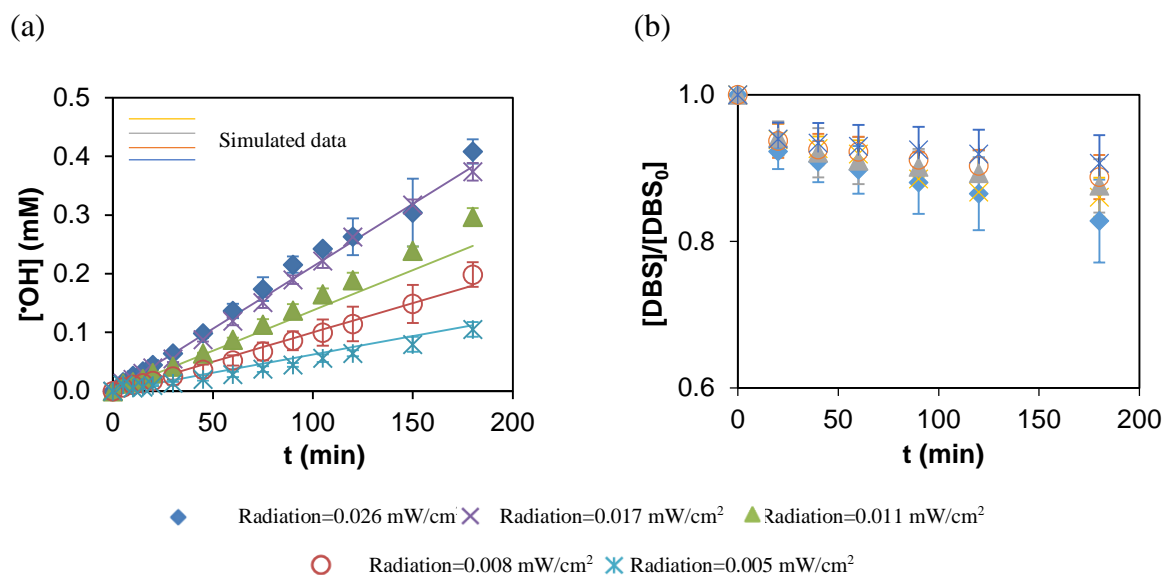


Fig. 2. Change with time at different radiation intensity of (a) $\cdot\text{OH}$ and (b) DBS. $[\text{DBS}]_0 = 0.144 \text{ mM}$, $[\text{TiO}_2]_0 = 12.5 \text{ mM}$

The DBS removed can be directly correlated to the radiation intensity and therefore with the $\cdot\text{OH}$ generated, under the hypothesis that in the experimental conditions the $\cdot\text{OH}$ generated 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 can be assumed that there is not mineralization, meaning that DBS degradation products remain in the oxidation medium at the same time that DBS is removed and $\cdot\text{OH}$ are generated. A determinant amount of $\cdot\text{OH}$ can be obtained varying radiation and TiO_2 concentration. Fig. 3 shows that it is better to represent contaminant removal as a function of $\cdot\text{OH}$. Hence, it can be conclude the adequacy of using the concentration of $\cdot\text{OH}$ as useful index of DBS degradation kinetics independent of the radiation value.

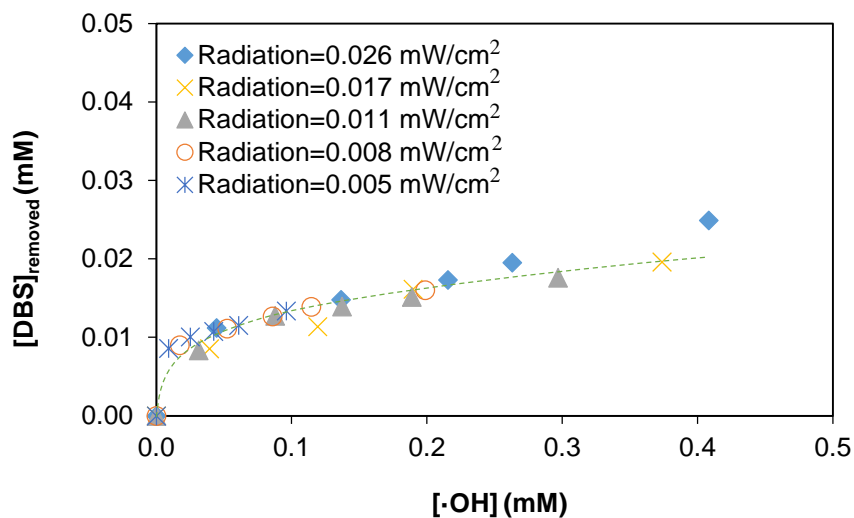


Fig. 3. DBS removed vs. the $\cdot\text{OH}$ generated. $[\text{TiO}_2]_0=12.5$ mM.

4.2. 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 and 25 mM for a fixed value of radiation. It is observed that the concentration of $\cdot\text{OH}$ in the medium changes

linearly with time. 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 $\cdot\text{OH}$ generation is smaller because the catalyst excess can lead to an increase in the opacity of the suspension and a decrease in light penetration (Kaneco et al., 2009; Sun et al., 2014). This trend is satisfactorily represented (Fig. 2(a)) by the logarithmic correlation shown in Eq. 2 with an average standard deviation of 0.00703 mM (Appendix A).

$$[\cdot\text{OH}] = (5.17 \cdot 10^{-4} \cdot \ln([\text{TiO}_2]) + 1.13 \cdot 10^{-3}) \cdot t \quad [2]$$

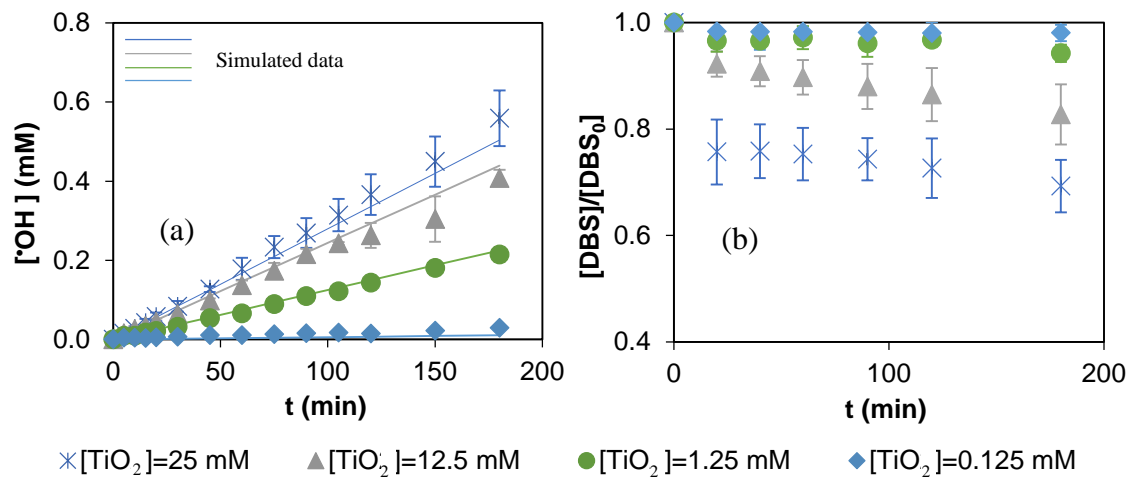


Fig. 4. Change with time of (a) $\cdot\text{OH}$ and (b) DBS through the oxidation process at different $[\text{TiO}_2]$.

$[\text{DBS}]_0 = 0.144 \text{ mM}$, radiation = 0.026 mW/cm^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)).

4.3. KINETIC MODELING

A fundamental step for an optimal process design must consider the determination of kinetic parameters. For an energetic efficient design, a kinetic model considering both catalyst dosage and radiation is feasible. Moreover, in this work the kinetic model will account for the rate of generation of the oxidizing OH radicals.

In order to mathematically describe the •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 radiation applied, Eq. 3

$$\frac{d [\bullet\text{OH}]}{dt} = k_{[\bullet\text{OH}]} \cdot [\text{TiO}_2]^m \cdot \text{Rad}^n \quad [3]$$

[•OH] is the concentration of •OH in the medium (in mM), t is the reaction time (in min), $k_{[\bullet\text{OH}]}$ is the kinetic constant (in $\text{mM} \bullet\text{OH} \cdot \text{cm}^2 \cdot \text{min}^{-1} \cdot \text{mW}^{-1} \cdot \text{mM TiO}_2^{-0.37}$), [TiO₂] is the catalyst dosage (in mM), m and n are experimental fitted parameters and Rad is the radiation applied (in mW/cm²).

The kinetic parameters $k_{[\bullet\text{OH}]} = 0.0371 \text{ mM} \bullet\text{OH} \cdot \text{cm}^2 \cdot \text{min}^{-1} \cdot \text{mW}^{-1} \cdot \text{mM TiO}_2^{-0.368}$ (T=25 °C) and m=0.368 and n=1 were obtained from regression of the experimental data to Eq. 3, leading to Eq. 4,

$$\frac{d [\bullet\text{OH}]}{dt} = 0.0367 \cdot [\text{TiO}_2]^{0.370} \cdot \text{Rad}^1 \quad [4]$$

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

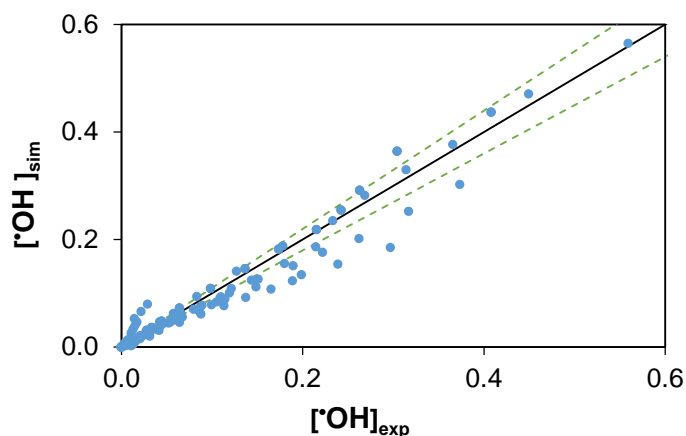


Fig. 5. Fitting of the experimental data of the $[\cdot\text{OH}]$ to the kinetic model proposed. $[\text{DBS}]_0=0.144\text{mM}$, radiation=(0.005-0.026) mW/cm^2 , $[\text{TiO}_2]=(0.125\text{-}25)$ mM .

Although some authors have proposed kinetic models for different compounds that consider the intensity of radiation and agree on its influence on the kinetics of the process (Meng et al. 2002; Blesa y Sánchez, 2004; Daneshvar et al. 2004; Ollis, 2005; Li et al. 2008; Wang et al. 2011), no agreement has been reached in terms of a unified kinetic model. Therefore, this work advances previous studies, proposing a kinetic model that considers $\cdot\text{OH}$ instead of time as main independent variable (Eq. 5). Moreover, radiation is also included in the model. .

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 $\cdot\text{OH}$ generation as well as DBS concentration (Eq. 5).

$$\frac{-d[\text{DBS}]}{dt} = k_{[\text{DBS}]} \cdot [\cdot\text{OH}] \cdot [\text{DBS}] \quad [5]$$

$[\text{DBS}]$ is the DBS concentration (in mM), t is the reaction time (in min), $k_{[\text{DBS}]}$ is the second order kinetic constant (in $\text{mM} \cdot \text{OH}^{-1} \cdot \text{min}^{-1}$) and $[\cdot\text{OH}]$ is the $\cdot\text{OH}$ concentration (in mM).

$k_{[\text{DBS}]}$ takes a value of $0.00404 \text{ mM} \cdot \text{OH}^{-1} \cdot \text{min}^{-1}$ at $25 \text{ }^\circ\text{C}$, therefore the kinetic model can be expressed by Eq. 6

$$-\frac{d[\text{DBS}]}{dt} = 1.49 \cdot 10^{-4} \cdot [\cdot\text{OH}] \cdot [\text{DBS}] \quad [6]$$

A parity graph of simulated versus experimental $[\text{DBS}]/[\text{DBS}]_0$ data is presented in Fig. 6. It can be seen that the 98 % of the simulated results fall within the interval $[\text{DBS}]/[\text{DBS}]_{0,\text{exp}} \pm 10 \% [\text{DBS}]/[\text{DBS}]_{0,\text{exp}}$.

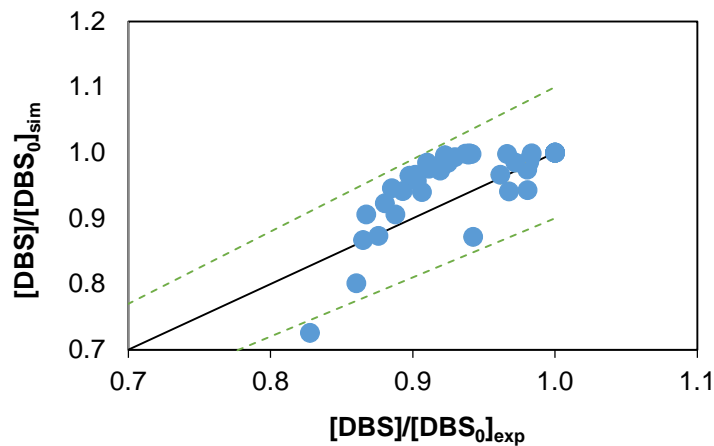


Fig. 6. Fitting of the experimental data to kinetic model proposed. $[\text{DBS}]_0 = 0.144 \text{ mM}$, radiation = $(0.005 - 0.026) \text{ mW/cm}^2$, $[\text{TiO}_2] = (0.125 - 25) \text{ mM}$.

Photocatalytic reaction generally occurs in two regimes with UV light intensity. For low radiation values below 1 mW/cm^2 Daneshvar et al. (2004) and Wang et al. (2011) 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 (Yu et al., 2007). Therefore, the model proposed in this work corroborates the existence of this regime. However, for higher intensities of radiation between 0.86 and 60 mW/cm^2 , Meng et al. (2002) and Li et al. (2008) observed that the reaction rate depends on the square of the intensity of radiation. In this case, the recombination rate is dominant (Yu et al., 2007).

5. 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 to radiation demand.

Furthermore, an indirect method has been used to determine the $\cdot\text{OH}$ concentration, which are the main oxidant specie, in order to correlate it with the radiation and the concentration of catalyst. This study has been applied to the photocatalytic degradation of the anionic surfactant DBS. Experimental results confirmed that the amount of $\cdot\text{OH}$ generated can be correlated to the DBS removal rate, contributing to a better understanding of the process. The $\cdot\text{OH}$ generation for a radiation intensity between 0.005 mW/cm^2 and 0.026 mW/cm^2 and a catalyst dosage between 0.125 mM and 25 mM is satisfactorily described by a model that takes into account both variables. Furthermore, for these experimental conditions, the DBS removal has been fitted to a second order kinetic model that includes the influence of the generated $\cdot\text{OH}$.

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7. APPENDIX A

To establish a relationship between the concentration of $\cdot\text{OH}$, reaction time and radiation applied, first it is necessary to correlate the concentration of $\cdot\text{OH}$ with the time (Fig. 2(a)) and then to relate the slopes obtained (m_1) with the radiation (Fig. A.1). The same procedure is used to obtain a relation between the concentration of $\cdot\text{OH}$, reaction time and catalyst dosage (Fig. A.2).

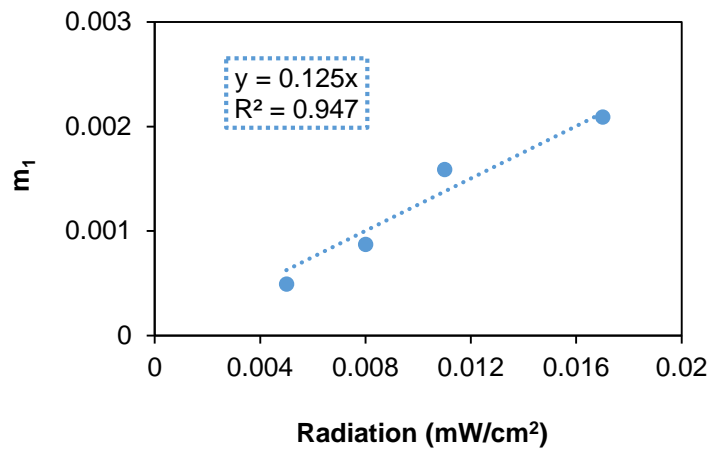


Fig. A.1. Relation between the slopes from the Fig. 2(a) and the radiation.

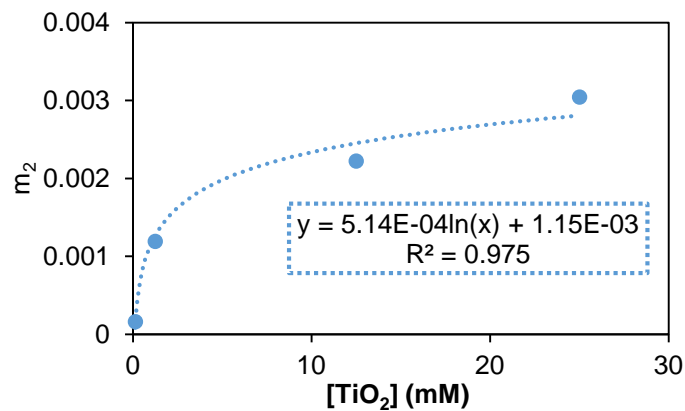


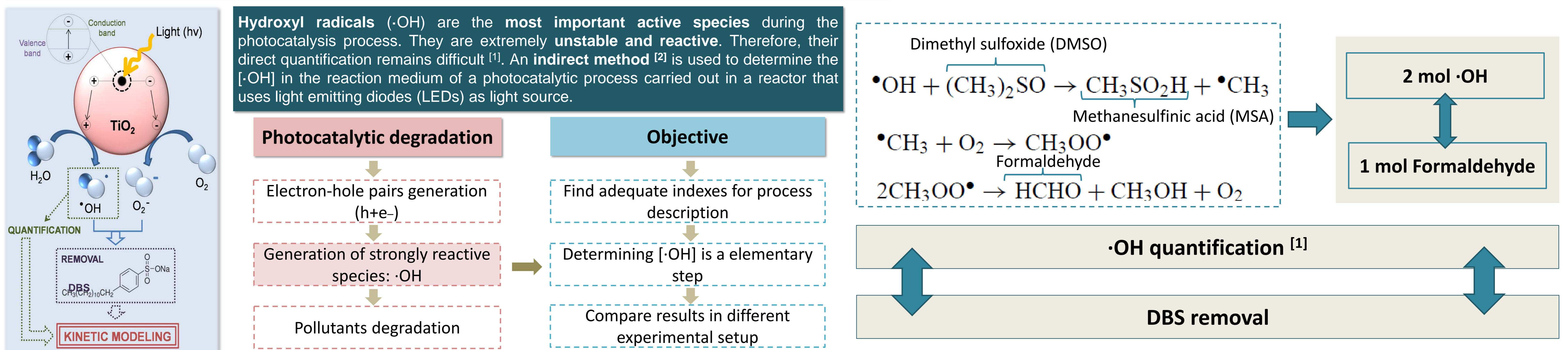
Fig. A.2. Relation between the slopes from the Fig. 4(a) and the catalyst dosage.

P. Ribao* and M.J. Rivero

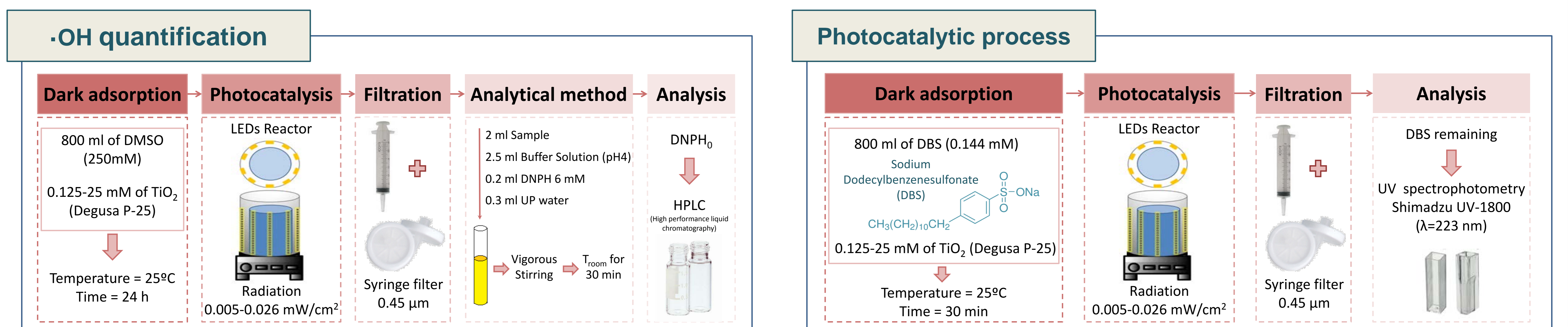
DPTO. Ingenierías Química y Biomolecular. Universidad de Cantabria

ETSIIyT. Avda. de los Castros s/n 39005 Santander. SPAIN ✉: ribaop@unican.es

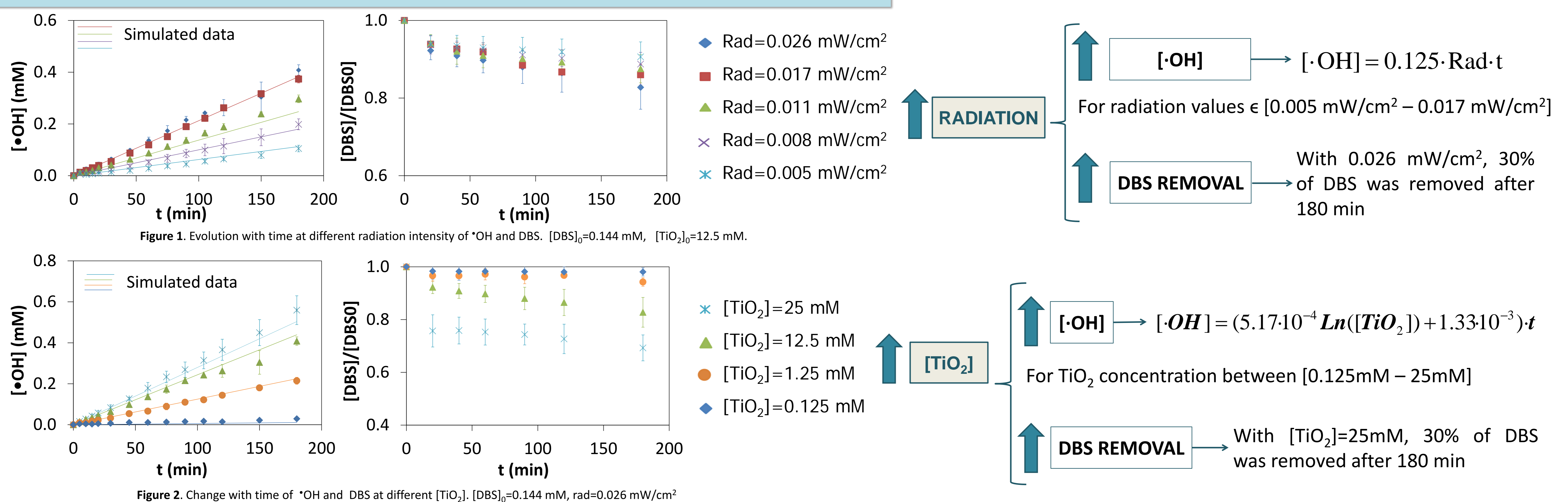
1. Hypothesis and objective



2. Experimental Methodology



3. Results: $\cdot\text{OH}$ generation and DBS removal



4. Conclusions

- ❖ The amount of $\cdot\text{OH}$ generated is correlated to the DBS removal, contributing to a better understanding of the process
- ❖ Catalyst concentration and light intensity show a coupled influence on the degradation yield
- ❖ The feasibility of applying UV-LEDs as light source in the photocatalytic degradation of DBS is showed

5. References

- [1] R.K. Nath, M.F.M. Zain, H.A.A. Kadhum, Journal of Applied Sciences Research, 8:8 (2012) 4147
- [2] C. Tai, J.F. Peng, J.F. Liu, G.B. Jiang, H. Zou. Anal. Chim. Acta 2004; 527: 73-80.

6. Acknowledgments

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.



MASTER EN INGENIERÍA QUÍMICA: “Producción y consumo sostenible”

Influence of Radiation and TiO_2 concentration on the $\cdot\text{OH}$ generation in a Photocatalytic LEDs Reactor. Application to removal of dodecylbenzenesulfonate (DBS).

Author: Paula Ribao Martínez

Advisor: Maria José Rivero

Environmental Technologies and Bioprocesses Research Group



**Chemical and Biomolecular Engineering Department
University of Cantabria (SPAIN)**



Contents

- 1** Problematic of emerging contaminants: DBS
- 2** Advanced oxidation process: Photocatalysis
- 3** Hydroxyl radical quantification and DBS degradation in LED reactor
- 4** Results: Hydroxyl radical generated and DBS removed
- 5** Kinetic modeling
- 6** Conclusions

1. Problematic of emerging contaminants: DBS

Emerging contaminants (ECs) are not necessarily new chemical pollutants, they may be substances that have been present in the environment for a long time but whose presence and significance are only now being recognized.

ECs as low as μg or ng concentrations can cause **adverse effects** on organisms.



Emerging contaminant list



Pharmaceutical compounds

Household cleaning products

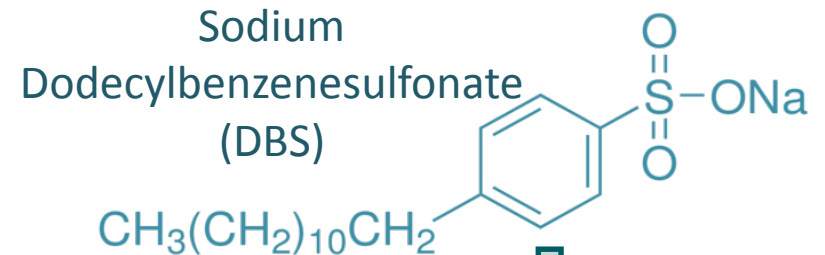


Personal care products

Pesticides and Herbicides



Anionic surfactant

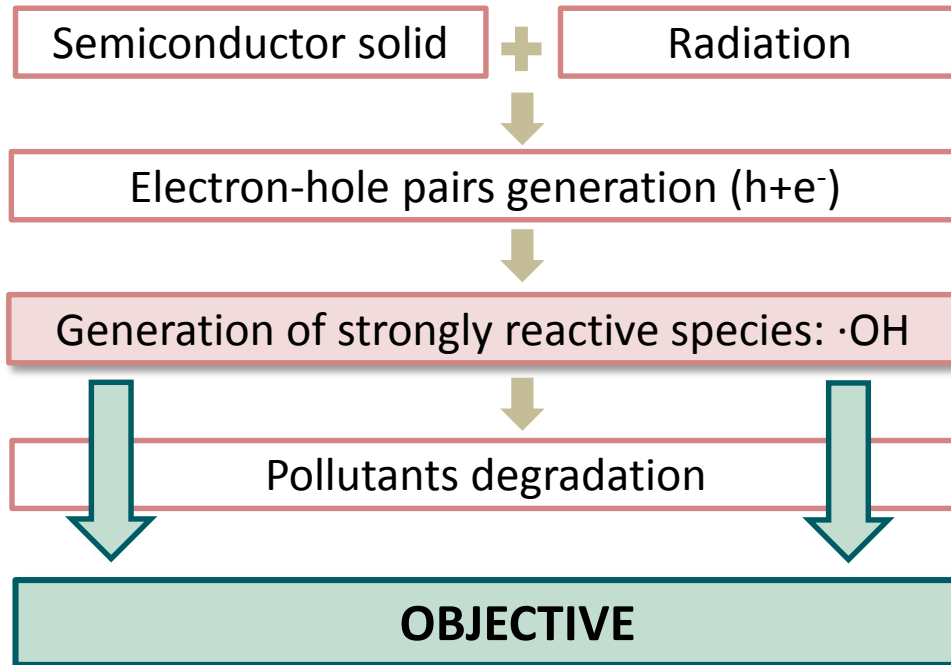


11-20% of the COD in municipal wastewater

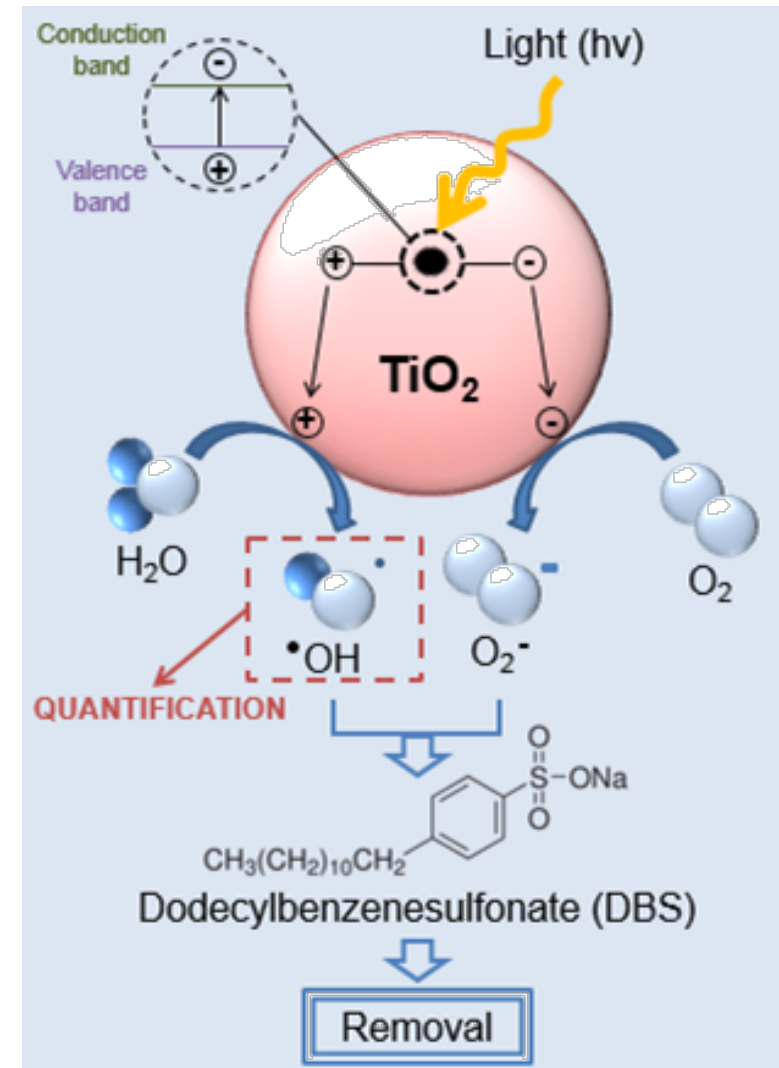
Adverse effects

- Toxicity
- Foam production in river
- Aquifers contamination
- Endocrine disruptor

2. Advanced oxidation process: Photocatalysis



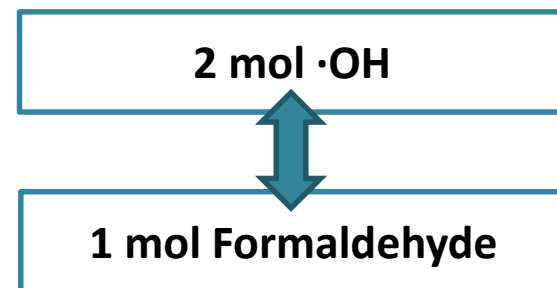
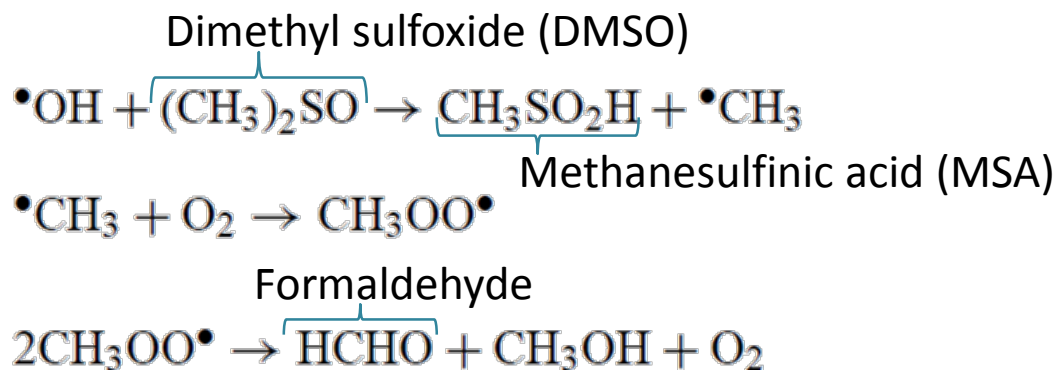
- Obtaining adequate indexes to compare the results obtained in different experimental setup designs
- Studying of the influence of the radiation and the catalyst dosage on the ·OH generation and DBS removal
- Proposing a kinetic model for ·OH generation and DBS removal



3. Hydroxyl radical quantification and DBS degradation

•OH QUANTIFICATION [1]

[1] C. Tai, J.F. Peng, J.F. Liu, G.B. Jiang, H. Zou, *Analytica Chimica Acta*, 527:1 (2004) 73-80



Dark adsorption

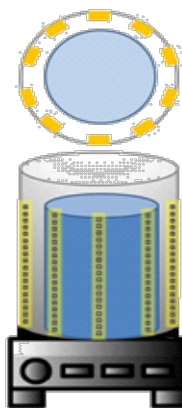
800 ml of DMSO
(250mM)

0.125-25 mM of TiO₂
(Degusa P-25)

Temperature = 25°C
Time = 24 h

Photocatalysis

LED Reactor



Radiation

0.005-0.026 mW/cm²

Analytical method

2 ml Sample
2.5 ml Buffer Solution
(pH4)
0.2 ml DNPH 6 mM
0.3ml UP water



Vigorous
Stirring → T_{room} for 30
min

Analysis

DNPH₀



HPLC
(High
performance
liquid
chromatography)



3. Hydroxyl radical quantification and DBS degradation

PHOTOCATALYTIC PROCESS

Dark adsorption

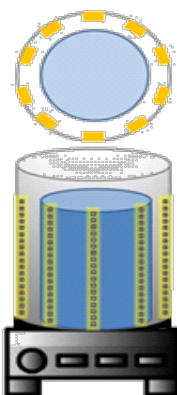
800 ml of DBS
(0.144 mM)

0.125-25 mM of TiO_2
(Degusa P-25)

Temperature = 25°C
Time = 24 h

Photocatalysis

LED Reactor



Radiation

0.005-0.026 mW/cm^2

Filtration



Syringe filter
0.45 μm

Analysis

DBS remaining

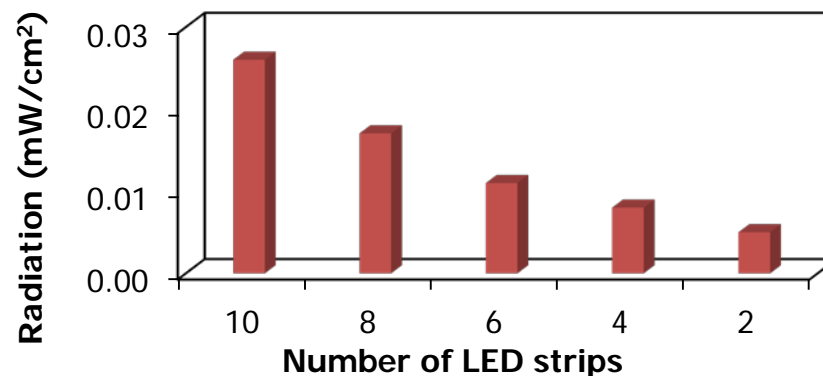
UV spectrophotometry

Shimadzu UV-1800
($\lambda=223 \text{ nm}$)

DETERMINATION OF THE RADIATION



A PCE-UV34 radiation meter
 $\lambda=(290-390) \text{ nm}$



4. Results: $\cdot\text{OH}$ generated and DBS removed

INFLUENCE OF THE RADIATION

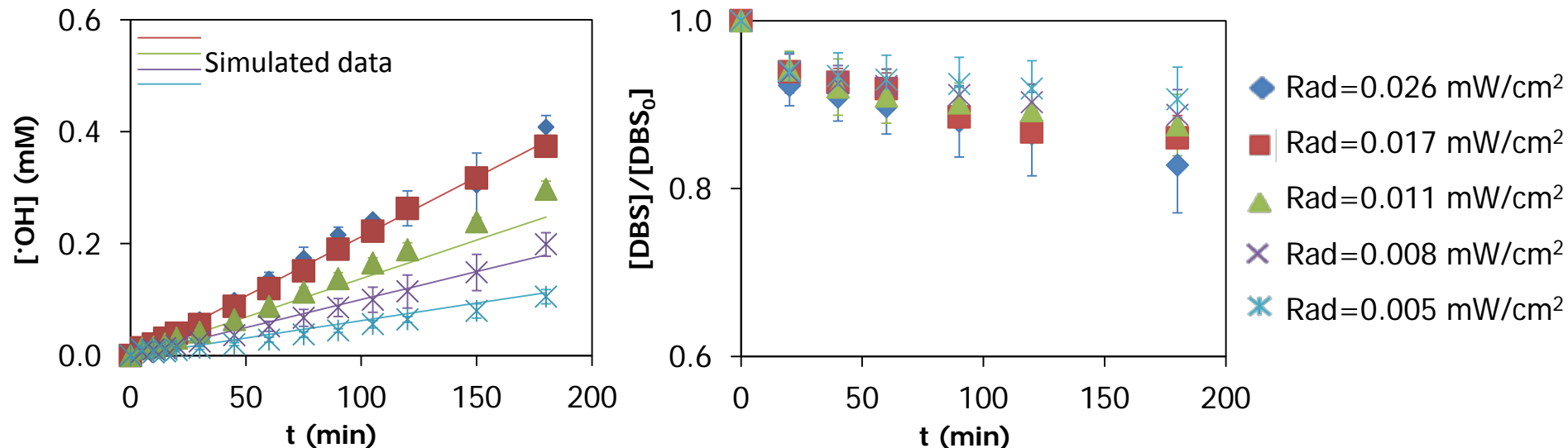


Figure 1. Evolution with time at different radiation intensity of $\cdot\text{OH}$ and DBS. $[\text{DBS}]_0=0.144$ mM, $[\text{TiO}_2]_0=12.5$ mM.

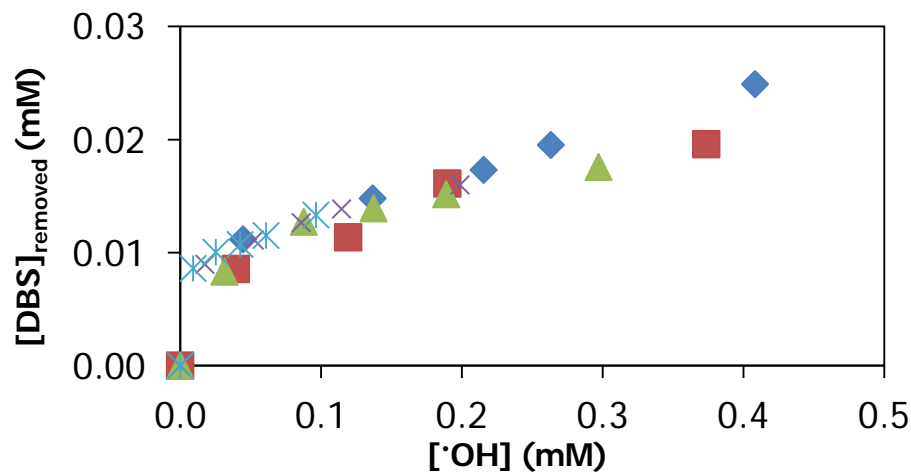
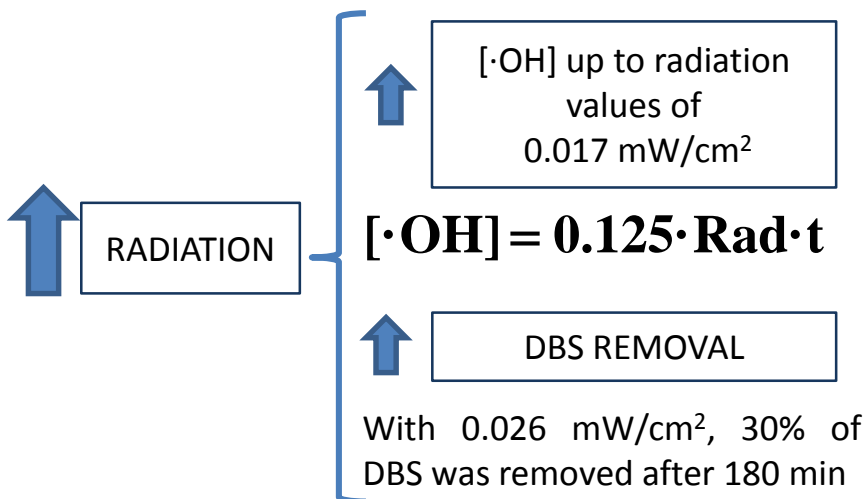


Figure 2. Relation between the $\cdot\text{OH}$ generated and DBS removed

4. Results: ·OH generated and DBS removed

INFLUENCE OF THE CATALYST DOSAGE

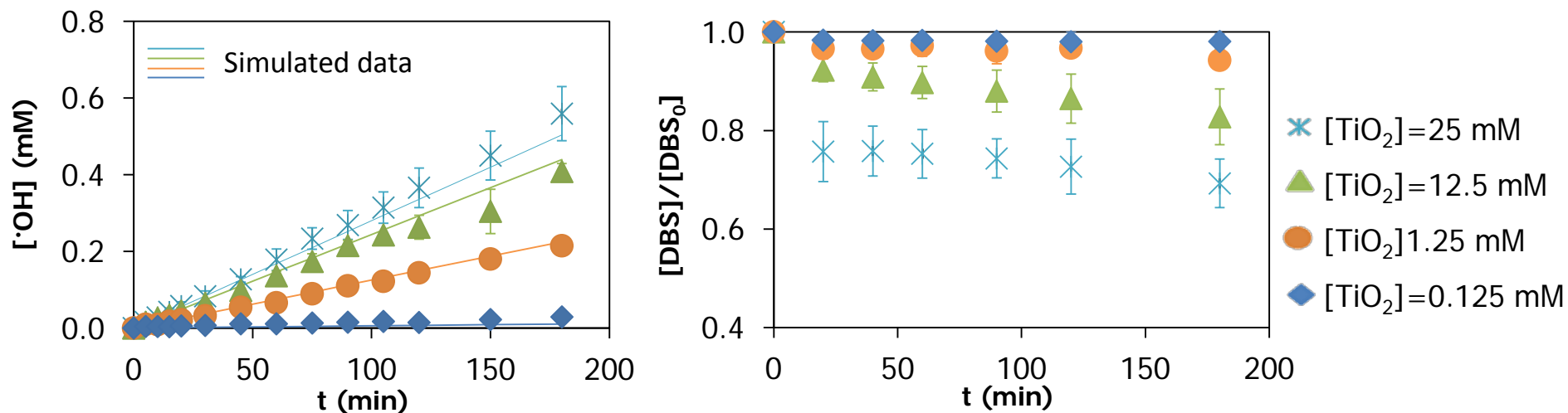
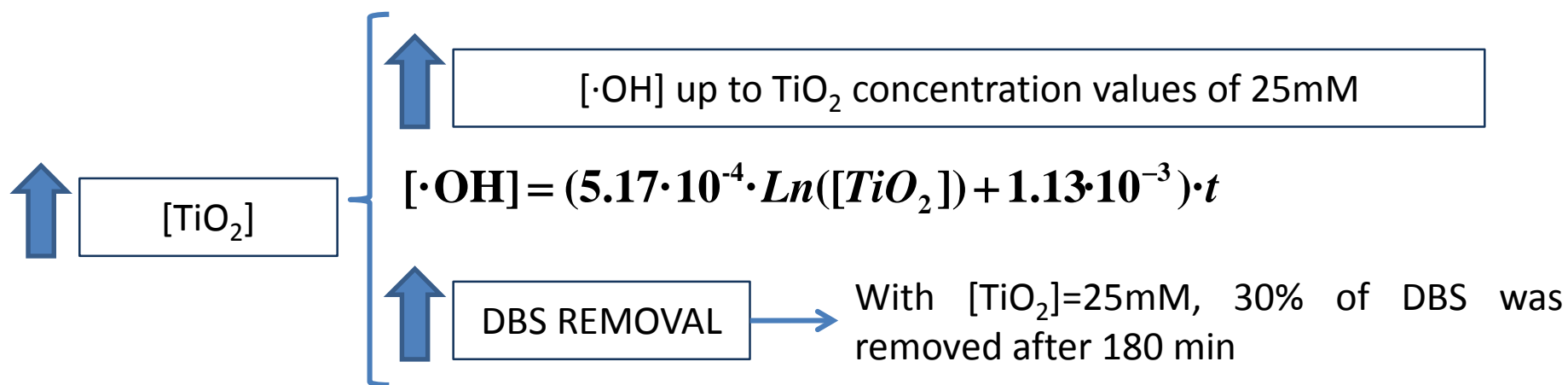


Figure 3. Change with time of $\cdot\text{OH}$ and DBS at different $[\text{TiO}_2]$. $[\text{DBS}]_0 = 0.144 \text{ mM}$, $\text{rad} = 0.026 \text{ mW/cm}^2$



5. Kinetic modeling

HYDROXYL RADICALS

$$\frac{d[\cdot\text{OH}]}{dt} = k_{[\cdot\text{OH}]} [\text{TiO}_2]^m \cdot \text{Rad}^n$$

$$\frac{d[\cdot\text{OH}]}{dt} = 0.0367 \cdot [\text{TiO}_2]^{0.370} \cdot \text{Rad}^1$$

in which $k_{[\cdot\text{OH}]}$ is the kinetic constant and m and n are experimental fitted parameters



Estimation tool Solver
(Microsoft Office)

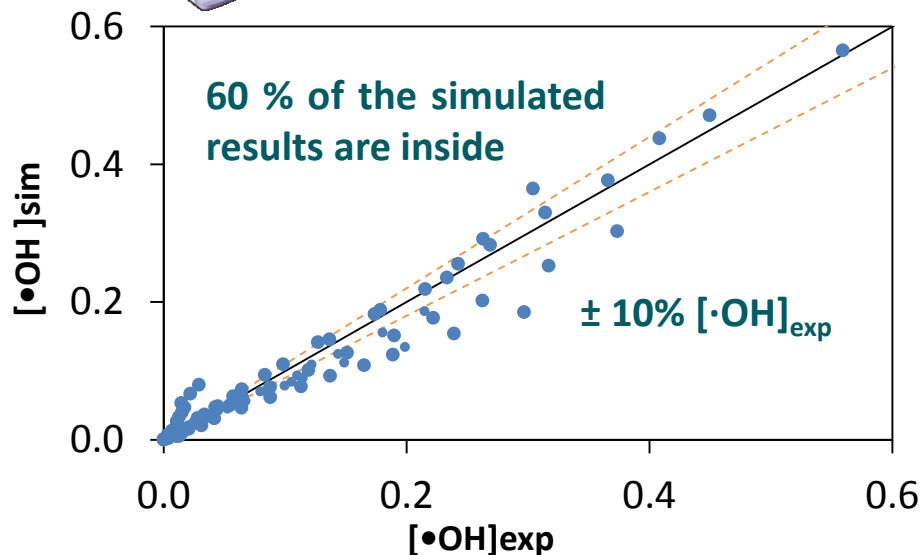
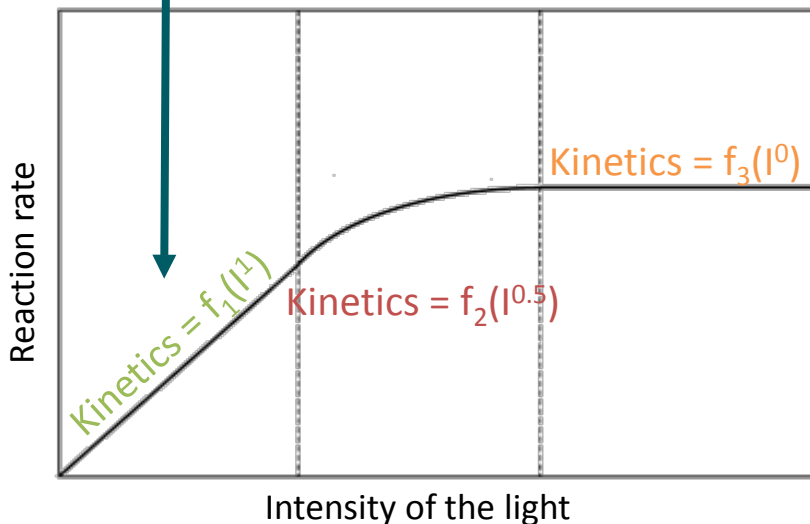


Figure 4. Kinetic modeling for $\cdot\text{OH}$ generation [2]

Figure 5. Fitting of the experimental data of the $[\cdot\text{OH}]$ to the kinetic model proposed. $[\text{DBS}]_0 = 0.144$ mM, radiation = (0.005-0.026) mW/cm², $[\text{TiO}_2] = (0.125-25)$ mM.

[2] M. A. Blesa, B. Sánchez. *Eliminación de contaminantes por fotocatalisis heterogénea*. CIEMAT, Madrid (2004)

5. Kinetic modeling

DBS REMOVAL

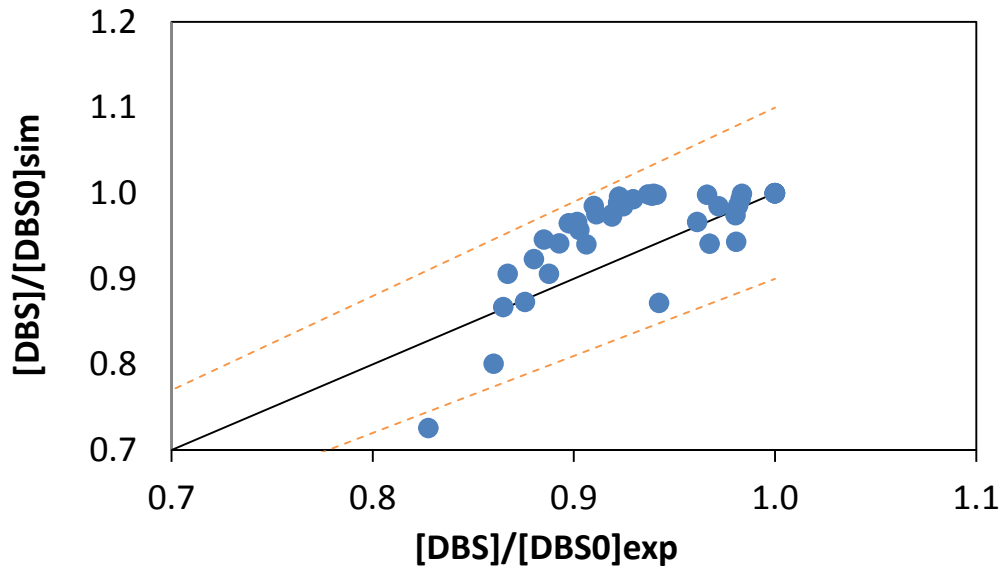
$$\frac{-d[\text{DBS}]}{dt} = k_{[\text{DBS}]} \cdot [\text{OH}\cdot] \cdot [\text{DBS}]$$

$$\frac{d[\text{DBS}]}{dt} = 1.49 \cdot 10^{-4} \cdot [\text{OH}\cdot] \cdot [\text{DBS}]$$

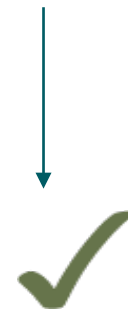
in which $k_{[\text{DBS}]}$ is the kinetic constant



Estimation tool Solver
(Microsoft Office)



98 % of the simulated results fall within the interval $[\text{DBS}]/[\text{DBS}]_{0,\text{exp}} \pm 10 \%$



The proposed kinetic model for DBS degradation shows a good fit with experimental results

Figure 6. Fitting of the experimental data to kinetic model proposed. $[\text{DBS}]_0 = 0.144$ mM, $\text{Rad} = (0.005-0.026)$ mW/cm², $[\text{TiO}_2] = (0.125-25)$ mM

6. Conclusions

The amount of $\bullet\text{OH}$ generated is correlated to the DBS removal, contributing to a better understanding of the process. Catalyst concentration and light intensity show a coupled influence on the degradation yield.

The $\bullet\text{OH}$ generation is satisfactorily described by a model that takes into account radiation and catalyst amount and the DBS removal is fitted to a second order kinetic model that includes the influence of the generated $\bullet\text{OH}$.

The feasibility of applying UV-LEDs as light source in the photocatalytic degradation of DBS is showed

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Environmental Applications

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Greece

SPEA8: 8th European Meeting on Solar Chemistry and Photocatalysis: Environmental Applications. Thessaloniki, Grecia

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THANK YOU FOR YOUR ATTENTION

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