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# PREPARATION OF C-$TiO_2$ NANOPHOTOCATALYST FOR THE DEGRADATION OF LIVOFLOXACINFROM WASTE WATER

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## ABSTRACT

Heterogeneous photocatalytic degradation of livofloxacin has been investigated in aqueous medium using visible light. The carbon doped titania has been prepared by sol-gel precipitation method. The rate of photocatalytic degradation of drug was monitored spectrophotometrically. The effect of variation of different parameters like pH, concentration of livofloxacin, amount of photocatalyst, dopant percentage and light intensity on the rate of photocatalytic degradation was also observed. A tentative mechanism for the photocatalytic degradation of livofloxacin has been proposed.

**Key words**: Heterogeneous, Nanophotocatalyst, C-$TiO_2$, Livofloxacin.

## INTRODUCTION

Most drug substances are persistent and slowly biodegradable compounds. Environmental studies show an increase of these substances in surface water due to their incomplete removal through sewage treatment plants. The photocatalytic decomposition of organic compounds of environmental concern (e.g. pesticides, dyes, etc.) has been studied extensively during the last 20 years and it has been demonstrated that heterogeneous photocatalysis using $TiO_2$ (anatase) as catalyst can be an alternative to conventional methods for the removal of such organic pollutants from water and air[1]. Additionally, an advantage of the photocatalytic process is its mild operating conditions and the fact that it can be powered by sunlight; thus, reducing significantly the electric power required and, therefore, operating costs[2]. Recently, a number of research groups have dealt with the homogeneous and heterogeneous photocatalytic decomposition of various types of drugs in the presence of near-UV (UV-A) or solar light with quite encouraging results[3,4]. Moreover, the incorporation of carbon into $TiO_2$ materials allows the synthesis of photocatalysts with improved efficiency and activity under visible light[5]. The extension of $TiO_2$ absorption in the visible region is required for majority of practical applications that utilize solar light or artificial visible light. Li et al.[6] prepared carbon-doped anatase $TiO_2$ by a facile hydrothermal process without adding additional carbon source. The as-prepared sample shows highly efficient photocatalytic activity, which only requires 4 min and is about 11 times higher than that of Degussa P25 $TiO_2$ in degradation of methyl orange dye under UV light irradiation. Surface photovoltage spectra and transient photovoltage suggest that the presence of interstitial carbons induced several localized occupied states in the gap, enhancing the separation extent and

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restrain the recombination of the photo-induced electron and hole carriers in $TiO_2$. Sakthivel et al.[7] prepared a carbon-modified titanium dioxide photocatalyst by the hydrolysis of titanium tetrachloride with tetrabutylammonium hydroxide followed by calcination at 400°C. They stated that the presence of a carbonate species (C–O bonds) created a variety of surface states. Thus, the superior photocatalytic activity of the carbon-doped $TiO_2$ was observed for the degradation of 4-chlorophenol and the azo dye remazol red solution in diffuse indoor daylight[7].

## EXPERIMENTAL

A stock solution of livofloxacin ($1.0 \times 10^{-3}$ M) was prepared in doubly distilled water. This stock solution was further diluted as and when required. The absorbance of this solution was determined with the help of Ultraviolet-Visible spectrophotometer (Model UV-1700 Pharmaspec) at $\lambda_{max}$ = 290 nm for livofloxacin. The solution of livofloxacin $4.00 \times 10^{-6}$ M was prepared in doubly distilled water and 0.10 g of carbon doped $TiO_2$ was added to it. The pH of reaction mixture was kept 8.5 and this solution was exposed to a 200 W tungsten lamp. A decrease in absorbance of drug solution was observed with increasing time of exposure.

The typical run for the the photocatalytic degradation of livofloxacin in the presence of carbon doped $TiO_2$ has been presented in Table 1 and graphically represented in Fig. 1.

**Table 1: A typical run**

pH = 8.5 C-$TiO_2$ = 0.10 g
[Livofloxacin] = $4.00 \times 10^{-6}$ M Light Intensity = 60.0 $mWcm^{-2}$

| Time (min.) | Absorbance (A) | 1 + log A |
|---|---|---|
| 0.0 | 0.2546 | 0.4058 |
| 20.0 | 0.2412 | 0.3824 |
| 40.0 | 0.2298 | 0.3613 |
| 60.0 | 0.2171 | 0.3366 |
| 80.0 | 0.2031 | 0.3077 |
| 100.0 | 0.1844 | 0.2857 |
| 120.0 | 0.1840 | 0.2648 |
| 140.0 | 0.17532 | 0.2438 |

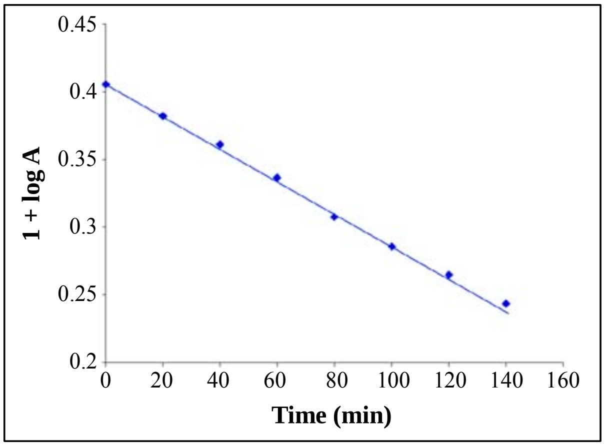

**Fig. 1: A typical run**

The absorbance of livofloxacin solution decreases with an increase in the time of irradiation, indicating that livofloxacin is consumed on irradiation. The plot of 1 + log A against time was linear, following pseudo-first order kinetics. The rate constant was measured with the expression k = 2.303 x slope with an optimum rate constant of $k = 5.41 \times 10^{-5}$ sec$^{-1}$.

## Effect of pH

The effect of pH on the rate of degradation of levofloxacin solution was investigated in the pH range 5.0-9.5. The results are given in Figure 2.

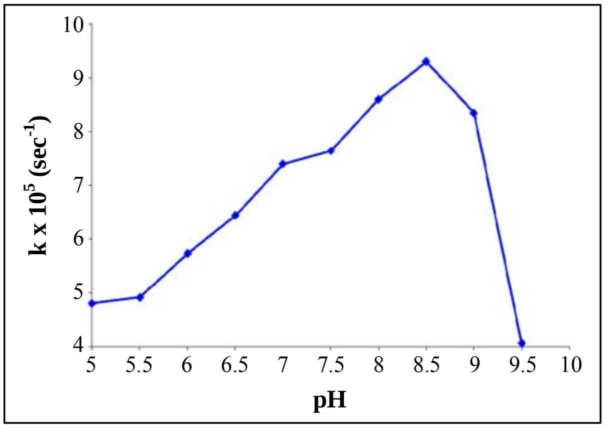

**Fig. 2: Effect of pH**

It has been observed that the rate of degradation increases with increase in pH upto 8.5. Further increase in pH resulted in a decrease in the rate of reaction. The increase in the rate of photocatalytic degradation with increasing pH may be due to generation of more $^{\bullet}$OH radicals, which are produced from the interaction of $^{-}$OH and hole (h$^{+}$) of the semiconductor. These $^{\bullet}$OH radicals are responsible for the oxidative degradation of livofloxacin. After optimum pH 8.5, the rate decreases on increasing pH further, because more $^{-}$OH ions are available and these will be adsorbed on the surface of the semiconductor making it negatively charged so that the approach of neutral or electron rich form of the drug towards negatively charged surface of semiconductor will be retarded. This will result into a decrease in the rate of degradation.

## Effect of Livofloxacin concentration

The effect of livofloaxcin concentration on its rate of degradation was studied at different concentrations varying from $1.0 \times 10^{-6}$ M to $30.0 \times 10^{-6}$ M keeping all other factors identical. The results are presented in Figure 3.

The rate of degradation increases on increasing the concentration of livofloxacin. The rate of photocatalytic degradation was found to decrease with an increase in the concentration of livofloxacin further. It can be explained on the basis of that on increasing the concentration of livofloxacin, more molecules are available for excitation and degradation. On increasing the concentration above $6.0 \times 10^{-6}$ M, the rate of reaction decreases, which can be explained that at higher concentration, the livofloxacin may start acting as a filter for the incident light. It will not permit the desired light intensity to reach the surface of the semiconductor and as a result, decrease in the rate of degradation of livofloxacin was observed.

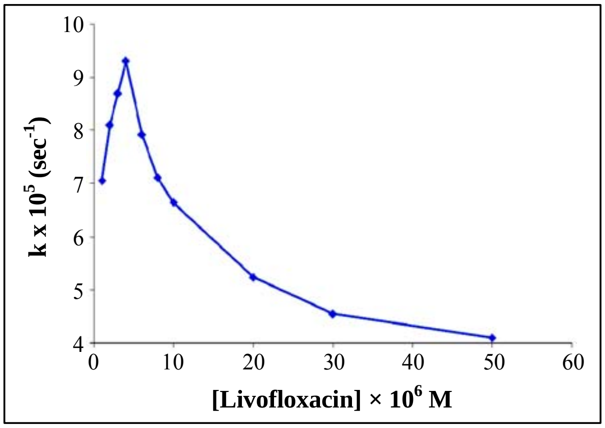

**Fig. 3: Effect of livofloxacin concentration**

### Effect of amount of photocatalyst

The effect of variation of amount of photocatalyst on the rate of photocatalytic reaction has also been observed. The results are summarized in the form of Figure 4.

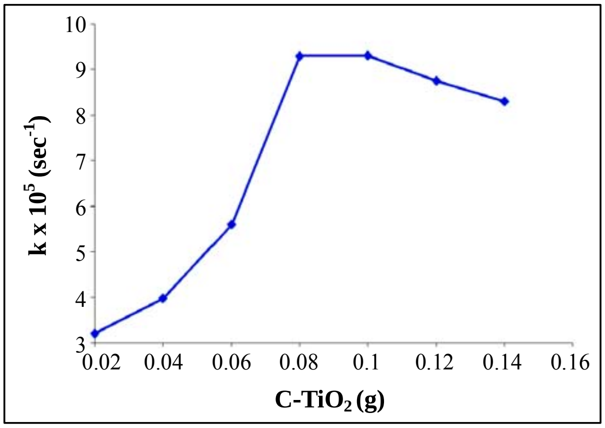

**Fig. 4: Effect of amount of photocatalyst**

It is clear from the above data that with increase in the amount of photocatalyst, the rate of reaction increases to a certain amount of catalyst (0.10 g), which may be regarded as a saturation point. Beyond this point, the rate of reaction decreases with increase in amount of photocatalyst. This may be explained by the fact that with the increase in its amount, the surface area of photocatalyst will increase. Hence, the rise in the rate of reaction has been observed. But after a certain limiting amount (0.10 g), if the amount of photocatalyst was further increased, the rate of degradation decreases, because it only increases the thickness of the layer of semiconductor and not the exposed surface area.

### Effect of percentage of dopant

The effect of percentage of dopant on the rate of degradation of livofloxacin was observed. The percentage was varied from 5-15% (Figure 5).

The rate of reaction was found to increase with increase in the percentage of dopant. The optimum rate constant was found at 15% dopant. It gives rise in the rate, which indicates that the percentage of dopant plays a major role in deciding the rate of photocatalytic degradation of livofloxacin.

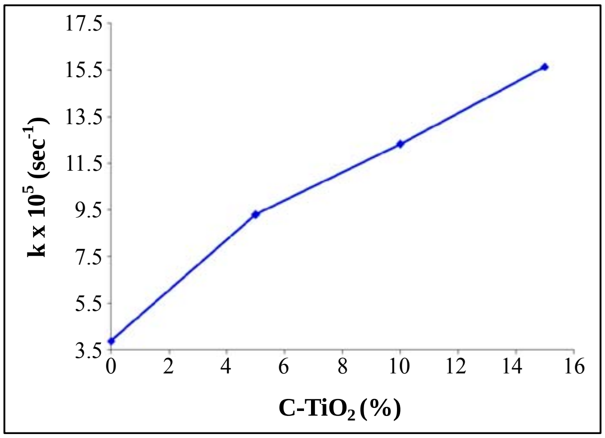

**Fig. 5: Effect of percentage of dopant**

## Effect of Light Intensity

The data indicate that as light intensity was increased, the rate of reaction also increases and maximum rate has been found at 60.0 $mWcm^{-2}$. The results are represent in Figure 6.

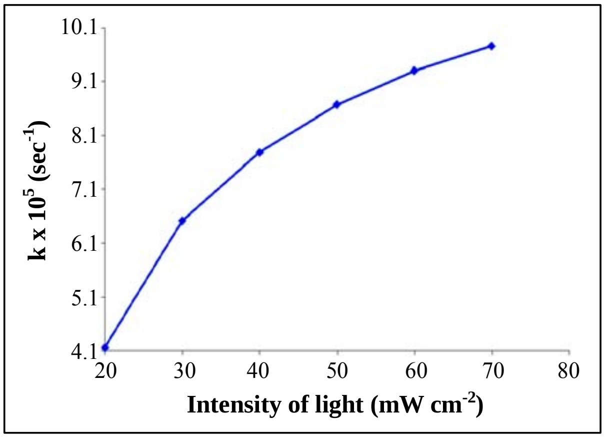

**Fig. 6: Effect of light intensity**

An almost linear relationship between light intensity and the rate of reaction was observed. It may be explained on the basis that as the light intensity was increased, the number of photons striking per unit time per unit area also increases, resulting into higher rate of degradation.

## Mechanism

On the basis of the experimental observations, a tentative mechanism of photocatalytic degradation of livofloxacin may be proposed as –

Livofloxacin (LV) absorbs radiation of suitable wavelength and it is excited to its first singlet excited state followed by intersystem crossing (ISC) to triplet state. On the other hand, the semiconducting carbon doped titanium dioxide also utilize the incident light energy to excite its electron from valence band to conduction band; thus, leaving behind a hole. This hole may abstract an electron from hydroxyl ions to generate hydroxyl radicals. These hydroxyl radicals will then oxidize the drug to products.

$$ {}^{1}LV_{0} \xrightarrow{h\nu} {}^{1}LV_{1} \qquad \ldots(1) $$

$$^{1}LV_{1} \xrightarrow{ISC} {}^{3}LV_{1} \qquad \ldots(2)$$

$$SC \xrightarrow{h\nu} e^{-}\ (CB) + h^{+}\ (VB) \qquad \ldots(3)$$

$$h^{+} + {}^{-}OH \longrightarrow {}^{\bullet}OH \qquad \ldots(4)$$

$$^{\bullet}OH + {}^{3}LV_{1} \longrightarrow \text{Products} \qquad \ldots(5)$$

The participation of $^{\bullet}OH$ radical as an active oxidizing species was confirmed by using hydroxyl radical scavenger (isopropanol), where the rate of degradation was drastically reduced.

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