Photocatalytic oxidation of ciprofloxacin under simulated sunlight

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ABSTRACT

Ciprofloxacin (CIP) is a famous synthetic chemotherapeutic antibiotic. It is widely found either in water or wastewater. In this study ciprofloxacin was photocatalytically degraded using commercial anatase titanium dioxide (TiO$_2$) under simulated sunlight. The rate of reaction was found to be affected by pH, TiO$_2$ concentration and antibiotic concentration. The best reaction rate was obtained in natural ciprofloxacin pH (5.8) and 1000 mg/L TiO$_2$. More titania concentration was found to reduce the reaction rate because of the limitation in light transmittance. From kinetic studies, the reaction was proved to proceed through adsorption step then photooxidation and obeys pseudo-first order kinetics.

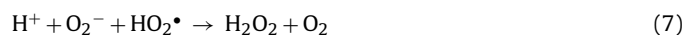© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Over the past few years, pharmaceuticals were considered as an emerging environmental problem due to their continuous input and persistence into the aquatic ecosystem even at low concentrations. After their use, human pharmaceuticals or their metabolites are excreted into the effluents and reach the sewage treatment plants (STPs). Unfortunately, conventional STPs are not able to degrade residues of pharmaceutical compounds, and as a result they are introduced into the aquatic environment. Residual amounts of pharmaceuticals can reach surface waters, groundwater or sediments. Many studies have reported a large number of pharmaceuticals at concentrations ranging from ng/L to mg/L in STP effluents, and in some cases up to several mg/L, in natural waters and even in drinking water [1–4].

After the introduction of the fluorinated quinolone norfloxacin in the early 1980s, successive drugs such as ciprofloxacin (CIP) or ofloxacin represent a significant advance in the history of infection control [5]. The fluoroquinolone group is one of the most important pharmaceuticals used worldwide for humans and veterinary purposes. The presence of broad-spectrum antibiotics like these in aquatic environments may pose serious threats to the ecosystem and human health by inducing proliferation of bacterial drug resistance [6,7].

The removal of such kind of pollutants from the environment became a mandatory issue. Unfortunately the low cost conventional degradation processes lack of enough efficiency for the removal of ciprofloxacin from water or wastewater [8]. Advanced oxidation processes (AOPs) provide a good tool for the destruction of organic contaminants. These processes rely on the production of reactive hydroxyl radicals that are able to oxidize almost all organic compounds. One of these processes is the heterogeneous photocataylsis; in which semiconductors are used as photocatalysts. Titanium dioxide is still the photocatalyst due to its coherent properties, e.g., chemically and biologically inactive, cheap, photostable, and very photoactive, although it does have a large band gap [9–11].

The mechanism of photocatalytic oxidation is presented in Eqs. (1)–(9) [12]. After receiving energy equal to or greater than the titania band gap (3.2 eV), an electron transfer to the conduction band leaving hole in the valence band. The electron and hole may recombine as one possibility. Another possibility is the reaction between photogenerated hole and adsorbed water or hydroxide ion to form hydroxyl radicals.

$$TiO_2 \xrightarrow{h\nu} e^- + h^+ \tag{1}$$

$$h^+ + RX_{ad} \rightarrow RX_{ad}{}^+ \tag{2}$$

$$h^+ \, H_2O_{ad} \rightarrow OH_{ad}{}^\bullet + H^+ \tag{3}$$

$$h^+ \, OH_{ad}{}^- \rightarrow OH_{ad}{}^\bullet \tag{4}$$

$$e^- + O_2 \rightarrow O_2{}^- \tag{5}$$

$$O_2{}^- + H^+ \rightarrow HO_2{}^\bullet \tag{6}$$

$$H^+ + O_2{}^- + HO_2{}^\bullet \rightarrow H_2O_2 + O_2 \tag{7}$$

$$H_2O_2 + h\nu \rightarrow 2OH^\bullet \tag{8}$$

$$OH_{ad}{}^\bullet + RX_{ad} \rightarrow Intermediate \tag{9}$$

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Fig. 1. Chemical structure of ciprofloxacin (CIP).
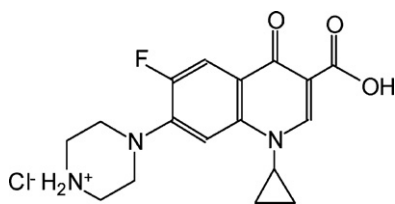
Table 1
Apparent rate constants of ciprofloxacin degradation using different TiO_2 concentrations and the corresponding $t_{0.5}$.

TiO_2 concentration (ppm)	K_{app} (min^{-1})	$t_{1/2}$ (min)
0	0.001	693.15
500	0.02	34.66
750	0.032	21.66
1000	0.04	17.33
1500	0.02	34.66

In the past few years, degradation of ciprofloxacin was studied using sonolysis [13] and Photo-Fenton [14]. This work aims to study the photocatalytic oxidation of ciprofloxacin as a model of pharmaceutical compounds under simulated sunlight, which hopefully will be reflected on the cost of treatment process. Different parameters have been investigated such as pH, ciprofloxacin concentration and titania concentration. Kinetic studies were also carried out.

2. Experimental

The photocatalyst, anatase titanium dioxide (99.9%), was purchased from Sigma–Aldrich Chemicals Company, Germany. Ciprofloxacin HCl (CIP) was kindly supplied by Unipharma Company for Pharmaceutical Industry, Egypt (Fig. 1). Sodium hydroxide and hydrochloric acid, used for pH adjustments, were purchased from Fluka Chemicals Company, Germany. All chemicals were used as received without any further purification.

Commercial visible metal halide lamp (HQI-T 250/Daylight, OSRAM GmbH, Germany) was used as the source of irradiation. The Luminous flux of irradiation is 20,000 lm with luminous efficacy of 82 lm/W.

Ciprofloxacin photodegradation was done in batch mode. The antibiotic solution was mixed with photocatalyst and stirred prior to the experiment to allow adsorption of ciprofloxacin on photocatalyst surface. Then, the lamp was switched on to start the photooxidation process. After pre-defined irradiation times, definite volumes of solution were sampled, then filtered (using 0.22 μm cellulose filter, Agilent, USA) to separate the photocatalyst. Degradation process was performed until complete mineralization of CIP. Following this procedure, different experimental conditions such as initial ciprofloxacin concentration, TiO_2 concentration and initial pH could be investigated.

The concentration CIP in the filtered portion was determined using high performance liquid chromatograph (HPLC Agilent 1100, USA) equipped with analytical column, Zorbax reversed C18 (4.6 mm i.d. × 250 mm, 5 μm). Before entering analytical column, samples were allowed to pass through guard cartridge system

(SB-C18) to keep analytical column clean. Both column and guard cartridge system were purchased from Agilent Company, USA. Oven temperature was kept at 35 °C during analysis. Isocratic elution was carried out using 0.017 M phosphoric acid and acetonitrile of ratio 80:20, respectively. Total flow rate was kept at 1 ml/min.

3. Results and discussion

3.1. Effect of catalyst dose on reaction rate

The concentration of photocatalyst is a critical parameter in photocatalytic oxidation. It affects on the reaction rate and consequently on the cost of treatment. The effect of TiO_2 concentration on 50 mg/L CIP conversion was studied in the range 0–1500 mg/L and natural solution pH of about 5.8. The obtained results are shown in Fig. 2a and b and the calculated $t_{1/2}$ is presented in Table 1. In absence of TiO_2, degradation is not possible which indicates that CIP cannot be degraded by photolysis only. Under all TiO_2 concentrations, the visible-assisted photooxidation process of CIP was found to follow pseudo-first order reaction kinetics. The rate of reaction was found to increase with the TiO_2 concentration (Fig. 2b) up to 1000 mg/L. After that a decline in reaction rate was observed which is due to the increase in turbidity of CIP solution caused by excess photocatalyst. This turbidity lowers the light transmittance inside the solution leading to lower light intensity reaching the catalyst surface. Thus, the optimum concentration can be concluded to be 1000 mg/L TiO_2 concentration.

The order of reaction in titania concentration can be deduced using the formula [15]: $\ln k_{app} = \ln k_1 + n \ln[TiO_2]$

Plot of the apparent rate constant (k_{app}) and TiO_2 load resulted in a straight line (Fig. 3) with $n = 1$, which reveals that rate of reaction depends on photocatalyst concentration as well. This is because addition of more TiO_2 to the reaction medium increases the total surface area exposed to light so that more free radicals would be generated. On the hand, the number of active sites available for CIP adsorption was enhanced by the addition of more TiO_2. These two factors explain the dependency of reaction rate on photocatalyst

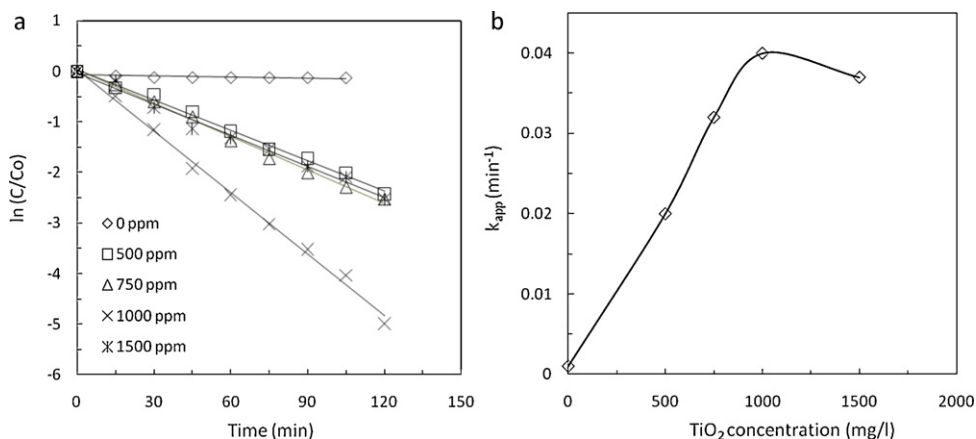**Fig. 2.** Effect of TiO_2 concentration on CIP photodegradation, (a) pseudo-first order kinetics of the reaction and (b) change in rate constant with TiO_2 concetration.

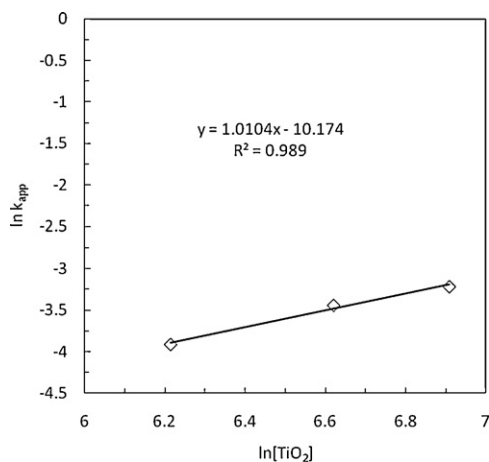**Fig. 3.** Order of reaction in TiO_2.

concentration. The above plot (Fig. 3) could only be applied at low catalyst dose. At high catalyst concentration opacity and aggregation of photocatalyst particles led to a deviation from linearity.

3.2. Effect of pH

The photooxidation of CIP does not depend only on TiO_2 concentration but also on pH value of CIP solution, since it determines the surface charge properties of the photocatalyst and therefore the adsorption behavior of the organic substrate. Therefore, the influence of pH on the degradation of CIP in aqueous suspensions of TiO_2 was studied at pH ranging from 3 to 9. Fig. 4a and b represents the conversion of cirpofloxacin as a function in time under different pH conditions and Table 2 summarizes the calculated k_{app} and $t_{1/2}$. From Fig. 4b the degradation rate constant of ciprofloxacin reached the maximum at pH 5.8, which is the natural pH of ciprofloxacin solution. This result differs from previous that obtained by An et al.[7]. In their study, they found that rate constant is nearly same for pH values 5, 7 and 9, which is not same to data obtained in this study. This discrepancy may be due to that ciprofloxacin hydrochloric acid was used in the current study instead of ciprofloxacin. The presence of hydrogen proton and chloride ion affects the natural pH of ciprofloxacin solution as well as the titania surface as will be discussed later. Under best conditions, i.e., pH 5.8 and 1000 mg/L TiO_2, photocatalytic degradation of CIP was found to proceed faster than sonolysis process (k_{app} = 0.0058 min^{-1}) [13] and slower than Photo-Fenton reaction using pillared iron catalyst (k_{app} = 0.533 min^{-1}) [14] under nearly same conditions. In case of Photo-Fenton process high concentration of hydrogen peroxide (60 mM) should be used to accelerate the reaction, which adds extra cost for the treatment of water or wastewater contaminated with CIP. This suggests that photocatalytic oxidation under sunlight is the best candidate for the treatment of water or wastewater contaminated with ciprofloxacin compound.

The interpretation of pH effect on the photocatalytic process is very difficult task because of its multiple roles such as electrostatic interactions between the semiconductor surface, solvent

Table 2
Apparent rate constants of ciprofloxacin degradation under different pH values and the corresponding $t_{0.5}$.

pH (−)	K_{app} (min^{-1})	$t_{1/2}$ (min)
3	0.021	33.01
6	0.040	17.33
7	0.034	20.39
9	0.024	28.88

Table 3
Apparent rate constants of degradation of ciprofloxacin of different initial concentration and the corresponding $t_{0.5}$.

Initial ciprofloxacin conc. (ppm)	K_{app} (min^{-1})	$t_{1/2}$ (min)
10	0.0671	10.33
25	0.041	16.91
50	0.040	17.33
75	0.026	26.66

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 the following equations [16,17]:

$$TiOH + H^+ \rightarrow TiOH^{2+} \tag{10}$$

$$TiOH + OH^- \rightarrow TiO^- + H_2O \tag{11}$$
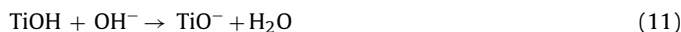
The point of zero charge (pzc) of the TiO_2 is reported at pH 6.25 [17]. Thus, the TiO_2 surface will remain positively charged in acidic medium (pH < 6.25) and negatively charged in alkaline medium (pH > 6.25). In this study it has been shown that the degradation of ciprofloxacin is strongly influenced by the reaction pH (Fig. 4). The best efficiency for the degradation of cirpofloxacin in natural pH (5.8) could be attributed to adsorption affinity. Fig. 5 represents the chemical structures of CIP under different pH values. Under acidic condition, CIP is positively charged which is same as TiO_2 surface resulting in repulsion between them. Furthermore, Cl^- may compete with water molecules for the adsorption on TiO_2 surface; this blocks the active sites of TiO_2 and hence production of hydroxyl radical decreases. On the other hand, both TiO_2 and CIP are negatively charged under basic conditions leading to the same phenomenon of repulsion between them and lower rate of reaction. The high rate of reaction in case of pH 5.8 (natural pH of CIP) might be due to the available protons from NH_2^+ and COOH groups of CIP, which interact with TiO_2 surfaces according to Eq. (10), i.e., protonation of TiO_2 by CIP itself. This leads to the formation of negatively charged CIP, molecules which can be adsorbed efficiently on the positively charged TiO_2 surface.

3.3. Effect of ciprofloxacin initial concentration

Another important factor that affects the photocatalytic degradation of organic pollutants is the initial concentration of the organic pollutant itself. Fig. 6 illustrates the change in CIP concentration as a function in time at 1000 ppm TiO_2 concentration and natural pH (5.8). Table 3 contains the calculated k_{app} and $t_{0.5}$. Comparing the obtained rate constants (Fig. 6b), it is obvious that the rate constant gradually decreases with the increase in initial CIP concentration because of the increase in Cl^- concentration. Cl^- scavenges simultaneously the holes and hydroxyl radicals (Eqs. (3) and (4)) resulting in prolonged reaction time. Formation of inorganic radical anions (e.g. $Cl^\bullet$, $ClOH^{\bullet-}$) under these circumstances is possible.

$$Cl^- + h_{vb}^+ \rightarrow Cl^\bullet \tag{12}$$

$$Cl^- + {}^\bullet OH \rightarrow ClOH^{\bullet-} \tag{13}$$

Although the reactivity of these radicals may be considered, they are not as reactive as h_{vb}^+ and $^\bullet OH$, and thus the observed retardation effect is still thought to be the strong adsorption of the anions on the TiO_2 surface [18].

Langmuir-Hinshelwood (LH) kinetics is the most commonly used kinetic expression to explain the kinetics of the heterogeneous catalytic processes. This mechanism proposes that both molecules adsorb and the adsorbed molecules undergo a bimolecular reaction, in this case hydroxyl radical and CIP. The Langmuir-Hinshelwood
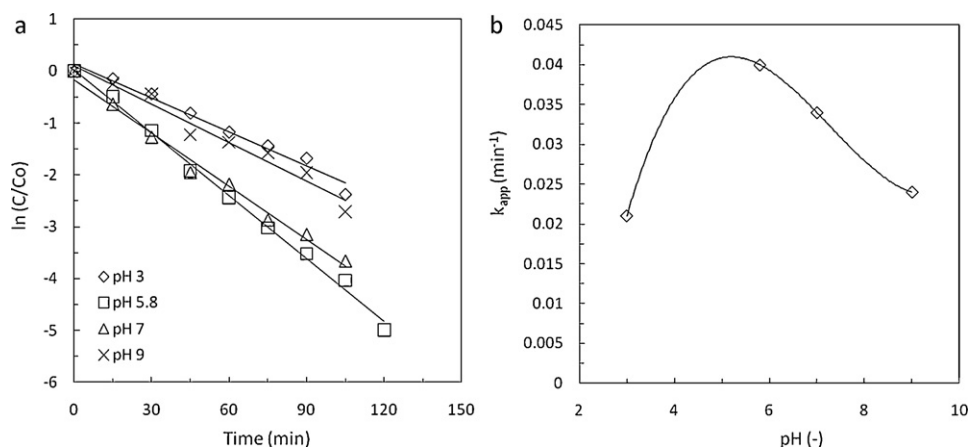
Fig. 4. Effect of pH on CIP photooxidation, (a) Pseudo-first order kinetics and (b) change in rate constant with pH value.
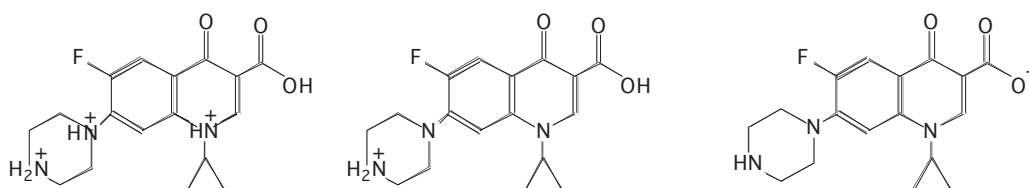

Fig. 5. Chemical structures of CIP under different pH values, (a) low pH value, (b) natural pH of CIP and (c) high pH value [12].

expression that explains the kinetics of heterogeneous catalytic systems is given by:

$$r = -\frac{dC}{dt} = \frac{k_r K C}{1 + KC}$$

where r represents the rate of reaction that changes with time. The term r is represented in terms of initial reaction rate, r_0 (mg/L min^{-1}), as a function of the initial CIP concentration, C_0 (mg/L), or in terms of C_e, where C_e is the equilibrium CIP concentration in solution after the completion of dark experiments. The initial rate of reaction as a function of C_0 and C_e is given by the following equations, respectively:

$$r_0 = \frac{k_r K C_0}{1 + K C_0}$$

$$r_0 = \frac{k_r K C_e}{1 + K C_e}$$

The parameters k_r and K, which are a function of C_0 or C_e can be predicted by linearizing the above equations as follows [19,20]:

$$\frac{1}{r_0} = \frac{1}{k_r} + \frac{1}{k_r K C_0}$$

where k_r is the reaction rate constant (min^{-1}), and K is the adsorption coefficient of the reactant onto the catalyst particles (L/mg). Plotting $1/r$ against $1/C_0$ (Fig. 7) gave a straight line with correlation coefficient $R^2 = 0.9513$, which reveals that adsorption step is involved in the photodegradation process (reactions (2) and (9)). The calculated adsorption coefficient and actual rate constant are 0.032 mg/L min^{-1} and 2.726 min^{-1}, respectively. The relatively high value of adsorption coefficient indicates that the adsorption of CIP on TiO$_2$ surface is favorable at natural CIP pH (5.8).
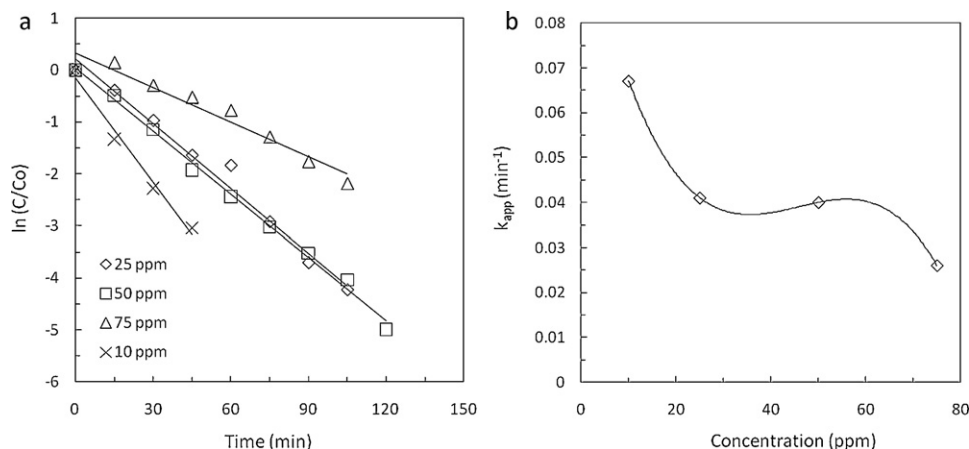

Fig. 6. Effect of CIP concentration on degradation process, (a) pseudo-first order kinetics and (b) change in rate constant with CIP concentration.
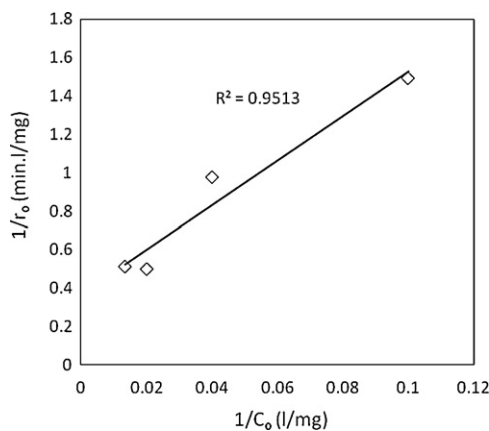
Fig. 7. L-H model verification.

4. Conclusions

Ciprofloxacin photocatalytic degradation using TiO_2 under simulated sunlight was found to obey pseudo-first order kinetics under the studied reaction conditions. Best degradation has been obtained at natural ciprofloxacin pH (5.8), 1000 mg/L of TiO_2 dose. Order of reaction in TiO_2 concentration was found to equal one indicating that catalyst concentration is important factor in the photocatalytic degradation. More catalyst concentration reduces the rate constant due to limitations of light transmittance. Application of L-H model revealed that degradation occurs through adsorption step. Adsorption was supposed to be high in case of pH 5.8 due to the static attraction between ciprofloxacin and TiO_2.

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