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EFFICIENT PHOTOCATALYTIC DEGRADATION OF MONOCHROTOPHOS CATALYZED BY C-TiO$_2$

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ABSTRACT

A visible-light responsive C-doped TiO$_2$ has been synthesized via sol–gel precipitation method, with different percentage of carbon dopant. The photocatalytic activity of carbon doped TiO$_2$ was evaluated by using monochrotophos as a model pollutant. The photocatalytic performance of the prepared photocatalysts was compared with the activity of pure TiO$_2$ under VIS irradiation. The carbon doped catalyst shows higher activity than the pure under visible light irradiation.

Key words: Titania, Carbon doped, Photocatalyst, Visible light activity, Monochrotophos.

INTRODUCTION

TiO$_2$ is one of the most promising photocatalysts due to its high reactivity under UV excitation and photochemical stability. One of the potential solutions for improving its efficiency is to extend its photoresponse from the UV region into the visible-light region, allowing more photons to be absorbed and utilized in decomposing the pollutants. Therefore, efforts have been made to modify TiO$_2$ by introducing various transition metal or nonmetal elements into its lattice. The photocatalytic efficiency of the TiO$_2$ system is strongly influenced by an electronic modification of the catalyst through deposition of metal particles[1-3], surface sensitization[4-7] and selective metal ion doping[8-10].

However, the photocatalytic processes do not occur effectively in TiO$_2$ photocatalyst under sunlight irradiation as approximately 4% of the total radiation of the solar spectrum is in the ultraviolet region only. Since nitrogen-doped TiO$_2$ in anatase form was reported as a visible light-sensitive photocatalyst[11], doping TiO$_2$ with some other non-metal elements has received much attention. In last decode, it has been demonstrated by many research groups that TiO$_2$ doped with non-metal elements such as nitrogen[12-14], boron[15], fluorine[16] sulphur[17] or carbon[18,19] showed response in the visible light region and relatively higher photocatalytic activity. Moreover, the incorporation of carbon into TiO$_2$ materials allows the synthesis of photocatalysts with improved efficiency and activity under visible light[20].

EXPERIMENTAL

Monochrotophosis is a typical pollutant (a pesticide). Therefore, monochrotophos was chosen as a

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*Author for correspondence; E-mail: sanyogitasharma22@gmail.com model contaminant and the its degradation was used to evaluate the photocatalytic performance. A 200 W tungsten lamp (Phillips) was used for irradiating the solution in the visible range. The intensity of light was measured with the help of solarimeter, Surya Mapi (Model CEL 201), in the unit of $mWcm^{-2}$. Ultraviolet-Visible spectrophotometer (Model UV-1700 Pharmaspec) was used for measuring absorbance at different time intervals.

The progress of reaction was observed by measuring absorbance of the reaction mixture containing organic pollutant and semiconductor at different time intervals (λ_{max} = 254 nm) during exposure. A decrease in the absorbance indicates that organic pollutant (pesticides) is degraded during this process. Some control experiments were also carried out. It was observed that the reaction takes place only in the presence of both, the light and semiconductor; thus, justifying that the reaction is a phototocatalytic reaction.

RESULTS AND DISCUSSION

The photochemical degradation of monochrotophos was observed. The results for a typical run are given in Table 1 and graphically represented in Figure 1.

Table 1: A typical run

pH = 6.5 C-TiO_2 = 0.10 g
[Monochrotophos] = 6.00×10^{-6} M Light intensity = 50.0 $mWcm^{-2}$

Time (min.)	Absorbance (A)	1 + log A
0.0	0.1936	0.2869
20.0	0.1871	0.2720
40.0	0.1822	0.2605
60.0	0.1766	0.2469
80.0	0.1740	0.2405
100.0	0.1675	0.2240
120.0	0.1622	0.2100
140.0	0.15922	0.2019

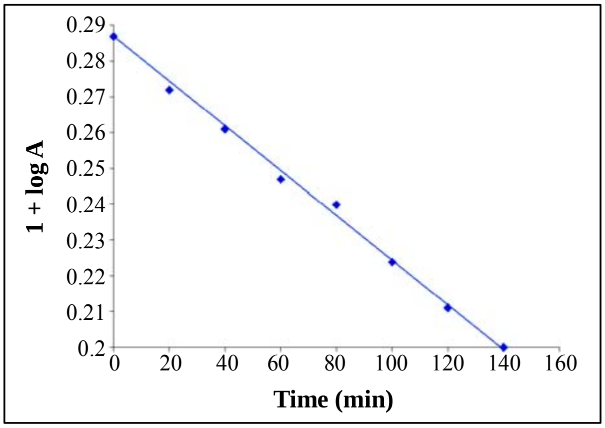

Fig. 1: A typical run

The absorbance of monochrotophos solution decreases with an increase in the time of irradiation, indicating that monochrotophosis was 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 $k = 3.11 \times 10^{-5} sec^{-1}$.

Effect of pH

The effect of pH on the rate of degradation of monochrotophos solution was investigated in the pH range for monochrotophos (5.0-9.5) and the results are reported Figure 2.

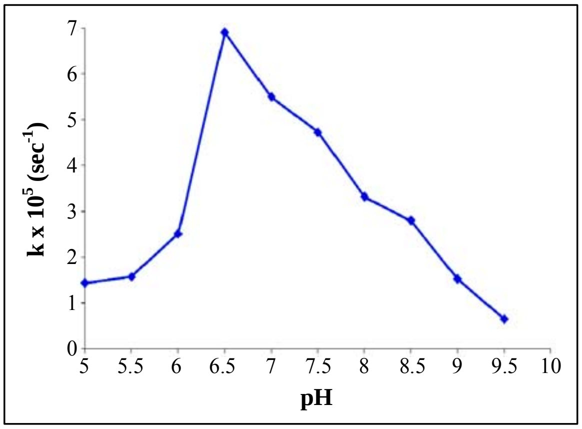

Fig. 2: Effect of pH

It has been observed that the rate of degradation increases with increase in pH upto 6.5 for monochrotophos. Further increase in pH resulted in a decrease in the rate of reaction. The increase in the rate of photocatalytic degradation with increase in pH may be due to more generation of $^{\bullet}OH$ 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 pesticide. After optimum pH 6.5, 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 pestictide towards negatively charged surface of semiconductor will be retarded. This will result into a decrease in the rate of degradation.

Effect of Monochrotophos concentration

The effect of monochrotophos concentration on the rate of its degradation was studied at different concentrations varying from 4.0×10^{-6} M to 30.0×10^{-6} M keeping all other factors identical. The results are reported in Figure 3.

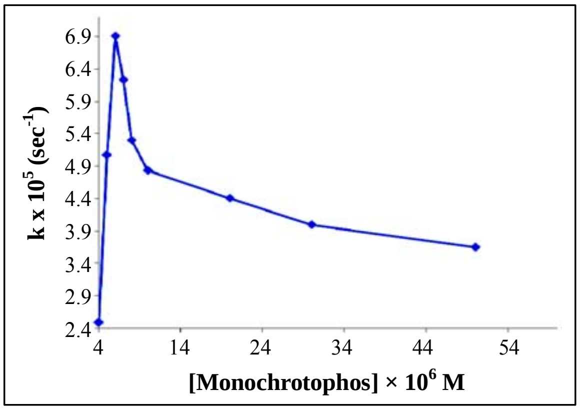

Fig. 3: Effect of monochrotophos concentration

The rate of photocatalytic degradation was found to increase with an increase in concentration of monochrotophos upto 6.00 × 10^{-6} M and then it decreases with an increase in the concentration of monochrotophos further. It can be explained on the basis of that on increasing the concentration of monochrotophos, more molecules are available for excitation and degradation. On increasing the concentration above 6.0 × 10^{-6} M, the rate of reaction decreases, which can be explained that at higher concentration of the monochrotophos may start acting as a filter for the incident light. It will not permit the desired light intensity to reach the surface of C-doped titania and as a result, decrease in the rate of degradation of monochrotophos was observed.

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 given in Figure 4.

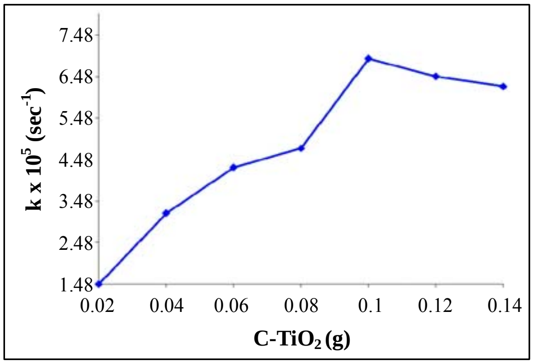

Fig. 4: Effect of amount of photocatalyst

It is clear from the above data that with increase in the amount of catalyst, 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 due the fact that with the increase in the amount of photocatalyst, its surface area will increase. Hence, the rise in the rate of reaction has been observed. But after a certain limiting amount of photocatalyst (0.10 g), if the amount of catalyst 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 monochrotophos was observed. The percentage was varied from 5-15% (Figure 5).

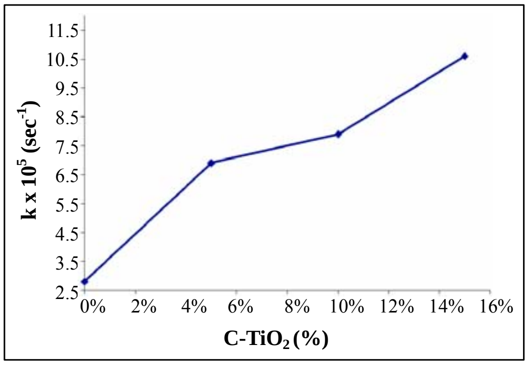

Fig. 5: Effect of percentage of dopant

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 as the percentage of dopant was increased, it indicates that percentage of dopant plays a major role in deciding the rate of photocatalytic degradation of monochrotphos.

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 50.0 mWcm^{-2} (Figure 6).

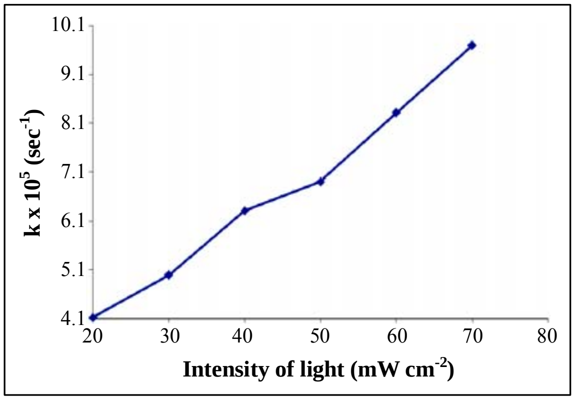

Fig. 6: Effect of light intensity

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

Mechanism

On the basis of the experimental observations, a tentative mechanism of photocatalytic degradation of monochrotophosmay be proposed as-

Monochrotophos (MP) absorbs radiation of suitable wavelengths 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 pesticide to products.

$$^{1}MP_{0} \xrightarrow{h\nu} {}^{1}MP_{1} \qquad \ldots(3.1)$$

$$^{1}MP_{1} \xrightarrow{ISC} {}^{3}MP_{1} \qquad \ldots(3.2)$$

$$SC \xrightarrow{h\nu} e^{-}\ (CB) + h^{+}\ (VB) \qquad \ldots(3.3)$$

$$h^{+} + {}^{-}OH \longrightarrow {}^{\bullet}OH \qquad \ldots(3.4)$$

$$^{\bullet}OH + {}^{3}MP_{1} \longrightarrow \text{Products} \qquad \ldots(3.5)$$

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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