PREPARATION AND USE OF C-TiO$_2$ FOR PHOTOCATLYTIC DEGRADATION OF AZURE-A

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ABSTRACT

Different methods are utilized for degradation of organic pollutants in treating effluents of various industries. Photocatalysis is an advanced oxidation technology for wastewater treatment. The present work presents the degradation of azure A by C-doped TiO$_2$, a nanophotocatalyst prepared by sol-gel method. The effect of various rate-affecting parameters are monitored spectrophotometrically. A tentative mechanism has been proposed based on experimental observations. The kinetic study of this system reveals that this reaction follows pseudo-first order kinetics.

Key words: Advanced oxidation technology, Photocatalysis, C-doped TiO$_2$, Nanophotocatalyst, Azure B, Sol-gel method.

INTRODUCTION

Dyes released from the industrial waste is one of the major factor responsible for the environmental pollution[1]. Out of various purification techniques like biological treatments[2] and traditional methods like ultra filtration, extraction and carbon adsorption[3], advanced oxidation processes (AOPs) have been proposed as a better alternative for waste water purification[4]. The photocatalytic process, a part of AOP, seems to be the most efficient method for water decontamination process. Photocatalysis involves strong oxidizing species such as hydroxyl radicals[6,7]. The rate of photocatalytic degradation depends on various parameters like ammount of semiconductor, initial concentration of the pollutant, pH, light intensity, addition of salts and oxidants, partial pressure of oxygen, etc. [8,9]. During the process, light is allowed to fall on the surface of a semiconductor, which results in migration of electron from valence band to the conduction band. This process involves three major steps:

(i) The production of electron-hole pair[10]

$$\text{Photocatalyst} + h\nu \longrightarrow e^- (CB) + h^+ (VB) \qquad \ldots(1)$$
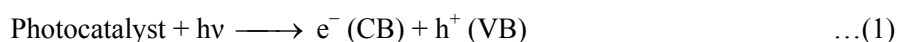
(ii) The separation of electrons and holes

$$e^- (CB) + h^+ (VB) \longrightarrow \text{Heat} \qquad \ldots(2)$$

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(iii) The oxidation and reduction

The charge is then migrated to the surface of the catalyst reacts with it then acts as oxidizing species likely to accept electrons or acts as reducing species likely to release electrons. In an aqueous medium, the hydroxyl groups OH, adsorbed on the surface of photocatalyst, react and produce free radicals $^{\bullet}$OH. In fact, the main reactions are [11]as follows:

$$h^+ + H_2O \text{ (Adsorbed)} \longrightarrow {}^{\bullet}OH + H^+ \qquad \qquad \text{...(3)}$$

$$h^+ + {}^-OH \text{ (Surface)} \longrightarrow {}^{\bullet}OH \qquad \qquad \text{...(4)}$$

Carbon-doped TiO_2 is thus used for photocatalytic degradation of Azure- A dye from water under solar light irradiation.
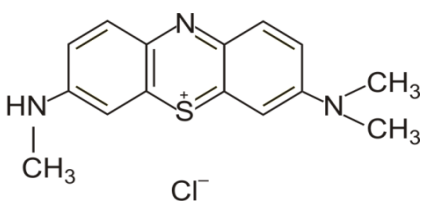
EXPERIMENTAL

IUPAC Name: N', N'-Dimethylphenothiazin-5-ium-3,7-diamine chloride

Molecular formula: $C_{14}H_{14}ClN_3S$

Molar mass: 291.8

Solubility: Water soluble

λ_{max}: 620-634 nm

Fig. 1: Structure of Azure A

A stock solution of Azure-A (1.0×10^{-3} M) was prepared in doubly distilled water by taking 0.02918 g of azure B dissolved in 100.0 mL of doubly distilled water so that the concentration of dye solution was 1.0×10^{-3} M. The stock solution was, further diluted as and when required. The absorbance of this solution was determined with the help of spectrophotometer at $\lambda_{max} = 635$ nm for Azure-A. The 50 mL dye solution was taken in four beakers.

- The first beaker was kept in dark,

- The second beaker was kept in light,

- The third beaker was kept in dark, which contains 0.10 g C-TiO₂,

- The fourth beaker containing 0.10 g C-TiO₂ was exposed to light.

 The absorbance of the solution in each beaker was measured with the help of a spectrophotometer after 3-4 hrs. It was observed that the absorbance of solutions of first three beakers remained almost same, while the solution of fourth beaker had a decrease absorbance.

A typical run

The solution of Azure-A 9.0×10^{-6} M concentration 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 at 9.0 and the solution was exposed to a 200 W tungsten lamp. A decrease in absorbance of dye solution was observed with increasing time of exposure.

The typical run for the photocatalytic degradation of Azure A in the presence of $C-TiO_2$ photocatalyst graphically represented in Fig. 2.

The absorbance of Azure-A solution decreases with an increase in the time of irradiation, which indicates decomposition of Azure-A. The plot of $1 + \log A$ against time was linear, following pseudo-first order kinetics. The rate constant was measured with the expression $k = 2.303 \times$ slope with an optimum rate constant of $k = 9.3 \times 10^{-4}$ sec^{-1}.
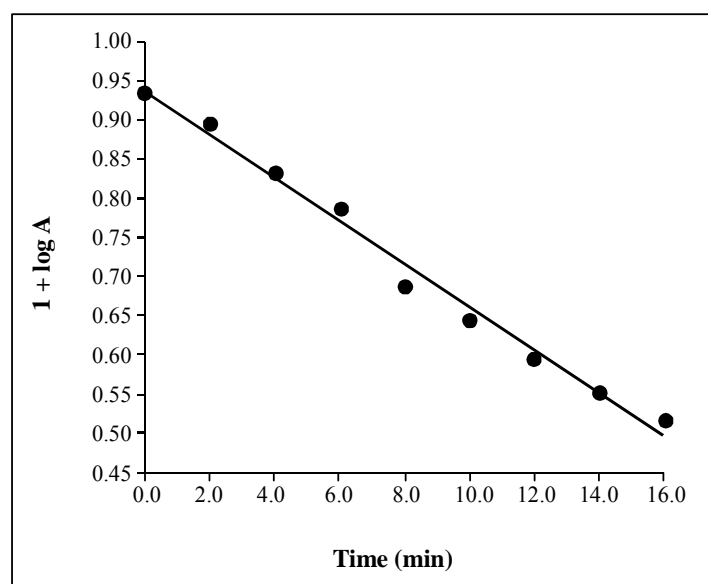
Fig. 2: A typical run

Effect of pH

The effect of pH on the rate of degradation of dye solution was investigated in the pH range 5.0 – 10.0. The results are presented in Table 2.

Table 2: Effect of pH

$[Azure-A] = 9.00 \times 10^{-6}$ M $C-TiO_2 = 0.10$ g

Light intensity = 60.0 mWcm^{-2}

pH	Rate constant (k) $\times 10^4$ (sec^{-1})
5.0	1.17
5.5	2.25
6.0	3.01

pH	Rate constant (k) $\times 10^4$ (sec^{-1})
6.5	3.87
7.0	4.24
7.5	6.17
8.0	6.75
8.5	7.78
9.0	**9.30**
9.5	7.14
10.0	3.13

The rate of degradation of azure-A increases with increase in pH and it reaches to a maximum at the pH 9.0. An increase in the rate of degradation with increase in pH is due to generation of more OH$^-$ ions. These ions donate an electron to holes at the semiconductor surface and $^\bullet$OH free radicals are formed. These free radicals cause oxidation of the dye and as a result, degradation takes place. On further increase in pH above 9.0, a decrease in the rate may be due to the fact that Azure-A now becomes almost neutral and there is no attraction between dye molecules and negatively charged surface of the semiconductor and hence, the rate of degradation is retarded.

Effect of Azure-A concentration

The effect of Azure-A concentration on the rate of degradation was studied at different concentrations varying from 0.8×10^{-5} M to 1.4×10^{-5} M keeping all other factors identical. The results are tabulated in Table 3.

Table 3: Effect of Azure-A concentration

pH = 9.0   Light intensity = 60.0 mWcm^{-2}
C-TiO$_2$ = 0.10 g

[Azure-A] $\times 10^5$ M	Rate constant (k) $\times 10^4$ (sec^{-1})
0.80	5.09
0.90	**9.30**
1.00	7.00
1.10	6.82
1.20	6.50
1.30	4.88
1.40	4.03

The data reveal that the rate of photocatalytic degradation of dye increases with an increase in concentration of the dye from 0.8×10^{-5} M to 0.9×10^{-5} M. It may be explained on the basis that with increase in concentration of dye, more dye molecules were available for excitation and consecutive energy transfer, which results in increase in the rate of photocatalytic degradation of the dye. The rate of photocatalytic degradation was found to decrease with an increase in the concentration of dye above 0.9 $\times$

10^{-5} M. It may be due to the fact that the dye itself may start acting as an internal filter for the incident light and it does not permit the desired light intensity to reach the semiconductor particles. As a result, the degradation rate decreases.

Effect of amount of semiconductor

The effect of amount of semiconductor on rate of degradation of Azure-A has been studied keeping all other factor identical. It was observed that the rate of photocatalytic degradation of Azure-A increases on increasing the amount of semiconductor, but after 0.10 g, the rate becomes virtually constant. The results are tabulated in Table 4.

Table 4: Effect of amount of semiconductor

[Azure-A] = 9.00×10^{-6} M   Light intensity = 60.0 mWcm^{-2}
pH = 9.0

C–TiO$_2$ (g)	Rate constant (k) $\times 10^5$ (sec^{-1})
0.02	4.54
0.04	5.99
0.06	7.00
0.08	6.96
0.10	**9.30**
0.12	9.28
0.14	9.31
0.16	9.30
0.18	9.27

The of photocatalytic degradation of Azure-A increases on increasing the amount of semiconductor. A maximum value was observed at the amount 0.10 g. It was evident that with increase in the amount of semiconductor, there was an increase in exposed surface area of the semiconductor, but after a certain limit (0.10 g), it become almost constant as any increase in the amount of semiconductor above this limit will not increase the exposed surface area.

Effect of light Intensity

The effect of light intensity on the photocatalytic degradation of Azure-A has investigated keeping all other factors identical. The results are reported in Table 5.

Table 5: Effect of light intensity

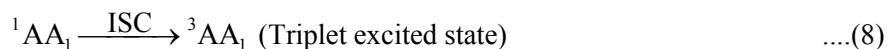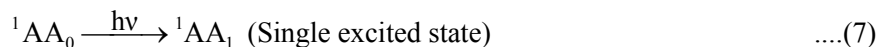[Azure-A] = 9.00×10^{-6} M   C–TiO$_2$ = 0.10 g
pH = 9.0

Light intensity (mWcm^{-2})	Rate constant (k) $\times 10^4$ (sec^{-1})
20.0	3.80
30.0	4.90

Light intensity (mWcm^{-2})	Rate constant (k) $\times 10^4$ (sec^{-1})
40.0	6.12
50.0	8.50
60.0	**9.30**
70.0	8.50

The results indicate that the rate of degradation of dye increases with increase in light intensity as the number of photons striking per unit area of C-TiO$_2$ increases per unit time. However, on increasing the intensity above 60.0 mWcm^{-2}, there was a decrease in the rate, which may be due to some thermal reactions.

Mechanism

On the basis of these observations, a tentative mechanism for photocatalytic degradation of Azure A dye is proposed as follows:

$$^1AA_0 \xrightarrow{\quad h\nu \quad} {}^1AA_1 \text{ (Single excited state)} \qquad ....(7)$$

$$^1AA_1 \xrightarrow{\quad ISC \quad} {}^3AA_1 \text{ (Triplet excited state)} \qquad ....(8)$$

$$SC \xrightarrow{\quad h\nu \quad} e^-(CB) + h^+(VB) \text{ or } SC^* \qquad ....(9)$$

$$h^+ + OH^- \longrightarrow {}^\bullet OH \qquad ....(10)$$

$$^\bullet OH + {}^3AA_1 \longrightarrow \text{Leuco AA} \qquad ....(11)$$

$$\text{Leuco AA} \longrightarrow \text{Products} \qquad ....(12)$$

Azure A absorbs radiations of desired wavelength and it is excited giving its first excited singlet state. Further, it undergoes intersystem crossing (ISC) to give its more stable triplet state. Along with this, the semiconducting carbon doped TiO$_2$ (SC) also utilizes this energy to excite its electron from valence band to the conduction band. An electron can be abstracted from hydroxyl ion by hole (h$^+$) present in the valence band of semiconductor generating $^\bullet$OH radical. This hydroxyl radical will oxidize Azure-A to its leuco form, which may ultimately degrade to products. It was confirmed that the $^\bullet$OH radical participates as an active oxidizing species in the degradation of Azure-A as the rate of degradation was appreciably reduced in presence of hydroxyl radical scavenger (2-propanol).

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