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Photodegradation of norfloxacin in aqueous suspensions of titanium dioxide

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Abstract

The photocatalytic degradation of an antibiotic norfloxacin [1-ethyl-6-fluoro-1,4-dihydro-4-oxo-7-(1-piperazinyl)-3-quinoline-carboxylic acid, **1**], has been investigated in aqueous suspensions of titanium dioxide (TiO_2) under a variety of conditions. The degradation was studied by monitoring the change in substrate concentration employing UV spectroscopic analysis technique and depletion in total organic carbon (TOC) content as a function of irradiation time. The degradation kinetics were investigated under different conditions such as different types of TiO_2, pH (ranging from 4 to 11), catalyst concentration (0.5–3 g L^{-1}), substrate concentration (0.15–0.5 mM) and in the presence of electron acceptor such as hydrogen peroxide (H_2O_2, 10 mM) besides molecular oxygen. Semiconductor titanium dioxide (Degussa P25) was found to be more efficient as compared with other photocatalysts.
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Keywords: Photocatalytic degradation; Antibiotic; Norfloxacin; Titanium dioxide; Semiconductor
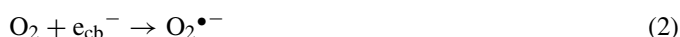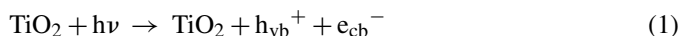
1. Introduction

Polluted water pose a serious problem to the environment. Besides water pollutants such as pesticides, dyes and surfactants, pharmaceuticals are an emerging class of aquatic contaminants. Both human and veterinary pharmaceuticals have been increasingly detected in sewage water, natural water, surface water and ground water [1–5]. The main problem regarding the pharmaceutical as pollutants is that their biological activity leads to adverse effects on aquatic ecosystems [2–7]. They also create adversely effects on soil organism. Pharmaceuticals enter into the aquatic environment mainly through treated and untreated sewage and human excretion into wastewater. They also enter into the aquatic system via dispersion of manure onto agricultural soils or via urban runoff from farms, where animals are even more overmedicated than humans. The waste pharmaceuticals and its derivatives also enter into the environment through effluents from pharmaceutical industries.

Among the antibiotic drugs, fluoroquinolone group is probably the most important class of synthetic antibiotics in human and veterinary medicines worldwide [8]. Norfloxacin is the major human-use fluoroquinolone. Fluoroquinolone are excreted largely unchanged and about less than 25% are metabolized in the body [9]. Thus most of the fluoroquinolone are pass out through human and animal excretion as such and enters into the water system. Most of the pharmaceutical compounds have polar structure, so they are not significantly adsorbed in the subsoil but they may leach into the groundwater aquifers from the contaminated surface water. Therefore many drugs are detected in sewage effluents, groundwater, surface and drinking water all over the world. Norfloxacin have been detected in wastewater streams as an organic pollutant [4,7]. Among many processes proposed and/or being developed for the destruction of the organic contaminants, biodegradation has received the greatest attention. However, many organic chemicals, especially those that are toxic or refractory, are not amendable to microbial degradation. Recently considerable attention has been focussed on the use of semiconductor as a means to oxidize toxic organic chemicals [10–13]. The photocatalysed degradation of various organic systems employing irradiated TiO_2 is well documented in the literature [11]. Briefly, when a semiconductor such as TiO_2 absorbs a photon of energy equal to or greater than its band gap width, an electron may be promoted from the valence band to the conduction band (e_{cb}^-) leaving behind an electron vacancy or

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"hole" in the valence band (h_{vb}^+). If charge separation is maintained, the electron and hole may migrate to the catalyst surface where they participate in redox reactions with sorbed species. Specially, h_{vb}^+ may react with surface-bound H_2O or OH^- to produce the hydroxyl radical and e_{cb}^- is picked up by oxygen to generate superoxide radical anion (O_2^-), as indicated in the following Eq. (1–3):

$$TiO_2 + h\nu \rightarrow TiO_2 + h_{vb}^+ + e_{cb}^- \tag{1}$$

$$O_2 + e_{cb}^- \rightarrow O_2^{\bullet-} \tag{2}$$

$$H_2O + h_{vb}^+ \rightarrow {}^{\bullet}OH + H^+ \tag{3}$$

It has been suggested that the hydroxyl radicals and superoxide radical anions are the primary oxidizing species in the photocatalytic oxidation processes. These oxidative reactions would result in the degradation of the pollutant and the efficiency of degradation will depend upon the oxygen concentration, which determines the efficiency with which the conduction band electrons are scavenged and the (e^-/h^+) recombination is prevented.

Photodegradation by direct excitation of few drugs have been reported earlier [14–19]. The model compound norfloxacin (**1**) is used as a synthetic broad-spectrum antibacterial drug. To the best of our knowledge no major effort have been made to study the photocatalytic degradation of this model compound. Therefore in this paper we present the results of our investigation of the photocatalysed degradation kinetics of norfloxacin in aqueous suspensions of TiO_2 under a variety of conditions. The aim of the present study was to determine the best photocatalyst among three different TiO_2 materials and find further means to accelerate the efficiency of the photocatalytic process.
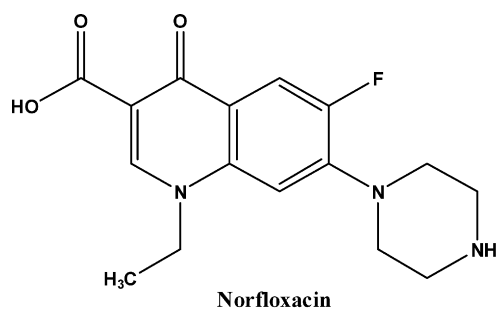
Norfloxacin

1-ethyl-6-fluoro-1,4-dihydro-4-oxo-7-(1-piperazinyl)-3-quinoline-carboxylic acid

$C_{16}H_{18}FN_3O_3$
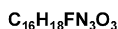
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2. Experimental methods

2.1. Reagents

The antibiotic sample norfloxacin (**1**) was obtained from Cipla, India and used as such without any further purification.

Double distilled water was employed in this study to make a solution for the irradiation experiments. The photocatalyst, titanium dioxide P25 (Degussa AG) was used in most of the experiments. Other catalyst powders, namely, Hombikat UV100 (Sachtleben Chemie GmbH) and PC500 (Millennium Inorganic Chemicals), were used for comparative studies. Degussa P25 contains 75% anatase and 25% rutile with a specific BET surface area of $50 \, m^2 \, g^{-1}$ and a primary particle size of 20 nm [20]. Hombikat UV100 consists of 100% pure anatase with a specific BET surface area of $250 \, m^2 \, g^{-1}$ and a primary particle size of 5 nm [21]. The photocatalyst PC500 has a BET-surface area of $287 \, m^2 \, g^{-1}$ with 100% anatase and primary particle size of 5–10 nm [22]. The other chemicals used in this study, such as sodium hydroxide, nitric acid and hydrogen peroxide are of reagent grade and were obtained from Merck.

2.2. Procedure

Solutions of desired concentrations of norfloxacin were prepared in double distilled water. Due to low solubility in water, aqueous solution of norfloxacin (**1**, 0.25 mM, pH 6.3) was prepared in 2 L double distilled water by adding 2 mL of 0.25 M aqueous NaOH solution for irradiation experiments. An immersion well photochemical reactor made of Pyrex glass was used in this study. The desired solution (250 mL) was poured into the reactor and the required amount of photocatalyst was added. The solution was stirred for at least 15 min in the dark to allow equilibration of the system. The zero time reading was obtained from a blank solution kept in the dark but otherwise treated similarly to the irradiated solution. The suspensions were continuously purged with molecular oxygen throughout each experiment. Irradiations were carried out using a 125 W medium pressure mercury lamp (Philips). IR fractions of radiation were eliminated by a water circulating "Pyrex" jacket. Samples (10 mL) were collected before and at regular intervals during the irradiation and centrifuged before analysis.

2.3. Analysis

The degradation was followed by measuring the change in absorption intensity at 284 nm using Shimadzu UV–vis Spectrophotometer (Model 1601). The mineralization was monitored by measuring the total organic carbon (TOC) content

with a Shimadzu TOC 5000A Analyzer by directly injecting the aqueous solution after centrifugation.

3. Results and discussion

3.1. Photocatalysis of TiO₂ suspensions containing norfloxacin (1)

Irradiation of an aqueous solution of norfloxacin (**1**, 0.25 mM, 250 mL) in the presence of TiO₂ (Degussa P25, 1 g L^{-1}) by the "pyrex" filtered output of 125 W medium pressure mercury lamp, lead to decrease in the absorption intensity as well as depletion in TOC content. Fig. 1 shows the change in absorption intensity and depletion in TOC content as a function of irradiation time for the photocatalytic degradation of norfloxacin in the absence and presence of the photocatalyst. Both the decomposition and mineralization curves can be fitted reasonably well by an exponential decay curve suggesting first order kinetics. For each experiment, the rate constant was calculated from the plot of natural logarithm of TOC and antibiotic concentration as a function of irradiation time. The degradation rate for the mineralization (depletion of TOC content versus irradiation time) and decomposition (decrease in absorption intensity versus irradiation time) was calculated using formula given below:

$$-\frac{\mathrm{d}[\mathrm{TOC}]}{\mathrm{d}t} = kc, \qquad -\frac{\mathrm{d}[A]}{\mathrm{d}t} = kc$$

TOC = total organic carbon, A = absorbance, k = rate constant, c = concentration of the pollutant.

Control experiments were carried out in all cases, employing unirradiated blank solutions. No observable loss of the compound takes when the irradiation was carried out in the absence of TiO₂. The zero irradiation time reading was obtained from blank solutions kept in the dark, but otherwise treated similarly to the irradiated solutions.
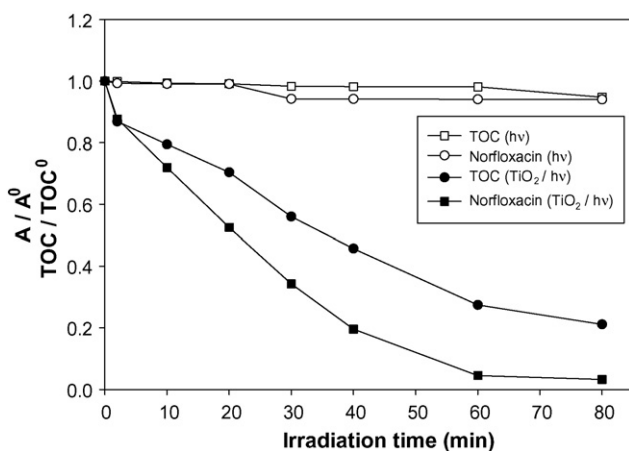

Fig. 1. Depletion in TOC and change in absorption intensity as a function of irradiation time for an aqueous solution of norfloxacin (**1**) in the presence and absence of photocatalyst. Experimental conditions: 0.25 mM norfloxacin, $V = 250$ mL, pH 6.3, photocatalyst: TiO₂ (Degussa P25, 1 g L^{-1}), immersion well photoreactor, 125 W medium pressure Hg lamp, absorbance was followed at 284 nm, cont. O₂ purging and stirring, irradiation time = 80 min.
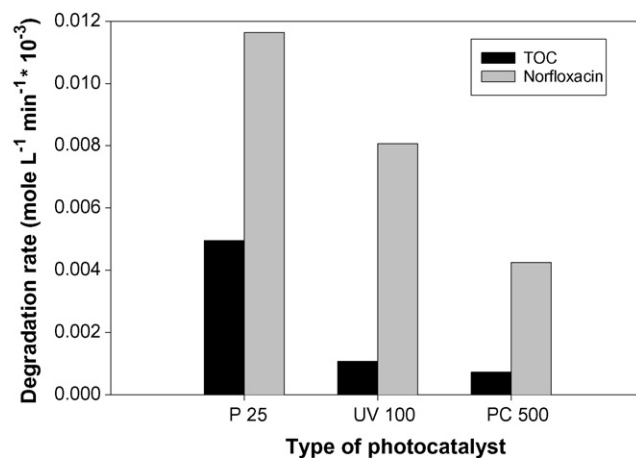

Fig. 2. Comparison of degradation rate for the mineralization (TOC depletion vs. irradiation time) and decomposition (change in absorption intensity vs. irradiation time) of norfloxacin (**1**) in the presence of different photocatalysts. Experimental conditions: 0.25 mM norfloxacin, $V = 250$ mL, pH 6.3, photocatalysts: TiO₂ Degussa P25 (1 g L^{-1}), Sachtleben Hombikat UV100 (1 g L^{-1}), PC500 (1 g L^{-1}), irradiation time = 80 min.

3.2. Comparison of different TiO₂ photocatalysts

Titanium dioxide, due to its higher photocatalytic activity, non-toxic nature, stability in aqueous solutions and relatively low cost, has demonstrated that degradation by photocatalysis could be a more efficient alternative as compared to the other wet oxidation techniques. Fig. 2 shows the degradation for the decomposition and mineralization of norfloxacin (0.25 mM) in the presence of different photocatalysts. It was observed that the degradation was slightly faster in the presence of Degussa P25, as compared to the other photocatalysts. Hence in all following experiments, Degussa P25 was used as the photocatalyst because this material exhibited the highest overall activity for the degradation of the model compound under investigation. The efficiency for the decomposition of the model compound was found to be higher as compared with the mineralization.

The results obtained for the photodegradation of the model compounds using different kinds of TiO₂ photocatalysts exhibiting different bulk and surface properties, i.e., impurities, lattice mismatches, or density of hydroxyl groups on the catalyst's surface, are apparently responsible for the photocatalytic activity, since they will affect the adsorption behavior of a pollutant or intermediate molecule and the lifetime and recombination rate of electron-hole pairs. Earlier studies have shown that Degussa P25 shows better activity for the photocatalytic degradation of a large number of organic compounds [11,23–24], whereas Lindner et al. [25] demonstrated that Hombikat UV100 is much more effective than P25 for dichloroacetic acid. Also Hombikat UV100 was found to be better for the degradation of benzidine, 1,2-diphenyl hydrazine [26] and remazol brilliant blue R [24] as shown in a recent study. These results have demonstrated that the activity of the photocatalysts not only depend upon the photocatalyst properties, but also on the type of the model pollutant.

The adsorption of an antibiotic norfloxacin on the surface of different photocatalyst (Degussa P25, Hombikat UV100,
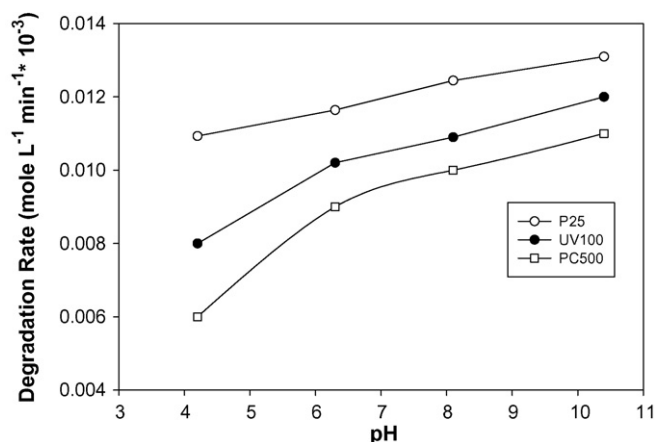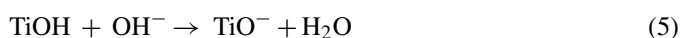
Fig. 3. Influence of pH on the degradation rate for the decomposition of norfloxacin (**1**). Experimental conditions: 0.25 mM norfloxacin, $V = 250$ mL, photocatalyst: TiO$_2$ Degussa P25 (1 g L^{-1}), Hombikat UV100 (1 g L^{-1}), PC500 (1 g L^{-1}), reaction pH (4.2, 6.3, 8.1 and 10.4), irradiation time = 80 min.

Fig. 4. Influence of substrate concentration on the degradation rate for the mineralization and for the decomposition of norfloxacin (**1**). Experimental conditions: substrate concentrations (0.15, 0.25, 0.35 and 0.50 mM), $V = 250$ mL, pH 6.3, photocatalyst TiO$_2$ (Degussa P25, 1 g L^{-1}), irradiation time = 80 min.

PC500) was investigated by stirring the aqueous solution in the dark for 24 h in a round-bottomed flask at different concentration such as 0.5, 1.0, 2.0 and 3.0 g L^{-1}. Analysis of the samples after centrifugation indicates no observable loss of the compound.

3.3. Effect of pH

Another important parameter in the photocatalytic reactions taking place on the semiconductor particulate surfaces is the pH of the solution, since it determines the surface charge properties of the photocatalyst and therefore the adsorption behaviour of the pollutants. Therefore, the influence of pH on the degradation of norfloxacin in aqueous suspensions of different types of TiO$_2$ was studied at pH ranging from 4 to 11. Fig. 3 shows the degradation for the decomposition of norfloxacin (**1**, 0.25 mM) as a function of reaction pH employing Degussa P25, Hombikat UV100 and PC500 (1 g L^{-1}). The degradation for the decomposition was found to increase with increasing pH from 4 to 11.

The interpretation of pH effects on the photocatalytic process is very difficult task because of its multiple roles such as electrostatic interactions between the semiconductor surface, solvent molecules, substrate and charged radicals formed during the reaction process. The ionization state of the surface of the photocatalyst can be protonated and deprotonated under acidic and alkaline conditions, respectively, as shown in following equations:

$$TiOH + H^+ \rightarrow TiOH_2^+ \tag{4}$$

$$TiOH + OH^- \rightarrow TiO^- + H_2O \tag{5}$$

The point of zero charge (pzc) of the TiO$_2$ (Degussa P25) is widely reported at pH ~ 6.25 [27]. Thus, the TiO$_2$ surface will remain positively charged in acidic medium (pH < 6.25) and negatively charged in alkaline medium (pH > 6.25). In this study it has been shown that the degradation for the model compound under investigation is strongly influenced by the reaction pH as
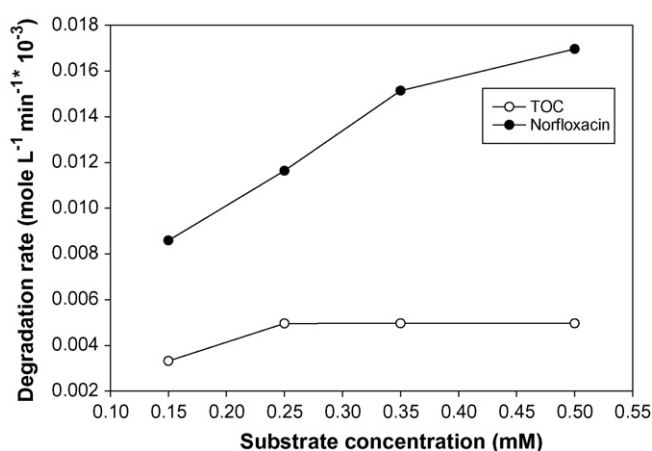
shown in Fig. 3. The better efficiency for the degradation of the compound 1 in alkaline pH could be attributed on the basis of efficient generation of hydroxyl radicals by TiO$_2$ with increasing concentration of OH$^-$.

The adsorption of an antibiotic norfloxacin on the surface of the photocatalyst (Degussa P25, 1 g L^{-1}) was investigated by stirring the aqueous solution in the dark for 24 h in a round-bottomed flask at different pH such as 4.2, 6.3, 8.1 and 10.4. Analysis of the samples after centrifugation indicates no observable loss of the compound.

3.4. Effect of substrate concentration

It is important both from mechanistic and from application point of view to study the dependence of photocatalytic reaction rate on the substrate concentrations. Hence the influence of substrate concentration on the degradation rate was studied at different concentrations varying from 0.15 to 0.50 mM under a UV light source. Fig. 4 shows the degradation for the decomposition and mineralization of norfloxacin as a function of substrate concentration employing Degussa P25 as photocatalyst (1 g L^{-1}). It could be seen from the figure that the degradation rate for the decomposition increases with the increase in substrate concentration. Whereas, its influence on the rate for the mineralization was not pronounced from 0.25 to 0.5 mM and found to be more or less same within the experimental error limits. It increases from 0.15 to 0.25 mM only.

As oxidation proceeds, less and less of the surface of the TiO$_2$ particle is covered as the pollutant is decomposed. Evidently, at total decomposition, the rate of degradation is zero and a decreased photocatalytic rate is to be expected with increasing irradiation time. It has been agreed, with minor variation that the expression for the rate of photomineralization of organic substrates with irradiated TiO$_2$ follows the Langmuir Hinshelwood (L-H) law for the four possible situations, i.e., (a) the reaction takes place between two adsorbed substances, (b) the reaction occurs between a radical in solution and an adsorbed

Table 1
Degradation rate for the decomposition of norfloxacin employing Degussa P25 at optimum pH 10.4 in the presence of different substrate and catalyst concentration

Parameters	Degradation rate for the decomposition ($\times 10^{-3}$ mol L^{-1} min^{-1})
Substrate concentration (mM)	
0.15	0.009
0.25	0.013
0.35	0.016
0.50	0.017
Catalyst concentration (g L^{-1})	
0.5	0.008
1.0	0.013
2.0	0.015
3.0	0.016

Experimental conditions: $V = 250$ mL, pH 10.4, photocatalyst TiO$_2$ (Degussa P25), immersion well photoreactor, 125 W medium pressure Hg lamp, absorbance was followed at 284 nm, cont. O$_2$ purging and stirring, irradiation time = 80 min.
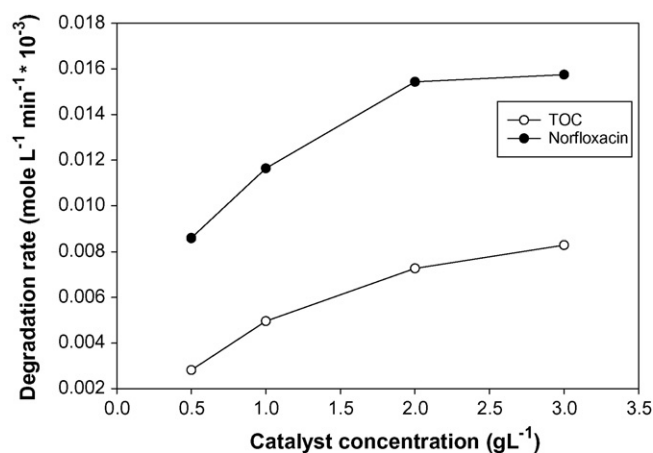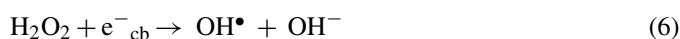

Fig. 5. Influence of catalyst concentration on the degradation rate for the mineralization and for the decomposition of norfloxacin (**1**). Experimental conditions: 0.25 mM norfloxacin, $V = 250$ mL, pH 6.3, photocatalyst: TiO$_2$ Degussa P25 (0.5, 1, 2 and 3 g L^{-1}), irradiation time = 80 min.

substrate molecule, (c) the reaction takes place between a radical linked to the surface and a substrate molecule in solution, and (d) the reaction occurs with both the species being in solution. In all cases, the expression for the rate equation is similar to that derived from the L-H model, which has been useful in modeling the process, although it is not possible to find out whether the process takes place on the surface, in the solution or at the interface. Our results, on the effect of the initial concentration on the degradation rate are in agreement with the assumption of the Langmuir Hinshelwood model.

The degradation of norfloxacin was also investigated at optimum pH 10.4 using different substrate concentration varying from 0.15 to 0.50 mM employing Degussa P25 as photocatalyst (1 g L^{-1}) as shown in Table 1. It could be seen that the degradation rate for the decomposition of norfloxacin increases with the increase in substrate concentration.

3.5. Effect of catalyst concentration

The influence of the photcatalyst concentration on the degradation for the decomposition and mineralization of norfloxacin (**1**, 0.25 mM) was investigated using different concentrations of Degussa P25 varying from 0.5 to 3 g L^{-1} as shown in Fig. 5. It can be seen from the figure that the degradation for the decomposition and mineralization of the model compound improved markedly.

Whether in static, slurry, or dynamic flow reactors, the initial reaction rates were found to be directly proportional to catalyst concentration, indicating a heterogeneous regime. However in some cases it was observed that above a certain concentration, the reaction rate even decreases and becomes independent of the catalyst concentration. This limit depends on the geometry and working conditions of the photoreactor and for a definite amount of TiO$_2$ in which all the particles, i.e., the entire surface exposed, are totally illuminated. When the catalyst concentration is very high, after traveling a certain distance on an optical path, turbidity impedes further penetration of light in

the reactor. In any given application, this optimum catalyst concentration [(TiO$_2$)OPT] must be determined, in order to avoid excess catalyst and ensure total absorption of efficient photons. As expected, increasing catalyst concentration leads to the increase in the degradation for the decomposition and mineralization of norfloxacin (**1**, 0.25 mM), shown in Fig. 5, which is due to increased number of the reaction sites due to more catalyst particles.

The degradation of norfloxacin (**1**, 0.25 mM) was also investigated at optimum pH 10.4 using different catalyst concentration (Degussa P25) ranging from 0.5 to 3.0 g L^{-1} as shown in Table 1. It could be found that the degradation rate for the decomposition of norfloxacin increases with the increase in catalyst concentration.

3.6. Effect of electron acceptor

One of the practical problems encountered while using TiO$_2$ as a photcatalyst is the undesired electron/hole recombination, which in the absence of proper electron acceptor or donor, is extremely efficient and thus represents the major energy wasting step limiting the achievable quantum yield. One strategy to inhibit electron–hole pair recombination is to add other (irreversible) electron acceptor to the reaction. In highly toxic wastewater where the degradation of organic pollutants is a major concern, the addition of inorganic ions to enhance the degradation rate may often be justified. In this connection, we have studied the effect of electron acceptor such as hydrogen peroxide on the photocatalytic degradation of the model compound **1**, under investigation. Fig. 6 shows the degradation for the decomposition and mineralization of norfloxacin (**1**, 0.25 mM) in the presence and absence of Degussa P25 (**1**, g L^{-1}) containing hydrogen peroxide as an electron acceptor. It was observed that hydrogen peroxide influenced the degradation rate. This acceptor is known to generate reactive radicals according to the following Eq. (6):
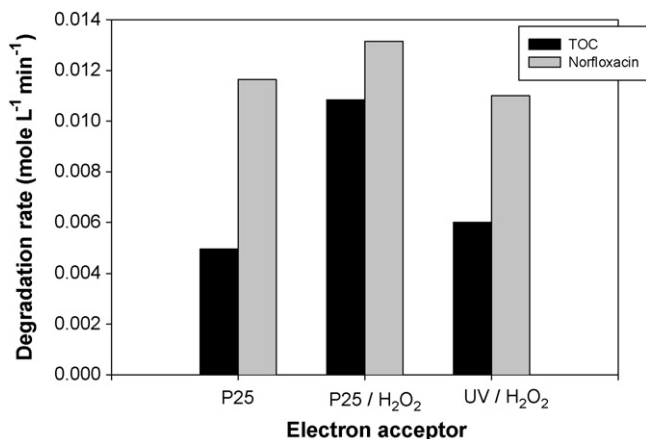
$$H_2O_2 + e^-_{cb} \rightarrow OH^\bullet + OH^- \tag{6}$$

Fig. 6. Comparison of degradation rate for the mineralization and for the decomposition of norfloxacin (**1**) in the presence of hydrogen peroxide. Experimental conditions: 0.25 mM norfloxacin, $V = 250$ mL, pH 6.3, photocatalyst: TiO$_2$ (Degussa P25, $1\,\mathrm{g\,L^{-1}}$), electron acceptor: H$_2$O$_2$ (10 mM), irradiation time = 80 min.

It was observed that the hydrogen peroxide markedly enhance the degradation for the decomposition and mineralization of norfloxacin. The respective one electron reduction potential (against NHE) of different species are ($E(\mathrm{O_2/O_2^{\bullet-}}) = -155$ mV, $E(\mathrm{H_2O_2/^{\bullet}OH}) = 800$ mV) [28]. From a thermodynamic point of view, the employed additives should therefore be more efficient electron acceptor than molecular oxygen.

4. Conclusion

The results of this study clearly indicate that TiO$_2$ can efficiently catalyse the photodegradation and photomineralization of the antibiotics derivative norfloxacin in the presence of light and oxygen. The photocatalyst Degussa P25 was found to be more efficient as compare to other photocatalyst TiO$_2$ powders. The addition of electron acceptor enhanced the degradation rate of the pollutants. The observations of these investigations clearly demonstrate the importance of choosing the optimum degradation parameters to obtain high degradation rate, which is essential for any practical application of photocatalytic oxidation processes. The best degradation condition depends strongly on the kind of pollutant.

Acknowledgements

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