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Photocatalytic degradation of 2,4-dichlorophenol by TiO_2/UV: Kinetics, actinometries and models

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Abstract

Heterogeneous photocatalysis has proved to be a useful tool for the degradation of water pollutants as it can be observed by the high number of references appeared the last 30 years. Despite this strong research, some points, as more satisfactory and accurate kinetic models, still have to be more developed. In this work, as reaction model, the photocatalytic treatment of 2,4-dichlorophenol has been studied by using TiO_2 in suspension as catalyst. The influence of different variables (TiO_2 concentration, pH effect, radiation) on the reaction rate has been tested. Afterwards, two new kinetic models are proposed. The first one takes into account the effect of intermediates in the degradation rate of the parent pollutant, which allows a better agreement for long time reactions. The second one attempts to include the radiation effect into the kinetic expression by means of a new term which refers to the absorbed light by the photocatalyst. Both models fit quite well with the experimental data and seem to be interesting future tools for the comparison and scaling-up of different photocatalytic systems.

Keywords: Photocatalysis; Radiation models; Reactor modelling; Pollutants treatment; Kinetic models

1. Introduction

In the last years, a big concern about the environment has emerged. One of the most striking problems is wastewater treatment and depuration. Biological systems are the most common treatment facilities used because they tend to be cheap and easy to operate. However, some industrial waste streams are not suitable for biological processes due to their high toxicity. In these cases, their treatment by traditional chemical processes, or incineration may be too energetically expensive or produce some hazardous final products, even more dangerous than the initial pollutants.

As a response to this problem, Advanced Oxidation Processes (AOPs) have appeared as potentially powerful methods for transforming pollutants into harmless substances [1–3]. AOPs are based on the generation of hydroxyl radicals ($OH^{\bullet}$). These radicals can degrade a big number of water pollutants, very frequent in industrial wastewater. However, their main disadvantage is that they require a high amount of energy or use of chemicals (H_2O_2, O_3, ...). This fact may add significant cost to the process, and therefore, may not be always suitable or competitive.

Among the AOPs, heterogeneous photocatalysis has been widely studied as an effective technology for the purification of water against a high number of pollutants [4–9], and it is under a constant research, as can be proved by the high number of references appeared in the last years [10]. This process is based on the utilisation of a catalyst (generally TiO_2) activated by the absorption of UV radiation. When this radiation with enough energy (over the TiO_2 band gap, approximately with $\lambda < 388$ nm) arrives to the surface of the catalyst, electrons may jump up from the valence band to the conduction band, and electron-hole pairs are created. Most of them are recombined and their energy is dissipated as heat. However, some can migrate to the surface of the catalyst where they can react with the substances adsorbed there. In the wastewater treatment, the most reasonable adsorbed substances are H_2O or OH^- due to their much higher concentration. It is generally accepted that both compounds can easily donate their electrons to the surface holes to generate $OH^{\bullet}$ radicals [11,12]. It is also necessary an electron acceptor to balance the process. Dissolved oxygen is believed to play mainly this role, generating more

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$OH^{\bullet}$ and $H_2O^{\bullet}$ [6,11]. Several authors have detected also, a direct reaction between the pollutants and the electron-hole pairs [13,14] but the extension of these reactions is a controversial matter [15]. Presumably, independently of the reaction pathway followed, most of the reactions take place very close to the catalyst surface so the pollutant adsorption is also very important.

Photocatalysis with TiO_2 presents some distinct advantages: high TiO_2 chemical stability in a large pH range, low cost of catalyst and chemicals, none or low inhibitions by common ions present in water, relatively mild reaction conditions required and success in the decomposition of several toxic refractory pollutants. To sum up, it can attack a wide variety of water pollutants, some of them very toxic for biological treatment, and in addition, photocatalysis is quite more inexpensive than the rest of AOPs if sun is used as radiation source. Although being a promising technology, it presents some obscure points; yet the wastewater to treat needs to be quite transparent at the spectral region semiconductor absorbs and, in some cases, the whole process is a bit slow because only about a 3% of solar radiation can be used. A great effort is being done to overcome these inconveniences and achieve a more competitive process [16].

Modelling of photocatalytic processes can be quite a complicated matter because it adds the radiation absorption to the classical aspects of the heterogeneous catalytic systems. Therefore, a lot of photocatalytic studies are focused on the usual issues of normal catalysis without light: degradation of pollutants, simple kinetics and mechanism reactions and enhancement of the conditions of operation (catalyst immobilisation and doped, optimal pH, etc.) [17–21]. There is another particular group, the main goal of which is the study of radiation phenomena: intrinsic study of the functioning of the catalyst, radiation models, reactors designs taking into account the radiation way, etc. [22–24,26–30,32]. Most of authors have studied both fields separately and a little effort to interconnect both of them has been done. The progressive union of both concepts here detailed will be necessary to be able to design efficient photocatalytic equipment and develop universal future useful tools that allow the scaling-up of this technique independently of the system employed.

The work reported here is part of a kinetic study on photocatalysis using a TiO_2 suspension. 2,4-dichlorophenol (DCP) has been chosen as the model pollutant, representing the chlorophenol family due to its environmental hazard. Degradation rates, influence of the amount of catalyst loaded, initial pH effect and other results are presented.

New models are proposed by considering the influence of intermediates and radiation on the reaction rate. First-order kinetic expression has often been used due to its simplicity [25] with good agreement for initial reaction times of a wide variety of pollutants. However, when experiment continues, it is observed that the degradation rate decreases more slowly. In that zone, kinetic data do not fit well first-order kinetics. This fact can be explained by the presence of intermediates that compete with the initial pollutant. By considering all that, the variation of the pollutant concentration during time is described by a model which includes the influence of the first intermediates present in the reaction medium. Thus, the kinetic equation takes the form:

$$r = k_1 c - k_2(c_0 - c) \tag{1}$$

where r is the intensive reaction rate, c_0 the initial concentration of pollutant, c the pollutant concentration at any time, k_1 the kinetic constant related to the pollutant decomposition and k_2 the kinetic constant associated to the intermediates decomposition. It is evidently an empirical equation, directly deduced from the common first-order kinetics equation. It is proposed because it is possible to apply Eq. (1), although the intermediates concentrations are not known, a very common problem in degradation of complex compounds. Although it is not really useful for mechanistic issues, it can be interesting for a simple description of the system behaviour and for scaling-up purposes.

Obviously, the reaction rate is also dependent on the amount of light absorbed by the catalyst. Not all the useful arriving radiation into the reactor is used to generate electron-hole pairs because part of it is lost in different ways: back-scattering, absorption in the liquid phase and transmittance. Thus, a new modification in the model is related to this last point, that is, trying to correlate the fraction of entering light absorbed by the catalyst (F_{abs}^{cat}) as function of catalyst concentration. In this way, if radiation is included into the kinetic model, a novel kinetic constant independent from the intensity of light arriving or the amount of catalyst loaded can be obtained. As a first approach to this objective, a first modification is done in the common first-order kinetics:

$$r_{TOC} = k_{ap} c_{TOC} = k' F_{abs}^{cat} c_{TOC} \tag{2}$$

where k_{ap} is the apparent kinetic constant, k' the real kinetic constant, F_{abs}^{cat} the amount of useful radiation absorbed by the catalyst and c_{TOC} the carbon found in the sample by means of TOC measurements at any time.

The estimation of F_{abs}^{cat} is not a simple matter, because the physical equations that could provide the fraction of absorbed light in a disperse media are only applicable to spherical particles (Mie equation), particles much more small than the radiation wavelength (Rayleigh equations) or much bigger (classical optics). In photocatalysis system, however, no one of these requirements are fulfilled.

Given that no theoretical equations can be applied, the only way to obtain F_{abs}^{cat} is experimental, combined, if the case, with some analytical models and computer simulations. In this way, from several works made in this sense, it is especially remarkable the owned to the Cassano's group [26–30]. These works are mainly based in reflectance–transmittance experiments and some cases can be solved analytically for photocatalytic systems with a simple geometry, although these models always require some

experimental parameter. Our alternative to these procedures consists on finding F_{abs}^{cat} by means of actinometric experiments.

In summary, this work is focused on characterising the behaviour of a photocatalytic system operating with a TiO_2 suspension and using the data obtained to test two new proposals that concern the effect of intermediates and radiation in the kinetic models.

2. Experimental

2.1. Chemicals

The TiO_2 samples used in this study were Degussa P25. 2,4-Dichlorophenol (99%) was supplied by Aldrich, while sulphuric acid (98%), sodium hydroxide (97%) and the reagents to carry out the actinometries, i.e., oxalic acid (99%), uranyl nitrate (98%) and potassium permanganate (99%) were obtained from Panreac. The chemicals were used without further purification. All solutions were prepared using ultra pure filtered Millipore water (18 μS cm^{-1}).

2.2. Reactor

The experimental set-up is shown in Fig. 1. It was composed by a tubular reactor made of quartz providing a length of 26 cm with an inner diameter of 1.95 cm. This reactor was located in the axis of two parabolic mirrors in a Solar Simulator "Solarbox" from CO.FO.ME.GRA, already described in previous papers [31,32]. 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. This design allowed to maintain constant the temperature in the whole system. The source of radiation was a Xenon lamp (PHILIPS XOF-15-OF, 1500 W), with a spectrum very close to the solar one in the UV range (see Table 1). It was placed in the upper part of the Solarbox, also in the axis of the parabolic mirrors.

2.3. Procedures

In order to carry out the photodegradation experiments, the 2,4-dichlorophenol solution was prepared to a concentration of 125 ppm, loaded to the reservoir tank (from 0.5 to 1.5 L) and circulated through the system for 10 min. Then a sample was taken. Afterwards, the desired amount of TiO_2 was added to the solution and the resulting suspension was recirculated again for an hour in the darkness to ensure that the adsorption equilibrium was achieved (after 15 min, the 2,4-dichlorophenol concentration remained practically unchangeable). Then the light was turned on and the photodegradation started. For 6 h, periodic samples were taken to follow the process and pH and temperature were measured. In the experiments where the initial pH was modified, it was adjusted by using NaOH and H_2SO_4 1 M solution.

The evolution of 2,4-dichlorophenol and the intermediates was tracked during the experiment by HPLC with a Waters Chromatograph (600 Controller Pump, 717 Photodiode Array Detector, Millenium 2.1 software, 717plus Autosampler). The detection wavelengths were 287 and 254 nm. The column was a TRACER EXTRASIL ODS2, 5 μm pore; 25 cm × 0.46 cm. A mixture of 40% of acetonitrile and 60% of water adjusted at pH 3 with phosphoric acid was chosen as the optimal mobile phase.

TOC was monitored with a Shimadzu TOC-V_{CSN} provided with an automatic autosampler. This measure allowed to follow the final mineralisation of the pollutant and its intermediates.

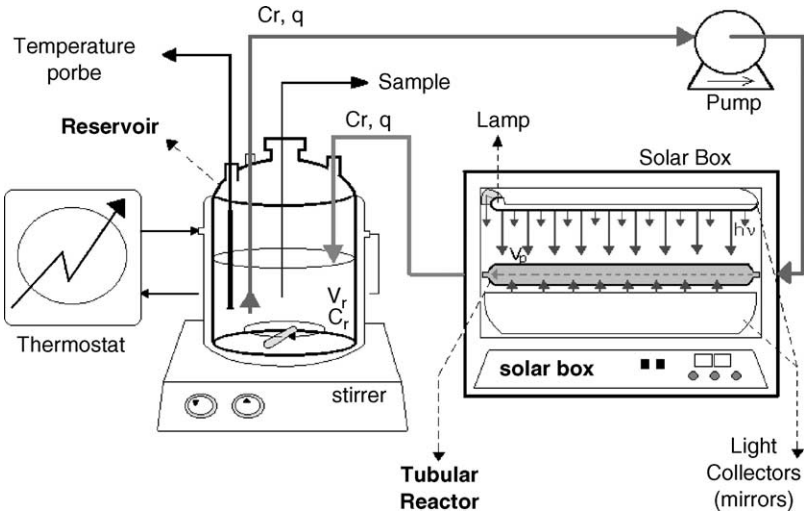

Fig. 1. Experimental set-up for the photodegradation and actinometric experiments.

Table 1
Spectrum of the lamp

λ (nm)	$f(\lambda)$	λ (nm)	$f(\lambda)$	λ (nm)	$f(\lambda)$	λ (nm)	$f(\lambda)$
300	0	335	0.00111	370	0.00210	405	0.00374
301	0	336	0.00114	371	0.00212	406	0.00380
302	0	337	0.00117	372	0.00214	407	0.00386
303	0	338	0.00120	373	0.00216	408	0.00392
304	0	339	0.00123	374	0.00218	409	0.00398
305	0.00002	340	0.00126	375	0.00220	410	0.00404
306	0.00004	341	0.00126	376	0.00222	411	0.00406
307	0.00006	342	0.00127	377	0.00224	412	0.00408
308	0.00008	343	0.00128	378	0.00226	413	0.00410
309	0.00009	344	0.00128	379	0.00228	414	0.00411
310	0.00011	345	0.00129	380	0.00230	415	0.00414
311	0.00015	346	0.00132	381	0.00231	416	0.00416
312	0.00018	347	0.00135	382	0.00232	417	0.00417
313	0.00022	348	0.00138	383	0.00233	418	0.00419
314	0.00025	349	0.00141	384	0.00234	419	0.00421
315	0.00029	350	0.00144	385	0.00235	420	0.00423
316	0.00033	351	0.00146	386	0.00236	421	0.00420
317	0.00037	352	0.00147	387	0.00237	422	0.00417
318	0.00041	353	0.00149	388	0.00237	423	0.00414
319	0.00045	354	0.00150	389	0.00238	424	0.00411
320	0.00049	355	0.00152	390	0.00239	425	0.00408
321	0.00053	356	0.00153	391	0.00249	426	0.00405
322	0.00057	357	0.00155	392	0.00260	427	0.00402
323	0.00061	358	0.00156	393	0.00270	428	0.00398
324	0.00064	359	0.00158	394	0.00281	429	0.00395
325	0.00068	360	0.00159	395	0.00291	430	0.00392
326	0.00077	361	0.00164	396	0.00302	431	0.00402
327	0.00085	362	0.00169	397	0.00313	432	0.00411
328	0.00094	363	0.00174	398	0.00323	433	0.00420
329	0.00102	364	0.00179	399	0.00334	434	0.00430
330	0.00111	365	0.00184	400	0.00345	435	0.00439
331	0.00111	366	0.00189	401	0.00351	436	0.00449
332	0.00111	367	0.00194	402	0.00356		
333	0.00111	368	0.00199	403	0.00362		
334	0.00111	369	0.00205	404	0.00368		

λ is the wavelength in nm; $f(\lambda)$ is the spectral distribution of the lamp.

Actinometric experiments were also made using the well-known oxalic–uranyl method [31,33,34], and the incoming radiation to reactor was evaluated. 0.05 M of oxalic acid and 0.01 M of nitrate of uranyl in a free pH medium were used. Under the tested experimental conditions, the uranyl (dissolved catalyst) absorbs the arriving radiation and then, attacks the oxalic acid. The degradation rate of oxalic follows a first-order kinetics with respect to the arriving radiation and zero order with respect to the concentration of uranyl or oxalate.

After that, a slight modification of the method was made, and different amounts of TiO_2 (from 0 to 2 g/L) were added to the system, without changing any other condition. Previously, it was checked that oxalic acid was not substantially adsorbed or degraded by the TiO_2. The removal of oxalic acid was never higher than 3% in the time and conditions of the experiment. Therefore, it was possible to do a first approach to the photocatalyst interaction with the entering light and evaluate, in an empirical way, the amount of useful radiation absorbed by the catalyst.

3. Results and discussion

3.1. Kinetic model and mass balances

In order to work with the proposed kinetic models, firstly the flow model of the system has to be known. As it has been described, the experimental installation consists of a continuous stirred tank reactor (the reservoir) and a small tubular reactor (the photoreactor). The tubular reactor is quite short and wide. It was checked that it does not have time by far to develop a plug-flow behaviour. Therefore, it is accepted that both parts follow a perfect mixing flow model. It is also assumed that the chemical reaction only takes place in the photoreactor [35]. The reaction rate is very slow and due to the small size of the photoreactor and high flowrate, it can be assumed that the pollutant concentrations in the photoreactor are practically the same as in the reservoir. In fact, it was observed that, for a time equal to the photoreactor residence time, only 0.035% of conversion was achieved.

Taking into account all those considerations, a mass balance around the system leads to:

$$-V_T \frac{\mathrm{d}c_\mathrm{r}}{\mathrm{d}t} = rV_\mathrm{p} \tag{3}$$

where V_T is the total volume of the system (it is assumed that the volume of the tubes connecting the reservoir and the photoreactor is negligible with respect to the volume of the reservoir and the photoreactor), V_p the volume of the photoreactor, c_r the pollutant concentration in the reservoir and t the time. This expression is very similar to the normal one applied to a batch reactor. However, it takes into account that only exists reaction in a small part of the total volume (approximately 1/10 of the volume).

Including the kinetic expression (Eq. (1)) into the last equation and integrating, expression (3) becomes:

$$c_\mathrm{r} = \frac{k_2 c_0 + k_1 c_0 \exp\left(-(V_\mathrm{p}/V_T)(k_1 + k_2)t\right)}{k_1 + k_2} \tag{4}$$

which relates the concentration in the reservoir with time being the boundary conditions: $c_\mathrm{r} = c_0$ when $t = 0$ and $c_\mathrm{r} = c_\mathrm{r}$ when $t = t$.

For the simplest case of $k_2 = 0$ (normally at the initial step of the reaction), Eq. (4) leads to an exponential decay:

$$c_\mathrm{r} = c_0 \exp\left(-\frac{V_\mathrm{p}}{V_T} k_1 t\right) \tag{5}$$

which describes the typical first-order kinetics observed by many authors during the initial moments of the process.

Eq. (3) should described the behaviour of the system in a more satisfactory way than the traditional first-order kinetics, since it includes the competition of the intermediates against the initial pollutant (Eq. (1)).

3.2. Radiation model

An attempt was made to estimate the radiation arriving to the reactor and the fraction of light absorbed by the catalyst

as function of catalyst concentration and its physical nature as well as function of the liquid absorbance. It was evaluated by means of actinometric experiments. The radiation emitted by the lamp was always constant. When adding TiO_2 to the actinometric solution, a direct competence for the entering radiation exists, so it is expected that the radiation absorbed by uranyl (employed to destroy the oxalic) will decrease. Consequently, it is assumed that when the photocatalyst is added, the radiation that is not absorbed by the actinometric solution anymore is absorbed by the TiO_2. Obviously, when the TiO_2 is loaded, part of the radiation cannot enter into the reactor due to the back scattering. But, on the other hand, it seems clear that once it is into the solution, part of the radiation cannot leave the system due to the same effect. Thus, it is considered that the available light into the reactor is approximately constant for all the experiments.

On this work, we call ''useful radiation'' that one useful for electron-hole pairs generation. The range of this radiation can be found in the literature. For Degussa P25, it is that one with a λ lower than 388 nm [36,41–43] and it corresponds almost exclusively to the total radiation absorbed by the TiO_2. Thus, only the radiation under 388 nm is considered from now on.

It can be assumed that the arriving radiation to the system was absorbed by the TiO_2 and the solution. Previous tests show that uranyl oxalate is not adsorbed on TiO_2. Thus, we can write:

$$F_{abs} = F_{abs}^{sol} + F_{abs}^{cat} \quad (6a)$$

where F_{abs} is the total useful radiation arriving to the system, F_{abs}^{sol} the arriving useful radiation absorbed by the solution and F_{abs}^{cat} the arriving useful radiation absorbed by the TiO_2. Obviously, the percentage of radiation absorbed for each one is function of the amount of TiO_2 loaded into the system. Therefore, the more quantity of TiO_2 loaded, the more amount of radiation will be absorbed by the TiO_2 particles, and the amount of radiation absorbed by the solution decreases.

According to all explained, it seems clear that the number of reactive points on the catalyst surface, which initiate the degradation (i.e., electron-hole pairs), are function of F_{abs}^{cat}. Therefore, it is logical to include this parameter into the kinetic equation.

To estimate F_{abs}^{cat} by means of Eq (6a), it is necessary to know previously F_{abs}. The actinometric experiments allow to calculate directly the amount of light absorbed by the solution (F_{abs}^{sol}). If $c_p = 0$ (being c_p the concentration of TiO_2 in the suspension), Eq. (6a) becomes:

$$F_{abs} = F_{abs}^{sol} \quad (6b)$$

Thus, doing an actinometry without loading TiO_2, F_{abs} can be measured directly. When titania is added, F_{abs}^{cat} has to be considered. Thus, for each concentration of TiO_2, F_{abs}^{cat} can be calculated by the difference between F_{abs} (the radiation absorbed by the actinometer when $c_p = 0$) and F_{abs}^{sol} for the considered concentration. It must be pointed again that only radiation below 388 nm is taken into account. It can be estimated easily since the actinometric method calculates the total radiation flow by adding the arriving radiation due to each wavelength λ_i. These contributions can be estimated since the requested parameters are conveniently tabulated [32,44–46].

As it was said before, it is possible to include radiation simply into the kinetic equation to find a real kinetic constant (k'), which should not to be depending neither on the amount of radiation emitted nor on the amount of catalyst loaded (Eq. (2)).

Eq. (2) must be also included into the flow model of the system. Doing an analogue mathematical development, and introducing Eq. (2) in Eq. (3) as in the previous case, the resulting equation is close to Eq. (5):

$$c_{TOC} = c_{TOC}^0 \exp\left(-\frac{V_p}{V_T} k_{ap} F_{abs}^{cat} t\right) \quad (7)$$

where c_{TOC}^0 is the initial concentration of TOC in the solution.

3.3. Degradation of DCP: optimal concentration of TiO_2

First, degradation of DCP for different amounts of TiO_2 was studied. In Fig. 2, DCP and TOC conversion values are presented. It can be seen how photocatalysis is capable of degrading DCP and its intermediates and proves to be an useful technique. The figure shows typical degradation curves. For DCP conversion, a fast degradation can be observed for initial times and later on it decreases. It is probably because for higher times, DCP has to compete with

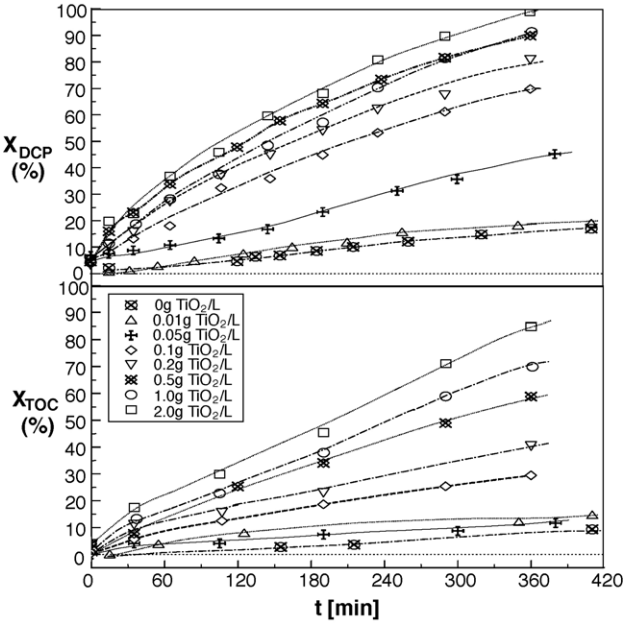

Fig. 2. DCP and TOC conversion vs. time for different amounts of TiO_2 loaded. $[DCP]_0$ = 125 ppm; flowrate = 27.5 mL/s; free pH (initially pH 5.5); T = 23 °C.

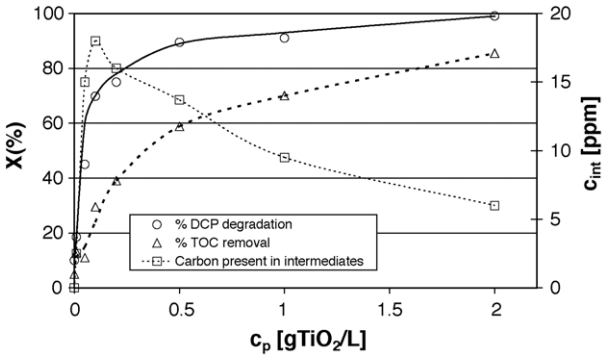

Fig. 3. Final DCP, TOC conversion and carbon present in intermediates compounds after 6 h of radiation for different amounts of TiO_2 loaded. $[DCP]_0 = 125$ ppm; flowrate = 27.5 mL/s; free pH (initially pH 5.5); $T = 23$ °C.

intermediates for the TiO_2 sites. However, TOC conversion increases quite more smoothly during all the experiment. The higher TOC removal achieved was for 2 g TiO_2/L, when about 85% of pollutant was mineralised after 6 h of radiation. It means that the global degradation of organic matter is quite mild along the experiment, although some compounds could present more affinity to be degraded.

It was attempted to study the behaviour of the process for different concentrations (c_p) of TiO_2 and find the most optimal value. From Fig. 2 data, Fig. 3 has been prepared. It illustrates the final conversion of TOC and DCP for different c_p after 6 h of radiation. For low c_p, it can be observed how the final DCP and TOC conversion increased rapidly with the amount of catalyst. However, for c_p higher than 0.5–1 g TiO_2/L the rising became fairly smoother, maybe because there existed a higher competence between TiO_2 particles for the arriving photons and not all the catalyst surface was used. The shape of the curve is more clear for the DCP. After 6 h of irradiation with 0.5 g TiO_2/L, a 90% of DCP had disappeared. For the same time, 2 g TiO_2/L, DCP degradation was over 99%, so the difference was patent but not really large. In the case of the TOC curve, although the rising was smoothed down for c_p higher to 0.5 g TiO_2/L, the plateau zone is never so flat as for DCP case. This is probably because, while almost all the DCP is exhausted, there was present high concentration of intermediates, yet decreasing the TOC value. According to this, 0.5 g TiO_2/L is chosen as the optimal value of operation.

3.4. Intermediates compounds analysis

A study of the intermediates was also made. The change of colour of the solution already warned about the presence of intermediates. In Fig. 3 is also depicted a curve which shows the amount of carbon present in the solution as intermediate compounds (TOC minus DCP carbon). It can be seen how, after an intermediate maximum, the decrease of them presented logically a parallel tendency to the TOC removal and how the presence of intermediates was quite important at the optimal value chosen for operating. Since the final mineralisation was not achieved, it is necessary to note which intermediates and their toxicity were present. HPLC results revealed the clear presence of seven intermediate compounds. All of them appeared at lower retention times than DCP. It means that they had a more hydrophilic structure than DCP. This agrees to the findings of other authors indicating that degradation products produced from photocatalytic oxidation usually present a more hydroxylated structure than the original molecule [41]. A preliminary study confirmed the existence of acids, some of them identified (maleic, acetic) for the lowest retention times. It was also corroborated by the fact that during the radiation period, pH decreases from 5.6 to about 2.7. Furthermore, two of the chromatogram peaks correspond to the retention time of 4-chlorophenol and phenol. These two intermediates are definitely uncommon in the DCP degradation; however, something similar was previously found by Pandiyan et al [25]. In consequence, more research has to be done in order to define them to ensure their identity accurately. It might be also pointed out that the only peaks detected for mineralisation higher than 70% were those associated to acids. It seems that these compounds are accumulated and degraded, once the rest of the substances are not present, probably because they are the last step of the degradation mechanism and they present lower affinity for the TiO_2. It is not a real inconvenient, since this type of compounds is normally less toxic and problematic than other more complex intermediates.

3.5. pH effect

It is known that pH can affect the mechanism and routes of degradation [7]. The TiO_2 point of zero charge (pzc) is between pH 5.6 and 6.4 [8,37]. Hence, depending on the pH the catalyst surface will be charged positively (for pH < pzc), negatively (for pH > pzc) or neutrally (for pH ≈ pzc). This characteristic affects significantly on the adsorption and desorption properties of TiO_2. Also, the structure of the pollutants will change with the pH. For example DCP has a $pK_a = 7.98$ and can be charged also positively or negatively on basis of the pH. To sum up, it seems clear that the interaction and affinity between both species will be different relying on the pH.

To study this aspect in our system, degradation experiments with different initial pHs (2, 5.5, 7.5, 11) in non-buffering conditions were made. The results obtained are presented in Fig. 4. It was found that pH has a pronounced influence on the mechanism pathway and final degradation of DCP. In all the cases, the pH decreased along the time, showing that more acidic species were appearing. Analysing the DCP curve, it can be observed how for pHs greater than 5.5, the final DCP removal decreased. For lower pH, the final conversion was practically the same. These results would suggest that the affinity between DCP and TiO_2 improves in acidic conditions. It is probably because

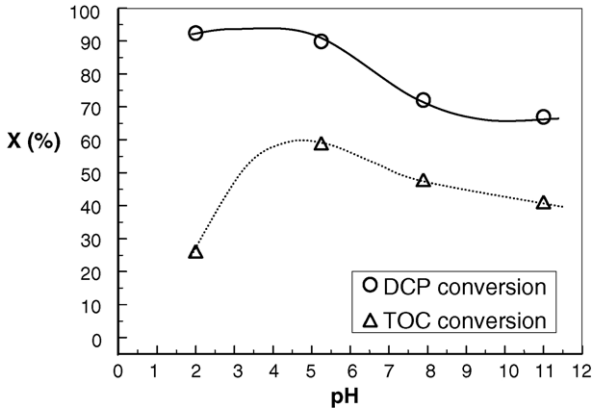

Fig. 4. Final TOC and DCP conversion after 6 h of illumination for different pHs in non-buffered conditions. $[DCP]_0$ = 125 ppm; flowrate = 27.5 mL/s; c_p = 0.5 g TiO_2/L; T = 23 °C.

DCP is mostly in the un-ionized form at acidic conditions and then, it could be more easily adsorbed onto the TiO_2 surface. On the other hand, for alkaline conditions, DCP and TiO_2 are mostly charged negatively so can exist a repulsion between both compounds. This fact would enhance other different degradation pathways which are slower as homogeneous mechanism. This assertion could be verified by means of the study of the HPLC chromatogram. It showed different intermediate peaks for the case of pH 11 compared with the rest of the pH chromatograms, pointing out that at pH 11 a different degradation pathway is followed with respect to the rest of pHs. These results seems also to show that for lower pH the degradation takes places through a reaction of the adsorbed compounds with the photo-generated holes. Meanwhile, for high pH compounds may react with diffuse $OH^{\bullet}$ radicals. It can be important and demand further research. Although for pH 11 the final degradation is worse, maybe the intermediates produced are less toxic or easy to degrade by other methods than those produced in the rest of conditions.

The curve referred to the TOC removal is a bit different. It shows a maximum for pH 5.5. Experiments for pH equal to 5.5, 7.5 and 11 followed the same trend explained for the curve of DCP removal. It might be explained because of the intermediate appeared. During the photocatalytic degradation of DCP, it is common to obtain carboxylic acid structures (actually some acids were detected by HPLC). At high pH, these compounds would be totally deprotonated and charged negatively. As for DCP, a repulsion would exist due to the negative charge of the TiO_2 surface so the adsorption and degradation would become more difficult. Another reason to explain the slowness of the process at high pH is the existence of carbonate ions which could scavenge the hydroxyl radicals or holes produced on TiO_2 surface to form less reactive carbonate radical $CO_3^{\bullet -}$ [38,39]. Therefore, there would be less available reactive points for the pollutants degradation and the mineralisation process would be slower.

Total mineralisation for pH 2 shows to be worse than for the rest of conditions. HPLC chromatograms revealed identical intermediates to those observed at pH 5.5 but in this case, the peaks which probably belonged to acids compounds were accumulated without being mineralised. Following with the previous deductions, it should be because bad interaction between the catalyst and those compounds existed. At low pH, probably most of the acids were protonated and it seems that those structures were barely attacked by the TiO_2. For slightly higher pHs, maybe the acid compounds were deprotonated and charged negatively and then, the interaction with the surface of the TiO_2 charged positively would be more efficient. Another fact to explain the low mineralisation at pH 2 could be that pointed by Chen et al [12]. They found that Cl^- ions have an inhibitory effect on the photodegradation, maybe because at so low pH value that ion can competitively adsorb on the surface of TiO_2 with big adsorption constant.

3.6. Kinetic model including intermediate compounds

As it has been seen, intermediate compounds play an important role in the photocatalytic degradation. Thus, they should appear in the kinetic model presented to avoid bad predictions for long reaction times, although some times these compounds cannot be quantified and then they are difficult to take into account. A new kinetic model including these compounds was presented before (Eq. (1)) in order to solve this problem. The experiments presented previously were fitted to this new model to test its validity. The degradation of DCP for different amounts of TiO_2 was fitted to Eq. (4) and the kinetic constants k_1 and k_2 compiled in Table 1 were obtained for each TiO_2 concentration. The agreement between experimental data and the model is quite satisfactory in all the cases. In Fig. 5, an example of this good agreement is presented. Again the optimal value for DCP photodegradation is found at c_p 0.5 g TiO_2/L. Once this value is exceeded, k_1 does not increase anymore. It is also noticeable that k_2 is generally rather smaller than k_1, which would mean that DCP degradation is quite favoured with respect to the rest of intermediates degradation.

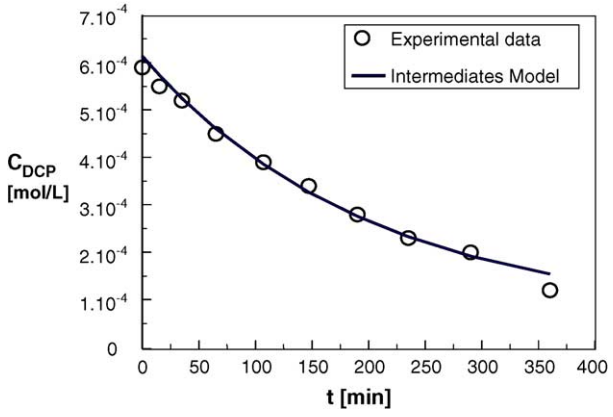

Fig. 5. DCP degradation vs. time. Experimental and theoretical (intermediate kinetic model) values are presented. $[DCP]_0$ = 125 ppm; flowrate = 27.5 mL/s; c_p = 0.5 g TiO_2/L; T = 23 °C.

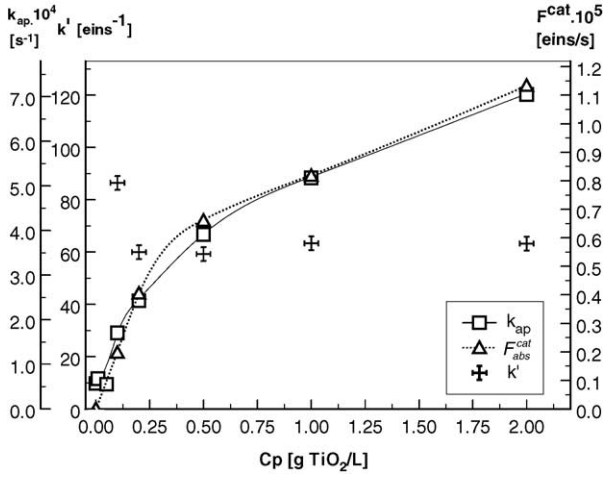

Fig. 6. Useful radiation absorbed by the catalyst, kinetic constants estimated for the TOC removal (k_{ap}, k') presented for different amounts of catalyst loaded. $[DCP]_0$ = 125 ppm; flowrate = 27.5 mL/s; free pH (5.6); T = 23 °C.

Although this model is empirical and has no mechanistic contributions, it can be very useful for scaling-up purposes because of its simplicity.

3.7. Kinetic model including radiation

Radiation is another variable that usually is not taken into account by kinetic models, although it has been proved by several authors [23,40] that degradation rate in photocatalysis depends strongly of the amount of radiation absorbed by the catalyst. For that reason, it is important to include this variable into the kinetic model in order to be able to compare systems more effectively and to develop an accurate and realistic model of the process. Previously, a novel kinetic model including the arriving radiation has been proposed (Eq. (2)) adding a new term (F^{cat}_{abs}). As explained in the Section 3.2, F^{cat}_{abs} can be easily estimated through actinometric measurements. The found values are shown in Fig. 6. For low c_p, F^{cat}_{abs} increases rapidly when the concentration of TiO_2 does it, probably because most of the surface of the photocatalyst is irradiated by light. For c_p over 0.5 g TiO_2/L, the rising of F^{cat}_{abs} is not so pronounced, maybe because of the stronger competition between the TiO_2 particles themselves for the light absorption.

In order to fit the new model to the experimental data presented above, the TOC values (and not the DCP ones) were chosen because it is believed that the final mineralisation of the pollutants is a more general aspect of the photocatalysis. Furthermore, F^{cat}_{abs} is used for the degradation of all the present pollutants and TOC values are more useful because they include the most of the given reactions in the solution.

Previously to the fitting of the model and to allow further comparisons, the apparent first-order kinetic constant (k_{ap}) was calculated for different concentrations of TiO_2 by fitting the experimental values to Eq. (7). The resulting k_{ap} are shown in Fig. 6 and in Table 1. The trend of the values is a typical one in this situations and very similar to that one where the optimal concentration of TiO_2 was discussed on basis of the TOC conversion (see Fig. 2). After a fast growing of k_{ap} with c_p, it becomes more steady for values of c_p higher than 0.5 g TiO_2/L. As it can be seen in Fig. 6, the general trend of this curve is completely parallel to the trend of F^{cat}_{abs} presented in the above paragraph. It seems to indicate a clear relationship between the degradation rate and the useful absorbed light.

Table 2
Kinetic constants estimated in this work

c_p	Intermediate model		Radiation model	
	k_1 (min^{-1})	k_2 (min^{-1})	Apparent k k_{ap} (min^{-1})	k corrected k' ($einstein^{-1}$)
0	0.012	0.045	0.003	–
0.01	0.007	0.014	0.004	–
0.05	0.017	0.004	0.003	–
0.1	0.034	0.003	0.01	86.4
0.2	0.045	0.005	0.015	59.9
0.5	0.062	0.007	0.023	59.2
1	0.060	0.007	0.031	63.3
2	0.066	0.009	0.042	62.2

k_1 and k_2 for the intermediates model and k' for the radiation model.

The experimental values were finally fitted to the new model (Eq. (7)). The resulting kinetic constants (k') are compiled in Table 2 and depicted in Fig. 6. It can be observed that the new kinetic constants are quite more invariable than the apparent ones. Thus, the model behaviour agrees notably with the hypothesis formulated: by considering the apparent kinetic constant (k_{ap}) as function of the light absorbed by the catalyst, a new kinetic constant (k') independent of the amount of TiO_2 was found.

The values of k' present a slight deviation for the experiment with less TiO_2 loaded. In that experiment, the degradation rate is quite slow and an important part is owned to the direct photolysis. When the concentration of the TiO_2 is increased, the degradation rate due to the photocatalysis increases rapidly and the contribution because of the photolysis can be underestimated. Thus, for the rest of values of c_p, k' is almost constant. Anyway, this deviation is not really important to invalidate the model because it happens for very low TiO_2 concentration that are not in the usual range of operation.

To sum up, the attempt to include the absorbed radiation into the kinetic model seems to be quite encouraging and the new models could explain more satisfactorily the behaviour of the system than the usual first-order kinetic models. k' has shown to be independent on the amount of catalyst loaded to the system. Furthermore, this constant is also independent on the radiation emitted by the lamp, since a variation in the radiation source would be automatically included in the term F^{cat}_{abs}.

It is normal to find difficult to compare photocatalytic works because of its strong dependence on the conditions of operation and set-up used. In this context, the obtained

kinetic constant k' can be a very useful parameter to compare photocatalytic processes independently of the operating device or the amount of catalyst used. Moreover, k' can be an interesting tool employed in the scaling-up of devices.

4. Conclusions

It has been proved that the heterogeneous photocatalysis using a suspension of TiO_2 can degrade effectively pollutants as DCP and can be a useful technique for the treatment and cleaning of wastewater. In 6 h of treatment with 2 g TiO_2/L loaded, more than 99% of DCP was degraded and a mineralisation up to 80% was achieved. In the experimental conditions tested, an optimal loading of 0.5 g TiO_2/L was fixed. The use of a bigger amount of TiO_2 do not enhance significantly enough the yield of the process.

It has been corroborated that pH is an important factor in the photocatalytic degradation mechanism. Different intermediate compounds and different removal of pollutants were detected depending on the pH. Thus, it is important to study the proper conditions of operation to find the pH which leads to an optimal degradation rate through compounds of low toxicity, if it is possible. In this work, it was found that the best degradation rate was for free pH (5.6).

An empirical kinetic model including the effect of intermediate compounds was presented. It tries to be more accurate for long-time reaction than the usual first-order kinetic models. It was fitted to the experimental data with good agreement. This model can be useful for scaling-up purposes.

Finally, a novel model containing the action of light was presented. In this case, a new term, which included the ''useful'' light absorbed by the TiO_2, was added. This term was estimated in basis on actinometric experiments. The new model was fitted to the experimental data with remarkable results. From this new model, a new kinetic constant k' was obtained.

The new kinetic constant obtained is independent on the amount of catalyst loaded and on the source of radiation. k' can be a very useful tool in the scaling-up and comparison of different systems due to its simplicity and applicability. Thus, the results are satisfactory enough to encourage further research in this topic.

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References

[1] S. Esplugas, J. Giménez, S. Contreras, E. Pascual, M. Rodríguez, Water Res. 36 (2002) 1034.
[2] M. Pera-Titus, V. García-Molina, M.A. Baños, J. Giménez, S. Esplugas, Appl. Catal. B: Environ. 47 (2004) 219.
[3] R. Andreozzi, V. Caprio, A. Insola, R. Marotta, Catal. Today 53 (1999) 51.
[4] Y. Ku, C.-B. Hsieh, Water Res. 26 (1992) 1451.
[5] J. Araña, J.A. Herrera Melián, J.M. Doña Rodríguez, O. González Díaz, A. Viera, J. Pérez Peña, P.M. Marrero Sosa, V. Espino Jiménez, Catal. Today 76 (2002) 279.
[6] K. Chhor, J.F. Bocquet, C. Colbeau-Justin, Mater. Chem. Phys. 86 (2004) 123.
[7] K. Chiang, T.M. Lim, L. Tsen, C.C. Lee, Appl. Catal. A: Gen. 261 (2004) 225.
[8] R. Terzian, N. Serpone, J. Photochem. Photobiol. A: Chem. 89 (1995) 163.
[9] J. Beltran De Heredia, J. Torregrosa, J.R. Dominguez, J.A. Peres, J. Hazard. Mater. B 83 (2001) 255.
[10] D.M. Blake, NREL/TP-510-31319, Colorado, USA, 2001.
[11] N.C. Baird, J. Chem. Educ. 74 (1997) 817.
[12] D. Chen, A.K. Ray, Water Res. 32 (1998) 3223.
[13] A. Houas, H. Lachheb, M. Ksibi, E. Elaloui, C. Guillard, J.M. Herrmann, Appl. Catal. B: Environ. 31 (2001) 145.
[14] E.R. Carraway, A.J. Hoffmann, M.R. Hoffmann, Environ. Sci. Technol. 28 (1994) 786.
[15] K. Ishibashi, A. Fujishima, T. Watanabe, K. Hashimoto, J. Photochem. Photobiol. A: Chem. 134 (2000) 139.
[16] K. Pirkanniemi, M. Sillanpää, Chemosphere 48 (2002) 1047.
[17] M. Sturini, E. Fasani, C. Prandi, A. Albini, Chemosphere 35 (1997) 931.
[18] H.D. Burrows, M.L. Canle, J.A. Santaballa, S. Steenken, J. Photochem. Photobiol. B: Biol. 67 (2002) 71.
[19] M. Adachi, Y. Murata, M. Harada, S. Yoshikawa, Chem. Lett. 29 (2000) 942.
[20] N.I. Al-Salim, S.A. Bagshaw, A. Bittar, T. Kemmitt, A.J. McQuillan, A.M. Mills, M.J. Ryan, J. Mater. Chem. 10 (2000) 2358.
[21] M.-C. Lu, G.-D. Roam, J.-N. Chen, C.-P. Huang, Water Res. 30 (1996) 1670.
[22] S. Malato, J. Blanco, A. Vidal, C. Richter, Appl. Catal. B: Environ. 37 (2002) 1.
[23] L. Vincze, T.J. Kemp, J. Photochem. Photobiol. A: Chem. 87 (1995) 257.
[24] O.M. Alfano, D. Bahnemann, A.E. Cassano, R. Dillert, R. Goslich, Catal. Today 58 (2000) 199.
[25] T. Pandiyan, O. Martínez Rivas, J. Orozco Martinez, G. Burillo Amezcua, M.A. Martinez Carrillo, J. Photochem. Photobiol. A: Chem. 146 (2002) 149.
[26] O.M. Alfano, M.I. Cabrera, A.E. Cassano, J. Catal. 172 (1997) 370.
[27] R.J. Brandi, O.M. Alfano, A.E. Cassano, J. Adv. Oxid. Technol. 3 (1998) 213.
[28] R.J. Brandi, O.M. Alfano, A.E. Cassano, Chem. Eng. Sci. 54 (1999) 2817.
[29] M.I. Cabrera, O.M. Alfano, A.E. Cassano, J. Phys. Chem. 100 (1996) 20043.
[30] M.I. Cabrera, O.M. Alfano, A.E. Cassano, J. Adv. Oxid. Technol. 3 (1998) 220.
[31] D. Curcó, S. Malato, J. Blanco, J. Giménez, Solar Energy Mater. Solar Cells 44 (1996) 199.
[32] D. Curcó, S. Malato, J. Blanco, J. Giménez, P. Marco, Solar Energy 56 (1996) 387.
[33] D.H. Volman, J.R. Seed, J. Am. Chem. Soc. 86 (1964) 5095.
[34] L.J. Heidt, G.W. Tregay, F.A. Middleton, J. Phys. Chem. 74 (1970) 1876.
[35] M.A. Grela, et al. Los mecanismos de destrucción de contaminantes orgánicos, in: M.A. Blesa (Ed.), Eliminación de Contaminantes por Catálisis Heterogénea, CYTED, La Plata, Argentina, 2001 , p. 103(Chapter 5).
[36] A. Mills, S. Le Hunte, J. Photochem. Photobiol. A: Chem. 108 (1997) 1.
[37] M.-C. Lu, G.-D. Roam, Chen FJ.-N., C.-P. Huang, J. Photochem. Photobiol. A: Chem. 76 (1993) 103.
[38] A.J. Feitz, T.D. Waite, Environ. Sci. Technol. 37 (2003) 561.

[39] P. Mazellier, E. Leroy, et al. New J. Chem. 26 (2002) 1784.
[40] J.M. Herrmann, Catal. Today 53 (1999) 115.
[41] M.R. Hoffmann, S.T. Martin, W. Choi, D.W. Bahnemann, Chem. Rev. 95 (1995) 69.
[42] R.I. Bickley, T. Gonzalez-Carreno, J.S. Lees, L. Palmisano, R.J.D. Tilley, J. Solid State Chem. 92 (1991) 178.
[43] A.L. Linsebigler, G. Lu, J.T. Yates, Chem. Rev. 95 (1995) 735.
[44] A.E. Cassano, Revista de la Facultad de Ingeniería Química, 37, Santa Fe, Argentina, 1968, 469 pp.
[45] M. Vicente, S. Esplugas, Afinidad 40 (1983) 453.
[46] J.F. Rabek, Experimental Methods in Photochemistry and Photophysics, Part 2, John Wiley and Sons, New York, 1982 (Chapter 27).