

$\text{Na}_{11}[\text{CuFeW}_{18}\text{O}_{62}]$ MEDIATED PHOTOCATALYTIC DEGRADATION OF BROMOCRESOL GREEN

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ABSTRACT

Potable water is a main need of everyone including human being, animal and plant kingdom. Effluents of different textile, dyeing and printing industries, which are being discharged in nearby water resources, are creating water pollution. Use of a semiconductor as photocatalyst is considered as a promising technology, which provides solution for this problem. In the present investigation, the photochemical degradation of bromocresol green by Well-Dawson heteropoly anion, $\text{Na}_{11}[\text{CuFeW}_{18}\text{O}_{62}]$ has been carried out. The rate of photocatalytic degradation of dye was observed spectrophotometrically. The effect of different parameters, which affect the rate of reaction; like pH, concentration of dye, amount of semiconductor and light intensity has been studied for the above system. Kinetic studies reveal that the photocatalytic process follows pseudo-first order kinetics. A tentative mechanism for the photocatalytic degradation of bromocresol green has also been proposed.

KEY WORDS: Water pollution, Semiconductor, Photocatalytic degradation, Bromocresol green, Well-Dawson heteropoly anion, $\text{Na}_{11}[\text{CuFeW}_{18}\text{O}_{62}]$.

INTRODUCTION

Dyes, phenols, pesticides, fertilizers, detergents and other chemical products are disposed off directly into the environment, without being treated, controlled or uncontrolled and without an effective treatment strategy. Using photocatalysis, organic pollutants can be completely mineralized reacting with the oxidizers to form CO_2 , water and dilute concentration of simple mineral acids. The semiconductor may be in the form of a powder suspended in the water or fixed on a support.

Photocatalytic reduction of the dye methylene blue by $\text{Bi}_2\text{S}_3/\text{CdS}$ nanocomposites was done by Kobasa and Tarasenko, (2002). CdO as a photocatalyst was introduced by Karunakaran and Senthilvelan, (2005) for the oxidation of aniline to azobenzene. Photoelectrocatalytic degradation of rose bengal has been carried out by Liu *et al.*, (2003). Arslan-Alaton, (2004) developed a new method for disperse dye decolourization using

photochemically active silicadodecatungstic acid and isopropanol redox system. Kaur *et al.*, (2011) synthesized La_2CoO_4 (lanthanum cobalt oxide) and studied its photocatalytic behaviour through bleaching of azure-B and yellowish orange dyes. The potential of a common semiconductor, ZnO , has been explored by Chakrabarti and Dutta, (2007) as effective catalyst for the photodegradation of two model dyes: methylene blue and eosin Y. The layered compound BiOCl was the first oxyhalide to be used as a photocatalyst and for its photocatalytic activity, the methyl orange dye degradation was chosen by Zhang *et al.*, (2006). Sharma *et al.*, (2011) used nickel sulphide as photocatalyst for the production of desalinated water. Oxidation of bismark brown-R (basic dye of azo series) with photo-Fenton reagent was investigated under ambient conditions by Sharma *et al.*, (2011).

The effectiveness of zinc-oxide mediated solar photocatalytic degradation of phenol was examined by Pardeshi and Patil, (2008). The photocatalysed

degradation of two selected pesticide derivatives such as dichlorvos and phosphamidon has been investigated by Rahman and Muneer, (2005) in aqueous suspensions of titanium oxide. A new TiO_2 -based photocatalyst with both B doping and Bi_2O_3 coupling ($\text{Bi}_2\text{O}_3/\text{TiO}_2\text{-xB}_x$) was synthesized by Su *et al.*, (2012) to degrade pentachlorophenol under visible light irradiation. Photocatalytic reaction of environmental pollutants Cr (VI) over CdS powder was observed by Wang *et al.*, (1992). Ameta *et al.*, (2006) used semiconducting iron (III) oxide as photocatalyst for bleaching of methylene blue, crystal violet and malachite green dyes. Han *et al.*, (2009) used heterogeneous photocatalysis involving titanium dioxide (TiO_2) for organic dyes degradation. Troupis *et al.*, (2007) carried out photocatalytic reductive destruction of azo dye naphthol blue black by polyoxometalate. Degradation of rhodamine B dye was investigated by Lei *et al.*, (2005) using immobilized polyoxometalate with H_2O_2 under visible light irradiation. Chen *et al.*, (2004) examined the photooxidation of rhodamine-B by visible light irradiation in the presence of POM ($\text{H}_4\text{SiW}_{12}\text{O}_{40}$) [12-tungstosilicic acid] and compared it with TiO_2 . Yanga *et al.*, (2005) prepared nanoporous polyoxotungstate anatase composite for the efficient degradation of dye pollutants. Gao *et al.*, (2009) studied photocatalytic properties of microspheres towards rhodamine B.

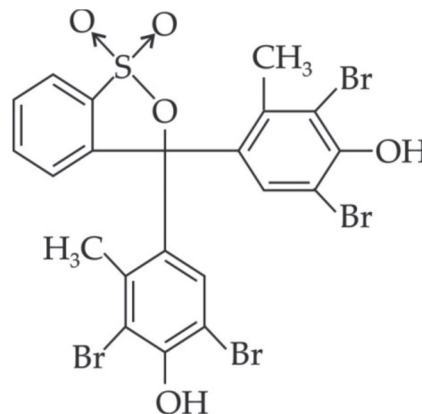
MATERIALS AND METHODS

Preparation of Well-Dawson Heteropoly Anion, $\text{Na}_{11}[\text{CuFeW}_{18}\text{O}_{62}]$ photocatalyst

Well-Dawson heteropoly anion was prepared by the reaction between cupric chloride, ferric chloride and sodium metatungstate. The mixture of 40 mL cupric chloride dihydrate $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ solution (1.1 g, 6.45 mmol) and 40 mL ferric chloride FeCl_3 (1 g, 6 mmol) was added dropwise to 100 mL sodium metatungstate solution prepared by dissolving (36.6 g, 110.96 mmol) with continuous stirring till constant pH. 10 mL of glacial acetic acid was added to maintain the acidic conditions. After the addition of 68 mL of the above mixed solution to sodium metatungstate solution, the pH of the final mixture became constant at 3.79. The mixture was refluxed for 4-5 hrs. It was ice cooled, filtered and the filtrate was left overnight for crystallization. Blue crystals were separated out, which were washed with n-hexane and preserved for the analysis. In the

present work, Well-Dawson heteropoly anion has been used as a photocatalyst for the degradation of dye bromocresol green.

Photocatalytic Degradation of Bromocresol green using $\text{Na}_{11}[\text{CuFeW}_{18}\text{O}_{62}]$ -Molecular formula of bromocresol green is $\text{C}_{21}\text{H}_{14}\text{Br}_4\text{O}_5\text{S}$



Structure of Bromocresol Green

Molecular weight of bromocresol green is 698.01

Solutions of the dye (bromocresol green) were prepared in doubly distilled water. The photocatalytic degradation was observed after addition of 0.10 g of Well-Dawson heteropoly anion, $\text{Na}_{11}[\text{CuFeW}_{18}\text{O}_{62}]$ to the dye solution. Irradiation was carried out in a glass vessel (Pyrex, 100 mL) with a 200 W tungsten lamp (visible light, Philips; light intensity = 50.0 mWcm^{-2}). The light intensities at various distances from the lamp were measured with the help of a solarimeter (Suryamapi CEL 201). A water filter was used to cut thermal radiations. A digital pH meter (Systronics Model 335) was used to adjust the pH of the solutions by the addition of previously standardized 0.1 N sulfuric acid and 0.1 N sodium hydroxide solutions.

Optical density of the dye solution was monitored at regular time intervals by spectrophotometer (Systronics Model 106). Controlled experiments were also carried out to confirm that reaction is photocatalytic in nature.

RESULTS AND DISCUSSION

The photocatalytic degradation of bromocresol green was observed at $\lambda_{\text{max}} = 620 \text{ nm}$. The plot of log O.D. v/s time was found to be a straight line. This indicates that the photocatalytic degradation of dye in presence of Well-Dawson heteropoly anion $\text{Na}_{11}[\text{CuFeW}_{18}\text{O}_{62}]$, follows pseudo-first order

kinetics and the rate constant of this reaction was determined using the following expression:

$$k = 2.303 \times \text{slope}$$

The observations for typical run are given in Table 1.

Table 1. A typical run

pH = 8.5 [Bromocresol green] = 1.70×10^{-5} M
Na₁₁[CuFeW₁₈O₆₂] = 0.10 g Light Intensity = 50.0 mWcm⁻²

Time (min.)	Optical Density (O. D.)	1 + log O. D.
0	0.692	0.8401
10	0.589	0.7701
20	0.490	0.6902
30	0.427	0.6304
40	0.363	0.5600
50	0.309	0.4899
60	0.269	0.4297
70	0.224	0.3503
80	0.200	0.3010
90	0.164	0.2148

Rate constant (k) = 2.61×10^{-4} sec⁻¹

Effect of pH

The effect of pH on photocatalytic degradation was investigated at different pH and the results are given in Table 2. The reaction rates were determined in the pH range 5.0–10.5 and the photocatalytic degradation of bromocresol green was found maximum at pH 8.5.

It has been observed that with an increase in pH, the rate of photocatalytic degradation of dye increases from 5.0 to 8.5. On further increasing the pH above 8.5 resulted into a decrease in the rate of

Table 2. Effect of pH

[Bromocresol green] = 1.70×10^{-5} M Na₁₁[CuFeW₁₈O₆₂] = 0.10 g
Light Intensity = 50.0 mWcm⁻²

pH	k × 10 ⁴ (sec ⁻¹)
5.0	0.57
5.5	0.65
6.0	0.79
6.5	1.06
7.0	1.25
7.5	1.71
8.0	2.10
8.5	2.61
9.0	2.42
9.5	2.18
10.0	1.78
10.5	1.56

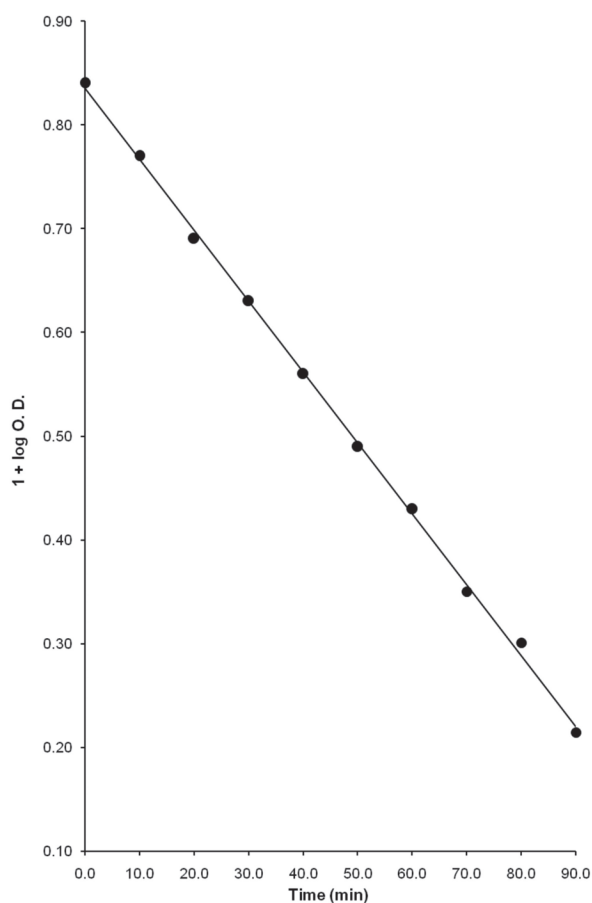


Fig. 1. Typical Run

photocatalytic degradation. These observations can be explained on the basis that as the pH of the solution was increased, more OH⁻ ions were available. These OH⁻ ions will generate more •OH radicals by combining with the hole of the semiconductor, which are considered responsible for oxidation of dye molecules. After a certain pH value, more OH⁻ ions will make the surface of semiconductor negatively charged and it restricts the approach of neutral dye molecules towards the semiconductor surface. This will result into a decrease in the rate of photocatalytic degradation of dyes.

Effect of dye concentration

Effect of variation of dye concentration was also studied by taking different concentrations of dye. The results are tabulated in Table 3. From the observed data, it is evident that the rate of photocatalytic degradation increases with increasing concentration of the dyes (i.e. from 1.00×10^{-5} M to 1.70×10^{-5} M).

This may be attributed to the fact that as the concentration of dyes was increased, more dyes molecules were available for excitation followed by inter system crossing and hence, there was an increase in the rate. The rate of photocatalytic degradation was found to decrease with an increase

Table 3. Effect of Bromocresol Green Concentration

pH = 8.5 $\text{Na}_{11}[\text{CuFeW}_{18}\text{O}_{62}] = 0.10 \text{ g}$ Light Intensity = 50.0 mWcm^{-2}	
[Bromocresol green] $\times 10^5 \text{ M}$	$k \times 10^4 (\text{sec}^{-1})$
1.00	1.11
1.10	1.24
1.20	1.43
1.30	1.62
1.40	1.79
1.50	1.90
1.60	2.34
1.70	2.61
1.80	1.91
1.90	1.62
2.00	1.19

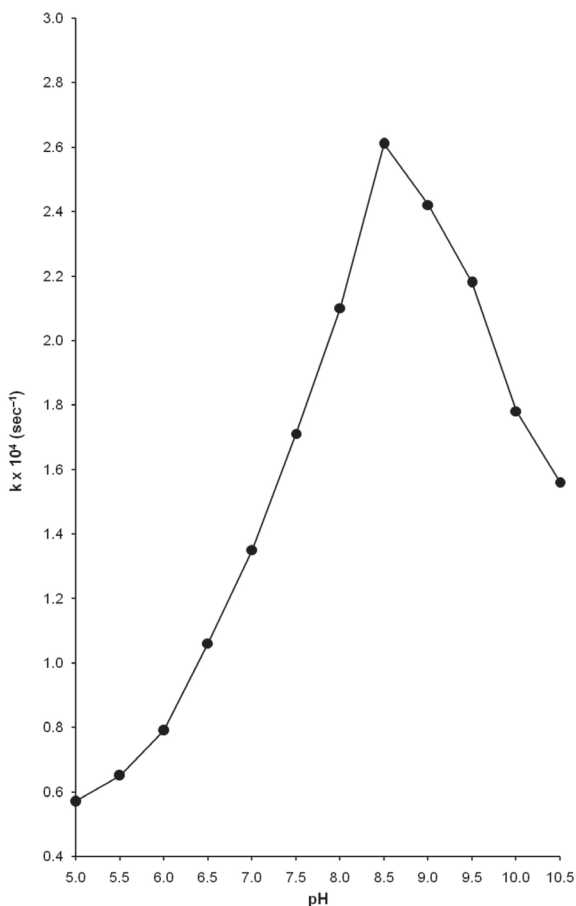


Fig. 2. Effect of pH

Table 4. Effect of Amount of Semiconductor

pH = 8.5 [Bromocresol green] = $1.70 \times 10^{-5} \text{ M}$ Light Intensity = 50.0 mWcm^{-2}	
Amount (g)	$k \times 10^4 (\text{sec}^{-1})$
0.02	0.41
0.04	0.70
0.06	1.05
0.08	1.65
0.10	2.61
0.12	2.58
0.14	2.58
0.16	2.60
0.18	2.64

in the concentration of dye further. Here, the dye molecules starts acting as filter for the incident light and they do not permit the desired light intensity to reach the semiconducting particles and thus results in decrease in the rate of the photocatalytic degradation of dye.

Effect of amount of semiconductor

The amount of semiconductor also affects the process of dye degradation. Different amounts of photocatalyst were used and the results are given in Table 4.

It has been observed that as the amount of semiconductor was increased, the rate of photodegradation of dye increases but ultimately, the reaction rate become virtually constant after a certain amount (0.10 g) of the semiconductor. This may be due to the fact that as the amount of semiconductor was increased, the exposed surface area also increases, but after a certain limit, if the amount of Well-Dawson heteropoly anion was further increased; there will be no increase in the exposed surface area of the photocatalyst. It may be considered like a saturation point above which any increase in the amount of semiconductor has negligible or no effect on the rate of photocatalytic

Table 5. Effect of Light Intensity

pH = 8.5 [Bromocresol green] = $1.70 \times 10^{-5} \text{ M}$ $\text{Na}_{11}[\text{CuFeW}_{18}\text{O}_{62}] = 0.10 \text{ g}$	
Intensity of light (mWcm^{-2})	$k \times 10^4 (\text{sec}^{-1})$
20.0	1.10
30.0	1.51
40.0	1.97
50.0	2.61
60.0	1.85
70.0	1.15

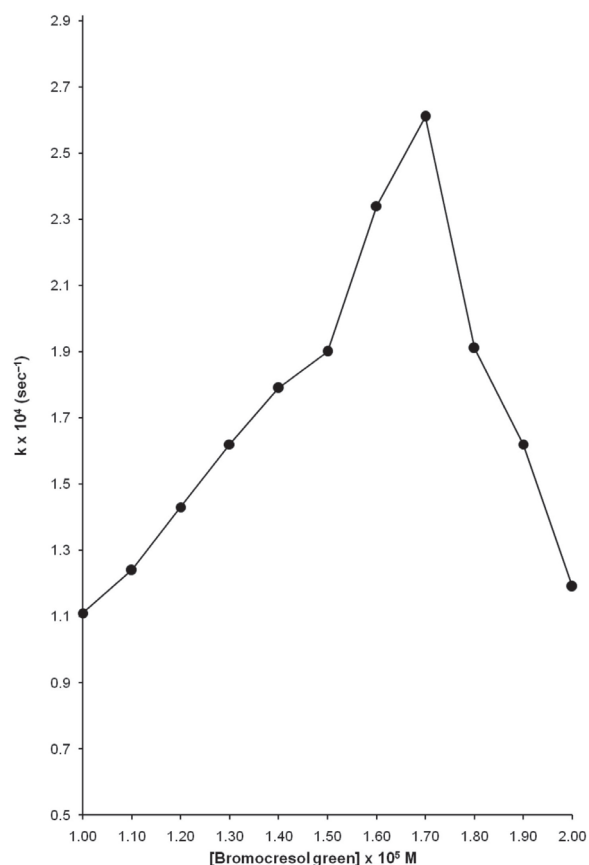


Fig. 3. Effect of Dye concentration

degradation of dye, as any increase in the amount of semiconductor after this saturation point will only increase the thickness of the layer at the bottom of the vessel.

Effect of light intensity

The effect of the variation of light intensity on the rate was also investigated and the observations are reported in the Table 5. The results indicate that degradation rate was enhanced as the intensity of light was increased, because any increase in the light intensity will increase the number of photons striking per unit area of semiconductor powder. An almost linear behavior between light intensity and rate of reaction was observed.

Mechanism

On the basis of these observations, a tentative mechanism for photocatalytic degradation of bromocresol green may be proposed as –

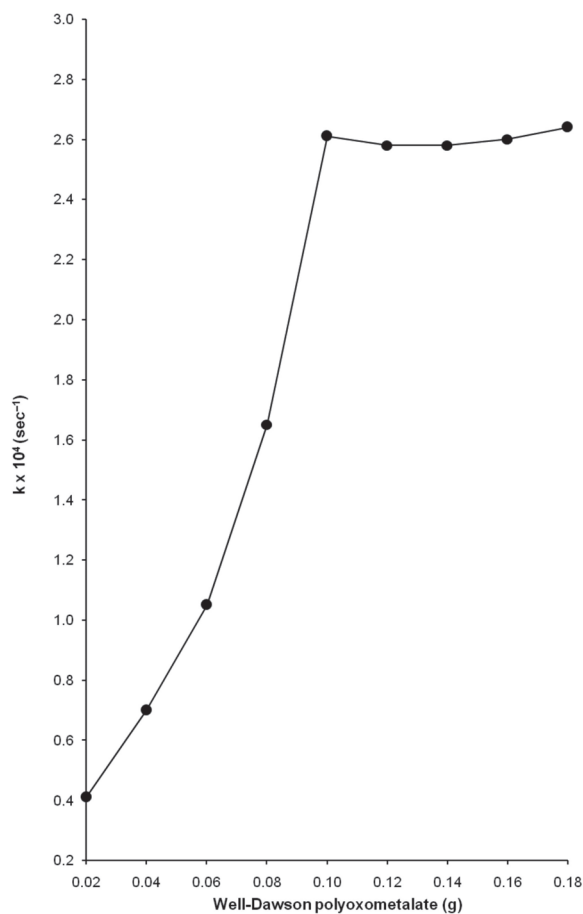
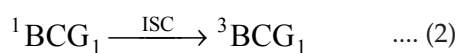
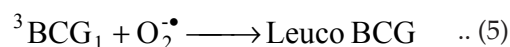


Fig. 4. Effect of Amount of semiconductor



Bromocresol green (BCG) absorbs radiations of suitable wavelength and gives rise to its excited singlet state. Then it undergoes intersystem crossing (ISC) to give the triplet state of the dye. On the other hand, the semiconducting Well-Dawson heteropoly anion (SC) also utilizes the radiant energy 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 ($\text{O}_2^{\bullet -}$). This anion radical will reduce the dye bromocresol green to its leuco form, which may ultimately degrade to products. It was also confirmed that this degradation proceeds through reduction and not oxidation. $\cdot\text{OH}$ radical does not

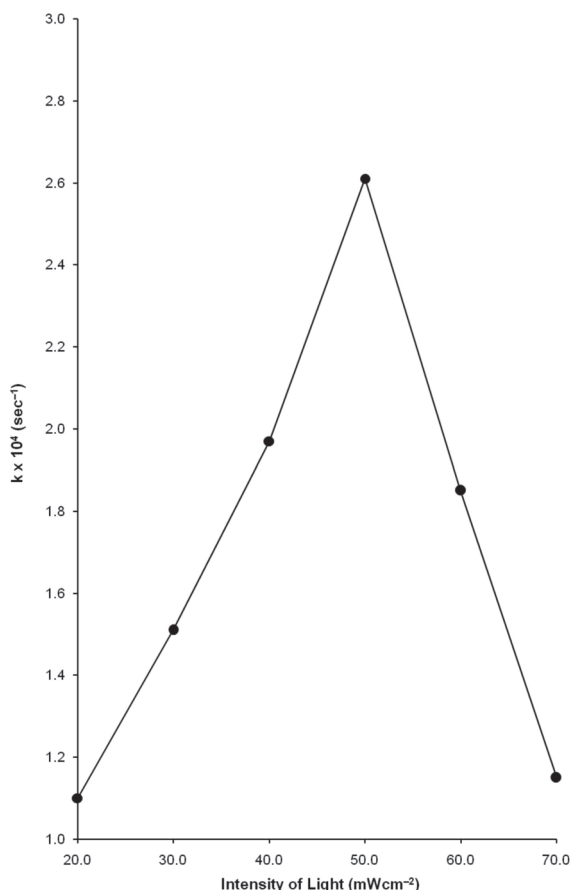


Fig. 5. Effect of Light Intensity

participate as an active oxidizing species as confirmed by using hydroxyl radical scavenger (2-propanol), where the rate of degradation was not affected appreciably.

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