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Evaluation of two types of TiO₂-based catalysts by photodegradation of DMSO in aqueous suspension

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ABSTRACT

Among the different methods to evaluate the photocatalytic activity of TiO₂-based photocatalysts, the most employed has been the methylene blue method. However, several questions have emerged during the last years about its reliability, because this compound can absorb light in the visible range. In this work a new compound is used as photocatalytic test-substance, the dimethylsulfoxide (DMSO), which will be used in the ISO standard (ISO/CD 10676) for the determination of the photocatalytic efficiency of systems used for water treatment. This solvent is a hydroxyl scavenging agent, which can interact with •OH. The study is focused on the degradation of this molecule by two different catalysts: Degussa P25 and Hombikat UV100. The reaction is studied by the monitoring of two of the intermediates formed during the reaction: the methansulfonate (CH₃SO₃⁻) and the sulfate (SO₄²⁻), by means of the ion chromatography technique, and by measuring the TOC. In general, TiO₂ Degussa P25 shows better results in terms of generation of two intermediates (methansulfonate and sulfate), TOC removal, and photonic efficiencies. Although Hombikat UV100 has six times larger specific surface than the other photocatalyst, the reason for the higher photoactivity of Degussa P25 can lie in the slower recombination rate of the electron/hole pairs, and also in the kind of aggregates formed in aqueous solution.

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1. Introduction

In the past two decades, TiO₂ photocatalysis has emerged as a promising process to be used for environmental applications, indeed, it is playing an important role in the purification of air and water media. More recently, photocatalysis is an important area of interest in terms of the development of coated materials. The mechanism of the photocatalysis is based on the use of a semiconductor, which can generate active oxidizing sites, when it is illuminated with photons whose energy is equal to or higher than the energy corresponding to the band-gap of the semiconductor. These photons are absorbed on the surface of the catalyst, and consequently, some electrons (e⁻) may jump from the valence to the conduction band. Thus, a photohole will be generated in the valence band, and these pairs, named electron/hole pairs, migrate to the surface of the catalyst. When they are not recombined, the electron/hole pairs can oxidize the water molecules and give rise to hydroxyl radicals. The

latter are responsible of the ultimate degradation of the molecules present in the medium [1–3].

Among all the different semiconductors, TiO₂ is the most used in the photocatalytic studies, because it is biologically and chemically inert, inexpensive and non-toxic. Numerous attempts have been made in order to increase the photoactivity of this catalyst, by means of doping or mixing with other semiconductors. Besides, other materials that are TiO₂-based are being synthesized for different purposes. In order to evaluate the efficiency of the different materials, the methylene blue test has been traditionally employed, together with other methods (i.e. stearic acid) [4–7].

However, several questions have emerged the last years, about the reliability of the methylene blue method as a photocatalytic activity test, due to the fact that this compound can absorb light in the visible range, and the test is based on the measurement of the decrease of its spectrum along the photocatalytic reaction. Other authors [8] claim that the difficulty of this method lies in the fact that the methylene blue can be adsorbed on the matrix of the photocatalytic material to be evaluated. The mentioned work already set the grounds for the standardization of an evaluation method for TiO₂-photocatalytic materials, by simultaneous determination of DMSO and its degradation products using anatase-type TiO₂-coated glass beads. Nevertheless, a comparison between different types of TiO₂ catalysts in suspension has not yet been made, in order to validate this technique as a possible standard method.

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Table 1

Comparison between two titania powders: Degussa P25 and Hombikat UV100 (Kirchnerova et al. [21]).

Characteristic	Degussa P25	Hombikat UV100
Composition by XRD	70% anatase/30% rutile	100% anatase, not fully crystalline
Apparent powder density (g/mL)	0.05	0.35
Primary crystallite size, XRD (nm)	30	<10
Morphology	Heterogeneous, wrinkled surface	Round agglomerated particles
Apparent particle size (μm)	<10	20–30
SSA _{BET} (m^2/g)	50	289; 189; 300
Weight loss on calcination (%)	<2 (1273 K)	<9 (1123 K); 8.8 (973 K)
Nitrogen adsorption isotherm	Hysteresis from 0.8 to 1 P/P_0	Hysteresis from 0.4 to 1 P/P_0
Pore volume (mL/g)	0.15	0.34
Pore size distribution	Little porosity, peak at 31.5 nm	Heterogeneous, peak at 3.5 nm Mesopores ~5.6 nm
Light absorptive characteristics	Peak at about 250 nm	Peak at about 310 nm
Phase transformation by milling	Fast to rutile only (in 12 h)	Slow, 30% brookite/anatase, 100 h
Particle size in water (μm)	0.7–10 (70%), 50–100 (10%); 5	0.3–6 (25%), 30–110 (65%); 60

This study is focused on the comparison of the photocatalytic activity of two different catalysts, Degussa P25 and Hombikat UV100, by measuring the degradation of dimethylsulfoxide (DMSO), which is used as the test-substance. Dimethylsulfoxide is a chemical compound with the formula $(\text{CH}_3)_2\text{SO}$. It is a colorless liquid and an important polar aprotic solvent that dissolves both polar and non-polar compounds, and is miscible in a wide range of organic solvents as well as water [9]. This solvent is a hydroxyl radical scavenging agent, which can interact with $\cdot\text{OH}$ ($k = 7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) [10]. The reason may be the easy access of the hydroxyl radical into the sulfoxides [11]. This skill has been profited by Tai et al. [12] to determine the generation of hydroxyl radicals in advanced oxidation processes.

The kinetics of the reaction of DMSO with $\cdot\text{OH}$ in the gaseous phase has been widely studied, since DMSO is a product of the photo-oxidation of dimethylsulfide [13,14]. Analogously, there are some studies of the reaction of DMSO with the hydroxyl radical in the aqueous phase [15–17], in which some intermediates generated through this reaction were proposed: methanesulfinic acid (MSI), methanesulfonic acid (MSA), formaldehyde and methane. Other authors [18] have focused on the kinetics of DMSO when it is degraded by means of advanced oxidation processes (i.e. $\text{Fe}^{2+}/\text{H}_2\text{O}_2$). Lee et al. [19] proposed a degradation pathway of this compound during the UV/ H_2O_2 treatment, being the final products of this reaction CO_2 and the sulfate anion.

In this way, the originality of this work lies in the use of DMSO as a new test-substance, because DMSO will be the model compound that will be used in the ISO standard (ISO/CD 10676) for the determination of the photocatalytic efficiency of systems to be used for water treatment. Since there is not a great deal of knowledge concerning the photocatalytic degradation of DMSO it is of utmost importance to generate more reliable data in this field, being this one of the objectives of this paper. It is reported the monitoring of two of the main intermediates of DMSO throughout its photocatalytic degradation: the methanesulfonate (CH_3SO_3^-) and the sulfate (SO_4^{2-}) by means of the ion chromatography technique, in order to develop a quality-test method to evaluate different photocatalytic materials. As mentioned, the study will be carried out both with Degussa P25 and Hombikat UV100. Finally, kinetic studies have been made, using the TOC values in order to calculate kinetic constants, to compare the reactions with the different catalysts.

2. Materials and methods

2.1. Chemicals

All reagents used in these experiments were of technical grade or better: KCl (Fluka >99.5%), K_2SO_4 (Fluka >99.0%), CH_3SOCH_3

(Riedel-de Haen, min. 99.5%), $\text{CH}_3\text{SO}_3\text{H}$ (Sigma–Aldrich, >99.5%), $\text{CH}_3\text{SO}_2\text{Na}$ (Sigma–Aldrich, 85%), HCOOH (Merck, 98–100%), Na_2CO_3 (Merck, min. 99.5%) and NaHCO_3 (Merck, min. 99.5%). The water used was Millipore ($18 \text{ M}\Omega \text{ cm}^{-1}$). The catalysts employed for the study were TiO_2 Degussa P25 and Hombikat UV100, being their main properties and characteristics summarized in Table 1.

2.2. Analytical methods

The methanesulfonate and the sulfate anions were measured by means of an ion chromatograph (ICS 1000, DIONEX) equipped with an automated autosampler (AS40, DIONEX). The column was a Dionex Ion Pac As9–HC (2 mm \times 250 mm). The mobile phase was a mixture of NaHCO_3 ($1.5 \times 10^{-3} \text{ M}$) and Na_2CO_3 ($8 \times 10^{-3} \text{ M}$). The flow rate was 0.3 mL min^{-1} . The TOC was determined with a total organic carbon analyzer (TOC-5000, SHIMADZU). The DMSO spectrum was analyzed in a UV-visible spectrophotometer (Cary 100 Bio, VARIAN). In order to measure the pH, a 691 Metronohm pH meter was used.

2.3. Degradation experiments

The experimental set-up was formed by a 500 mL cylindrical quartz reactor (182 mm \times 80 mm). The reactor is placed under the Solar Simulator Philips HB 541 solar simulator, equipped with 8 lamps (1000 W). The solution is being continuously stirred by a magnetic stirrer (Ikamag Reg).

2.3.1. Experimental procedure

The compound chosen to perform the evaluation of the different catalysts is the dimethylsulfoxide (DMSO). Solutions of different concentrations (0.25–1.0 mM) were prepared in 0.5 L volumetric flasks. The volumetric flask is covered to avoid any loss due to volatility. The catalysts are used in the same way in which they are supplied by the manufacturer. The amount needed for the experiment is weighed in a scale, using a rectangular-shaped plastic, specially made to handle these types of materials. 500 mL of DMSO solution together with the catalyst were added to the reactor. This suspension was then stirred in the dark for 30 min, in order to reach the equilibrium concentration of DMSO. Once the solution has been stirred for 30 min, the reactor is placed under the Solar Simulator.

Sample withdrawal is made through an entrance located in the cap of the reactor. The withdrawal is carried out by means of a syringe, and 10 mL per sample are taken. This volume is then centrifuged for 30 min, in order to separate the catalyst from the solution. The collected solution is then poured into two vials, one to be used for the ion chromatography and the other for the total organic carbon (TOC) analysis. Afterwards, 10 mL of sample are

Table 2
Comparison of the results obtained with Degussa P25 (A) and Hombikat UV100 (B) in terms of generation of methansulfonate and its corresponding photonic efficiency (ξ_{MSA}), generation of sulfate and its corresponding photonic efficiency (ξ_{SA}) and percentage of TOC removal in each case.

	Cat	[Cat] (g L ⁻¹)	MSA _{max} ^a (μM)	MSA _{end} ^b (μM)	ξ_{MSA} (mol Einstein ⁻¹)	SA _{max} ^a (μM)	SA _{end} ^b (μM)	ξ_{SA} (mol Einstein ⁻¹)	% TOC _{end} (mg CL ⁻¹)
1	A	0.4	426	202	0.278	234	234	0.015	73
2	A	1.0	381	205	0.240	177	177	0.013	55
3	A	1.6	395	233	0.234	136	136	0.011	34
4	B	0.4	150	140	0.034	40	40	0.008	24
5	B	1.0	244	220	0.067	37	37	0.010	31
6	B	1.6	257	241	0.089	25	25	0.011	48

^a Maximum generation.

^b Generation at the end of the experiment.

Table 3
Comparison of the results obtained with Degussa P25 (A) and Hombikat UV100 (B) (1 g L⁻¹) in terms of generation of methansulfonate and ξ_{MSA} , generation of sulfate and ξ_{SA} , and percentage of TOC removal in each case.

	DMSO ₀ (mM)	Cat	MSA _{max} ^a (μM)	MSA _{end} ^b (μM)	ξ_{MSA} (mol Einstein ⁻¹)	SA _{max} ^a (μM)	SA _{end} ^b (μM)	ξ_{SA} (mol Einstein ⁻¹)	% TOC _{end} (mg CL ⁻¹)
1	0.25	A	179	20	0.121	179	179	0.014	88
2	0.50	A	381	205	0.240	177	177	0.013	55
3	1.00	A	916	838	0.296	92	92	0.011	48
4	0.25	B	160	137	0.083	28	28	0.011	45
5	0.50	B	244	220	0.067	37	37	0.010	31
6	1.00	B	607	607	0.130	22	22	0.010	14

^a Maximum generation.

^b Generation at the end of the experiment.

taken to measure the pH (691 Metronohm pH), along the process. Once the pH has been measured the sample is taken back to the tank. The experiments are all made at room temperature, being the deviation of this variable along the reaction lower than 2 °C.

2.3.2. Evaluation of the incoming radiation

With the value of the power (I) entering the system (1.4 mW cm⁻²), the photonic flow emitted by a monochromatic energy source (F) can be calculated by Eq. (1):

$$F = \frac{IA}{hcN_A} \lambda \quad (1)$$

where I is the incident power on the surface of the system, A is the area through which the radiation enters the reactor (50.26 cm²), considering that the radiation enters the system exclusively through the upper side of the reactor, h is the Planck's constant (6.626×10^{-34} J s), c is the speed of light (3×10^8 m s⁻¹), N_A is the Avogadro's number (6.023×10^{23}) and $\lambda = 350$ nm.

The resulting photon flow (F) is 2.058×10^{-5} Einstein s⁻¹, with which the corresponding apparent photonic efficiencies for every experiment have been calculated (see Tables 2 and 3). The apparent photonic efficiency is defined as the ratio of the photogenerated reaction rate at initial conditions, to the rate of incident photons:

$$\xi = \frac{R}{F} \quad (2)$$

where R is the initial reaction rate (mols⁻¹) of the photogenerated species, and F is the incident photonic flow (2.058×10^{-5} Einstein s⁻¹). The resulting photonic efficiency will be in mol Einstein⁻¹.

3. Results and discussion

3.1. Detection of the intermediates by ion chromatography

High performance ion chromatography was used as the analytical technique to detect the different compounds generated during the photocatalytic degradation of DMSO. Although the main compound, DMSO, could not be monitored using this technique (under the conditions employed in this study), two different anions were found: methansulfonate (MSA⁻) (Rt=4.5 min) and sulfate (SA⁻)

(Rt= 18 min). The appearance of these anions in the solution can also be justified by the decrease of the pH along the reaction, which was also monitored. The drop of the pH at the end of the experiments was around 0.5–1.0 units.

The photocatalytic degradation of DMSO is expected to be due to the attack of the hydroxyl radical to the molecule, resulting in the progressive mineralization of DMSO, highlighted by the decay of TOC in the solution. Fig. 1 shows the degradation of a solution of DMSO during the time in terms of MSA⁻ and SA⁻ generation and TOC reduction.

Surprisingly, no presence of methansulfinate (CH₃SO₂⁻) was detected in any of the samples. As reported previously by Veltwisch et al. [11], the general reaction for sulfoxides with the hydroxyl would be the following:



Hence, the formation of methanesulfinic acid (MSI) would be expected throughout the reaction of DMSO and the radicals •OH, before the generation of methanesulfonic acid (MSA). In order to elucidate why this substance was not generated during the reaction, an experiment was made, in which methansulfinate (MSI⁻) was photo-degraded with P25. Fig. 2 shows the results obtained

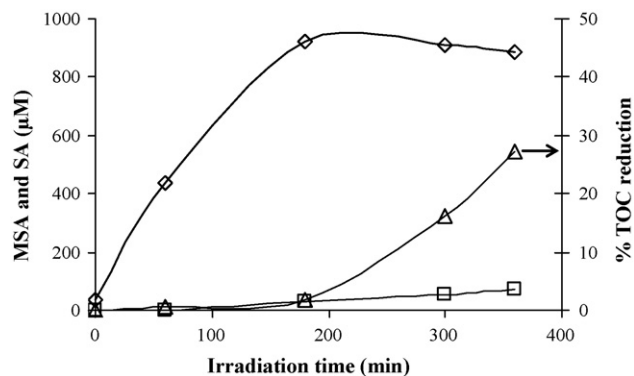


Fig. 1. Generation of methansulfonate and sulfate and % TOC reduction (DMSO=1 mM, P25=0.4 g L⁻¹, irradiation time=6 h and volume=500 mL). MSA⁻ (◇), SA⁻ (□), % TOC reduction (△).

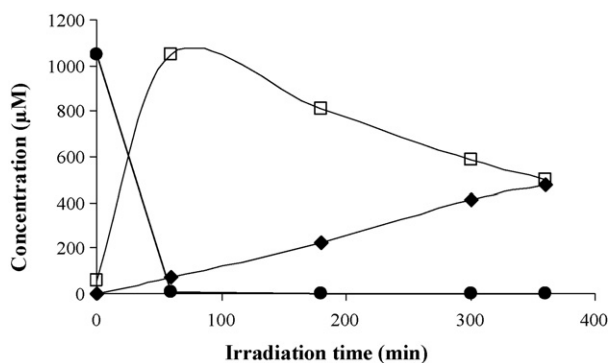


Fig. 2. Evolution of the photocatalytic degradation of MSI^- with DP25 ($[\text{MSI}]_0 = 1 \text{ mM}$, pH free, catalyst = 0.4 g L^{-1} , volume = 500 mL and reaction time = 6 h). MSI^- (●), MSA^- (□), SA^- (◆).

for this experiment, in terms of MSA^- and SA^- formation, from the photodegradation of MSI^- .

The experiment was running at free pH, being the initial pH of this experiment 3.20. As it can be observed, the experiment begins with negligible amounts of MSA^- in the solution, and the maximum generation of this species is reached within the first hour of reaction, which could indicate the fact that MSI^- is transformed entirely into MSA^- very fast. The generation of SA^- follows a gradual and linear increase during the time, not reaching the maximum value after 6 h.

The fact that MSI^- is entirely transformed into MSA^- within the first hour of reaction could explain why MSI^- was not present in the first sample of each experiment (taken after 1 h), because it is very susceptible to be oxidized and it immediately disappears. Bardouki et al. [16] studied the reaction of MSI^- (0.7 mM) with hydroxyl radicals (obtained from the H_2O_2 photolysis), and they found that MSA^- was the major end product of the reaction, with a yield close to unity. Russell and Scaduto [17] found that MSI^- in incubations with hydroxyl radicals' generation led to stoichiometric production of MSA^- . Other authors [20] concluded that MSI^- reacts very fast with the radical ($k = 6.2\text{--}12 \times 10^9 \text{ mol L}^{-1} \text{ s}^{-1}$). These results stress the fact that MSI^- may be only an intermediate in the reaction of DMSO with $\bullet\text{OH}$, through which it would lead to the formation of MSA^- , and subsequently SA^- .

Formaldehyde is other intermediate prone to be generated during the reaction of DMSO with $\bullet\text{OH}$ [10,19], but unfortunately it could not be detected in the HPLC, under the conditions employed for the study.

3.2. Influence of the amount of catalyst

Before tackling the comparison of the photoactivity of both catalysts, it would be interesting to differentiate Degussa P25 and Hombikat UV100, according to their physical properties.

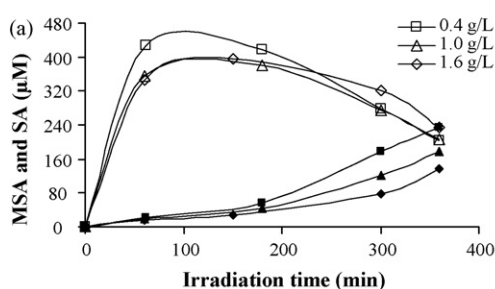


Table 1 summarizes the main characteristics of these photocatalysts according to some authors [21]. The major difference between these catalysts is that Degussa P25 consists of a mixture of anatase and rutile (70/30% or 80/20%), and Hombikat UV100 is exclusively anatase, besides the surface area, which is four to five times higher in the case of Hombikat UV100.

Firstly, the degradation experiments were focused on the effect of the amount of catalyst on the process. The amount of catalyst was changed, while the others parameters remained constant (initial concentration of DMSO, pH and volume). The interval of catalyst amounts was: $0.4\text{--}1.6 \text{ gTiO}_2 \text{ L}^{-1}$. The summary of these experimental results are presented in **Table 2**.

The comparison of the photocatalytic degradation with DP25 and HUV100 are depicted in **Fig. 3**, in terms of production of MSA^- and SA^- , during 6 h of reaction.

As it can be observed in **Fig. 3(a)**, MSA^- concentration increases at the beginning and reaches a maximum corresponding to the 85% of the releasable stoichiometric amount in the case of $0.4 \text{ g DP25 L}^{-1}$, and almost 80% in the other two cases. From this maximum, the amount of MSA^- decreases, due to the generation of other intermediates from its degradation.

It seems that the same amount of MSA^- is generated in the cases of 1.0 and $1.6 \text{ g DP25 L}^{-1}$, being the maximum of the generated MSA^- slightly higher for a catalyst concentration of 0.4 g L^{-1} . This fact could point out that the adsorption of the different species present in the solution is more noticeable when the catalyst concentration is higher than 0.4 g L^{-1} . It could be also explained by considering that scattering or competition for the photons between the particles of the catalyst grows when the catalyst concentration does it, avoiding the increase of the photodegradation of DMSO.

With regards to the generation of SA^- , it needs more time to increase, since the source of SA^- may be merely the degradation of MSA^- . Surprisingly, the amount of SA^- decreases when the amount of catalyst increases (see **Fig. 3(a)**). In the most favorable case ($0.4 \text{ g DP25 L}^{-1}$), the generated SA^- does not reach the 55% of the stoichiometric maximum releasable from the degradation of MSA^- .

The adsorption of SA^- on the surface of the catalyst could be an explanation, under the conditions employed for the study, since the pH range of the whole experiment is lower than 4.5, where the TiO_2 is positively charged, and so there would be attraction between the surface of the catalyst and the anion, which would cause the extinction of the sulfate anion to some degree.

On the other hand, the low SA^- generation yields observed for both catalysts might be due to the fact that sulfate ions, as inorganic ions, can inhibit the photodegradation in two ways: competitive adsorption with DMSO on TiO_2 surface and trapping positive holes (h^+) and hydroxyl radicals ($\bullet\text{OH}$), through reactions (4) and (5) [22].

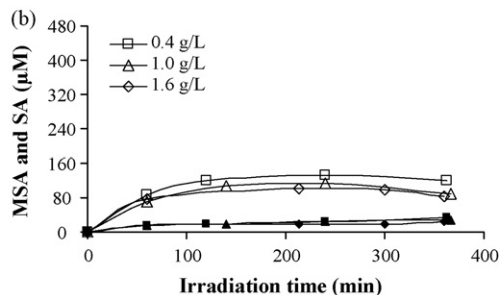


Fig. 3. Methansulfonate generation and sulfate generation for different amounts of DP25 (a) and HUV100 (b) (DMSO = 0.5 mM , pH = free, irradiation time = 6 h and volume = 500 mL). MSA^- (empty symbols), SA^- (full symbols).

Thus, reactions (4) and (5) would lead to the extinction of this species (SA^-) in the solution, acting as a hydroxyl scavenger. This fact would explain the low yields of SA^- generation observed for DP25 and HUV100. If DP25 exhibits a high photoactivity (see Figs. 3(a) and 4(b)), the generation of hydroxyl radicals would also be high, and the reactions above explained would be more favored with a higher concentration of TiO_2 .

Mori et al. [8], who worked with coated TiO_2 material, obtained similar results than those obtained in the present work with TiO_2 in suspension, when monitoring the concentration of MSA^- and SA^- along the photocatalytic experiment: the MSA^- reaction rate is very high and it reaches the maximum relatively fast. On the contrary, the SA^- reaction rate is almost negligible within the first stages of the reaction, and then it starts increasing gradually, reaching the maximum concentration at the last stage of the experiment. In the mentioned study, it can be seen that the slow SA^- reaction rate is a consequence of the behavior of both MSI^- and MSA^- . SA^- does not start to be present in the solution till MSI^- is totally degraded as a consequence of the photocatalytic reaction, and the gradually increase of SA^- starts when the MSA^- is slowly decreasing.

Analogously to the experiments carried out with the catalyst DP25, the amount of Hombikat UV100 was varied, while the other parameters remained constant ($DMSO_0$, pH and volume). The interval was the same than with DP25: 0.4–1.6 g HUV100 L^{-1} . Results are depicted in Fig. 3(b). In this case, the best values of MSA^- generation (see Table 2) were obtained for the highest amount of catalyst (1.6 g HUV100 L^{-1}), contrary to what happened with DP25. The maximum percentage of MSA^- generated is only the 52% of the releasable stoichiometric amount in the most favorable case (1.6 g HUV100 L^{-1}).

On the other hand, the values of SA^- generation can be considered to remain constant with the different amounts of HUV100 in solution, reaching only the 8% of the stoichiometric amount of the possible releasable from the maximum MSA^- generated, at conditions of 0.4 g HUV100 L^{-1} .

Photonic efficiencies (ξ , mol Einstein $^{-1}$) have also been calculated and they are likewise presented in Table 2. The photonic efficiency has been calculated in all cases as the initial reaction rate of the photogenerated moles of the compound to the rate of the radiation entering the system (Eq. (2)). As it can be seen, the tendencies of all evaluated parameters: ξ_{MSA^-} , ξ_{SA^-} , and TOC removal for both catalysts (experiments 1–3 and 4–6) are opposite: whereas these parameters decrease with the amount of DP25-catalyst, those belonging to Hombikat UV100 increase with the concentration of catalyst.

The reason could be the kind of aggregates formed in each case, which could either favor or avoid the scattering phenomena in the solution: Degussa P25 is composed of loose aggregates of TiO_2 , whereas Hombikat UV100 particles are highly agglomerated TiO_2 , which could avoid interferences of the particles of the catalyst with each other in the solution, hence the scattering phenomena would be minimized. Degussa P25 TiO_2 suspension may be thus more opaque than Hombikat UV100, under the employed conditions [23]. In agreement with this hypothesis, Table 1 shows the different particle size of both catalysts: Degussa P25 has a particle size lower than 10 μm and Hombikat UV100 has a particle size of 20–30 μm . This fact would imply a different sensitivity of these two titania powders to the incident light intensity: In case of Degussa P25 particles, radiation would reach more easily the first layer of the particles, being the other layers covered by the particles located in layers above them, i.e. a large part of the particles are not being excited by the photons. On the contrary, the catalyst Hombikat UV100 would form fewer but larger particles in aqueous medium, because it is highly agglomerated. The radiation can reach relatively easier the lower layers because solutions of Hom-

bikat UV100 are less opaque than the other with DP25, i.e. there is more distance between the particles of the catalyst.

The work presented by Colón et al. [24] also states the different characteristics of both catalysts: Degussa P25 has a wrinkled surface, and Hombikat UV100 particles are spherical, formed by small subparticles highly agglomerated, which makes the global surface area higher than that of DP25 (as it can be seen in Table 1).

The higher size of these agglomerates in solution could explain why the scattering influences more when working with Degussa P25. Vione et al. [25] compared the degradation of two substances by means of Degussa P25 and TiO_2 Wackherr, coming to similar conclusions. Thus, phenol degradation in the presence of TiO_2 “Wackherr” continues to increase with increasing photocatalyst loading, and the authors attributed this fact to the lower radiation scattering in the UV region of this catalyst, because it has got a higher particle size than Degussa P25.

Finally, it must be remarked that the photonic efficiencies corresponding to the catalyst Degussa P25 are much better than those of Hombikat UV100, due to the higher generation yield of the evaluated species coming from the degradation of DMSO. It seems that Degussa P25 has a higher photoactivity, despite the more abundant scattering phenomena occurring with this catalyst.

There are several theories that explain why Degussa P25 exhibits a higher photoactivity than other photocatalysts. Some authors [26,27] attribute this property to the slow recombination electron/hole taking place on the surface of P25, different from other photocatalysts like UV100. Other authors [28] explain its higher activity because of its structure formed by a mix of the phases anatase and rutile, being the activity of the latter greater than the activities of the pure crystalline phases. Any of the mentioned reasons would explain the higher photogeneration of MSA^- and SA^- obtained by Degussa P25.

On the contrary, the photonic efficiencies of HUV100 are lower but they can still grow up with the increasing loaded catalyst in the solution, because, as already explained above, the scattering phenomena are lower than with DP25. However, the ranking of catalysts will depend on the test molecule as well: e.g., in case of dichloroacetic acid (DCA), Hombikat UV100 yields significantly higher photonic efficiencies [29]. In this way, as pointed out in Section 1, one of the purposes of this work is to explore the ability of DMSO in the discerning of the efficiency of different photocatalysts, because DMSO will be used in the ISO/CD 10676 for the determination of the photocatalytic efficiency of systems to be used for water treatment. Thus, according to the results obtained in this section, DMSO can be useful for these purposes and can aid to unify the parameters used for photocatalysts comparison.

3.3. Influence of the initial concentration of DMSO

A group of experiments were made, in which the initial concentration of DMSO was varied, and the rest of parameters remained constant. Fig. 4 depicts the results obtained in MSA^- and SA^- generation for the following DMSO initial concentrations: 0.25, 0.5 and 1 mM.

As expected, the generation of the different species coming from the degradation of the target compound increases as long as the concentration of DMSO is higher, except for the sulfate ion in the case of Degussa P25, which undergoes a slightly decrease with $[DMSO]_0$.

In Fig. 4(a), it can be observed that, when DMSO concentration is 1 mM, the reached amount of MSA^- is 91% of the stoichiometric amount releasable from the degradation of DMSO. The most remarkable aspect is the large amount of MSA^- obtained at the highest DMSO concentration, because this is not conveyed in a higher generation of SA^- . On the contrary, the SA^- generation seems

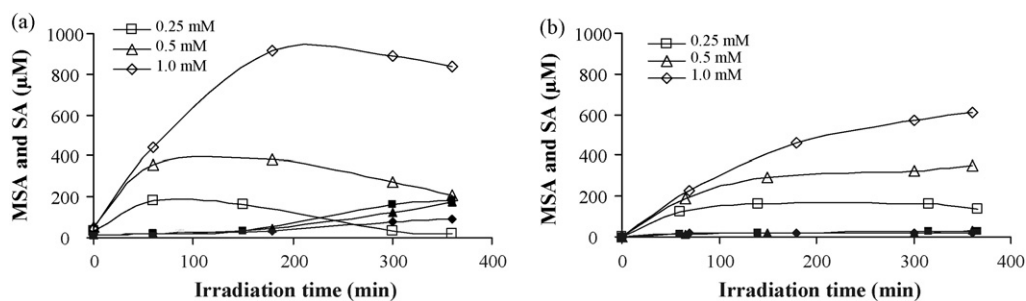


Fig. 4. Methansulfonate and sulfate generation for different amounts of initial concentration of DMSO. DP25 (a) and HUV100 (b) (catalyst = 1.0 g L^{-1} , pH = free, irradiation time = 6 h, volume = 500 mL). MSA⁻ (empty symbols), SA⁻ (full symbols).

to be independent on the initial concentration of DMSO, during the 6 h of reaction.

Fig. 4(b) will be used to explain how the variation of the initial concentration of DMSO can influence the process, when working with Hombikat UV100. The stoichiometric amounts of the generated MSA⁻ are around 64 and 69%, when the initial concentration of DMSO is 0.25 and 0.5 mM, respectively. This percentage decreases slightly to 60% when the initial concentration of DMSO is 1.0 mM, probably due to the presence of more intermediates in the solution generated from the degradation of MSA⁻. A maximum of MSA⁻ is hardly reached at the end of the experiment, after 6 h of irradiation. SA⁻ generation seems to be very inefficient in terms of the percentage of SA⁻ obtained from the maximum MSA⁻ yielded in the reaction (considering that MSA⁻ is the only source of this substance).

As expected, the TOC reduction (see Table 3) for both catalysts has a descendent tendency as long as DMSO₀ becomes higher, due to the increase of the amount of the intermediates present in the solution, since more time is needed to mineralize the molecules in solution.

The photonic efficiencies obtained in case of MSA⁻ are 1.5–3.5 times higher when working with DP25. In this case, the parameter ξ_{MSA} is clearly enhanced when DMSO₀ increases. It is not so clear with Hombikat UV100, although it could be concluded that the overall tendency is ascendant. This must be due to the higher generation of MSA⁻ when the source of this compound (DMSO) also rises.

The most outstanding fact is that the photonic efficiencies of SA⁻ with DP25 have a slightly descendant tendency, being in the case of HUV100 almost constant for the different DMSO concentrations. As already explained, the low yield of SA⁻ generation might be the reaction of this species with the hydroxyl radicals present in the medium (Eqs. (4) and (5)). Nevertheless, there are other intermediates arising from the photodegradation of DMSO (methansulfinate acid, formaldehyde, etc.), which may hinder the generation of sulfate ions by reacting either with the hydroxyl radicals present in the medium, or with the MSA and/or MSI, giving

rise to other intermediate. This fact implies that the monitoring of SA⁻ as a tool to evaluate different photocatalysts is not reliable by itself.

3.4. Comparison of the kinetics between Degussa P25 and Hombikat UV100

As previously mentioned, the HPLC technique was useful to measure the amounts of MSA⁻ and SA⁻ generated during the process, but unfortunately, the values of DMSO during the experimental time could not be analyzed under those conditions. This fact limited the approach to a wide range of kinetic models, e.g. the globally used Langmuir–Hinshelwood model, which can normally fit the experimental data of most photocatalytic reactions. Instead of this, a simple zero-order model has been proposed, that could fit the kinetics for the reactions occurring with DP25 and HUV100 (Eq. (6)):

$$C = C_0 - kt \quad (6)$$

where C is the concentration of TOC inside the reactor, C_0 is the initial concentration of TOC, k is the apparent kinetic constant and t is the time. Radiation effects are included in the apparent kinetic constants. Since all factors that may affect the radiation (geometry, lamp spectrum, location of the reactor in the simulator, etc.) have been kept constant along all experiments, it can be assumed that radiation affected in the same way all the experimental data. Fig. 5 shows how the data fit the zero-order model, for a given amount of catalyst of 1.0 g L^{-1} .

The first stretch of the curve formed by the data of DP25 fits relatively well to a zero-order kinetic, but as long as the reaction time increases, the curve formed by the experimental data becomes more exponential and thus the data do not fit the model. Regarding the experiments carried out with the catalyst HUV100, they fit better the zero-order equation, and the curve of experimental data does not become exponential during the time of the experiment.

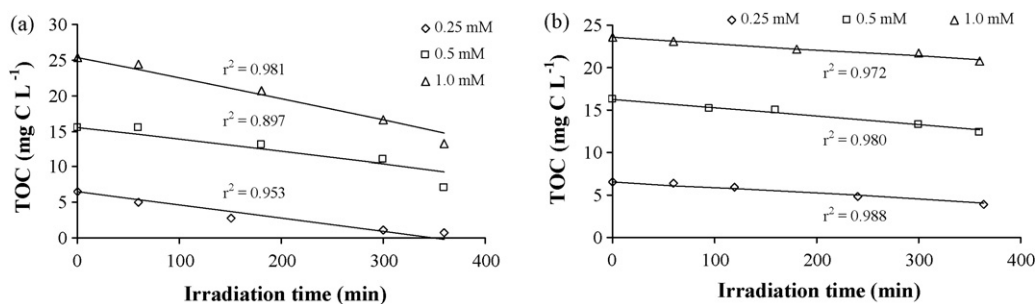


Fig. 5. Fitting of the experimental data to the zero-order kinetic model: (a) DP25 and (b) HUV100 (catalyst = 1.0 g L^{-1} , V = 500 mL, irradiation time = 6 h, pH = free).

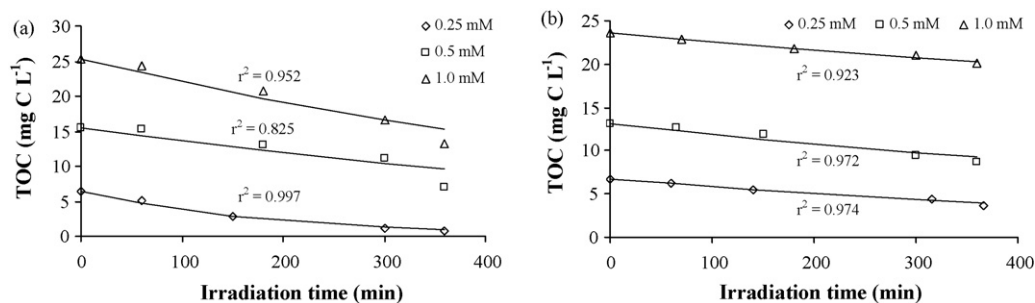


Fig. 6. Fitting of the experimental data to the first-order kinetic model: (a) DP25 and (b) HUV100 (catalyst = 1.0 g L⁻¹, V = 500 mL, irradiation time = 6 h, pH = free).

Table 4

Comparison of the different kinetic constants for the zero-order and first-order kinetics model.

	DMSO ₀	Degussa P25 ^a	Hombikat UV100 ^a
Zero-order (mg m ⁻² min ⁻¹)	0.25	7.41 × 10 ⁻⁴	6.37 × 10 ⁻⁵
	0.5	6.81 × 10 ⁻⁴	8.83 × 10 ⁻⁵
	1.0	11.81 × 10 ⁻⁴	7.40 × 10 ⁻⁵
First-order (min ⁻¹ m ⁻²)	0.25	21.4 × 10 ⁻⁵	11.52 × 10 ⁻⁶
	0.5	5.26 × 10 ⁻⁵	7.68 × 10 ⁻⁶
	1.0	5.64 × 10 ⁻⁵	3.33 × 10 ⁻⁶

^a Considered SSA values: 50 m² g⁻¹ (P25) and 250 m² g⁻¹ (UV100) [21].

A first-order model could also be applied to both reactions, whose mathematical expression would correspond to Eq. (7).

$$C = C_0 \exp(-kt) \quad (7)$$

Experimental data obtained with HUV100 and DP25 together with the theoretical data are shown in Fig. 6.

The experimental data corresponding to initial concentrations higher than 0.5 mM do not fit the model. On the contrary, improvements are obtained with the series belonging to [DMSO]₀ = 0.25 mM for both catalysts, although only Degussa P25 has a good correlation factor. It must be taken into account that the studied kinetic equations consider the concentration of all the organic molecules present in the solution, since the parameter employed is the TOC. In order to have a better fitting, it would be necessary to have the data of the concentration of every species formed during the reaction, however, in order to evaluate both kinetic models, a new kinetic constant (*K*) has been calculated (Eq. (8)).

$$K = \frac{k}{C_p \text{SSA}} \quad (8)$$

where *k* is the apparent kinetic constant, SSA is the specific surface area (BET), in m² g⁻¹ and C_p is the amount of catalyst in g L⁻¹. Table 4 shows the values of this kinetic constant for all reactions taken into account in both kinetic models.

From the results of Table 4, again DMSO shows a good sensibility in the discerning of photocatalysts efficiencies and its goodness as a new test-substance. Regarding the variation of the kinetic constants, the most stable one can be found in the case of zero-order equation with HUV100, because the kinetic constants seem to be less dependent on the variations of the initial concentration of DMSO. All cases show much higher values of this kinetic constant when working with DP25, around 10 times higher than those belonging to HUV100 catalyst, which is explained by the higher activity in the surface of the particles of Degussa P25. This catalyst seems to have the best values of the apparent kinetic constants also in case of the zero-order model (with the first-order one there is a sharp increase when [DMSO]₀ < 0.5 mM).

4. Conclusions

The comparison of the photocatalytic efficiencies of Degussa P25 and Hombikat UV100 has been made by using DMSO. Reliable data have been obtained confirming the goodness of DMSO for photocatalysts comparison, in order to be employed as an ISO standard in water media systems. In general, the catalyst Degussa P25 can yield higher photonic efficiencies for the generation of MSA and SA than Hombikat UV100. The differences detected between the two tested catalysts are probably due to the kind of aggregates formed in each case: Degussa P25 is composed of loose aggregates of TiO₂, whereas Hombikat UV100 particles are highly agglomerated TiO₂, giving rise to less opaque solutions where the scattering phenomena are minimized. Besides this reason, it should be taken into consideration the slower recombination rate of electron/hole pairs of Degussa P25, which causes higher efficiencies when working with this catalyst. On the other hand, the low yields of SA generation in both cases can be attributed to the reaction of the sulfate ions with the hydroxyl radicals, which may act as scavengers in solution. With regards to the kinetic equation, HUV100 seems to fit well the zero and the first-order equations. DP25 fit slightly better the first-order equation, due to the more exponential shape of the curves obtained with this catalyst. When comparing the kinetic constants, the conclusion is that the best fitting takes place in the case of the zero-order model applied to the catalyst HUV100.

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