



PHOTOCATALYTIC DEGRADATION OF CRYSTAL VIOLET USING NICKEL CONTAINING POLYTUNGSTOMETALATE

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ABSTRACT

Advanced Oxidation Processes (AOPs) are considered as promising technology for waste water treatment. Photochemistry, which is a part of AOPs plays an important role in solving the problem of removal of various organic pollutants from effluents of various industries. In the present work, the photocatalytic degradation of crystal violet has been investigated in aqueous solution using nickel containing polytungstometalate under different conditions. The progress of reaction was monitored spectrophotometrically. The effect of different parameters, which affect the rate of degradation of dye; such as effect of pH, dye concentration, amount of polytungstometalate and light intensity were studied. A tentative mechanism involving hydroxyl radicals as an active oxidizing species has also been proposed.

Key words: Polytungstometable, CRYSTAL violet, Phtocatalytic degradation.

INTRODUCTION

Environmental problem caused by toxic organic pollutants from the domestic and industrial output is now the subject of considerable concern from environmental remediation point of view. In the past decades, great effort has been made using widely called “Advanced Oxidation Technologies (AOTs)” for treatment of these recalcitrant pollutants to more biodegradable compounds or their mineralization into CO₂ and other inorganics.

It has been estimated that the amount of solar energy reaching the Earth every day is more than that mankind could use for three decades. In whole energy of incoming solar spectrum, ultraviolet radiation (400 nm) accounts to only less that 4%. Hence, effective utilization of the visible light of solar radiation (as in the photosynthesis of plants) is a long dream of any photochemical researcher.

The most important aspect of photocatalysis is a focus probably on metal oxide semiconductor for degradation of organic pollutants in water at ambient conditions, using inexpensive and clean solar light and hole as the energy source and oxidant, respectively. The main advantage of this method is that a lot of organic pollutants can be mineralized completely into CO₂, H₂O and inorganic ions.

Activated charcoal adsorption was used for color removal in minor amounts but it is an expensive method and had high regeneration cost. Photocatalysis is a promising technology for degradation of these water pollutants. Many semiconductors like TiO_2 , ZnO , Fe_2O_3 , CdS , Sb_2S_3 etc. have already been used as photocatalysts for degradation of many dyes molecules into harmless or less harmful products. Various researchers have used different semiconductors as photocatalyst for degradation of dyes.

The effectiveness of zinc oxide mediated solar photocatalytic degradation of phenol was examined by Pardeshi and Patil¹. Degradation and mineralization of two agricultural organic pollutants (Diazinon and Imidacloprid as N-heterocyclic aromatics) in aqueous solution by photocatalysis using immobilized titania nanoparticles were investigated by Mahmoodi et al.² The chemical degradation of pesticide methomyl in water by Fenton ($\text{H}_2\text{O}_2/\text{Fe}^{2+}$) and photo-Fenton ($\text{H}_2\text{O}_2/\text{Fe}^{2+}/\text{UV}$) processes was investigated by Tamimi et al.³

Photodegradation of crystalene blue using sunlight and TiO_2 was investigated by Nogueria and Jardin⁴. Hg (II) ions were photocatalytically eliminated from aqueous solutions in presence of ZnO powder⁵. Ameta et al.⁶ investigated the effect of surfactants on photobleaching of basis blue -24. Cao and Suils⁷ reported photooxidation of propan-2-ol to acetone using amorphous manganese oxide as catalyst. Sharma et al.⁸ carried out the photocatalytic bleaching of crystal violet in aqueous suspension of zinc oxide. Mansilla and Villasnov⁹ investigated ZnO catalysed photodegradation of Kraft-black liquor, which is an effluent from pulp paper industries. Wang and Zhuang¹⁰ carried out the photocatalytic reduction of (VI) over CdS powder under visible light. Ameta et al.¹¹ used semiconducting iron (III) oxide as photocatalyst for bleaching of crystalene blue, crystal violet and malachite green dyes.

Tangestaninejad et al.¹² have prepared a new photocatalyst, nanoporous anatase TiO_2 crystalline particles coupled with $\text{Na}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ Keggin units, TiO_2 -PVMo. Dey and Sharma¹³ have described the chemistry of POMs inorganic complexes composed of transitional metals mainly Mo, W and V and their catalytic effect on nitration of the phenols, acetylation of alcohols, phenols, and their derivatives. Lee et al.¹⁴ reported the use of zero valent iron, which was used for the reductive transformation of halo- and nitrocompounds. Chen et al.¹⁵ studied photooxidation of a dye (rhodamine-B) by visible-light irradiation in the presence of TiO_2 . Yajun et al.¹⁶ have used polyoxometalates as photocatalyst for the degradation of crystal orange. Wang and Yang¹⁷ carried out photocatalytic degradation of crystal orange with phosphotungstic acid. Kim et al.¹⁸ observed simultaneous conversion of dye and hexavalent chromium in visible light illuminated aqueous solution of polyoxometalate as an electron transfer catalyst. Kato et al.¹⁹ have studied EDTA-reduction of water to molecular hydrogen catalyzed by visible-light-responsive TiO_2 -based materials sensitized by Dawson and Keggin- type rhenium (V)-containing polyoxotungstates.

EXPERIMENTAL

Materials and methods

Preparation of nickel containing polytungstometalate photocatalyst

$\text{Na}_{12}[\text{CuNiW}_{18}\text{O}_{62}]\cdot 23\text{H}_2\text{O}$

150 mL of sodium tungstate solution was prepared by dissolving (34.8 g, 105.5 mmol). To the above solution, 25 mL cupric chloride prepared by dissolving (1.0 g, 5.86 mmol) and 40 mL of nickel chloride solution prepared by dissolving (1.4 g, 5.89 mmol) were added dropwise with continuous stirring till constant pH. 10 mL of glacial acetic acid was added. The mixture was refluxed for 4 hrs and left overnight for slow cooling. Shining blue crystals obtained were washed with n-hexane and preserved for analysis. Nickel containing polytungstometalate was used as a photocatalyst for the degradation of crystal violet.

Degradation of crystal violet using nickel containing polytungstometalate

Molecular formula of crystal violet is $C_{24}H_{28}N_3Cl$

1.0×10^{-3} M solution of crystal violet dye was prepared in doubly distilled water and was diluted as and when required. The photocatalytic degradation was observed upon addition of 0.10 g of nickel containing polytungstometalate 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 are measured with the help of a solarimeter (Suryamapi CEL 201). A water filter was used to cut off 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 at regular time intervals was monitored to know the progress of the photocatalytic reaction. Controlled experiments were also carried out to confirm that reaction is neither photochemical nor thermal, but it was photocatalytic.

RESULTS AND DISCUSSION

The photocatalytic degradation of crystal violet was observed at $\lambda_{\text{max}} = 590 \text{ nm}$. The observations for typical run are given in Table 1. The plot of log OD v/s exposure time was found to be a straight line, as shown in Fig. 1. This indicates that the photocatalytic degradation of dye in presence of nickel containing polytungstometalate follows pseudo first order kinetics and the rate constant for this reaction was determined using the expression: $k = 2.303 \times \text{slope}$.

Table 1: Typical run

pH = 6.5		[Crystal violet] = 1.60×10^{-5} M
Amount of semiconductor = 0.10 g		Light intensity = 50.0 mW cm^{-2}
Time (min.)	O.D.	$1 + \log \text{O.D.}$
0	0.524	0.7193
20	0.447	0.6503
40	0.380	0.5798
60	0.331	0.5198
80	0.292	0.4654
100	0.248	0.3945
120	0.211	0.3243
140	0.184	0.2648
160	0.160	0.2401
180	0.140	0.1461
$k = 1.22 \times 10^{-4} \text{ sec}^{-1}$		

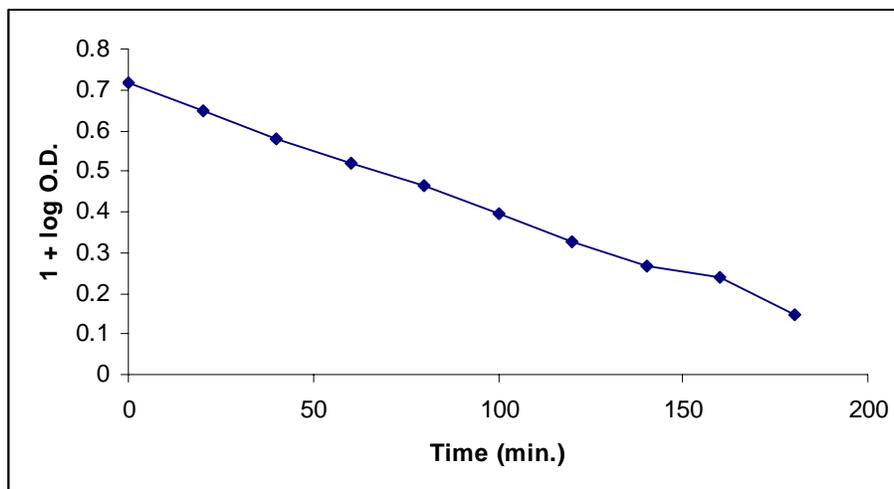


Fig. 1: Typical run

Different factors, which affect the rate of the reaction, were studied.

Effect of pH

The effect of pH on photocatalytic degradation of dye was investigated. The reaction rates were determined in the pH range 5–10.0 and the results are given in Table 2.

Table 2: Effect of pH

[Crystal violet] = 1.60×10^{-5} M

Amount of semiconductor = 0.10 g

Light intensity = 50.0 mWcm^{-2}

pH	Rate constant $k \times 10^4 \text{ (s}^{-1}\text{)}$
5.0	0.70
5.5	0.88
6.0	1.04
6.5	1.22
7.0	0.92
7.5	0.75
8.0	0.60
8.5	0.37
9.0	0.29
9.5	0.18

Maximum photocatalytic degradation of crystal violet was found at pH 6.5. It has been observed that with an increase in pH, the rate of photocatalytic degradation of dye increases from 5.0 to 6.5. Further increase in the pH resulted into a decrease in the rate of photocatalytic degradation. These observations can be explained on the basis that as the pH of the solution increases, more OH^- ions are available. OH^- ions will generate more $\cdot\text{OH}$ radicals by combining with the hole of the semiconductor. These $\cdot\text{OH}$ are considered

responsible for this photocatalytic degradation. After a certain pH value, more OH⁻ ions will make the surface of semiconductor negatively charged and the approach of neutral dye molecules towards the semiconductor surface is retarded. This will result into a decrease in the rate of photocatalytic degradation of dye.

Effect of dye concentration

Effect of variation of dye concentration was also studied by taking different concentrations of dyes. The results are tabulated in Table 3.

Table 3: Effect of dye concentration

pH = 6.5
Light intensity = 50.0 mWcm⁻²

Amount of semiconductor = 0.10 g

[Crystal violet] x 10 ⁵ M	Rate constant k x 10 ⁴ (s ⁻¹)
0.50	0.43
0.70	0.51
0.90	0.67
1.10	0.81
1.30	0.90
1.50	1.01
1.60	1.22
1.70	1.04
1.80	0.87
2.00	0.69
2.20	0.53

From the above data, it is evident that the rate of photocatalytic degradation increases with increasing concentration of the dyes (i.e. from 0.7 x 10⁻⁵ M to 1.7 x 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 consecutive oxidation and hence, there was an increase in the rate. The rate of photocatalytic degradation was found to decrease with an increase in the concentration of dye further. Here, the dye starts acting as a filter for the incident light and it does not permit the desired light intensity to reach the semiconducting particles and thus, decreasing the rate of the photocatalytic degradation of dyes.

Effect of amount of semiconductor

The amount of semiconductor also affects the process of dyes degradation. Different amounts of photocatalyst were used (from 0.02 g to 0.16 g) 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 also increases. Ultimately, the reaction rate becomes almost constant after a certain amount (0.10 g) of 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 nickel containing polytungstometalate 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 effect on the rate of photocatalytic bleaching of dyes 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 reaction vessel.

Table 4: Effect of amount of semiconductor

pH = 6.5

[Crystal violet] = 1.60×10^{-5} M

Light intensity = 50.0 mWcm^{-2}

Amount of semiconductor (g)	Rate constant $k \times 10^4 \text{ (sec}^{-1}\text{)}$
0.02	0.38
0.04	0.57
0.06	0.78
0.08	0.94
0.10	1.22
0.12	1.20
0.14	1.22
0.16	1.21
0.18	1.20

Effect of light intensity

The effect of the variation of light intensity on the rate was investigated (from 20.0 mWcm^{-2} to 70.0 mWcm^{-2}) and the observations are reported in the Table 5.

Table 5: Effect of light intensity

pH = 6.5

[Crystal violet] = 1.60×10^{-5} M

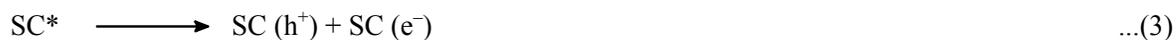
Amount of semiconductor = 0.10 g

Light intensity (mWcm^{-2})	Rate constant $k \times 10^4 \text{ (s}^{-1}\text{)}$
20.0	0.36
30.0	0.52
40.0	0.88
50.0	1.22
60.0	1.15
70.0	1.04

The results indicate that degradation action was accelerated as the intensity of light was increased upto 50.0 mWcm^{-2} . This may be attributed to an increase in the number of photons striking per unit area per unit time with increase in light intensity. On further increase in the light intensity retards the rate, due to some thermal side reactions.

Mechanism

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



Crystal violet (MV) absorbs radiation of suitable wavelength and it is excited to its first excited singlet state followed by intersystem crossing (ISC) to triplet state. On the other hand, the semiconducting nickel containing polytungstometalate also utilized the incident light energy to excite its electron from valence band to conduction band, which creates a electron-hole pair. Dissolved oxygen reacts with the electron located in the conduction band of semiconductor forming oxygen radical anion. This radical anion reacts with proton forming hydrogen peroxide radical, which in turn will oxidize the dye to its leuco form. This leuco form ultimately degrades to the products. It was also confirmed that $\bullet\text{OH}$ radical does not act as oxidizing species, as the reaction rate remains almost unaffected in the present of $\bullet\text{OH}$ radical scavenger, isopropanol.

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