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Study of the wavelength effect in the photolysis and heterogeneous photocatalysis

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Abstract

In this work, photocatalytic and photolytic degradation of two model pollutants has been done. The chosen substances were 2,4-dichlorophenol (DCP) and sulfamethoxazole (SMOX), both with different absorptive properties in the UV range. The experiments were carried out under UV-A and concomitant UV-ABC radiation, studying the effect of each type of radiation on each type of degradation. Different kinetic orders were applied to the experimental series, results were fitted to the time and incident radiation. Also, the photon flow absorbed by the suspension and the quantum yield was measured for each condition tested. It was found that UV-ABC radiation can be more efficient than UV-A, although it depends also on the properties of the pollutant. It was demonstrated that the plotting of compounds degradation versus the incident UV radiation offers more accurate perspectives in establishing comparisons between different radiation sources. In this way, the conclusions are very similar to those obtained calculating the quantum yield, which is probably one of the best options to analyze a process.

Keywords: Dichlorophenol; Sulfamethoxazole; Photocatalysis; Photolysis; UV radiation; Radiation wavelength; Quantum yield

1. Introduction

Heterogeneous photocatalysis has been one of the most studied oxidation processes over the last decades, because of its efficiency in the treatment of a wide variety of pollutants in wastewaters [1–3]. In these processes, TiO_2 is the most employed catalyst. As known, electron-hole pairs can be generated in titania when it absorbs radiation with an energy level higher than the one corresponding to the band gap (3.2 eV for titania), that is, radiation with a wavelength (λ) lower than 387 nm, corresponding to the UV region of the electromagnetic spectrum (200–380 nm). On the other hand, photolysis is other phenomenon that can take place, when a solution is irradiated. The mechanism of the photolysis is based on the fact that the chemical species undergo photochemical reactions, by which molecules are broken down into smaller molecules, merely through the absorption of light.

The photon flux necessary to initiate these processes can be supplied whether by the sunlight, or by artificial lamps. There is a broad variety of artificial radiation sources when working at the laboratory: black, germicide, solar simulating lamps, etc. The most commonly used are usually high-, medium- and low-pressure mercury lamps, and xenon lamps, to generate UV radiation [4].

Photocatalytic studies are normally carried out under UV-A (320–380 nm) and UV-B (280–320 nm) radiation range [5,6], since this is the spectrum range of the solar radiation, in the UV range, arriving at the surface of the earth and photocatalysis is commonly understood as a process to be used with solar energy. In fact, the UV-C radiation emitted by the lamps mentioned above is normally cut off by filters or by the material of the photoreactor. On the contrary, very little work has been made under UV-C radiation to study the efficiency or parallel effects of photochemical reactions occurring. Chun et al. [7] studied the photocatalytic oxidation of phenol under UV light at $\lambda > 330$ nm and $\lambda > 200$ nm, and they obtained a slightly better response in the last case, both with and without catalyst. Matthews and McEvoy [8] obtained similar results, when working on the degradation of phenol and salicylic acid employing radiation of 254 and 350 nm. The considerably more effectiveness of 254 nm radiation was attributed to the shorter penetration capability of the higher energy photons, so there

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Nomenclature

A	Absorbance [−]
c	concentration of pollutant [mol/L]
DCP	2,4-dichlorophenol
F_{abs}	photonflow absorbed by the catalyst [Einstein/s]
F_0	reactor incident photonflow [Einstein/s]
f_λ	ratio of Einsteins of wavelength λ and total incident Einsteins (in the considered range)
k_r	DCP or SMOX first-order pseudokinetic constant considering incoming photonflow as independent variable [$\mathrm{Einstein}^{-1}$]
$k_\mathrm{r}^{\mathrm{TOC}}$	TOC zero order kinetic constant considering incoming photonflow as independent variable [mol/s]
k_t	DCP or SMOX first order pseudokinetic constant considering time as independent variable [s^{-1}]
$k_\mathrm{t}^{\mathrm{TOC}}$	TOC zero order kinetic constant considering time as independent variable [mol/s]
l	distance that the light travels through the material (path length) [cm]
Q	incoming photons to the reactor [Einstein] in the considered part of the spectrum
qy	quantum yield.[mol degraded/Einstein absorbed]
SMOX	sulfamethoxazole
T	Transmittance [−]
TDAB	low-pressure metal organic chemical vapor deposition titanium dioxide alumina beads
TOC	total organic carbon [ppm]
α	absorption coefficient or molar absorptivity. [L/(cm mol)]
λ	wavelength [nm]

were more electron-hole pairs available for the target compounds. Most recently, Puma and Yue [9] followed this trend and compared the effectiveness of UV-A and concomitant UV-ABC in the photocatalytic and photolytic degradation of 2-chlorophenol, obtaining a slight higher yield for the UV-ABC radiation. A similar study and results were obtained by Lee et al. [10] but using TDAB instead of TiO_2. Cao et al. [11] used different glass filters to work at 300 or 350 nm and degraded chlorfenapyr using photocatalytic and photolytic processes. Again, the 300 nm radiation demonstrated to be more efficient that the longer one. Some different results were obtained by Wong and Chu [12], who photodegraded alachlor by means of 254, 300 and 350 nm radiation, finding that the best quantum yield was obtained at 300 nm, followed by the one at 254 nm and finally 350 nm. In summary, it seems that the lower the wavelength of the radiation, the better efficiency is obtained, although some authors disagree about this point. Unfortunately, some of the studies do not consider the incident photonflow as an important parameter. When a filter is placed between the lamp and the reactor, part of the available radiation is lost, and therefore a lower degradation must be expected for the same time of irradiation. The same may occur when the lamp is changed. It is also important to control the lamp aging, since spectral energy distributions and intensities can change along the time [13]. Actually, only Puma and Yue [9] and Wong and Chu [12] take some of these facts into account to some extent, and they do not come exactly to the same conclusions. Therefore, it is not totally clear from the previous literature, if the most energetic radiation is more efficient than the less energetic one or if the results are disguised by some other considerations.

When the effectiveness of photocatalysis and photolysis are compared in the degradation of wastewaters, the former usually yields to a higher degradation rate than the latter, due to the enhancing effect of the catalyst on the use of the light. It is a subject of discussion how much the photolysis interferes in the photocatalysis process, since it is important to know the extension of the photocatalytic process to understand it [12]. A first clue about the importance of the photolysis can be obtained comparing the absorbance spectrum of the target compounds with the emission spectrum of the lamp [14]. Obviously, if the compounds can absorb light in the region of the lamp emission, both the catalyst and the molecules will compete for the photons. Nevertheless, one of the two mechanisms, either photolysis or photocatalysis, may predominate in the process. How important is the photolysis on the photocatalytic process might be deduced from the study of the reaction pathways.

The aim of the present work is to determine the importance of the photolysis in a photocatalytic process, by studying the degradation of two organic compounds, under UV radiation of $\lambda > 235$ nm (UV-ABC) and $\lambda > 300$ nm (mainly UV-A). It is also focused on the effectiveness of each type of radiation in a photocatalytic process, paying special attention to the incoming and absorbed radiation in the system. To reach these goals, photooxidation of two model compounds (2,4-diclhorophenol (DCP) and sulfamethoxazole (SMOX)) has been done. These substances can absorb light until a wavelength of 315 nm. Although both compounds absorb approximately in the same range of the UV spectrum, SMOX retains quite higher amount of radiation than DCP. Thus, it is also possible to study the effect when working in a medium more or less avid for the entering radiation.

These chemicals are also chosen because both are typical and toxic pollutants, and SMOX is in addition an emerging pollutant. DCP is a key intermediate in the synthesis of the herbicide 2,2-DT, and it is classified as a toxic, non-biodegradable compound [15] and it is usually chosen as a representative of chlorophenol's family. SMOX is an antibiotic commonly used in the treatment of urinary tract infections [16].

2. Materials and methods

2.1. Chemicals

The chemicals used in these experiments were 2,4-dichlorophenol (>98%, Merck), sulfamethoxazole (100%, Sigma), uranyl nitrate (98%, Panreac), oxalic acid (99.5%, Panreac), potassium permanganate (>99%, Panreac), acetonitrile (99.8%, isocratic grade for HPLC, Merck), ortophosphoric acid (85%, Panreac) and Millipore water (Milli-Q Millipore system with a 18 MΩ/cm resistivity). TiO_2 Degussa P25 was used as catalyst.

As commented in the Introduction section, DCP and SMOX absorb radiation in a similar range of the UV spectrum, but sulfamethoxazole absorbs quite more radiation than DCP. Fig. 1 shows both absorption spectra, and it can be observed how DCP needs about four times the concentration of SMOX to reach the same absorptivity. f_λ is the fraction of incoming light absorbed by the pollutants. It is explained in more detail in Section 2.5.

2.2. Analytical methods

The DCP and SMOX concentrations were measured by using a Waters' HPLC (photodiode array detector 996, auto sampler 717, controller 600) equipped with Millennium software. The reverse-phase column was a Tracer Extrasil ODS2. The mobile phase was a mixture of water, acetonitrile and phosphoric acid (60:40:5%) isocratically delivered by a pump at a flow rate of 1 mL/min. The wavelength of the UV absorbance detector was 287 nm for DCP and 270 nm for SMOX. The total organic carbon was measured using a TOC analyzer (Shimadzu TOC-VCSN) provided with an auto-sampler. The DCP and SMOX spectrum were determined with a Spectrophotometer (Perkin-Elmer, Lambda 20) that supplies values of absorbance versus wavelength (λ). The samples were filtered before analysis by 0.22 μm PVDF filters (Millipore).

2.3. Reactors and procedure

The experimental set-up was formed by a tubular reactor made of quartz, with a length of 26 cm and an inner diameter of 1.97 cm. This reactor was located in the axis of two parabolic mirrors in a Solar Simulator "Solarbox" from COFOMEGRA (Milan, Italy). Both mirrors ensured that all the radiation emitted by the lamp was mostly used and arrived perpendicularly to the reactor. The solution to be treated was recirculated to the reactor from a reservoir tank, the temperature of which was controlled by means of a thermostatic bath (Selecta Frigiterm S382, Abrera, Barcelona, Spain). This design allowed controlling the temperature in the whole system. The source of radiation was a Xenon lamp (PHILIPS XOP-15- OF, 1000 W), whose spectrum is very close to the solar one in the UV range. It was placed in the upper part of the Solarbox, also in the axis of the parabolic mirrors [17].

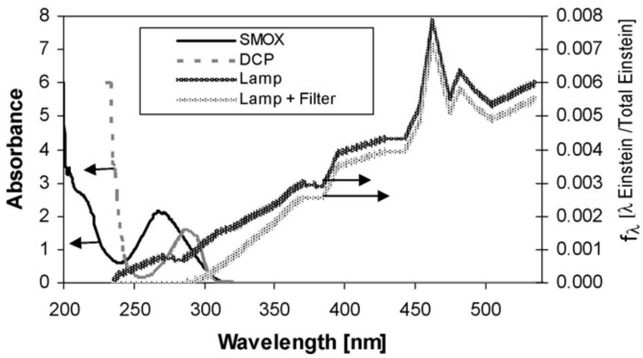

Fig. 1. Absorbance spectrum of DCP and SMOX (right axis) and lamp spectrum when the filter is placed (UV-A radiation) and without the filter (UV-ABC) (left axis). [DCP] = 120 ppm [SMOX] = 30 ppm.

Carrying out the photodegradation experiments, solutions of 2,4-dichlorophenol and sulfamethoxazole were prepared (100–120 mg/L), loaded in the reservoir tank (1 L) and circulated through the system (27.5 mL/s) in the darkness together with 0.5 g TiO_2/L to ensure that the adsorption equilibrium was achieved (after 15 min, both the 2,4-dichlorophenol and SMOX concentrations remained practically constant). Then the light was turned on and the photodegradation started. Periodic samples were taken to monitor the process. All the experiments were made at free, non-buffered pH.

2.3.1. Filters limiting spectrum of xenon lamp

The experimental set-up explained above was operated with and without limiting radiation filters. Two spectral distributions were studied:

(a) Light emission starting at 235 nm (UV-ABC), which corresponds to the experiment carried out *without any filter.*
(b) Light emission starting at 300 nm (mainly UV-A), which corresponds to the experiment carried out *with a soda-lime glass UV filter* placed in a filter support system.

Fig. 1 shows the spectral distribution of the lamp radiation either alone or using the filter.

2.4. Actinometric experiments

Actinometric experiments were performed to determine the amount of radiation emitted by the lamps and transferred into the reactors. The method is based on the well-known photochemical decomposition of oxalic acid in the presence of uranyl [18]. On basis of the available data (reactor geometry, lamp spectrum and quantum yield), the incident photon flow for the different conditions was found [19]. They are shown in Table 1.

An annular reactor was used to estimate the photonflow absorbed by the suspension in each experimental condition. The actinometric solution was placed in the outer jacket and the studied suspension was placed in the inner reactor. By difference with a blank of water, it was possible to determine the radiation absorbed both by the catalyst and the solution. This method has been explained in detail elsewhere [20]. The absorption values are also shown in Table 1.

2.5. Estimation of photonflow absorbed by the solutions

When no catalyst was loaded to the wastewater, the actinometric method was not sensitive enough to measure the photonflow absorbed by the studied pollutants with an acceptable degree of error. Therefore, to estimate the photonflow absorbed by the solutions of DCP and SMOX, it was assumed they followed Beer–Lambert's law:

$$A = -\log(T) = \alpha \times l \times c \tag{1}$$

where A is the absorbance (measured directly by the spectrophotometer), T is the transmittance, α is the absorption

Table 1
Incident and absorbed photonflow (into brackets, the % of light absorbed by the medium in the UV range), kinetic constants fitted vs. time, regression coefficient for each lineal fitting, and accumulated UV radiation and quantum yield for DCP and SMOX removal

	Radiation UV-ABC				Radiation UV-A			
	0 g TiO_2 / L + DCP sol	0.5 g TiO_2 / L + DCP sol	0 g TiO_2 / L + SMOX sol	0.5 g TiO_2 / L + SMOX sol	0 g TiO_2 / L + DCP sol	0.5 g TiO_2 / L + DCP sol.	0 g TiO_2 / L + SMOX sol	0.5 g TiO_2 / L + SMOX sol
Incident $F_0 \times 10^6$ UV [Einstein/s]	6.30	6.30	6.30	6.30	4.41	4.41	4.41	4.41
Absorbed $F_{abs} \times 10^6$ UV (f_λ)[Einstein/s]	0.61 (9.8%)	5.31 (84.4%)	2.3 (37%)	5.46 (86%)	0.05 (1.2%)	3.71 (84.2%)	0.28 (6.5%)	3.88 (88%)
$k_t \times 10^4$ [min^{-1}]	29.8	67.2	144.0	66.7	2.6	38.0	13.2	33.2
R^2	0.996	0.977	0.983	0.994	0.972	0.999	0.985	0.999
$k_t^{TOC} \times 10^7$ [mol/min]	11.6	84.4	25.3	25.4	0.5	52.0	3.5	18.5
R^2	0.928	0.997	0.984	0.935	0.999	0.999	0.990	0.950
k_r [Einstein^{-1}]	7.9	17.8	38.1	17.6	1.0	14.3	5.0	12.5
R^2	0.996	0.977	0.983	0.994	0.972	0.999	0.985	0.999
k_r^{TOC} [Einstein/mol]	3.1	22.3	6.7	6.7	0.22	19.6	1.3	7.0
R^2	0.928	0.997	0.984	0.935	0.999	0.999	0.990	0.950
qy % [mol/Einstein]	6.1	1.6	7.9	1.0	6.3	1.3	3.8	0.7
qy^{TOC} % [mol/Einstein]	3.1	2.6	1.8	0.8	1.4	2.3	2.0	0.8

coefficient or the molar absorptivity of the absorber, l is the distance that the light travels through the material (the path length) and c the concentration of pollutant.

The absorbance was measured by means of a spectrophotometer, in a 1 cm path length cuvette. Thus, the absorptivity could be calculated for each wavelength. Using the Eq. (1), the fraction of light absorbed by the pollutants (f_λ) could be estimated, in a system like the reactor employed (1.97 cm inner diameter and 125 ppm of diluted pollutant), assuming that the entire light was incoming perpendicularly to the reactor due to the collector effect. Obviously, f_λ was calculated for each wavelength by using the spectrum emitted by the xenon lamp. The amount of the incoming UV radiation (with and without filter) absorbed by DCP, was about 1.2% and 9.8%, respectively, and on the other hand, SMOX absorbs 6.5% and 37% of the incoming UV radiation with and without the filter. These values were multiplied by the incoming UV radiation flow obtaining the absorbed UV radiation F_{abs}, was calculated, as shown in Table 1.

3. Results and discussion

3.1. Degradation experiments

Fig. 2 depicts the photocatalytic and photolytic degradation of DCP when using UV-ABC and UV-A as radiation source. All the series are plotted versus time and the removal of DCP and TOC is included. The photocatalytic experiments with UV-ABC reach a higher degradation and mineralization of DCP, in agreement with most of the results found in the literature. Actually, the photocatalytic DCP degradation and the TOC removal was about 20% higher with UV-ABC than with UV-A. In case of the DCP photolysis, the observed degradation was about 60% by using UV-ABC, and about 10%, when using UV-A radiation. This value was expected since DCP does not practically absorb in this spectrum range. Finally, it is noteworthy, although it is common for UV-C wavelengths, to point out that the TOC removal using photolysis was less than 10% for both radiation types, probably due to the formation of some intermediates which cannot be photolytically degraded in this range of radiation. If both processes are compared, photocatalytic process is always much faster than the photolytic degradation of DCP. Therefore, it is obvious the interest of using photocatalysis in the treatment of this type of pollutant.

As it was previously mentioned, it is very important, when working with photocatalysis, to consider the arriving radiation at the system. When the influence of this parameter is considered, the interpretation of the experimental results can change. Thus, Fig. 3 represents the same degradation experiments shown in

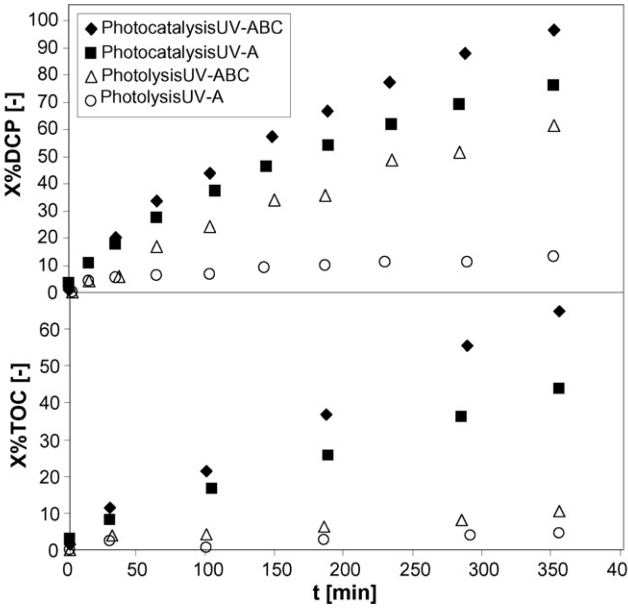

Fig. 2. DCP (upper box) and TOC (lower box) conversion vs. time, using UV-A and UV-ABC radiation in photocatalytic and photolytic experiments. Experimental conditions as detailed in Section 2.3.

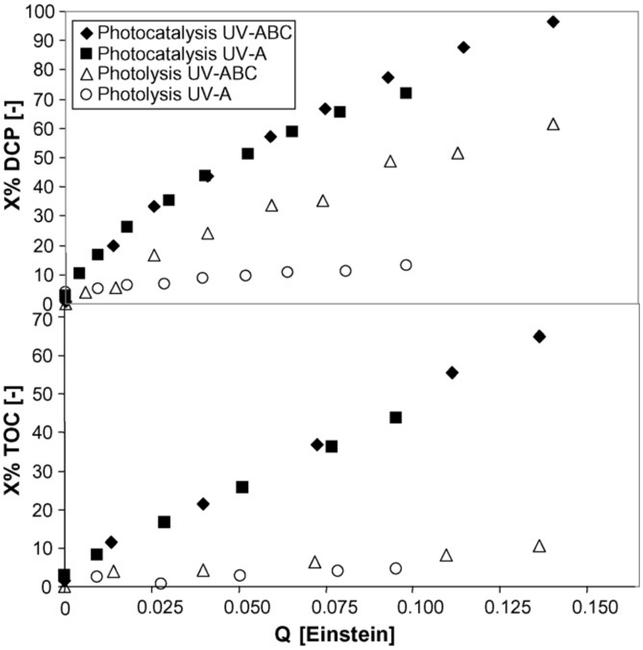

Fig. 3. DCP (upper box) and TOC conversion (lower box) vs. accumulate incoming UV radiation "Q", using UV-A and UV-ABC radiation in photocatalytic and photolytic experiments. Experimental conditions as detailed in Section 2.3.

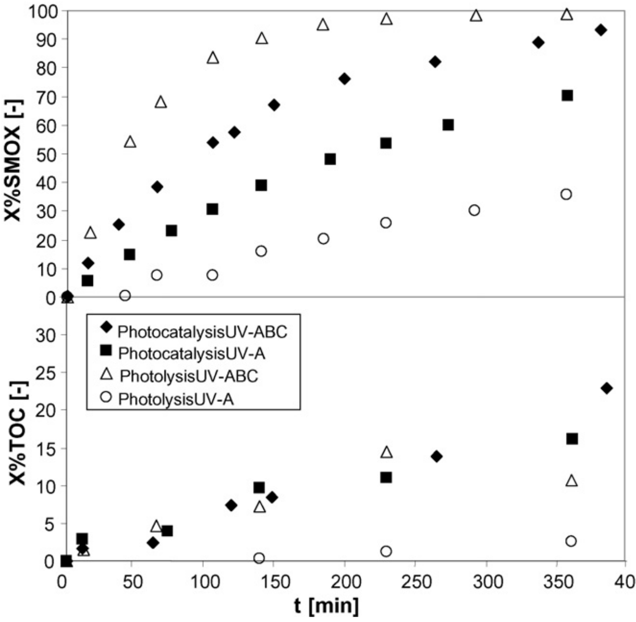

Fig. 4. SMOX (upper box) and TOC conversion (lower box) vs. time, using UV-A and UV-ABC radiation in photocatalytic and photolytic experiments. Experimental conditions as detailed in Section 2.3.

Fig. 2, but the degradation and the TOC are represented versus the accumulated incident radiation.

This parameter, as explained in the previous section, was determined by means of actinometric experiments and presented in Table 1 as "incident F_0". It is interesting to remark that only a 70% of the emitted UV radiation arrives at the system when the filter was placed. Although the value of F_0 is not actually the radiation absorbed by the TiO_2 (the useful one), it is much more accurate to represent the degradation experiments versus this variable (Q) instead of time, being the experiments compared much more precisely. In this way, Fig. 3 shows that the degradation of DCP using UV-A is much closer to that obtained when using UV-ABC, if only the incoming UV radiation is considered.

If the TOC is analyzed, the obtained results are practically the same when UV-A or UV-ABC radiation is used, for both photocatalysis and photolysis. Thus, it has been proved that the conclusions found when plotting the experiments versus time or F_0 may be different. Hence, it is important to pay attention to the amount of UV radiation arriving to the system, and it must be carefully considered when different radiation sources are employed or the photonflow is not constant (e.g. if sunlight is used).

The experiments of SMOX degradation versus time are presented in Fig. 4. All the conditions and graphics are equivalent to those shown for DCP. In these experiments, the behavior of the series is different to that found for DCP. SMOX degrades faster in the experiments without TiO_2 and with UV-ABC, and it has been completely degraded in 200 min. This agrees the fact that SMOX absorbs about four times more radiation than DCP in this part of the spectrum (see Fig. 1 and Section 2.5), being more easily photolytically degraded. Actually, photolysis is still faster than photocatalysis when UV-ABC radiation is used, probably because the catalyst absorbs an important part of the UV spectrum (so there is no much available radiation for the SMOX photolytic degradation) but photocatalysis is not so efficient as photolysis. This point will be developed later. When the filter is placed, the photolytic degradation of SMOX decreases dramatically, since a very small fraction of light may be absorbed. If the photocatalytic experiments with TiO_2 are compared, the series using concomitant UV-ABC radiation are again much faster than the series using UV-A radiation. Fig. 4 shows also that all the series of TOC mineralization present a similar trend. All the series exhibit a moderate disappearance rate and only the experiments done without catalyst and with UV-A radiation are practically zero. The rest of them are quite similar, although the photocatalytic experiment with UV-ABC radiation seems to be slightly faster than the others.

If SMOX degradation is presented versus the incoming energy Q (Fig. 5), trends do not change as clearly as in the case of DCP. Photolysis is again the fastest way to degrade SMOX with UV-ABC radiation, followed by photocatalysis with UV-ABC radiation, photocatalysis with UV-A radiation and photolysis with UV-A radiation. In spite of this fact, the differences between all the series are not so large when the experiments are plotted versus Q, as in the case of DCP series. If TOC is analyzed, all the experimental series are quite similar for all the tested conditions and only the experiments carried out without catalyst and with UV-A radiation were clearly slower. TOC mineralization was much slower than that corresponding to DCP mineralization due to the presence of some intermediates not easily attacked by the radicals or to the more complicated structure of SMOX. Therefore, SMOX mineralization requires a longer time of operation.

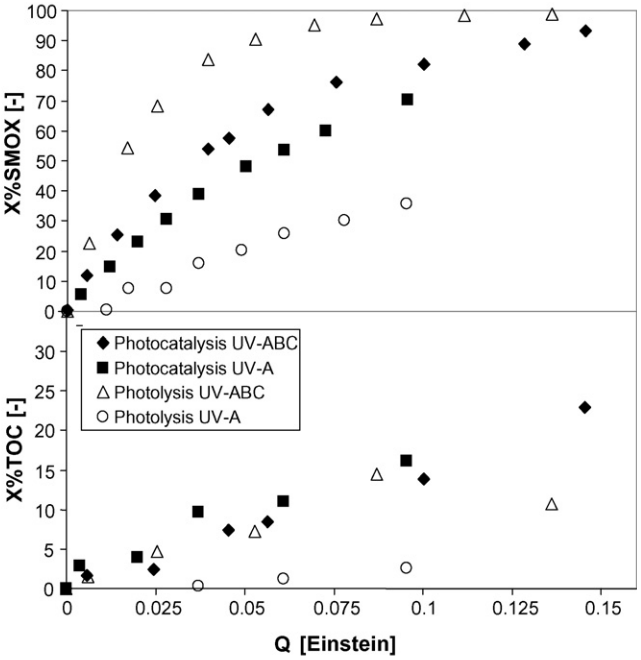

Fig. 5. SMOX (upper box) and TOC conversion (lower box) vs. accumulate incoming UV radiation "Q", using UV-A and UV-ABC radiation in photocatalytic and photolytic experiments. Experimental conditions as detailed in Section 2.3.

3.2. Kinetic fitting

For a more objective analysis, all the series were fitted to different kinetic equations. In the case of the DCP and the SMOX degradation, the experimental series were fitted to a typical first order kinetic equation:

$$r = k \times c \tag{2}$$

where r is the degradation rate of the substance, k is the pseudo-first order kinetic constant and c the pollutant concentration. The decay of SMOX and DCP versus time was fitted to the kinetic model and k_t [min^{-1}] (see Table 1) was obtained. It was also fitted to the decay versus Q, and then k_r [Einstein^{-1}] (see Table 1) was obtained.

The TOC mineralization series were fitted to a zero order kinetic model:

$$r^{\mathrm{TOC}} = k^{\mathrm{TOC}} \tag{3}$$

where r^{TOC} is the mineralization rate of TOC and k^{TOC} is the zero order kinetic constant. Analogously, the kinetic model was fitted to a decay of TOC versus time and Q. Thus, k_t^{TOC} and k_r^{TOC} were obtained for each pollutant and each type of radiation. (see Table 1). All the series fitted quite satisfactorily to the proposed equations, so the obtained kinetic constants seems to be appropriate to compare the effectiveness of all the conditions tested.

Once Figs. 2–5 have been analyzed, all the assumptions previously proposed are confirmed by the calculated values of the kinetic constants. When the kinetic constants were fitted employing time as variable, always the concomitant UV-ABC radiation proved to be faster than UV-A radiation, for both the disappearance of the target compound and the TOC. The difference can be up to 10 times higher for the photolytic k_t's of DCP. The minor differences found between UV-A and UV-ABC are for photocatalytic kinetic constants (between 1.2 and 2 times higher), but also in these ones, the use of the full spectrum leads to a best performance. In the case of the degradation of DCP, the photocatalytic kinetic constants k_t are 2 and 14 times higher than the photolytic ones when using UV-ABC and UV-A, respectively. Obviously, DCP practically does not absorb UV-A radiation, and it cannot be directly degraded. Thus, the difference regarding the photocatalysis is very important. If the behavior of SMOX is analyzed, it is found again that the kinetic constant for the photolysis with UV-ABC radiation is the highest one. It is obvious that if the light source provides UV-ABC radiation, is better to operate without catalyst because the degradation becomes less effective. However, if the radiation source is UV-A (e.g. sunlight), kinetic constants show that photocatalysis is about 2.5 times better than photolysis.

If the kinetic constants are fitted to the incident UV radiation (k_r), the difference between the constants k_r is not as significant as in the last case. As it was already seen in the plotting of the experimental data, UV-ABC radiation proves to be again more effective than UV-A, but these results are not as clearly better as the ones fitting with time. The differences between both photolytic kinetic constants k_r are still quite important, but it is only due to the fact that SMOX and DCP absorbs scarcely in the UV-A region, and the direct photolysis can hardly practically take place. On the other hand, if the photocatalytic k_r's are compared, the difference between the use of UV-A and UV-ABC is not so significant. In the case of DCP, photocatalytic k_t and k_t^{TOC} when using UV-ABC were 40% higher than when UV-A is used. Meanwhile, k_r and k_r^{TOC} were only 15% higher when using UV-ABC radiation. Something similar can be concluded analyzing the SMOX degradation kinetic constants: if the photocatalytic process is considered, the difference between the kinetic constants comes from 50 to 30%, fitting to time or radiation, respectively. Besides, the obtained photocatalytic k_r^{TOC} for SMOX removal with UV-A radiation is still slightly higher than with UV-ABC. These conclusions were quite expected because the incident radiation when the filter is placed is not the same. However, they are highlighted here since a lot of literature references present experimental data only versus time, although it would be much more accurate to consider the entering radiation, especially when different radiation sources are used. As it was mentioned in Section 1, some authors do not forget this aspect of the study. However, the importance of incident useful radiation is sometimes wrongly underestimated. It is also important not to rely only on the power data supplied by the manufacturer of the lamp, because it could not be very accurate or it could change along the time due to the aging of the lamp. Therefore, the best option is always to carry out some periodical actinometric or radiometric measurements in order to be precise in the estimation of the incident photonflow, which is a key variable of the process.

3.3. Absorbed photons flow and quantum yield

In the Sections 2.4 and 2.5 it was briefly explained the measurement of the absorbed radiation by the TiO_2. The results are presented in Table 1, showing that the SMOX and DCP suspensions practically absorb the same amount of radiation, around 85% of incident UV light and also absorb approximately the same fraction of UV-ABC and UV-A radiation. According to some authors [21,22], TiO_2 presents a maximum absorbance around 300 nm. This absorbance decreases faster for higher wavelengths than for lower ones. Hence, it would be expected that the absorbed fraction of UV-A radiation was a little bit lower than the fraction considering the entire spectrum (UV-ABC). The TiO_2 absorbance in each part of the spectrum may not be as different as it was expected or the fraction of UV-BC (about a 30% of the total UV light) is not important enough to modify the overall values.

Another fact to point out is related to the effect of solved substances in the suspension when total absorption is considered. Although SMOX absorbs almost four times more UV radiation than DCP, within the same wavelength range, it does not seem to affect the total absorption of the suspension: regardless of the characteristics of tested substances, the final amount of UV absorbed radiation was always the same. A possible explanation is the lost of a part of the incident radiation, due to the back scattering, but the fraction ‘‘entering’’ the reactor is absorbed either by the TiO_2 or by the solution. The fraction of back-scattered light would be only a consequence of the amount of TiO_2 present in the suspension since the chosen homogeneous solutions do not present a high refraction index. Therefore, for this type of compounds the amount of radiation absorbed is probably only controlled by the catalyst loaded to the system. Unfortunately, it is not possible to determine in this work which fraction of light is absorbed by the catalyst and which fraction is absorbed by the solution. However, in the next section, on the basis of the found intermediates, some predictions may be attempted. Due to the strong absorption of UV light by TiO_2, it can be expected that the catalyst absorbed most of the entering radiation.

Once the absorbed photons flow and the degradation rates are known, the quantum yield can be calculated at the different tested conditions. In the case of the degradation of DCP and SMOX, the quantum yield has been calculated as the ratio of the initial degradation rate and the photons flow absorbed by the suspensions. Initial degradation rate has been chosen since, in this period, there is no interference with the intermediates generated. Thus, the obtained quantum yield will be much more accurate because it only includes the degradation of the target compound. In the case of the TOC mineralization, since it follows a zero order kinetic and includes all the organic matter in the solution, the quantum yield has been calculated as the direct ratio of the degradation rate and the absorbed photon flow. The obtained quantum yields are shown in Table 1. Analyzing the results, it can be checked that all the quantum yields referred to photolysis are from two to eight times higher than those referred to photocatalysis. It seems than photolysis is much more efficient than photocatalysis but, unfortunately, these compounds absorbs considerably less light than TiO_2, becoming the overall photolytic degradation rate slower than the photocatalytic one.

If the effectiveness of each type of radiation is compared in the photocatalytic series, it is found that, in general, UV-ABC radiation exhibits a better quantum yield than UV-A. In spite of this, the difference of effectiveness shown by the two types of radiation was not so high as other authors reported elsewhere [7,9,11]. In the case of DCP, the photocatalytic quantum yield using concomitant UV-ABC radiation was about 20% higher than the one using UV-A. If SMOX values are examined, this difference increases up to 30%. Some authors [8,9] consider that this effect may be due to a lower recombination of electrons and holes in TiO_2 when using UV-ABC radiation, since the lower wavelengths present a minor penetration capacity. Hence, the distance to the surface is shorter and there is not so much time for the recombination.

When TOC mineralization is considered, the differences of quantum yields for each type of radiation are much lower. For DCP mineralization, the quantum yield obtained by using UV-ABC radiation is only 10% higher than that using UV-A. In the case of SMOX mineralization, there is almost no difference and both types of radiation show a similar capacity of mineralization. Obviously, TOC mineralization is a complex issue, since several compounds are present in the solution with different relations and crossed effects. It is possible to find substances which either are difficult to be removed or present a slow degradation rate and, therefore, the mineralization rate will be also slower.

The type of radiation employed seems to affect the photolytic process in a different manner. With regards to DCP degradation, a similar quantum yield was obtained by using UV-A and UV-ABC radiation. However, TOC mineralization proved to be 54% faster when UV-ABC radiation was used. The quantum yield for the SMOX degradation rate was 50% higher if UV-ABC radiation was used, but the TOC mineralization was slightly lower. Thus, type of radiation seems to affect each substance in a different way, probably depending on the degradation pathway and characteristics of the initial compound and intermediates. The generated intermediates may absorb strongly in a specific region of the spectrum, changing the measured results. Hence, general conclusions could not be established on the effect of the radiation on the photolysis, since they may be different for each substance. When it is accurately calculated, the quantum yield is a parameter generally accepted as an objective and independent way for the evaluation of efficiency of a process. It is noteworthy that the ratios of the quantum yields are much more similar to the ratios of the kinetic constants obtained by using the incident radiation than those obtained by fitting the degradation rates to time. Thus, it is confirmed again the convenience of using the incident radiation when comparisons between different processes or systems were carried out.

3.4. Analysis of the intermediates

In Fig. 6, two chromatograms of DCP and SMOX degradation are shown. The chromatograms correspond to the photocatalytic experiments when using UV-A and UV-ABC

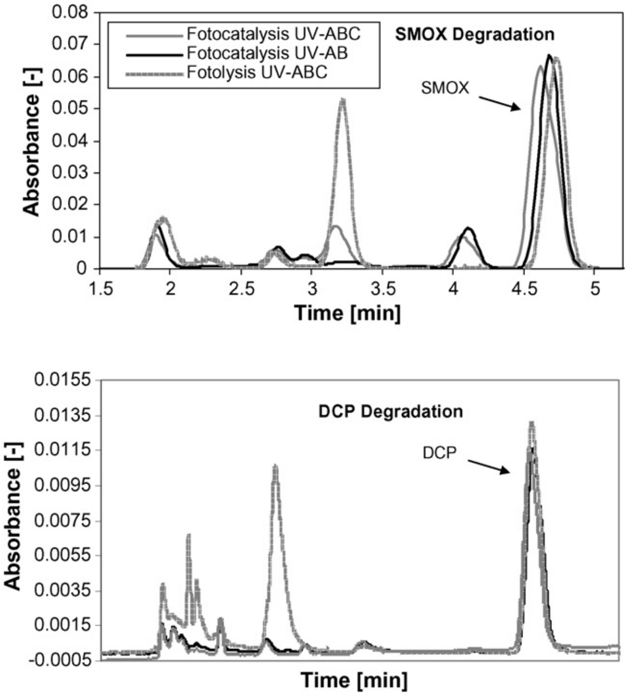

Fig. 6. SMOX (upper box) and DCP (lower box) chromatograms at the same degradation values, series with photocatalysis + UV-A, photocatalysis + UV-ABC and photolysis + UV-ABC are shown. The last peak of each box corresponds to the target compound.

radiation and the one obtained in the photolytic experiment done with UV-ABC radiation, all of them at the same degradation level of the target compound. In the case of DCP degradation, both experiments done with TiO_2 present exactly the same chromatogram, regardless of the type of the radiation used. Therefore in both cases the degradation pathway is the same. Previously it has been proved that the photolytic degradation of DCP is negligible when using UV-A radiation. Thus, it can be assumed that, in the series done with TiO_2 and UV-A, the entire degradation is due to the photocatalytic process. According to this, the fact that the chromatogram of the photocatalytic experiment done with UV-ABC radiation is equal to its analogous done with UV-A would indicate that in both cases the dominant process is photocatalysis, and photolysis is not important. It can be confirmed analyzing the chromatogram of the photolytic experiment. There is a characteristic intermediate at 5.5 min which is not present in the experiments carried out with TiO_2 (it was verified by comparing the residence time and the absorbance spectrum). Thus, the minor importance of photolysis in DCP degradation seems to be clear also when UV-ABC radiation is used.

In the case of SMOX degradation, some differences turn up. Again, the chromatograms of both photocatalytic experiments are very similar. However, when the photocatalysis is done with UV-ABC radiation, a new peak appears. This peak is not present in the chromatogram of the photocatalysis done with UV-A radiation. If the chromatogram of the photolytic experiments is now analyzed, this new peak is a characteristic peak of the photolytic degradation pathway of the SMOX. Therefore, it seems clear that the oxidation is due to concomitant photolysis and photocatalysis. It is difficult to estimate the importance of each process in the overall degradation of the pollutant. However, a rough estimation can be done. In the case of the photocatalytic degradation, the common peak owns an area about five times smaller than the area found for the same peak in the photolytic experiment (considering the same decay of SMOX). Therefore, if it is considered that the rate of the photolytic process is proportional to the presence of this intermediate, photolysis would be responsible of 20% of the SMOX degradation in the experiments done with TiO_2 and UV-ABC radiation. Obviously, it is a risky assumption, since the intermediate can be also degraded photocatalytically. However, it can give an idea on the importance of photolysis in a photocatalytic process like this and the importance of the absorbance presented by the solution in which the catalyst is suspended.

4. Conclusions

A deep comparison of the efficiency of UV-A and UV-ABC in photocatalytic and photolytic degradation has been done, using SMOX and DCP as model pollutants. It has been proved that UV-ABC radiation is more effective than UV-A, although when the incident UV radiation is used instead of time in order to present the results, the enhancement is proved not to be so important. Thus, best results were obtained when calculations are made using the UV radiation arriving at the reactor instead of time. The SMOX and DCP decay were fitted to a first order kinetic model, meanwhile the TOC mineralization of both were fitted to a zero order kinetic model. In all cases, the fitting was quite successful. It was found that photocatalysis is always faster than photolysis when operating with UV-A radiation. When operating with UV-ABC radiation, SMOX proved to be degraded faster with photolysis, probably because this substance absorbs a lot of radiation. The photonflow absorbed by the solutions/suspensions was also estimated. It was found that the suspensions absorbed approximately the same fraction of incident radiation, independently of the optical properties of the tested substances dissolved in the solution (about 85% of UV radiation), and this value was also the same for UV-A and UV-ABC radiation. Quantum yield for the different conditions tested were calculated, and photolysis presented a higher quantum yield than photocatalysis. The ratios of the quantum yields were closer to the ratios of k_r and k_r^{TOC} than to k_t and k_t^{TOC}. This fact shows again that is better to use the UV radiation arriving at the reactor, instead of time of the experiment, at least when different radiation sources or systems are used or the photonflow is not the same. Finally, a brief analysis of the intermediates was done. For DCP, which absorbs moderately in the UV range, the predominant degradation pathway is the photocatalytical one, for both UV-A and UV-ABC radiation. However, for SMOX, which absorbs up to four times more than DCP in the same region, photolysis seems to compete with photocatalysis in the degradation of this pollutant when UV-ABC radiation is used. It was roughly estimated that photolysis may be responsible of 1/5 of the degradation in some moments of the process.

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