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# CHROMIUM PYROPHOSPHATE AS VISIBLE LIGHT PHOTOCATALYST FOR DEGRADATION OF AZURE B

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## ABSTRACT

Photocatalytic degradation of Azure B was carried out in presence of $Cr_4(P_2O_7)_3$ as photocatalyst under visible light irradiation. Effect of various parameters like pH, dye concentration, amount of $Cr_4(P_2O_7)_3$, light intensity etc. was studied to obtain optimum conditions. Tentative mechanism has been proposed for this reaction.

**Key words**: Chromium pyrophosphate, Degradation, Azure B, Photocatalysis, Visible light.

## INTRODUCTION

Environment or nature gifted by God is very precious thing, which is to be cared by human being. Increasing industrialization in developing countries generates problem of environmental pollution. Most of textile industries' waste contains dyes, which is major constituent for water pollution. The main objective of the present work is to purify this polluted water. Lot of research work is being done in this area to degrade dyes and remove polluting chemical substances by using photocatalyst $TiO_2$[1,2], ZnO[3-5], ZnS[6] and CdS[7].

Adsorption, osmosis, flocculation, bioremediation and other techniques have been used to remove dyes from water bodies, but all such methods suffer from various drawbacks. Photochemistry using semiconductor nanoclusters is involved in waste treatment methods called Advanced Oxidation Processes (AOPs) such as photo-Fenton, photocatalysis and sonolysis. Photocatalytic bleaching of dyes in waste water is a promising process. As a result, extensive work has been done in this area and now a days special attention is given towards enhancing activity of photocatalyst especially $TiO_2$[8-12]. Less attention has been paid towards search of materials as a photocatalyst. Here, an effort has been made to use chromium pyrophosphate as a photocatalyst to degrade azure B dye.

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## EXPERIMENTAL

### Photocatalytic degradation of azure B

The stock solution of dye was prepared in distilled water and diluted as and when required. The pH of the solution was adjusted by diluted NaOH and diluted HCl and determined by a pH meter (pH pen type). Solution of dye was taken in a beaker and known amount of $Cr_4(P_2O_7)_3$ was added. The beaker was covered with water filter to avoid any thermal radiation. The solution was irradiated by a visible tungsten filament lamp and the absorbance was recorded spectrophotometrically (Systronics, Model 106).

### Preparation of semiconductor

The semiconductor was prepared by making separate clear solutions of $CrCl_3$ and $Na_4P_2O_7 \cdot 6H_2O$ in water and precipitated by mixing these solution. Then it was filtered. The solid was washed with distilled water several times and it was allowed to dry at room temperature and then at 80 $^0$C. A light bluish powder was obtained, which was used for further experiment as a photocatalyst.

## RESULTS AND DISCUSSION

The plot of absorbance versus time was found to be a straight line suggesting that degradation of azure B by $Cr_4(P_2O_7)_3$ follows pseudo-first order rate law. Rate constants were calculated as follows-

$$k = 2.303 \times \text{slope} \quad ...(1)$$

The data of typical run is given in Table 1 and shown graphically in Fig. 1.

**Table 1: A typical run**

| **Time (min)** | **[Azure B] = 1.00 x $10^{-5}$M<br>pH = 7.0<br>$Cr_4(P_2O_7)_3$ = 0.15 g<br>Light intensity = 50.0 mWcm$^{-2}$** | |
|---|---|---|
| | **O.D.** | **1 + log O.D.** |
| 15.0 | 1.108 | 1.0445 |
| 30.0 | 0.944 | 0.9750 |

Cont…

| Time (min) | **[Azure B] = 1.00 x $10^{-5}$M**<br>**pH = 7.0**<br>**$Cr_4(P_2O_7)_3$ = 0.15 g**<br>**Light intensity = 50.0 mWcm$^{-2}$** | |
|---|---|---|
| | **O.D.** | **1 + log O.D.** |
| 45.0 | 0.800 | 0.9031 |
| 60.0 | 0.700 | 0.8451 |
| 75.0 | 0.585 | 0.7672 |
| 90.0 | 0.512 | 0.7093 |
| 105.0 | 0.452 | 0.6551 |
| 120.0 | 0.404 | 0.6064 |
| | $k_1 = 1.57 \times 10^{-4}$ $s^{-1}$ | |

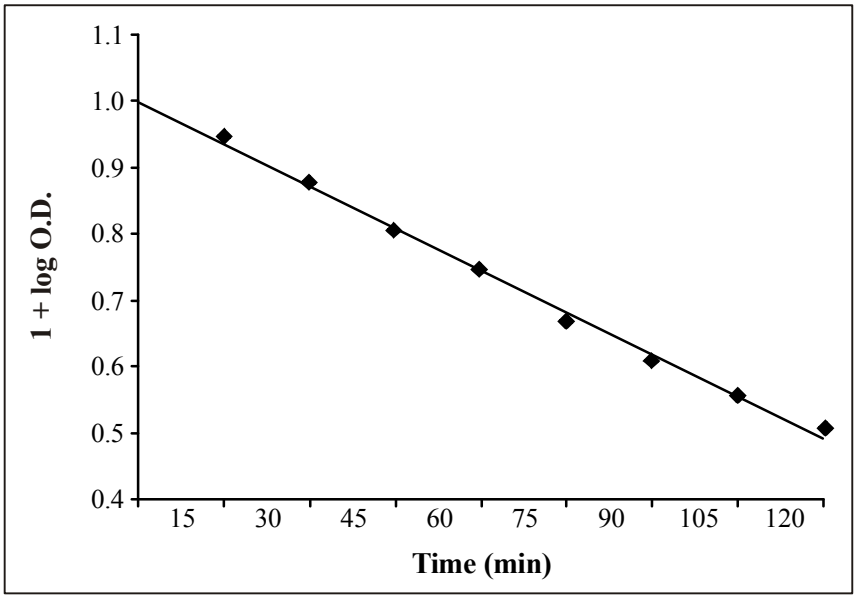


**Fig. 1: A typical run**

## Effect of pH

Photocatalytic degradation was carried out keeping other parameters constant. The effect of pH variation on the rate is given in following Table 2 and represented graphically in Fig. 2.

**Table 2: Effect of pH**

| pH | [Azure B] = 1.00 x $10^{-5}$M<br>$Cr_4(P_2O_7)_3$ = 0.15 g<br>Light intensity = 50.0 mWcm$^{-2}$ |
|---|---|
| | k x $10^4$ ($s^{-1}$) |
| 6.0 | 0.80 |
| 6.5 | 0.94 |
| 7.0 | 1.27 |
| 7.5 | 1.57 |
| 8.0 | 0.91 |
| 8.5 | 0.85 |

With increasing pH, degradation of azure B increases and at pH 7.5, maximum degradation was observed. Above pH 7.5, degradation of dye decreases and hence, effect of other parameters was studied at pH 7.5.

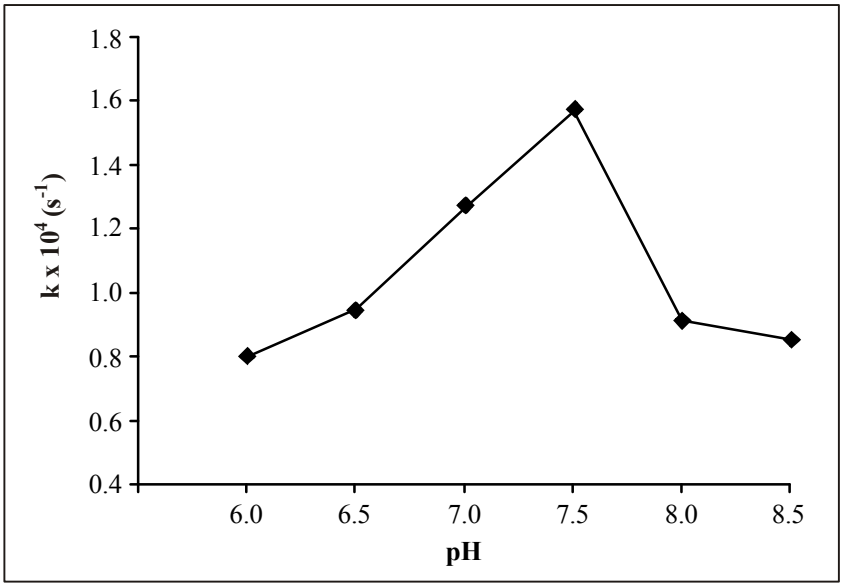


**Fig. 2: Effect of pH**

**Effect of amount of photocatalyst**

The effect of amount of photocatalyst on degradation rate was also observed. The results are reported in Table 3 and presented in Fig. 3

**Table 3: Effect of amount of photocatalyst**

| Amount (g) | **pH = 7.5**<br>**[Azure B] = 1.00 x $10^{-5}$M**<br>**Light intensity = 50.0 mWcm$^{-2}$** |
|---|---|
| | **k x $10^4$ ($s^{-1}$)** |
| 0.05 | 0.62 |
| 0.10 | 0.96 |
| 0.15 | 1.57 |
| 0.20 | 1.57 |
| 0.25 | 1.54 |

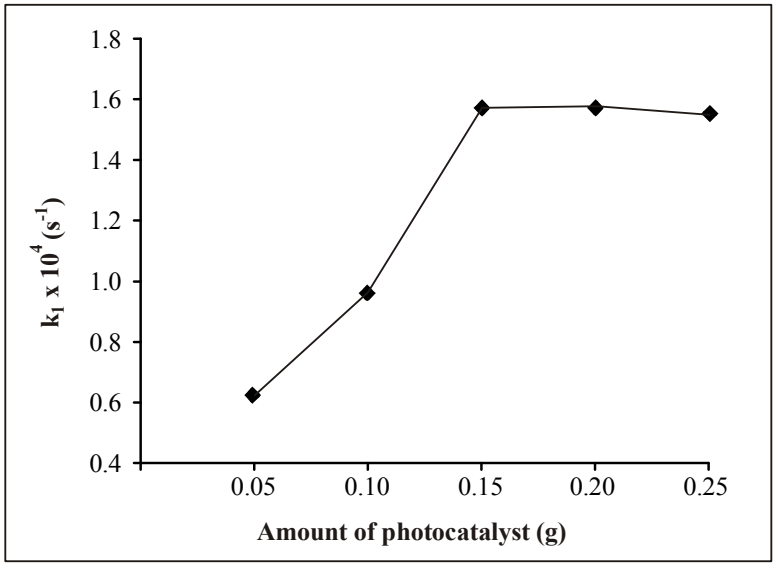


**Fig. 3: Effect of amount of photocatalyst**

Quantity of photocatalyst was varied keeping all other parameters constant. It was observed that up to 0.15 g of $Cr_4(P_2O_7)_3$, the rate of degradation increases. Then it remains almost constant because particle settled at the bottom of vessel in a layered form, so only

upper layer is excited affecting the degradation process of the dye.

**Effect of concentration of azure B**

**Table 4: Effect of concentration of azure B**

| **[Azure B] x $10^5$ M** | **pH = 7.5**<br>**$Cr_4(P_2O_7)_3$ = 0.15 g**<br>**Light intensity = 50.0 mWcm$^{-2}$** |
|---|---|
| | **k x $10^4$ ($s^{-1}$)** |
| 0.5 | 0.96 |
| 1.0 | 1.57 |
| 1.5 | 1.45 |
| 2.0 | 1.23 |
| 2.5 | 0.90 |

It is explained on the basis that with increasing concentration up to 1.00 x $10^{-5}$M, rate of degradation increases. Then increasing concentration of the dye further, rate decreases as at higher concentrations, the dye solution is dark in colour and it will not permit the desired number of photons to reach the surface of catalyst and as a result, the rate of reaction decreases.

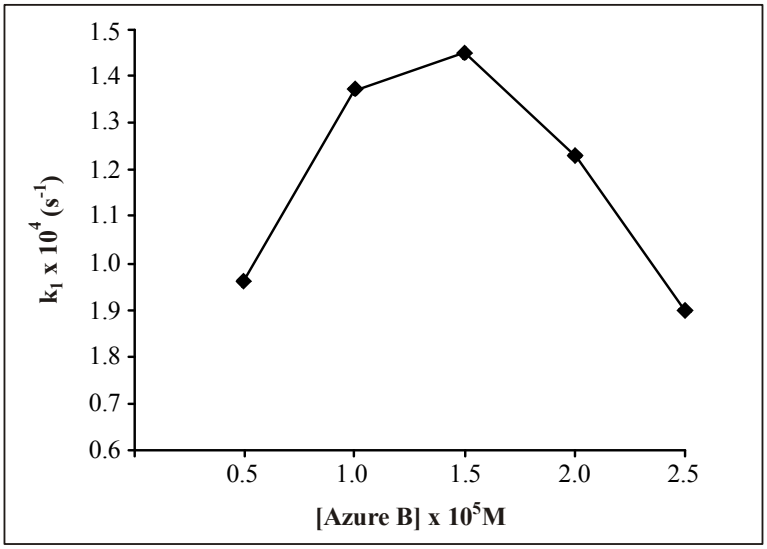


**Fig. 4: Effect of azure B concentration**

**Effect of light intensity**

The effect of light intensity on the rate of degradation of dye was observed by increasing distance between the reaction vessel and light source.

**Table 5: Effect of light intensity**

| **Light intensity ($mW\ cm^{-2}$)** | **pH = 7.5<br>$Cr_4(P_2O_7)_3$ = 0.15 g<br>[Azure B] = $1.00 \times 10^{-5}$M** |
|---|---|
| | **$k \times 10^4$ ($s^{-1}$)** |
| 30.0 | 1.47 |
| 40.0 | 1.53 |
| 50.0 | 1.57 |
| 60.0 | 1.62 |
| 70.0 | 1.86 |

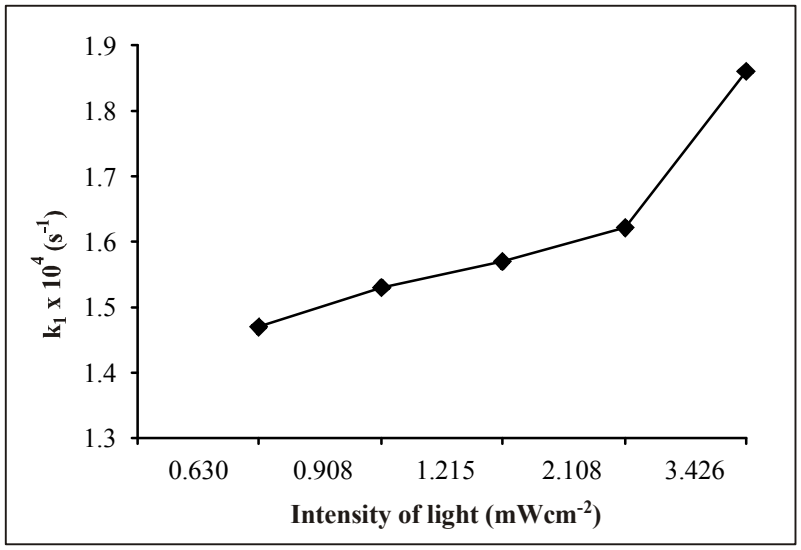


**Fig. 5: Effect of light intensity**

It was observed that the rate of reaction increases with increasing light intensity. The increasing light intensity increases the number of photons to excite dye molecules and as a result, the dye degradation rate also increases. But at higher intensities of light, thermal

degradation is possible and hence, just to avoid thermal degradation, light intensity 50.0 $mWcm^{-2}$ was used.

## MECHANISM

On the basis of experimental observations, a tentative mechanism has been proposed as,

$$^1Dye_0 \longrightarrow {}^1Dye_1 \text{ (Singlet excited state)} \quad ...(2)$$

$$^1Dye_1 \xrightarrow{ISC} {}^3Dye_1 \text{ (Triplet excited state)} \quad ...(3)$$

$$SC \longrightarrow e^- + h^+ \text{ or } SC^+ \quad ...(4)$$

$$h^+ + OH^- \text{ (from base)} \longrightarrow {}^{\bullet}OH \quad ...(5)$$

$$^3Dye_1 + {}^{\bullet}OH \longrightarrow \text{Products} \quad ...(6)$$

Dye absorbs the light of suitable wavelength and gets excited to its first excited singlet state. This state gets converted to corresponding triplet state through inter system crossing. On the other hand, the semiconductor also gets excited by absorbing light and an electron is excited from its valence band to conduction band leaving behind a hole. This hole abstracts an electron from $OH^-$ ions generating $^{\bullet}OH$ free radicals. The dye is now being bleached by this free radical. The participation of $^{\bullet}OH$ radical was confirmed by using its specific scavenger i.e. 2-propanol, which almost stops the bleaching reaction.

## REFERENCES

1. R. W. Matthews and S. R. Mecvercy, J. Photochem. Photobiol., **64A**, 23 (1992).
2. M. Trillas, J. Peral and X. Domenech, Appl. Catal., **3**, 45 (1993).
3. Ajay Sharma, P. Rao, R. P. mathur and S. C. Ameta, J. Photochem. Photobiol., **86 A**, 197 (1995).
4. P. Rao, G. Patel, S. L. Sharma and S. C. Ameta, Toxicol. Environ. Chem., **65**, 155 (1997).
5. A. Akyol, H. C. Yatmaz and M. Bayramoglu, Appl. Catal. B: Environ., **54**, 19 (2004).
6. W. Hetterich and H. Kisch, Chem. Ber., **15**, 121 (1988).
7. K. J. Green and R. Rudham, J. Chem. Soc., **88**, 3599 (1992).

8. A. Di Paola, E. Garcia-Lopez, S. Ikeda, G. Marci, B. Ohtani and L. Palmisano, Catal. Today, **75,** 87 (2002).

9. H. Chun, T. Yuchao and T. Hongxiao, Catal. Today, **90**, 325 (2004).

10. J. Zhu, W. Zheng, B. He, J. Zhang and M. Anpo, J. Mol. Catal. A: Chem., **216**, 35 (2004).

11. M. Kang, S. J. Choung and J. Y. Park, Catal. Today, **87**, 87 (2003).

12. M. I. Franch, J. A. Ayllon, J. Peral and X. Domenech, Catal. Today, **101**, 245 (2005).

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