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Removal of drugs in aqueous systems by photoassisted degradation

M. ADDAMO, V. AUGUGLIARO, A. DI PAOLA*, E. GARCÍA-LÓPEZ, V. LODDO, G. MARCÌ and L. PALMISANO
Dipartimento di Ingegneria Chimica dei Processi e dei Materiali, Università di Palermo, Viale delle Scienze, 90128, Palermo, Italy
*(*author for correspondence, e-mail: dipaola@dicpm.unipa.it)*

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Abstract

Aqueous solutions of tetracycline, lincomycin and ranitidine were irradiated with UV light in homogeneous and heterogeneous systems. Two commercial polycrystalline TiO_2 powders (Degussa P25 and Merck) were used as photocatalysts. After 5 h, an appreciable photolytic degradation of tetracycline and ranitidine was observed while the degradation of lincomycin was noticeably lower. As far as the mineralization is concerned, a small decrease of the TOC values was measured in the case of tetracycline whereas negligible variations were found for lincomycin or ranitidine. The presence of the photocatalysts greatly enhanced the degradation rates of the drugs with respect to those observed during the homogeneous experiments. The Langmuir–Hinshelwood kinetic model adequately describes the experimental results and both the pseudo-first order kinetic constants of the reactions and the adsorption constants were calculated. Merck TiO_2 was more active than P25 Degussa for the photodegradation of tetracycline and ranitidine, whereas both photocatalysts showed similar performances for lincomycin. In the presence of TiO_2 Degussa P25, tetracycline was almost completely mineralized, but the reduction of the initial TOC was ca. 60% in the case of lincomycin and ranitidine. A less significant mineralization was observed by using Merck TiO_2.

1. Introduction

The presence of pharmaceuticals and their metabolites in aquatic environments has raised increasing concern in recent years [1]. These molecules are often excreted via urine or faeces when non-metabolized and enter into wastewater [2]. They are present in sewage systems after therapeutic use and can be exceptionally degraded by micro-organisms [3]. Approximately 70% of drugs are excreted and hardly degraded biologically. Removal percentages ranging between 60 and 90% have been recently obtained for a variety of medium polar drugs during sewage treatments in German municipal plants [4]. Most drugs are designed to be persistent, so that they retain their chemical structure long enough to do their therapeutic work. The continuous inlet of these molecules to effluents enables them to remain in the environment for a significant period of time [5]. The risks to the environment have led to a regulation on new pharmaceuticals in the USA and a draft on environmental risk assessment of new pharmaceuticals has been proposed in the EU [6].

In this work, the photodegradation and mineralization of some pharmaceuticals often present in wastewater, i.e. tetracycline, lincomycin and ranitidine, have been investigated. Tetracycline and lincomycin are antibiotics of broad and medium spectrum, respectively. Both drugs are extensively used for the treatment of bacterial infections in human and veterinary medicine. Polar antibiotics excreted by humans are not eliminated effectively in the sewage treatment plants [4] and they contaminate the receiving water. The most dangerous effect of antibiotics in the environment is the development of multi-resistant bacterial strains that can no longer be treated with the presently known drugs. Ranitidine competitively inhibits the action of histamine on the H_2-receptors of parietal cells and reduces the gastric acid secretion under daytime and nocturnal basal conditions. It is widely prescribed for the treatment of peptic ulcer, reflux oesophagitis and dyspepsia [7].

The photooxidation of aqueous solutions of the three drugs was carried out by irradiation with UV light in the absence and in the presence of TiO_2 which has been successfully used as a photocatalyst to oxidize many organic compounds in aquatic environments [8]. The use of two commercial TiO_2 powders allowed determination of the influence of the type of photocatalyst on the kinetics of degradation.

2. Experimental details

Tetracycline, lincomycin and ranitidine were purchased from Aldrich and were used without further purification. The structural forms of these molecules are reported in Figure 1.

The irradiation experiments were carried out in a 0.5 L Pyrex batch photoreactor with a 125 W medium pressure Hg lamp (Helios Italquartz) immersed in the reacting solution and axially positioned. The IR component of the incident beam, as well as any radiation below 300 nm was eliminated by the circulation of cooling water through a Pyrex jacket surrounding the lamp. The photon flux emitted by the lamp, measured using a radiometer (UVX Digital) against the external wall of the photoreactor containing only pure water, was 8.5 mW cm^{-2}.

The initial concentrations of the drugs were 10, 20 and 50 mg L^{-1} and the corresponding pH values ranged between 5.7 and 6.0. Oxygen was continuously bubbled into the reacting system before and throughout the duration of the runs which lasted 3–7 h. The temperature inside the photoreactor was about 313 K during all the experiments.

Samples for analysis were withdrawn from the photoreactor at fixed intervals of time. The quantitative determination of each drug was performed by HPLC analysis by using a Varian chromatograph equipped with a C-18 column (LUNA 5 micron-C18, 4.60 × 250 mm from Phenomenex). For tetracycline analysis, a mixture of acetonitrile and an aqueous solution (20 mM) of potassium dihydrogenphosphate (35:65 v/v) was used as the mobile phase. For lincomycin and ranitidine, the eluant was a mixture of acetonitrile and an aqueous solution (40 mM) of potassium dihydrogenphosphate (25:75 v/v). A flow rate of 0.8 cm^3 min^{-1} was maintained during the analyses. A detector UV–Vis was operated at 275, 210 and 312 nm for tetracycline, lincomycin and ranitidine, respectively. The mineralization of the drugs was monitored by determining the total organic carbon (TOC) by means of a TOC Shimadzu 5000 A analyser, provided with an autosampler ASI 5000 A. Absorption spectra of the withdrawn samples were recorded by a UV–visible Shimadzu 2401 PC spectrophotometer, in order to study the evolution of the drugs and of their intermediate products during the course of the reactions.

Commercial TiO_2 Degussa P25 (BET specific surface area = 50 m^2 g^{-1}, 80% anatase, 20% rutile) and TiO_2 Merck (BET specific surface area = 10 m^2 g^{-1}, 100% anatase) were used as photocatalysts for the heterogeneous photodegradation experiments. The suspensions were magnetically stirred during the runs. Before analysis, the samples were separated from the catalyst by filtration through a 0.45 μm cellulose acetate membrane (HA, Millipore). The amount of catalyst able to absorb almost all the impinging photons was determined by performing measurements of the light transmitted through aqueous suspensions containing different quantities of powder. The optimal amounts of catalyst were 0.4 and 1 g L^{-1} for Degussa P25 and Merck, respectively.

3. Results and discussion

Preliminary tests were carried out in the dark in order to determine the influence of oxygen and/or TiO_2 on the

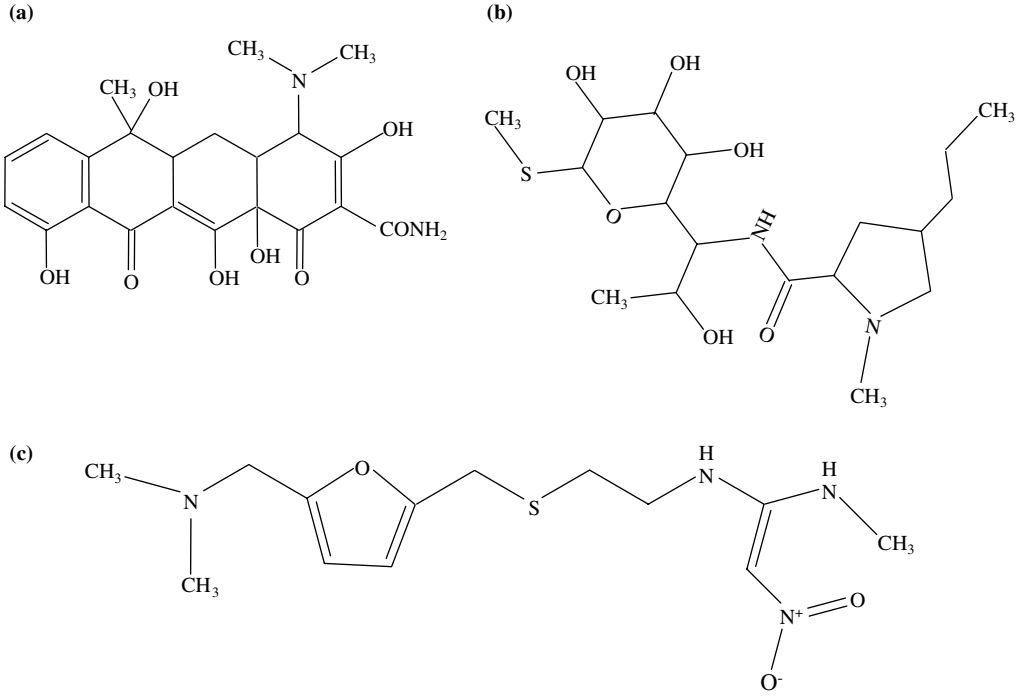


Fig. 1. Structural forms of (a) tetracycline, (b) lincomycin and (c) ranitidine.

degradation of all substrates, under the same experimental conditions of the photodegradation experiments. No degradation was observed in the presence of O_2. A small decrease in the initial concentration of the different drugs occurred in the presence of TiO_2, due to weak adsorption of the substrates onto the photocatalyst surface. This behaviour was reversible, since photodesorption of the molecules occurred when the lamp was turned on.

3.1. *Photochemical degradation*

Photolytic reactions were carried out at three different initial concentrations of the drugs. Figure 2 shows the disappearance of tetracycline, lincomycin and ranitidine in aqueous solutions containing 50 mg L^{-1} of drug, as a function of the irradiation time. An appreciable photolytic degradation of tetracycline and ranitidine was observed and ca. 70% of these molecules disappeared in 5 h. In contrast, only 20% of lincomycin was photodegraded during the same irradiation time. This feature can be explained by comparing the absorption spectra of the substrates with the emission spectrum of the lamp as shown in Figure 3. Both ranitidine and tetracycline reveal absorption bands that partially overlap the emission peaks of the lamp. However, lincomycin shows no significant absorption in the wavelength emission range of the lamp.

Figure 4 shows the variation of TOC as a function of irradiation time during the homogeneous degradation experiments. The TOC values of tetracycline slowly decreased during the first 4 h of irradiation, reaching a steady-state value corresponding approximately to ca. 90% of the initial organic carbon quantity. The small diminution of TOC suggests the formation of stable photodegradation products having a number of carbon atoms not much different from that of the initial molecule. In the case of lincomycin and ranitidine, practically no variation of the TOC values was observed during irradiation.

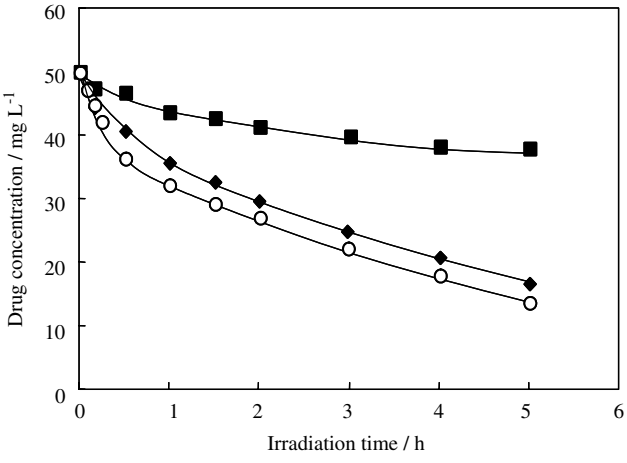


Fig. 2. Photochemical degradation of aqueous solutions of tetracycline (◆), lincomycin (■) and ranitidine (○). Initial drug concentration 50 mg L^{-1}.

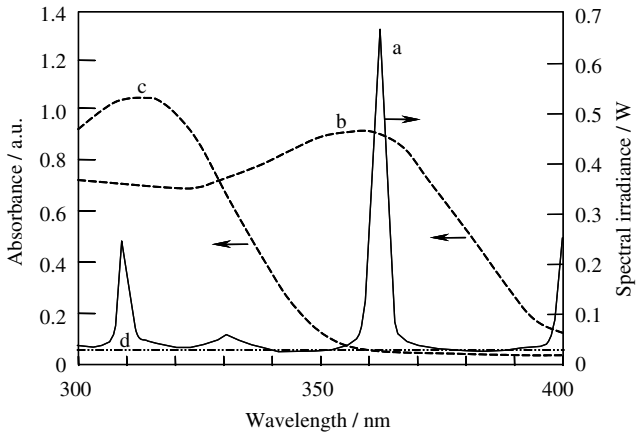


Fig. 3. Absorption spectra of aqueous solutions (50 mg L^{-1}) of (b) tetracycline, (c) ranitidine and (d) lincomycin compared with the emission spectrum of the lamp (a).

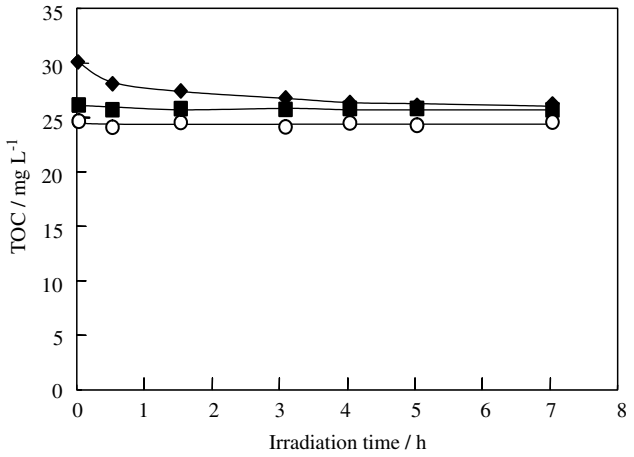


Fig. 4. Variation of TOC during the photochemical experiments with tetracycline (◆), lincomycin (■) and ranitidine (○). Initial drug concentration 50 mg L^{-1}.

3.2. *Photocatalytic degradation*

Figure 5 shows the concentration values of tetracycline, lincomycin and ranitidine versus the irradiation time for runs carried out by using TiO_2 Degussa P25 and TiO_2 (Merck). The presence of the photocatalysts greatly enhanced the reaction rates with respect to those observed for the degradation of the same compounds during the homogeneous photochemical experiments. In the presence of TiO_2 Degussa P25 (Figure 5a) or TiO_2 (Merck) (Figure 5b) more than 98% of the three drugs disappeared within about 2 h. The transformation of the three compounds was faster when TiO_2 P25 was used as the photocatalyst. The rate of degradation of ranitidine was always higher than that of the other drugs by using both types of photocatalyst.

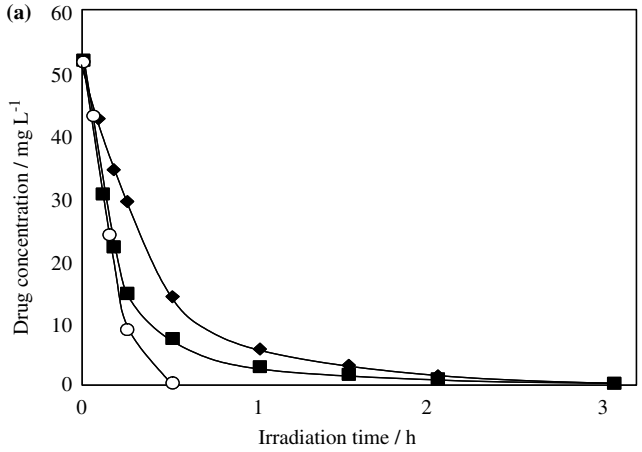


Fig. 5. Photocatalytic degradation of aqueous suspensions of tetracycline (◆), lincomycin (■) and ranitidine (○) by using (a) TiO_2 Degussa P25 and (b) TiO_2 Merck as photocatalysts. Initial drug concentration 50 mg L^{-1}.

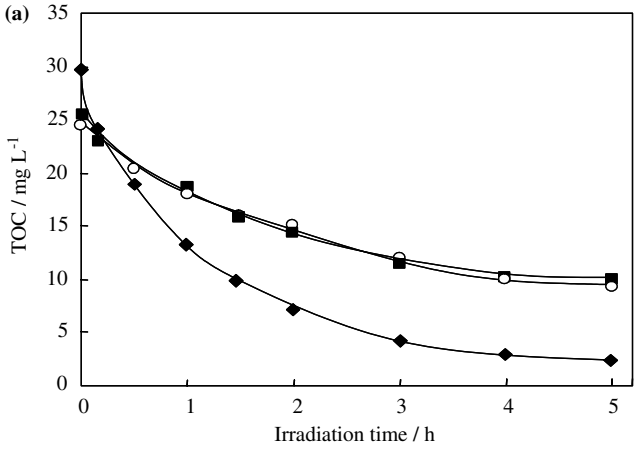


Fig. 6. Variation of TOC during the photocatalytic experiments with tetracycline (◆), lincomycin (■) and ranitidine (○) by using (a) TiO_2 Degussa P25 and (b) TiO_2 Merck as photocatalysts. Initial drug concentration 50 mg L^{-1}.

Figure 6 shows the variation of the TOC values determined during the photocatalytic degradation of 50 mg L^{-1} of the three drugs. After 5 h irradiation, tetracycline was mineralized almost completely in the presence of P25 whereas only 50% of substrate was transformed with Merck TiO_2. In the case of lincomycin and ranitidine, *ca.* 60% of the two drugs was mineralized with P25 but a less significant mineralization was observed using Merck TiO_2. It is worth noting that the efficiency of P25 was also always higher if the runs were carried out using 0.2 g L^{-1} of catalyst, corresponding to the same value of the Merck TiO_2 surface area.

3.3. *Mechanistic aspects*

The homogeneous photodegradation of an organic compound generally starts from an electronic excited state:

$$R \xrightarrow{h\nu} R^* \quad (1)$$

The excited R* species can (i) undergo homolytic bond scission to form radicals that eventually react to give final products with or without the participation of molecular oxygen:

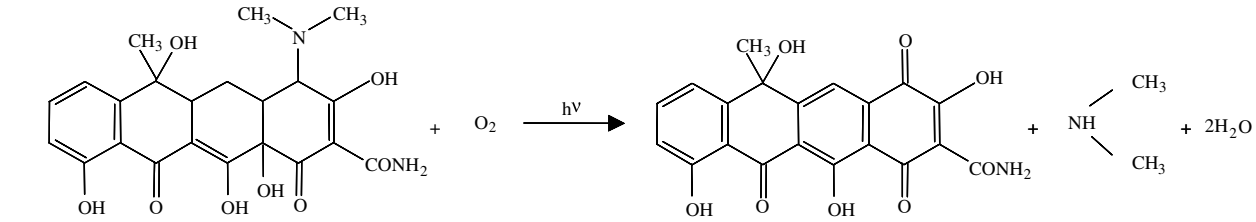
$$R^* \rightarrow R_1^\bullet + R_2^\bullet \rightarrow \text{products} \quad (2)$$

or (ii) initiate a process of electronic transfer with oxygen molecules:

$$R^* + O_2 \rightarrow R^{\bullet+} + O_2^{\bullet-} \quad (3)$$

Equation 3 is a typical quenching reaction. The formed radical cation, $R^{\bullet+}$, can undergo hydrolysis or mesolytic bond scission to low weight products. The superoxide radical, $O_2^{\bullet-}$, is a very strong oxidant species and is able to degrade many aromatic species [9].

The observation of the absorption UV–Vis spectra (Figures 7–9) of the samples withdrawn during the occurrence of the homogeneous experiments reveals the course of the reactions. Spectrum 1 of Figure 7a, obtained before irradiation of tetracycline, reveals two major absorption bands at 275 and 355 nm. Absorption slowly decreases with irradiation time. The fall in the absorbance at 355 nm is accompanied by a very weak absorption in the visible region that can be attributed to the formation of 4a,12a-anhydro-4-oxo-4-dedimethylaminotetracycline [10, 11]:



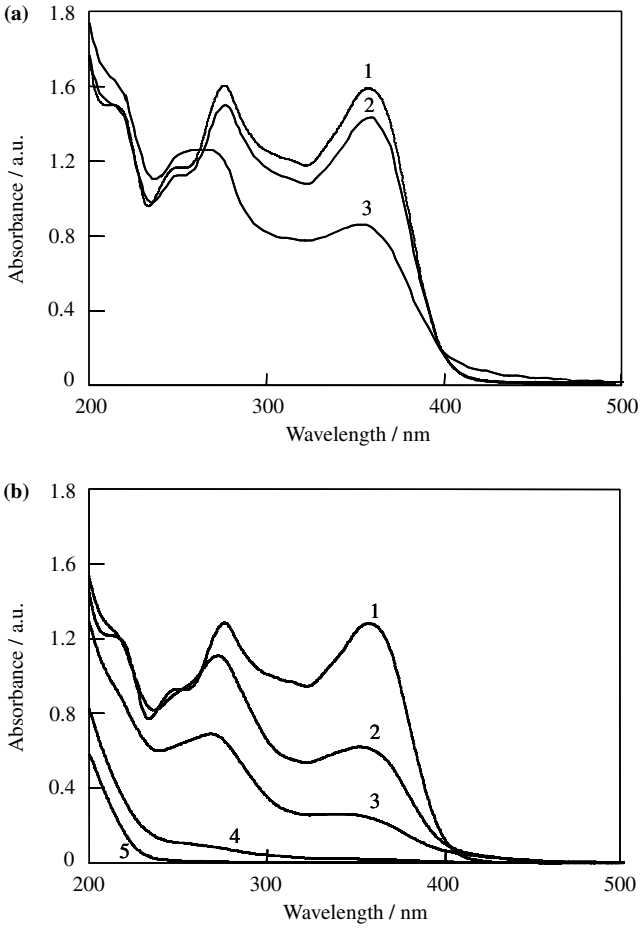


Fig. 7. Changes in absorption spectra during the photodegradation of a 50 mg L^{-1} aqueous solution of tetracycline. (a) Homogeneous degradation: spectra 1–3 denote irradiation for 0, 120 and 360 min, respectively. (b) Heterogeneous photocatalytic degradation in the presence of TiO_2 Degussa P25: spectra 1–5 denote irradiation for 0, 30, 60, 90 and 120 min, respectively.

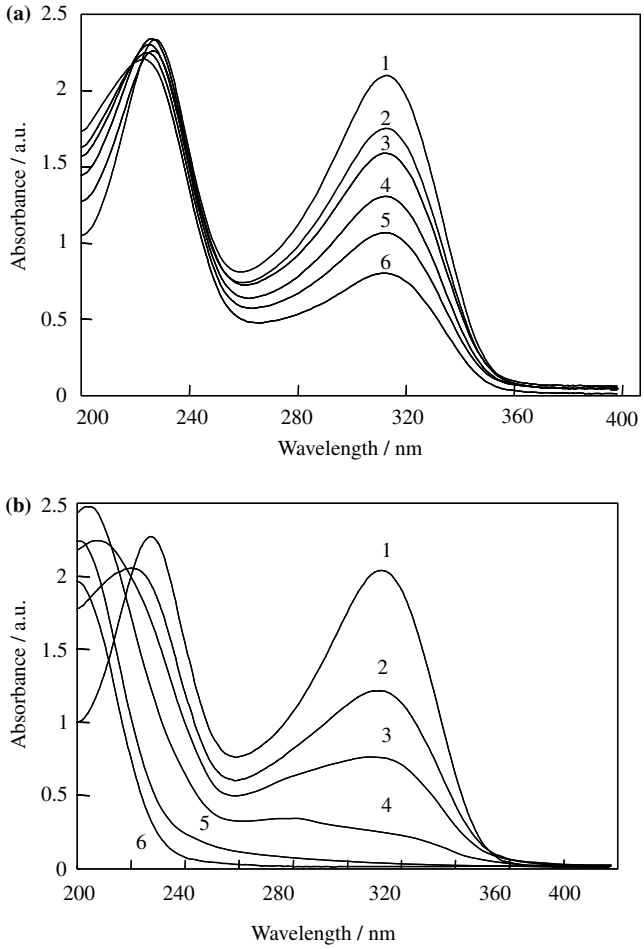
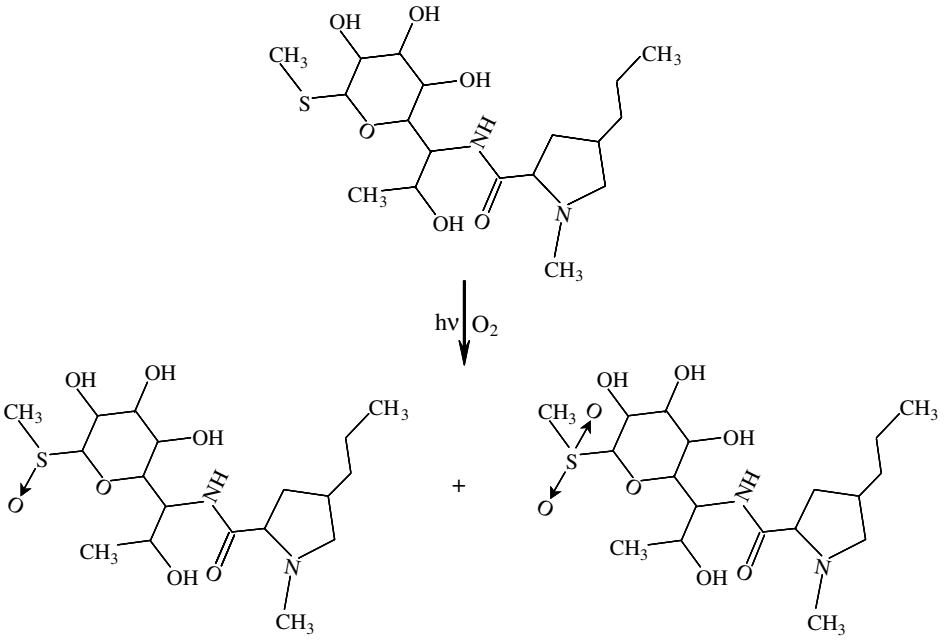


Fig. 8. Changes in absorption spectra during the photodegradation of a 50 mg L^{-1} aqueous solution of ranitidine. (a) Homogeneous degradation: spectra 1–6 denote irradiation for 0, 60, 120, 180, 240 and 360 min, respectively. (b) Heterogeneous photocatalytic degradation in the presence of TiO_2 Degussa P25: spectra 1–6 denote irradiation for 0, 15, 30, 60, 120 and 360 min, respectively.

Tetracycline photodecomposes easily and is converted to many decomposition compounds [11–18]. Side-chain degradations by deamination, desulfuration and dealkylation are typical of many photolytic processes [19–22]. Photodeamination occurs when tetracycline is irradiated with UV light [11–13]. The removal of volatile dimethylamine, which requires the loss of only 2 atoms of carbon with respect to the 22 atoms of tetracycline, explains the small variation of the TOC values reported in Figure 4.

Figure 8a shows the absorption spectra obtained before and during the photochemical degradation of ranitidine. Spectrum 1, obtained before irradiation, reveals two major absorption bands at 224 and 312 nm, which are related to the nitroethenediamine moiety and the furanyl group, respectively [23]. Absorption at 312 nm decreases during irradiation, accompanied by a decreased absorption shifted towards wavelengths lower than 220 nm. The absorption spectra of lincomycin, reported in Figure 9a, reveal no characteristic bands.

The evolution of the UV–Vis spectra of ranitidine and lincomycin is indicative of the progressive conversion of the two substrates in compounds having the same initial carbon content as indicated by the constant values of TOC observed during irradiation. The photochemical oxidation of lincomycin probably leads to



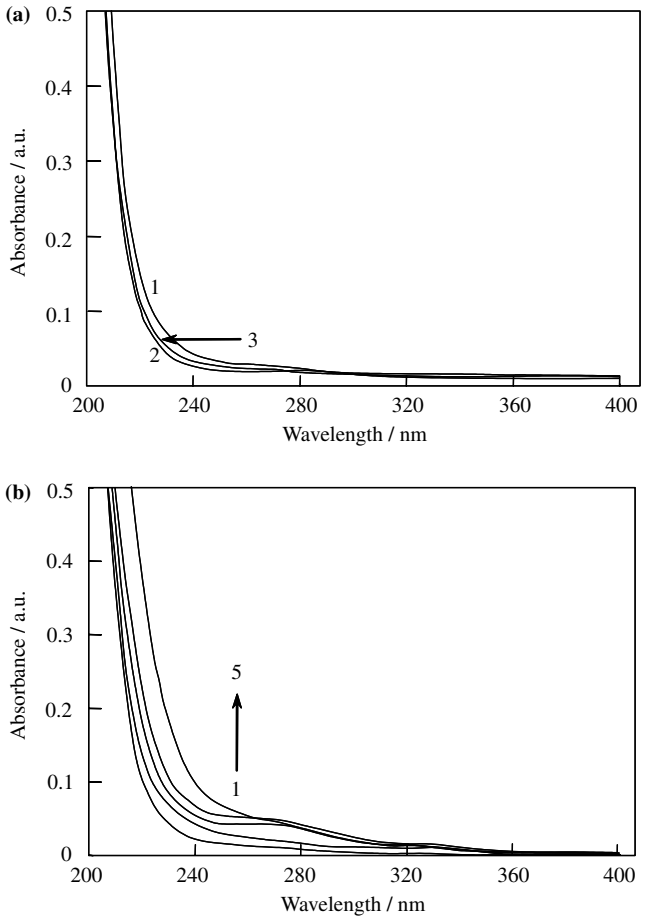


Fig. 9. Changes in absorption spectra during the photodegradation of a 50 mg L^{-1} aqueous solution of lincomycin. (a) Homogeneous degradation: spectra 1–3 denote irradiation for 0, 30 and 300 min, respectively. (b) Heterogeneous photocatalytic degradation in the presence of TiO_2 Degussa P25: spectra 1–5 denote irradiation for 0, 30, 90, 120, and 240 min, respectively.

the conversion of the thiomethyl group into sulfoxide and sulfone derivatives already obtained by Pospíšil et al. [24, 25] using H_2O_2 under both acid and alkaline conditions:

Similarly, N-oxide and S-oxides might be the products resulting from the oxidation of ranitidine [26, 27].

As far as the mechanism of the heterogeneous photocatalytic reaction is concerned, it is well known that the primary step following radiation absorption is the generation of electrons and holes within the TiO_2 particle [28]:

$$TiO_2 + h\nu \rightarrow TiO_2 + e^-_{CB} + h^+_{VB} \quad (4)$$

Electrons and holes thus separated migrate to the surface of the particles where they can either recombine or participate in interfacial oxidation and reduction reactions.

In aqueous solutions, the oxidation of a pollutant has been attributed to the reaction of the positive holes with adsorbed water or hydroxyl groups to form hydroxyl radicals $OH^\bullet$ which then react with the pollutant [29]:

$$H_2O + h^+_{VB} \rightarrow OH^\bullet + H^+ \quad (5)$$

$$OH^- + h^+_{VB} \rightarrow OH^\bullet \quad (6)$$

$OH^\bullet$ can also be formed via the superoxide radical anion $O_2^{\bullet -}$ obtained by reaction of the photogenerated electrons with adsorbed oxygen:

$$O_2 + e^-_{CB} \rightarrow O_2^{\bullet -} \quad (7)$$

$$O_2^{\bullet -} + H_2O \rightarrow HO_2^\bullet + OH^- \quad (8)$$

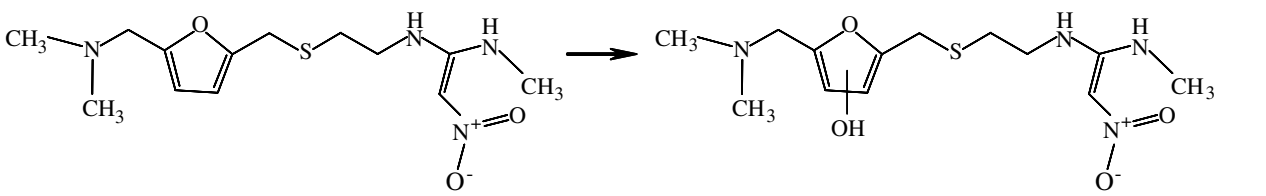
$$HO_2^\bullet + H_2O \rightarrow H_2O_2 + OH^\bullet \quad (9)$$

Figures 7–9 also show the absorption spectra of the three drugs recorded in the presence of Degussa P25. The spectra obtained by using Merck TiO_2 (not reported for the sake of brevity) were very similar indicating that the photocatalytic degradation pathways were the same. The temporal evolution of the spectral changes occurring during the photocatalytic degradation of tetracycline is displayed in Figure 7b where spectrum 1 was obtained in the presence of the catalyst before irradiation. The absorbance of tetracycline (see spectrum 1 of Figure 7a) decreased by ca. 20% after addition of TiO_2, reflecting the extent of adsorption of tetracycline on the TiO_2 surface in the dark. UV light irradiation of the aqueous suspension caused a decrease of absorbance with increasing time. The well-defined absorption bands disappeared after 120 min confirming the complete photodegradation of tetracycline in the presence of TiO_2 and oxygen.

During the initial period of the TiO_2-assisted photoprocess, the degradation of tetracycline occurs through two competitive reactions: (i) photodeamination and (ii) cleavage of the ring structure. The deamination reaction is probably predominant both in the homogeneous and the heterogeneous systems. The progressive addition of $OH^{\bullet}$ radicals to the aromatic rings leads to the formation of oxygenated aliphatic intermediates, as already reported for various aromatic polynuclear compounds [30–32], and finally to the formation of CO_2.

The fast initial decrease of TOC shown in Figure 6a, reflects the fast disappearance of tetracycline. The slow mineralization observed towards the end of the process can be attributed to difficult oxidation of the intermediates originated by the fission of the various benzene rings.

Figure 8b shows the absorption spectra recorded during the photocatalytic degradation of ranitidine. The disappearance of the absorption bands at 312 and 224 nm during irradiation and the appearance of a broad band shifting progressively towards lower wavelengths are ascribable to the continuous transformation of the substrate and of the intermediate species. The presence of the heterocyclic ring allows the electrophilic addition of the $OH^{\bullet}$ radicals in the 3- or 4-position:



probably followed by the cleavage of the molecule on either side of the sulphur atom [33] and the progressive formation of CO_2.

The spectra of lincomycin, reported in Figure 9b, revealed a progressive small increase in the absorbance during irradiation, accompanied by the appearance of a small broad band at 270 nm. One of the primary degradation stages is the desulfuration of the molecule [24, 25] since sulfate ions were detected from the beginning of irradiation. The oxidation attack probably involves the introduction of one oxygen in the pyrrolidine moiety and the cleavage of the amide bond [25].

The different mineralization rates observed when either the photon flow absorbed by the two photocatalysts or the surface areas were equal, are not easily explained. They can be attributed to the different surface physico–chemical and/or intrinsic electronic properties of the two catalysts. This kind of behaviour has been previously observed for other kinds of molecules [34–36].

TiO_2 Degussa P25 powder is constituted mainly by plate-like particles mainly exposing (001) and (010) surface planes whereas Merck TiO_2 consists of large roundish microcrystals with sharp edges corresponding to the interplanar spacing of (101) planes of anatase [34]. The two photocatalysts have different adsorption capacity for the substrates, the intermediate species and O_2, probably due to a different surface hydroxyl density and to the higher basicity of Degussa P25 with respect to Merck TiO_2 [34–36]. Moreover Degussa P25 is a mixture of anatase and rutile and the presence of rutile may positively influence the mineralization rate.

3.4. *Kinetic aspects*

Under the reaction conditions used for carrying out the photochemical degradation runs, it is reasonable to assume that the photon absorption rate is far higher than the bond scission rate, since the lifetime of the excited state is normally stabilized by solvent interaction. In the presence of a large excess of an external oxidizing agent such as molecular oxygen, the quenching of the excited state (Equation 3) is not a limiting step. By hypothesizing that the absorption of light is uniform in the reaction volume and the lifetimes of radicals and other reactive species are sufficiently long so that uniform concentrations throughout the reaction volume result from diffusion, it can be assumed that the rate of drug degradation by homogeneous photochemical reaction, $(-r_{homo})$, has the following form [37]:

$$(-r_{homo}) = -\frac{1}{V}\frac{dN_D}{dt} = -\frac{dC_D}{dt} = k_{homo} I_a^n C_D^{\alpha} C_{Ox}^{\beta} \quad (10)$$

where V is the reaction volume, N_D the moles of drug, t the time, C_D and C_{Ox} the molar concentration of drug

and oxygen, k_{homo} the rate constant, I_a the absorbed photon flow, n is an exponent ranging between 0.5 and 1, α and β the reaction orders of the drug and the oxygen, respectively.

The small decrease in TOC (see Figure 4) and the evolution of the UV–Vis spectra suggest that the optical properties of the reacting solution do not change greatly in the course of the photochemical degradation so that it may be assumed that the drug and its degradation intermediates have similar extinction coefficients. On this basis the Ia term may be assumed constant in the course of the photoreaction.

All the experimental data obtained from the photochemical runs showed exponential decreases of substrate concentration versus irradiation time, thus indicating first order kinetics with respect to the drug concentration. By considering that the oxygen concentration in the solution is kept constant during the photoprocess, the reaction rate, Equation 10 can be written in the following way:

$$(-r_{homo}) = -\frac{dC_D}{dt} = k'_{homo} C_D \tag{11}$$

where k'_{homo} is the pseudo-first order rate constant and is equal to $k_{homo} I_a^n C_{Ox}^{\beta}$. It should be noted that k'_{homo} depends inversely on the initial drug concentration whatever the n value. Equation 11 can be easily integrated with the limiting condition that at the beginning of the reaction, $t = 0$, the substrate concentration is the initial one, $C_D = C_{D,0}$. The integral relationship between C_D and t is therefore:

$$C_D = C_{D,0} \exp(-k'_{homo} t) \tag{12}$$

By applying a least squares best fitting procedure to the reactivity data, the values of the observed rate constants for each drug were determined. Table 1 reports the k'_{homo} values obtained from runs carried out at different initial concentrations. The results confirm the lower reactivity of lincomycin with respect to that of tetracycline and ranitidine. The figures reported in Table 1 indicate that, as expected, the values of k'_{homo} decrease with increasing initial drug concentration.

As far as the heterogeneous photocatalytic degradation is concerned, the reactivity data fit exponential curves, quite well indicating that the degradation rate follows first order kinetics, as reported in the literature for most of the investigated organic substrates [38–43].

Table 1. Values of the observed rate constants, k'_{homo}, obtained by the photochemical experiments

C_0 mg L^{-1}	$k'_{homo} \times 10^4$ s^{-1}		
	Tetracycline	Ranitidine	Lincomycin
10	2.43	2.65	0.63
20	0.96	1.99	0.25
50	0.56	0.66	0.13

It is useful to stress that the homogeneous reaction occurs contemporaneously with the heterogeneous one. The presence of the photocatalyst in the reacting medium strongly reduces the intensity of the radiant field inside the medium. It can therefore be reasonably hypothesized that in the presence of the photocatalyst the contribution of the homogeneous photoreaction to the overall drug degradation can be neglected. The rate of the heterogeneous photocatalytic reaction, $(-r_{hete})$, can be expressed in terms of the Langmuir–Hinshelwood model as:

$$(-r_{hete}) \equiv -\frac{1}{S}\frac{dN_D}{dt} = -\frac{V}{S}\frac{dC_D}{dt} = k''\theta \tag{13}$$

where S is the surface area of the photocatalyst, k'' the surface rate constant, and θ, the drug fractional site coverage given by:

$$\theta = \frac{K_D C_D}{1 + K_D C_D + \sum K_I C_I} \tag{14}$$

where K_D and K_I are the equilibrium adsorption constants of the drug and of the intermediate products, and C_D and C_I the drug and intermediate product concentrations in the fluid phase, respectively. By hypothesizing that the interactions of the drug and the intermediate products with the catalyst surface are similar, it can be assumed that the values of the equilibrium adsorption constants are approximately equal [41, 44] and the following relationship is obtained:

$$-\frac{dC_D}{dt} = \frac{S}{V}\left(\frac{k'' K_D}{1 + K_D C_{D,0}}\right) C_D = \frac{S}{V} k_{hete} C_D \tag{15}$$

where $C_{D,0}$ is the initial drug concentration and k_{hete} is the observed first order rate constant. Equation 15 can be integrated with the limiting condition that at the beginning of the reaction, $t = 0$, the substrate concentration is the initial one, $C_D = C_{D,0}$. The integral relationship between C_D and t is therefore:

$$C_D = C_{D,0} \exp\left(-\frac{S}{V k_{hete}} t\right) \tag{16}$$

By applying a least squares best fitting procedure to the experimental data, the values of the observed rate constants were determined and are reported in Table 2.

Table 2. Values of the observed rate constants, k_{hete}, obtained by the photocatalytical experiments carried out in the presence of different catalysts

C_0 mg L^{-1}	$k_{hete} \times 10^7$ m s^{-1}					
	Tetracycline		Ranitidine		Lincomycin	
	Merck	Degussa	Merck	Degussa	Merck	Degussa
10	1.68	0.89	3.48	2.21	2.56	2.14
20	0.97	0.61	2.19	1.14	1.19	1.16
50	0.67	0.36	1.08	0.62	0.61	0.53

Table 3. Values of k'' and K calculated for both catalysts

	Tetracycline		Ranitidine		Lincomycin	
	Merck	Degussa	Merck	Degussa	Merck	Degussa
$k'' \times 10^8$ mol s^{-1} m^{-2}	1.01	0.54	2.0	1.13	0.82	0.72
$K \times 10^4$ M^{-1}	2.40	2.85	3.78	3.80	7.74	7.77

The dependence of k_{hete} on the initial drug concentration may be linearized by considering its definition and the following relationship is obtained:

$$\frac{1}{k_{hete}} = \frac{1}{k''} C_{D,0} + \frac{1}{k'' K_D} \quad (17)$$

Equation 17 represents a straight line in a $1/k_{hete}$ versus $C_{D,0}$ coordinate system. The values of k'' and K_D for each drug have been obtained by means of a least squares best fitting procedure and are reported in Table 3. For tetracycline and ranitidine Merck TiO_2 is more active than Degussa P25, whereas for lincomycin both photocatalysts show similar performances.

4. Conclusions

Heterogeneous photocatalysis may be successfully applied to degrade drugs such as tetracycline, lincomycin and ranitidine present in wastewater. Homogeneous irradiation leads to partial degradation of the three substrates and causes almost negligible mineralization. The photocatalytic degradation increases both the reaction rates of the main compounds and the mineralization of the organic intermediates. First order kinetics adequately describe the experimental results and allows determination of the values of the homogeneous and the heterogeneous kinetic constants of the degradation reactions in the presence of both the catalysts.

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