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Photocatalytic Degradation of Ciprofloxacin Hydrochloride using Carbon-doped Titanium dioxide

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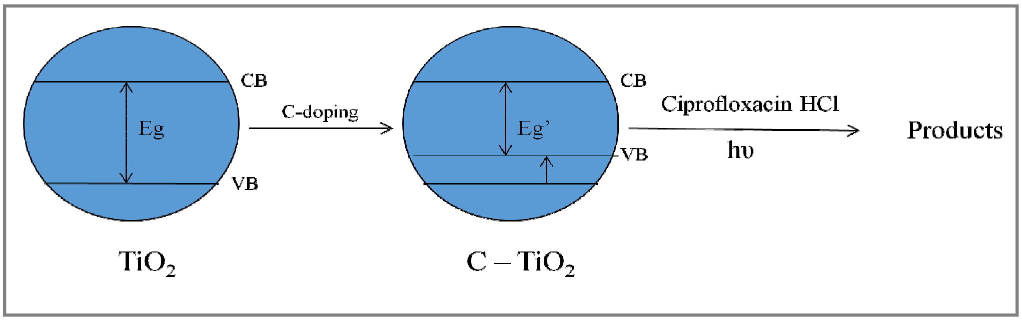
ABSTRACT

Ciprofloxacin hydrochloride was degraded photocatalytically by using carbon doped titanium dioxide in the presence of light. Doping of titanium dioxide with carbon was done using glucose as a dopant. Photocatalytic activity of this catalyst was evaluated by degradation of Ciprofloxacin hydrochloride. A 200W tungsten lamp was used for irradiation. Progress of the reaction was followed spectrophotometrically by measuring the absorbance of the reaction mixture at regular time intervals. The effect of variations of different parameters like pH, drug concentration, amount of semiconductor and effect of light intensity on the rate of degradation was also observed to achieve the optimum rate of photodegradation. These are: pH = 3.4; [Ciprofloxacin hydrochloride] = 2.00×10^{-5}M; C-TiO_2 = 0.12 g and light intensity = 60.0 mW cm^{-2}.

Graphical Abstract



Keywords: Ciprofloxacin HCl, Titanium dioxide, Semiconductor, Photocatalytic degradation.

INTRODUCTION

World is in the grip of severe water pollution. Industrial effluents, chemical spills and agricultural runoff are main sources from which a large number of organic substances are introduced into the water system. Adsorption processes are used for removal of organic pollutants from industrial wastewater [1]. Environmental photochemistry utilizes semiconductors in order to remove dyes from the polluted water [2, 3]. The presence of medicinally active drugs in the aquatic environment has become a burning issue in environmental chemistry. Quite a good number of pharmaceuticals and several drug metabolites have already been detected in the aquatic environment posing a threat to life in general. Several drugs have been found in effluent samples and also in surface water located downstream from municipal sewage treatment plants [4]. Most of these pharmaceuticals are commonly used as antibiotics, and their presence may contribute to antibacterial resistance in human beings, resulting in increased hospitalization as well as increased treatment costs. Risk assessment of antibiotic residues in different water sources in India has been carried out by Mutiyar and Mittal [5]. They also discussed key issues and challenges. Ciprofloxacin, a fluoroquinolone antibiotic, seems to present the greatest risk in India. Photocatalysis involves degradation of water contaminants, which are chemically stable and resistant to biodegradation. These are not effectively removed by usual wastewater treatment techniques such as activated carbon adsorption, chemical oxidation, biological treatment and membrane separation. Semiconductor mediated photocatalytic process is a promising technique with a great potential as a sustainable treatment technology because it is low cost and environment friendly [6].

TiO_2 is a photocatalyst suitable for industrial use at present and may be in the future also. This is because TiO_2 has the most efficient photoactivity, highest stability and low cost. Pelaez *et al.* [7] reviewed visible light active titanium dioxide photocatalysis for environmental applications. Oxidation of sulfamethoxazole and related antimicrobial agents by TiO_2 photocatalysis was studied by Hu *et al.* [8]. Photodegradation of amoxicillin, streptomycin, erythromycin and ciprofloxacin by UV and UV/TiO_2 processes was investigated by Palmisano *et al.* [9]. Photostability of four antibiotics: amoxicillin, streptomycin, erythromycin and ciprofloxacin, with and without TiO_2 catalysis was compared.

Removal of organic pollutants from the pharmaceutical effluent by TiO_2 was studied by Lakshmi *et al.* [10]. Photocatalytic removal of organics and its degradation efficiency was assessed by determining reduction in the COD values. Phenol photodegradation with oxygen and hydrogen peroxide over TiO_2 and Fe-doped TiO_2 was carried out by Adan *et al.* [11]. Catalyst was calcined at 450°C preferably using hydrogen peroxide as an oxidant agent for relatively low doping level (ca. 0.7 wt.%),where an enhancement in photocatalytic activity was observed.

Synthesis and characterization of $Fe_3O_4/SiO_2/TiO_2$ nanoparticles and their effectiveness in photocatalytic degradation of 2-chlorophenol in simulated wastewater was studied by Rashid *et al.* [12]. Sun *et al.* [13] reported photocatalytic decomposition of 4-chlorophenol over an efficient N-doped TiO_2 under sunlight irradiation. The band gap of the N-doped TiO_2 was found to be 3.12 eV, which was slightly lower than that of pure TiO_2 (3.15 eV). The degradation of 4-chlorophenol using the pure TiO_2 was 66.2%, while for N-doped TiO_2, it was 82.0%.

Sambandam *et al.* [14] synthesized visible light active carbon-loaded anatase TiO_2 (C-TiO_2) nanocrystals in different shapes (spherical, distorted spherical, rice grain and hexagonal morphologies) with a particle size range in between 50-70 nm. They used microwave-assisted route in the solution state for their preparation. It was reported that band gap was shifted to the visible region due to C loading. A rapid degradation of an endocrine disrupting agent (carbamazepine) by the rice grain shaped C-TiO_2 was attributed to the large surface area (229 m^2 g^{-1}). Photocatalytic degradation of reactive blue 19 (RB-19) and reactive red 76 (RR-76) dyes in the industrial wastewater has been investigated by Helmy *et al.* [15] using TiO_2, C-doped TiO_2(C-TiO_2), S-doped TiO_2 (S-TiO_2) and C,S co-doped TiO_2 (C,S-TiO_2) nanoparticles. These undoped and doped TiO_2 were synthesized via sol-gel process. The degradation efficiency of RB-19 and RR-76 photocatalytic degradation attained 100% on 1 h irradiation under visible light.

Kandira stone, which is commonly used as a cladding material for building stone has been used for the removal of an antibiotic Ciprofloxacin hydrochloride (CIP) from its aqueous solution [16]. The adsorption kinetics, equilibrium and thermodynamics between the adsorbent surfaces and CIP were examined. Ciprofloxacin degradation was also observed by Hayder *et al.* [17] in the presence of 0.01 mg mL^{-1} of TiO_2. About 90 and 70% of its original concentration was eliminated in 120 min on irradiation by UV lamp and visible light, respectively, while insignificant degradation was observed on irradiation in absence of TiO_2.

MATERIALS AND METHODS

Chemicals and reagents: Titanium dioxide, D-(+)-glucose anhydrous, sodium hydroxide and sulphuric acid were used in present investigations. These were purchased from Hi-Media Laboratories Pvt. Ltd., India. All the chemicals and reagents used were of analytical grade and used without further purification.

Drug: Ciprofloxacin hydrochloride ($C_{17}H_{21}ClFN_3O_4$), drug is effective in the treatment of a wide variety of infections which includes skin and bone infections, lower respiratory tract infections¸ acute urinary-tract infections etc., and was procured from Department of Pharmacy, MLS University, India. The molecular weight of Ciprofloxacin hydrochloride is 385.8 g mol^{-1} and λ_{max} is 270 nm. The chemical structure of the drug is shown in figure 1.

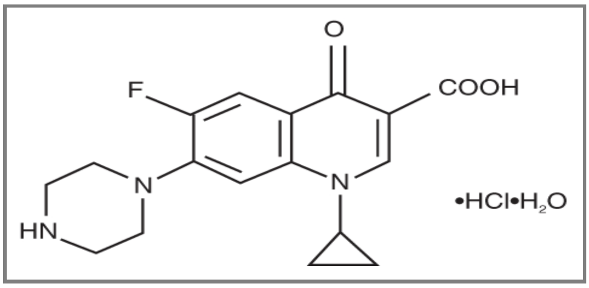


Figure 1. Chemical structure of Ciprofloxacin HCl.

Synthesis of carbon-doped titanium dioxide: Carbon-doped titanium dioxide was prepared by using glucose as dopant. An aqueous solution of 1% glucose was prepared by dissolving 0.50 g glucose in 50 mL water. This solution was slowly added into 10 g titanium dioxide and was mechanically stirred for 1 h. This solution was aged for 24 h and then dried at 50ºC in an oven for 3 h. It was further dried in an oven at 110ºC for 3 h and then it was crushed with mortar and pestle. The powder received was then calcined at 586ºC for 3 h in a muffle furnace.

Photocatalytic degradation of drug: A stock solution of Ciprofloxacin hydrochloride (1.0×10^{-3} M) was prepared by dissolving 0.0386 g of Ciprofloxacin hydrochloride in 100 mL of doubly distilled water. The absorption maximum of the drug was determined with the help of a Ultraviolet-Visible spectrophotometer (Model UV-1700 Pharmaspec). The pH of the solution was adjusted by the addition of 0.1 N sodium hydroxide and 0.1 N sulphuric acid solutions. Working solution of 2.00 x 10^{-5} M concentration of Ciprofloxacin hydrochloride was prepared by diluting the stock solution. 0.10 g of photocatalyst was added in 50 mL solution.The reaction mixture was exposed to a 200 W tungsten lamp (Philips) and about 3 mL aliquot was taken out every 30 min. Suryamapi (CEL Model TM 201) was used to measure the light intensity of light. A water filter was used to cut off thermal radiations.

RESULTS AND DISCUSSION

Photocatalytic degradation of drug: About 3.0 mL of the solution was taken out at regular time intervals from the reaction mixture and absorbance was measured spectrophotometrically at λ_{max} 270 nm. A decrease in absorbance of the drug was observed with increasing time of exposure. A plot of 1 + log A versus time was linear and followed pseudo-first order kinetics.

The rate constant was calculated by the expression, k = 2.303 × slope.

A typical run for the photocatalytic degradation of drug is given in table 1 and graphically represented in figure 2. Rate constant, (k) with TiO_2 = 1.34×10^{-5} sec^{-1}, rate constant (k) with C-TiO_2 = 2.04×10^{-5} sec^{-1}.

Table 1. Typical runs of Ciprofloxacin HCl degradation

Time (min)	TiO_2		Carbon-doped TiO_2	
	Absorbance	1 + log A	Absorbance	1 + log A
0.0	0.666	0.8234	0.664	0.8221
30.0	0.650	0.8129	0.637	0.8041
60.0	0.632	0.8007	0.611	0.7860
90.0	0.619	0.7917	0.592	0.7723
120.0	0.602	0.7796	0.570	0.7559
150.0	0.589	0.7701	0.550	0.7403

pH = 3.4, Drug concentration = 2.00×10^{-5} M,
Amount of photocatalyst = 0.12 g, Light intensity = 60.0 $mWcm^{-2}$

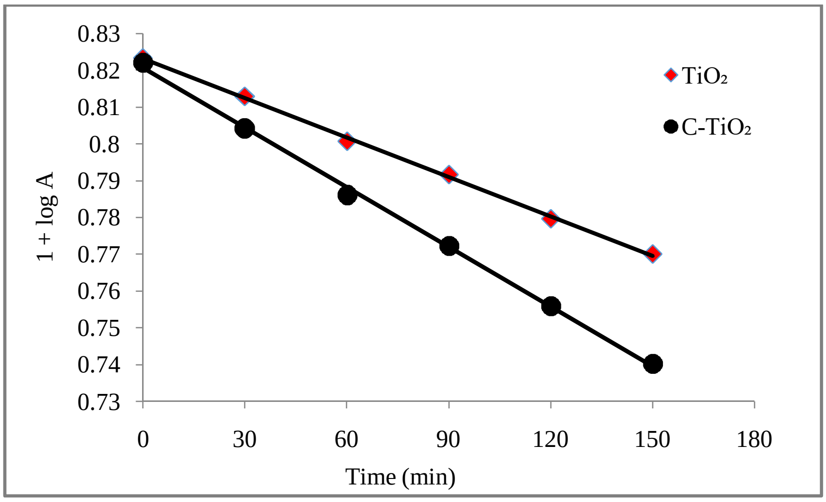


Figure 2. Plot of 1 + log A versus time for a typical run.

Effect of different variables on photocatalytic degradation of drug

Effect of pH: The pH of the Ciprofloxacin hydrochloride solution was varied from 2.6 to 3.6. The results are reported in figure 3. As observed, the rate of reaction increases with increasing pH of the solution up to pH 3.4. However, a further increase in pH of solution resulted in decreased reaction rate. An increase in the rate of photocatalytic degradation of Ciprofloxacin hydrochloride with increase in pH may be due to generation of more $HO_2^{\bullet}$ radicals, which are produced from the reaction between $O_2^{\bullet-}$ ions and hole (h^+) of the semiconductor. $O_2^{\bullet-}$are formed by the abstraction of an electron from conduction band of the semiconductor by dissolved oxygen. Above pH 3.4, a decrease in the rate of photocatalytic degradation of the drug was observed, which may be due to the fact that cationic form of Ciprofloxacin hydrochloride is converted in its almost neutral form, which faces less or no attraction towards the charged semiconductor surface due to absorption of H^+ ions. As a result, reaction rate decreases. Drug concentration = 2.00×10^{-5} M , Amount of photocatalyst = 0.12 g, Light intensity = 60.0 $mWcm^{-2}$.

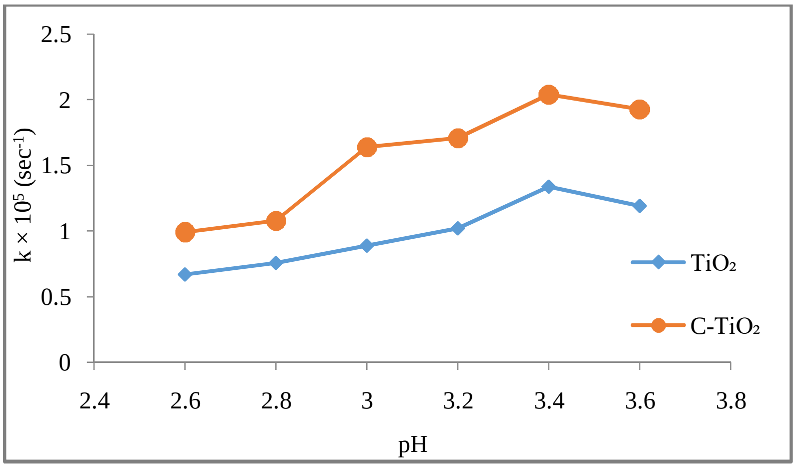


Figure 3. Effect of pH on degradation of Ciprofloxacin hydrochloride.

Effect of drug concentration: The effect of variation of drug concentration on the degradation was studied by taking different concentrations of drug. The results are summarized in figure 4. It has been observed that the rate of photocatalytic degradation increases with an increase in the concentration up to 2.00 x 10^{-5} M. With further increase in the concentration of drug, rate of photocatalytic decomposition decreases. It can be explained on the basis of the fact that as the concentration of drug was increased, more drug molecules were available causing hindrance in the mobility of Ciprofloxacin towards semiconductor surface and as a result, rate decreases. pH = 3.4, Amount of photocatalyst = 0.12 g, Light intensity = 60.0 $mWcm^{-2}$.

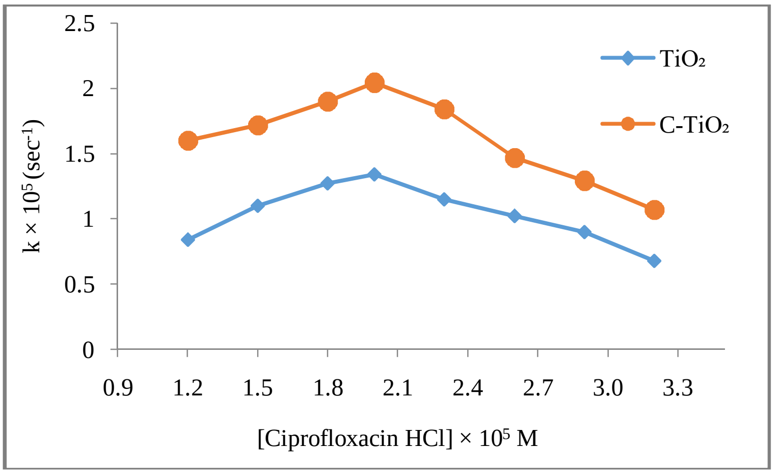


Figure 4. Effect of drug concentration on degradation of Ciprofloxacin hydrochloride.

Effect of amount of photocatalyst: The amount of photocatalyst was varied from 0.02 to 0.20 g and the results are given in figure 5. These results showed that an increase in the amount of photocatalyst from 0.02 to 0.12 g increased the photodegradation efficiency, as the exposed surface area of the semiconductor also increases and after that any further increase in catalyst above 0.12 g, only thickness of photocatalyst increases as it will form multilayers. As a consequence of multilayer formations, e^--h^+ recombination becomes easier and hence, the rate of degradation decreases. pH = 3.4, Drug concentration = 2.00 × 10^{-5} M, Light intensity = 60.0 $mWcm^{-2}$.

Effect of light intensity: The effect of light intensity has been studied in the range from 20.0 to 70.0 $mWcm^{-2}$ and the observations are summarized in figure 6. The data indicate that on increasing the intensity of light, the rate of reaction also increases up to 60.0 mW cm^{-2}, because on increasing the

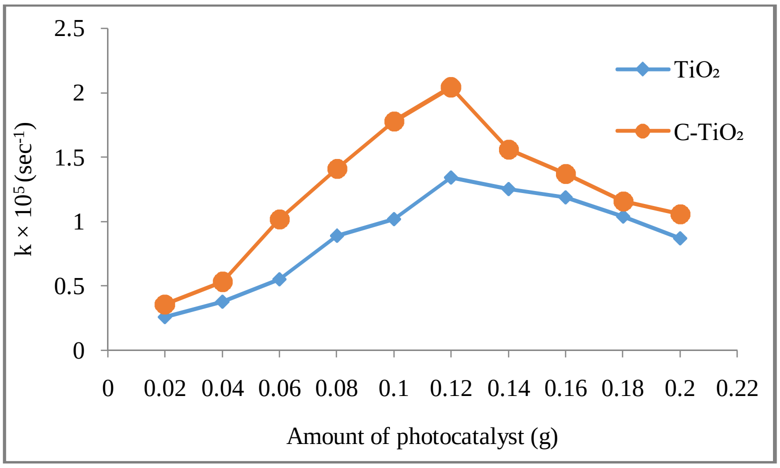


Figure 5. Effect of amount of photocatalyst on degradation of Ciprofloxacin hydrochloride.

intensity, the number of photons striking per unit area per unit time will also increase. A small decrease in the rate on further increasing light intensity may be due to some thermal or side reactions. pH = 3.4, Drug concentration = 2.00×10^{-5} M, Amount of photocatalyst = 0.12 g.

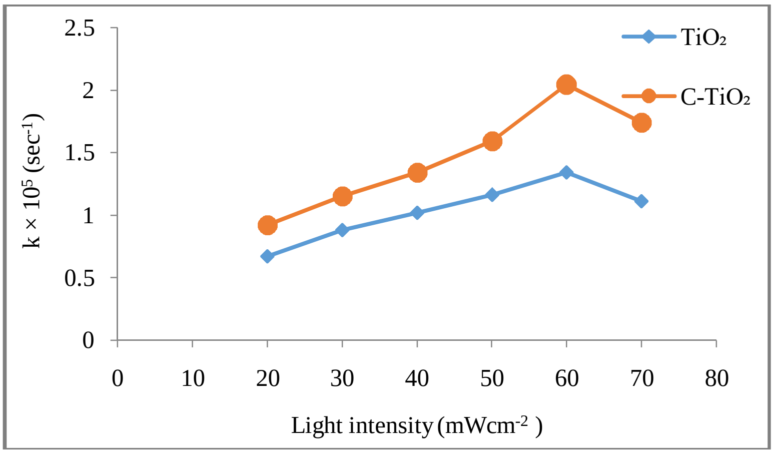


Figure 6. Effect of light intensity on degradation of Ciprofloxacin hydrochloride.

Mechanism: On the basis of these observations, a tentative mechanism for photocatalytic degradation of Ciprofloxacin hydrochloride (CH) may be proposed as–

$$^{1}CH_{0} \xrightarrow{h\nu} {}^{1}CH_{1} \quad \ldots(1)$$

$$^{1}CH_{1} \xrightarrow{ISC} {}^{3}CH_{1} \quad \ldots(2)$$

$$C\text{-}TiO_{2} \xrightarrow{h\nu} e^{-}(CB) + h^{+}(VB) \quad \ldots(3)$$

$$e^{-}(CB) + O_{2}(\text{dissolved oxygen}) \longrightarrow O_{2}^{\bullet-} \quad \ldots(4)$$

$$O_{2}^{\bullet-} + H^{+} \longrightarrow HO_{2}^{\bullet} \quad \ldots(5)$$

$$^{3}CH_{1} + HO_{2}^{\bullet} \longrightarrow \text{Products} \quad \ldots(6)$$

Ciprofloxacin hydrochloride (CH) absorbs radiations of suitable wavelength and transforms to its first excited singlet state. Then it undergoes intersystem crossing (ISC) to give the triplet state of the drug. The semiconductor (SC) also utilizes the light to excite its electron from valence band to the conduction band. This electron will be abstracted by oxygen molecule (dissolved oxygen) generating superoxide anion radical ($O_2^{\bullet-}$). This $O_2^{\bullet-}$ radical will react with H^+ to give $HO_2^{\bullet}$ radical. This $HO_2^{\bullet}$ radical will degrade the drug Ciprofloxacin hydrochloride to products. In presence of hydroxyl radical scavenger (2-propanol), the reaction rates were found to be unaffected. This shows that this degradation proceeds through oxidation by some other species than $^{\bullet}OH$ radical. $O_2^{\bullet-}$ is not stable in acidic medium and therefore, $HO_2^{\bullet}$ radical will be the main active oxidizing species in the degradation of Ciprofloxacin hydrochloride.

APPLICATION

Photocatalysis finds applications in solar cells, generation of hydrogen as fuel, and killing certain pathogens apart from wastewater treatment. This process is a part of advanced oxidation processes (AOPs) and can degrade toxic organic contaminants to their small fragments, which are almost harmless.

CONCLUSION

The carbon-doped titanium dioxide was successfully prepared by using glucose as dopant. At optimum conditions, the rate of degradation of Ciprofloxacin hydrochloride in presence of TiO_2 and C-doped TiO_2 was obtained as 1.34 x 10^{-5} and 2.04 x 10^{-5} sec^{-1}, respectively. Results indicate that carbon-doped titanium dioxide shows more photocatalytic activity than titanium dioxide (almost 52.2% higher). It was observed that various variables such as the pH of the reaction mixture, concentration of drug, amount of semiconductor and light intensity affect the rate of drug degradation.

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