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Photodegradation of pharmaceutical drugs in aqueous TiO_2 suspensions: Mechanism and kinetics

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Abstract

The degradation and mineralization of Tamoxifen (TAM) and Gemfibrozil (GEM) drugs, whose molecular structures exhibit ethereal bonds, have been carried out by irradiating aqueous suspensions of TiO_2 with near-UV light at pH 10. Two commercial polycrystalline TiO_2 powders (Degussa P25 and Merck) were used as the photocatalysts. A remarkable TAM degradation and the formation of stable intermediates which are not mineralized occur in homogeneous system under irradiation through the breakage of the ethereal O–C (sp^3) bond. Heterogeneous photocatalysis plays a minor role on TAM oxidation; in fact the addition of the photocatalyst does not modify the pathway and the rate of primary steps of TAM degradation but it determines the complete mineralization of intermediate products. In irradiated homogeneous solutions GEM undergoes a small partial oxidation while the addition of the photocatalyst determines its complete and fast degradation and mineralization. The identification of some stable intermediate compounds allows one to hypothesise that the breakage of the ethereal bond is also occurring in the primary steps of GEM photocatalytic oxidation. The disappearance rate of TAM is higher than that of GEM both in homogeneous and heterogeneous systems, while the total organic carbon concentration decreases more quickly for GEM. For both drugs the photoreactivity results in homogeneous system indicate a first order kinetics with respect to the drug concentration. The GEM photocatalytic results have been modelled by the Langmuir–Hinshelwood relation which allows one to determine the values of the kinetic constants and the equilibrium adsorption constants. TiO_2 Degussa P25 showed to be the most active photocatalyst for both the degradation and mineralization of GEM.

Keywords: Drug photodegradation; Gemfibrozil; Tamoxifen; Heterogeneous photocatalysis; Titanium dioxide

1. Introduction

In recent years an increasing attention has been devoted to pharmaceutical compounds as a class of environmental pollutants [1–8]. The reason why they may be dangerous for the environment is that these substances, generally developed with the aim to perform a biological effect on human beings, may also affect other living organisms in a non-predictable way. These compounds enter the aquatic environment after their ingestion and subsequent excretion either without modifications or in the form of non-metabolized parent compounds [6]. More than 4000 molecules are the active principles of more than 10,000 drugs derived from them. Several investigations have shown evidence that some pharmaceutical compounds are not eliminated during wastewater treatments and also not biodegraded in the environment [9,10]. Indeed, a large variety of pharmaceutical compounds has been frequently found in sewage treatment plant effluents and river water at concentrations up to several mg L^{-1} [11]. Pharmaceutical substances have been detected in small creeks and big rivers such as Rhine, Elbe, Neckar, Danube, and Po [12].

Heterogeneous photocatalysis can be used to eliminate organic and inorganic compounds from wastewater in the presence of semiconductor oxides [13–16]. This method has been found effective for the mineralization of drugs and their metabolites in aqueous phase [17,18].

In this paper the photocatalytic degradation and mineralization of two pharmaceuticals, Gemfibrozil (5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoic acid, hereafter indicated as GEM) and Tamoxifen (*Z*)-2-[4-(1,2-diphenylbut-1-enyl)phenoxy]-*N*,*N*-dimethyl-ethanamine, hereafter indicated as TAM), were studied. GEM is a fibrate hypolipidemic agent clinically effective

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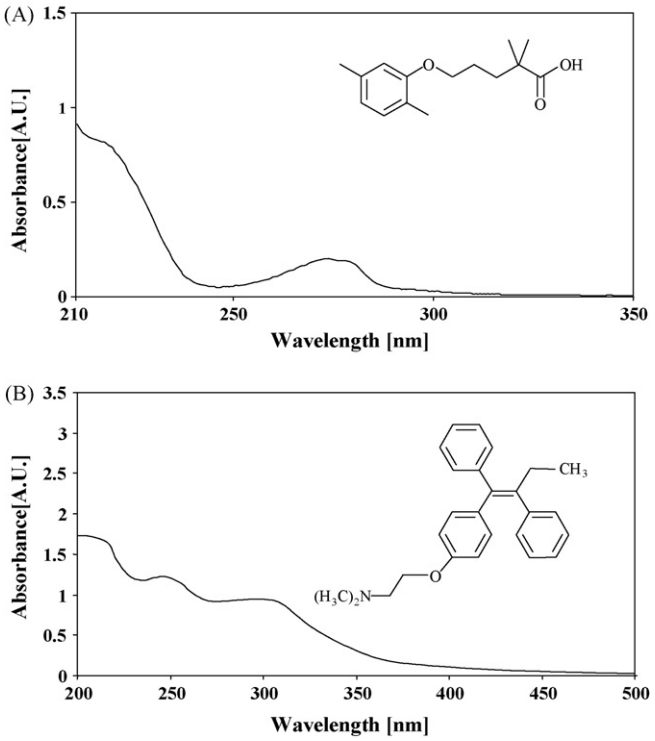


Fig. 1. Absorbance spectra of aqueous solutions (25 mg L^{-1}) of Gemfibrozil (A) and Tamoxifen (B) at pH 10. The structures of the drugs are also reported.

in lowering the incidence of coronary heart diseases [19]. From an environmental point of view GEM can be found at the outlet of water treatment plants and in mud and soil to which it shows some affinity owing to its acidic properties and high value of the octanol/water partition coefficient. The nonsteroidal antiestrogen TAM is a drug extensively used in the treatment and prevention of breast cancer. Fig. 1(A) and (B) report GEM and TAM structural forms, respectively. It may be noted the presence of an O–C (sp^3) ethereal bond both in GEM and TAM molecules.

The aim of this work was to investigate the mechanism and the kinetics of the photodegradation of GEM and TAM dissolved in water. A particular attention was devoted to the stability of the two ethereal bonds in the two different drugs. The degradation of these molecules was carried out by irradiation with near UV light in the absence and in the presence of two kinds of commercial TiO_2 samples, i.e. Degussa P25 and Merck. The influence of the initial drug concentration, the presence and type of the photocatalyst on the photoprocess performance, were studied.

2. Experimental

A Pyrex batch photoreactor of cylindrical shape, with volume of 0.5 L, was used for performing the reactivity experiments; the details of the experimental setup are reported in Ref. [17]. The photoreactor was provided with ports in its upper section for the inlet and outlet of gases and for sampling. A magnetic bar guaranteed a satisfactory suspension of the photocatalyst and the uniformity of the reacting mixture. A 125 W medium pressure Hg lamp (Helios Italquartz) was axially immersed within the photoreactor and it was cooled by water circulating through a Pyrex thimble; the temperature of the suspension was about 300 K. The radiation energy impinging on the suspension had an average value of 10 mW cm^{-2}; it was measured by using a radiometer UVX Digital, at $\lambda = 360$ nm.

The aqueous solution was saturated by bubbling O_2 at atmospheric pressure for 30 min in the dark and then the lamp was turned on. The gas was continuously bubbled also during the runs. Photoreactivity runs were carried out in the absence of photocatalysts for checking the occurrence, if any, of homogeneous degradation of drugs.

The initial concentration of the drugs for the photochemical and the photocatalytic runs was in the 5–50 mg L^{-1} range. The initial pH of the solutions was about 10 for both the drugs, alkaline conditions were chosen because the solubility of GEM is very low at acidic pH's. Samples were withdrawn for analysis at fixed intervals of time. The quantitative determination of each drug concentration was performed by using a HPLC Beckman Coulter (System Gold 126 Solvent Module and 168 Diode Array Detector), equipped with a Luna 5 μ Phenyl-Hexyl column (250 mm long × 2 mm i.d.). The eluent (flow rate: 0.33×10^{-2} cm^3 s^{-1}) was a solution composed by 40% of an aqueous solution of H_3PO_4 0.4%, w/w and 60% of acetonitrile for GEM, while it was a solution composed by 60% of an aqueous solution of HCOOH 0.1%, w/w and by 40% of acetonitrile for TAM. It is worth noting that, before carrying out the TAM analyses, all the withdrawn samples of suspension were acidified at ca. pH 2 with H_2SO_4 to induce desorption of TAM.

The quantitative determination of anionic species was carried out by using an ionic chromatograph system (Dionex DX 120) equipped with an Ion Pac AS14 4 mm column (250 mm long, Dionex). Aqueous solutions of $NaHCO_3$ (1 mM) and Na_2CO_3 (8 mM) were used as eluents at a flow rate of 1.67×10^{-2} cm^3 s^{-1}. The mineralization of the drugs was monitored by determining the total organic carbon (TOC). These measurements were carried out by means of a TOC Shimadzu 5000A analyzer, provided with an automatic autosampler injector ASI 5000 A. The absorption spectra of the withdrawn samples were recorded in a UV–vis Shimadzu 2401 PC spectrophotometer.

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 the photocatalysts. A quantity of 0.4 g L^{-1} of catalyst was used for all the runs. It allowed to absorb all the impinging photons emitted by the lamp. Before analysis the samples were separated from the catalyst by filtration through a 0.45 μm cellulose acetate membrane (HA, Millipore).

In order to determine the intermediate degradation products, GC-mass analyses were carried out by using a Hewlett Packard 1800A GCD System equipped with a polyethylenglycol crosslinked Innowax Fused Silica capillar polar column (60 m × 0.25 mm i.d. × 0.25 μm). The aqueous samples were mixed with diethyl ether in order to extract the organic compounds and then the organic surnatant was analysed.

Gemfibrozil, Tamoxifen citrate salt, and all the other chemicals used were reagent grade from Aldrich and they were used without further purification.

3. Results

Under the used experimental conditions no degradation of GEM and TAM was observed without irradiation in the presence of bubbling oxygen and/or of the photocatalyst.

Experiments of dark adsorption of the drugs on TiO_2 at room temperature were carried out for 30 min before starting the irradiation. A negligible adsorption was showed by GEM, whereas TAM showed a very strong adsorption (almost all the drug adsorbed for the small initial concentrations used).

The UV–vis absorption spectra of GEM and TAM aqueous solutions used for the photoreactivity runs are reported in Fig. 1(A) and (B), respectively. Negligible absorption at wavelengths higher than 300 nm can be observed for GEM, while a significant absorption was showed by TAM.

Fig. 2 shows the results of GEM photoreactivity runs carried out in homogeneous system. GEM exhibited a very small photodegradation, while no measurable mineralization was observed (TOC results not showed for the sake of brevity). Figs. 3 and 4 show GEM and TOC (in the insets) concentration trends during photodegradation runs carried out with Merck and Degussa P25, respectively. The TOC results indicate that the mineralization starts to be important when GEM concentration reaches low values. For the highest initial concentration of GEM the irradiation times needed for the drug complete disappearance were about 3.0 h (10.8 ks) and 0.5 h (1.8 ks) and the times of complete mineralization were 15 h (54 ks) and 3.2 h (11.5 ks) for Merck and Degussa P25, respectively. On this basis TiO_2 Degussa P25 seems to be more effective than Merck both for GEM degradation and mineralization. In any case the presence of the catalyst allowed the complete drug degradation together with its complete mineralization.

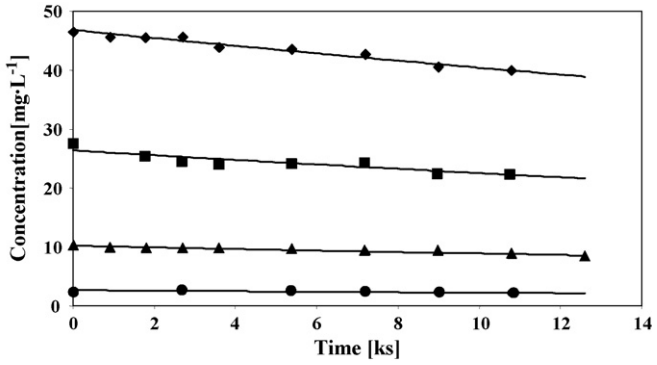


Fig. 2. GEM concentration vs. irradiation time for homogeneous degradation. ◆, 47 mg L^{-1}; ■, 28 mg L^{-1}; ▲, 10 mg L^{-1}; ●, 2.5 mg L^{-1}.

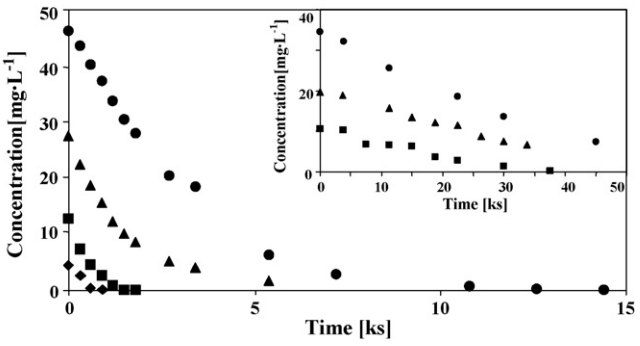


Fig. 3. GEM concentration vs. irradiation time for photocatalytic degradation carried out with TiO_2 Merck. In the inset TOC concentration for the same runs. ●, 47 mg L^{-1}; ▲, 28 mg L^{-1}; ■, 11 mg L^{-1}; ◆, 4 mg L^{-1}.

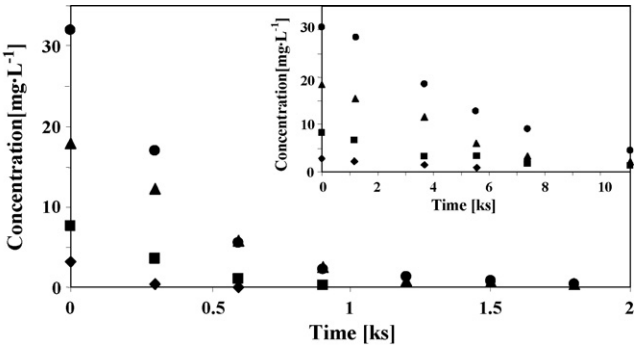


Fig. 4. GEM concentration vs. irradiation time for photocatalytic degradation carried out with TiO_2 Degussa P25. In the inset TOC concentration for the same runs. ●, 32 mg L^{-1}; ▲, 17 mg L^{-1}; ■, 8 mg L^{-1}; ◆, 2.5 mg L^{-1}.

Fig. 5 reports the results of TAM homogeneous and heterogeneous photodegradation as TAM concentration versus irradiation time; in the inset the corresponding TOC values are reported.

For the homogenous run reported in Fig. 5 the TAM concentration became negligible after 20 min (1.2 ks) of irradiation, whereas no evidence of mineralization was found for all the duration of the run (18 h, i.e. 64.8 ks). As it may be noted from the data reported in Fig. 5, the addition of the catalyst to the reacting system has a detrimental effect on the TAM degradation rate, being this effect more important for Merck catalyst. In fact the irradiation times needed for the TAM complete disappearance were about 60 min (3.6 ks) and 83 min (5 ks) for Degussa P25 and Merck, respectively. Nevertheless it is worth noting that the presence of the photocatalyst positively affected the mineralization rate as the TOC values continuously decreased with the irradiation time. Times for complete mineralization were ca. 22 h (79.8 ks) and 28 h (100.8 ks) for

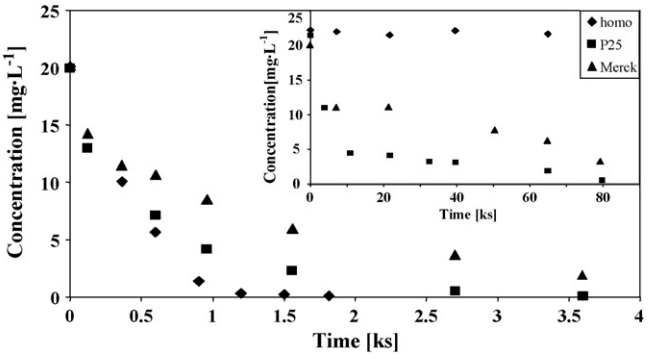


Fig. 5. TAM concentration vs. irradiation time for photoreactivity runs carried out: ◆, in homogeneous condition; ■, with TiO_2 Degussa P25; and ▲, with TiO_2 Merck. In the inset TOC concentration for the same runs.

Degussa P25 and Merck, respectively. Degussa P25 seems to be more photoactive than Merck, both for GEM and TAM mineralization.

GC-mass analyses showed that the main intermediate of GEM photochemical degradation is 5-(2-methyl,5-methanal)-2,2-dimethylpentanoic acid, i.e. a methyl group of the aromatic ring is oxidised to –CHO, while in the presence of catalyst the main intermediates were 2,5-dimethylphenol and 2,2-dimethylpentanoic acid, i.e. the breakage of the ethereal O–C (sp^3) bond occurred.

As far as TAM is concerned, GC-mass analyses evidently showed that both the homogeneous photochemical process and the heterogeneous one produced the same intermediate compounds; in particular the formation of 2,6-di(1,1-dimethylethyl)-4-methylphenol was observed together with oxalate, acetate, formate ions, and acetaldehyde. This finding, along with the observation that the degradation rate of TAM does not substantially increase in the presence of photocatalyst, suggests that the photocatalytic mechanism plays a minor role with respect to the photochemical one on the initial steps of TAM degradation. The great photoreactivity of TAM molecule was confirmed by a run carried out in homogeneous system by using distilled water completely degassed before the addition of TAM and by bubbling dinitrogen in the course of the irradiation. It was found that the absence of oxygen in the solution did not affect TAM degradation that occurred at a rate lower than that with oxygen but produced the same intermediate products. The important role played by the photocatalytic mechanism is however that of degrading quickly the TAM intermediate products as indicated by the TOC continuous decrease. Moreover nitrate ions were not detected in the course of TAM homogeneous degradation; these ions only appeared in the course of photocatalytic runs.

4. Discussion

4.1. Mechanistic aspects

The homogeneous photochemical degradation of an organic compound generally starts from an electronic excited state following the radiation absorption:

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

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:

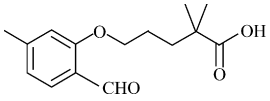
$$R^* \rightarrow R_1^{\bullet} + R_2^{\bullet} \rightarrow \text{products} \quad (2)$$

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

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

The formed radical cation, $R^{\bullet+}$, can undergo hydrolysis or mesolytic bond scission to low weight products. The superoxide radical, $O_2^{\bullet-}$, is able to induce the degradation of many aromatic species [20].

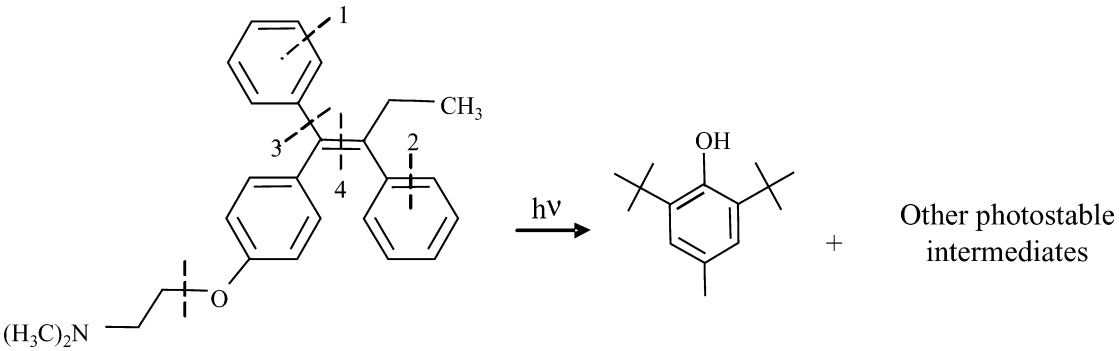
The reactivity results show that the homogeneous photochemical process of GEM degradation is very slow and produces traces of the following aldehyde intermediate, as firstly reported by Cermola et al. [21]:



i.e. there is a partial oxidation of the 2-methyl group of aromatic ring while the ether C–O–C bonds are not modified.

The very low photoreactivity of GEM molecule in homogeneous system is completely justified by the fact that the radiation reaching the solution has wavelengths higher than 300 nm due to the filtering effect of Pyrex glass present between the lamp and the solution. At those wavelengths GEM shows a negligible absorbance (see Fig. 1(A)). On the contrary TAM molecule undergoes a fast photodegradation through a photochemical process which breaks the ethereal O–C (sp^3) bond present in the lateral chain and produces stable intermediates that cannot be mineralized, as shown by the TOC results reported in the inset of Fig. 5. Really TAM shows significant absorption also at wavelengths higher than 300 nm, although the high photoreactivity found can not be straightforwardly related only to this feature. TAM molecule, in fact, is *per se* more reactive with respect to GEM, due to the lower stability of the O–C (sp^3) bond whose breakage produces more highly stable phenoxyde radicals. The presence of three aromatic rings in the molecule, instead of one as in the case of GEM, can induce a more significant electron delocalization.

By considering that TAM homogeneous photodegradation gives rise to the formation of 2,6-di(1,1-dimethylethyl)-4-methylphenol together with oxalate, acetate, formate ions, acetaldehyde, a likely scheme of this reaction is the following one:

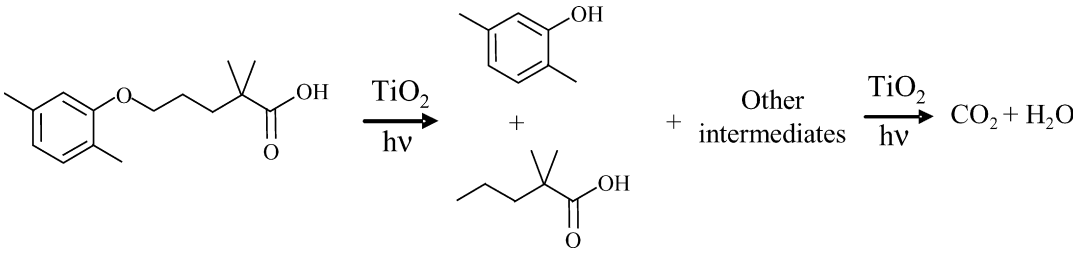


(4)

It can be tentatively hypothesised that the breakage of the ethereal bond of the not aromatic linear chain with the formation of OH group is followed by the opening of two aromatic rings (1 and 2 in the scheme) and the entrance of the other substituents in *ortho* position with respect to OH. The subsequent breakage of bonds 3 and 4 (see the scheme) leads to the formation of the methyl group in *para* position.

As far as the mechanism of the heterogeneous photocatalytic reaction is concerned, the primary step following the radiation absorption by the photocatalyst is the generation of electron–hole pairs that migrate to the surface of the particles where they can participate to redox reactions. In aqueous solutions, the oxidation of organic species has been attributed to the trapping reaction of the positive holes with adsorbed water or with hydroxyl groups to form $HO^{\bullet}$ radicals responsible for the primary oxidant attack [22]. $HO^{\bullet}$ radicals can also be formed *via* the superoxide radical anion $O_2^{\bullet -}$ obtained by reaction of the photogenerated electrons with adsorbed oxygen.

By taking into account the results obtained by the photoreactivity runs and by GC-Mass analyses, GEM heterogeneous photocatalytic oxidation, can be represented as follows:



(5)

The ethereal bond present in the GEM linear chain is destabilised by the presence of an aromatic group, but its breakage occurs only in the presence of the irradiated photocatalyst.

The rate of TAM photodegradation in the heterogeneous systems was lower than that in homogeneous one. By considering that the rate of TAM degradation through the homogeneous photochemical process depends on the radiation intensity profile inside the solution, the rate decrease in heterogeneous system may be attributed to the fact that the dispersed solid particles absorb photons and then lower the light intensity under which the homogeneous process proceeds. Moreover the rate decrease in heterogeneous system together with the finding that the same intermediate compounds were produced by the homogeneous and heterogeneous process is a clear clue that the heterogeneous photocatalytic mechanism plays a minor role on the initial steps of TAM degradation. Nevertheless only the presence of irradiated photocatalyst gave rise to TAM complete mineralization (see Fig. 5, inset), indicating that heterogeneous photocatalysis plays a fundamental role for the subsequent oxidation steps.

This finding suggests that nitrogen atoms remain bonded to organic chains and only in the presence of TiO_2 and light their oxidation to nitrates can be achieved:

$$\mathrm{TAM} \xrightarrow{h\nu} \text{photostable intermediates} \xrightarrow[h\nu]{TiO_2} CO_2 + H_2O + {NO_3}^- \tag{6}$$

4.2. Kinetic aspects

Under the reaction conditions used for carrying out the photochemical degradation runs of GEM and TAM, it is reasonable to assume that the lifetime of the excited state is normally stabilized by solvent interaction. In the presence of a large excess of an external oxidizing agent as molecular oxygen, the excited state is quenched at diffusion rate according to Eq. (3). By hypothesizing that the lifetimes of radicals and other reactive species are sufficiently long, it can be assumed that the rate of drug degradation by the homogeneous photochemical reaction, $(-r_{\mathrm{homo}})$, has the following form [23]:

$$(-r_{\mathrm{homo}}) = -\frac{1}{V}\frac{dN_D}{dt} = -\frac{dC_D}{dt} = \Phi I_a = \frac{\Phi I_0[1-\exp(-1\varepsilon C_D)]}{1} \tag{7}$$

where V is the reaction volume, N_D the drug moles, t the irradiation time, C_D the drug molar concentration, Φ the primary quantum yield, I_a and I_0 the absorbed and incident photon flows, l the light path length and ε the molar extinction coefficient of the drug.

At the experimental conditions used in this work GEM solutions show a small radiation absorption in the 300–320 nm range (see Fig. 1(A)) while TAM solutions a relevant absorption in the 300–400 nm range (see Fig. 1(B)). As the main emission peaks of the lamp are 310 and 365 nm (in the range 300–400 nm), the ε value for GEM was evaluated at the radiation wavelength of 310 nm while that for TAM at 337.5 nm (mean value between 310 and 365 nm); the values are 67 and 1158 $M^{-1}\,cm^{-1}$ for GEM and TAM, respectively. It is worth noting that photons corresponding to 310 nm wavelength could be responsible for the breakage of the O–C (sp^3) bond in homogeneous system for TAM. By considering that l is equal to 2.5 cm and the highest initial concentrations used for GEM and TAM are 1.8×10^{-4} M (45 mg L^{-1}) and 5.38×10^{-5} M (20 mg L^{-1}), respectively, it may be assumed that $\exp(-\varepsilon l C_D) \cong 1 - \varepsilon l C_D$. On this ground Eq. (7) can be

rewritten as:

$$(-r_{\text{homo}}) = \frac{dC_D}{dt} = k'_{\text{homo}} C_D \quad (8)$$

where k'_{homo} is the pseudo-first order rate constant and it is equal to $\Phi I_0 \varepsilon$. Eq. (8) can be easily integrated with the limiting condition that at $t = 0$ the drug concentration is the initial one, $C_{D,0}$, giving:

$$C_D = C_{D,0} \exp(-k'_{\text{homo}} t) \quad (9)$$

By applying a least square best fitting procedure to the experimental data, the values of k'_{homo} were calculated for all the runs ($R^2 > 0.98$). The average values are 1.47×10^{-5} and 3.11×10^{-3} s^{-1} ($R^2 > 0.98$) for GEM and TAM, respectively.

Owing to the fact that heterogeneous photocatalysis plays a minor role on degradation of TAM molecule, the kinetic modelling of heterogeneous system is here carried out only with the GEM results. By considering that in the presence of the catalyst the contribution of homogeneous photochemical degradation of GEM is negligible, the rate of the heterogeneous photocatalytic reaction, $(-r_{\text{hete}})$, can be expressed in terms of the Langmuir–Hinshelwood model as:

$$(-r_{\text{hete}}) \equiv -\frac{1}{S}\frac{dN_D}{dt} = -\frac{V}{S}\frac{dC_D}{dt} = k'' \theta_D \theta_{Ox} \quad (10)$$

where S is the surface area of the photocatalyst, k'' the surface rate constant, θ_D and θ_{Ox} the fractional site coverage by GEM and oxygen, respectively. The θ_D term is given by the Langmuir relationship:

$$\theta_D = \frac{K_D C_D}{1 + K_D C_D + \sum K_I C_I} \quad (11)$$

where K_D and K_I are the equilibrium adsorption constants of GEM and of its intermediate products, and C_D and C_I the GEM and its intermediate products concentrations in the liquid phase, respectively. By hypothesising 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. Moreover, in the time needed for GEM disappearance the TOC concentration did not vary strongly suggesting that the mineralization and the production of volatile compounds during GEM degradation is small; it may be therefore assumed that $C_D + \sum C_I \cong C_{D,0}$. Under the previous hypotheses, the following approximation may be assumed:

$$K_D C_D + \sum K_I C_I \approx K_D C_{D,0} \quad (12)$$

By substituting Eqs. (11) and (12) into Eq. (10), the following relationship is obtained:

$$-\frac{dC_D}{dt} = \frac{S}{V}\left(\frac{k' K_D}{1 + K_D C_{D,0}}\right) C_D = k_{\text{obs}} C_D \quad (13)$$

in which $k' = k'' \theta_{Ox}$ is constant as the oxygen concentration was always the same during the runs. Integration of Eq. (13) with the usual limiting condition that at $t = 0$, $C_D = C_{D,0}$ gives:

$$C_D = C_{D,0} \exp(-k_{\text{obs}} t) \quad (14)$$

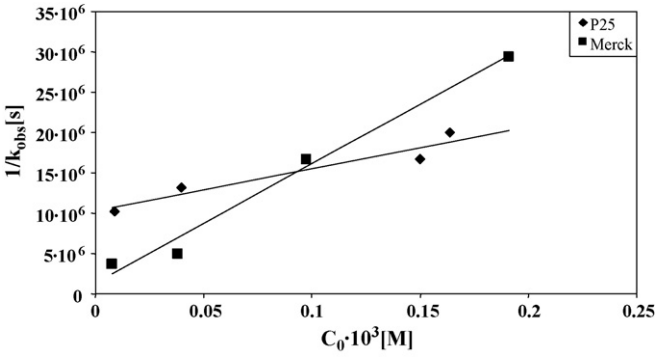


Fig. 6. $1/k_{\text{obs}}$ vs. initial GEM concentrations. The straight lines represent Eq. (15), the fitted model.

By applying a least square best fitting procedure to the experimental data, the values of the observed rate constants were determined.

The k_{obs} values depend on the initial GEM concentration by the following equation:

$$\frac{1}{k_{\text{obs}}} = \frac{V}{S}\left(\frac{1}{k' K_D} + \frac{C_{D,0}}{k'}\right) \quad (15)$$

Fig. 6 shows the $1/k_{\text{obs}}$ values versus $C_{D,0}$ for each photocatalyst. By applying a least square best fitting procedure to the data the values of k' and K_D were determined; the values of k' are 1.91×10^{-8} and 6.78×10^{-9} mol m^{-2} s^{-1} and those of K_D 5.11×10^3 and 1.07×10^5 M^{-1} for Degussa P25 and Merck, respectively. It is worth noting that a straightforward correlation between the equilibrium adsorption constants given by the Langmuir–Hinshelwood kinetic model and the adsorption properties measured in the absence of radiation is generally very difficult because the catalyst surface is strongly modified under irradiation by phenomena of photoadsorption, photodesorption and electron/hole trapping.

5. Conclusions

In homogeneous irradiated system TAM molecule underwent a strong degradation while GEM only a very slow partial oxidation but no evidence of mineralization was found for both drugs. The heterogeneous photocatalytic method was able to mineralize both GEM and TAM molecules and for the last one also the complete oxidation of nitrogen to NO_3^- was achieved. The best performance of the photocatalytic process was obtained with TiO_2 Degussa P25 sample with respect to the Merck one. The initial stage of GEM photocatalytic degradation gave rise to the breakage of the ethereal O–C (sp^3) bond, present also in TAM molecules. This mechanism also occurs in the homogeneous photodegradation of TAM. The presence of three aromatic rings near the TAM ethereal bond, in fact, strongly decreases its stability due to the electron delocalization effect. Phenoxyde radicals deriving from the attack to the TAM

ethereal bond can be formed more easily because they are more stable. This effect is so high that TAM molecule could be degraded in homogeneous solution with the radiation alone.

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