Journal of Current Chemical & Pharmaceutical Sciences

J. Curr. Chem. Pharm. Sc.: 6(1), 2016, 8-16
ISSN 2277-2871

PHOTOCATALYTIC BLEACHING OF XYLIDINE PONCEAU USING WELL-DAWSON CATALYST

UMA VYAS, CHETNA KHATRI and SHOBHA KANWAR and AJAY SHARMA*

Department of Chemistry, Govt. College, SIROHI – 307001 (Raj.) INDIA

(*Received : 13.02.2016; Accepted : 26.02.2016*)

ABSTRACT

The photocatalytic degradation of xylidine ponceau was carried out by using Well-Dawson catalyst in the presence of light. Well-Dawson catalyst was synthesized by using cupric chloride dihydrate, chromium chloride and sodium tungstate. It has been utilized for degradation of xylidine ponceau dye. A 200 W tungsten lamp was used for irradiation. Progress of the reaction was followed kinetically by measuring absorbance of the reaction mixture at various time intervals. The effect of variations of different parameters like pH, dye concentration, amount of semiconductor and effect of light intensity on the rate of degradation was also observed.

Key words: Photocatalytic bleaching, Xylidine ponceau, Dye degradation.

INTRODUCTION

Water pollution is one of the major problems faced by humanity. Industrialization, urbanization and increase in human population are responsible for water pollution. Effluents from different dyeing, textile and printing industries also pollute their nearby natural water resources. Heterogeneous photocatalysis is one of the promising technologies for the degradation of dyes. Xylidine ponceau can be decomposed by using Well-Dawson catalyst.

Photodegradation of methylene blue using MnO_2 supported POM was studied by Kannan et al.[1] Wang et al.[2] studied visible photocatalytic degradation of rhodamine B using Keggin type–Fe(III) substituted phototungustic heteropoly anion as a photocatalyst. The chemistry of POM's inorganic complexes, which are composed of transition metals like V, W and Mo have been explained by Deva and Sharma[3]. Troupis et al.[4] carried out the photocatalytic reductive oxidative degradation of acid orange-7 by using polyoxometallate while polyoxometallate based photocatalyst assembled with cucurbit [6] uril-via-hydrogen bonds for degradation of azo dyes was developed by Cao et al.[5]

Two new inorganic-organic hybrid compounds based on well-defined Keggin type polyoxometallate and copper-bis (triazole) assemblies namely $[Cu_3(L)_3(PMo_{12}O_{40})_2].9H_2O(1)$ and $[Cu_3(L)_3(PW_{12}O_{40})_2].9H_2O(2)$ [L=1, 4-bis(1, 2, 4-triazol-1-ylmethyl)-benzene], have been synthesized by Wu et al.[6] while Wang and Yang[7] synthesized phosphotungstic and silicotungustic acid. They investigated their photocatalytic

Available online at www.sadgurupublications.com
*Author for correspondence; E-mail: ajay395@gmail.com

activity in the degradation of organic dye methyl orange. Neto et al.[8] studied the properties, characterization and photochromic behavior of phophotungstic acid-ormosil nanocomposites. Tungstophosphoric acid (TPA) immobilized on NH_4Y and ZSM5 Zeolites was prepared by Marchena et al.[9]

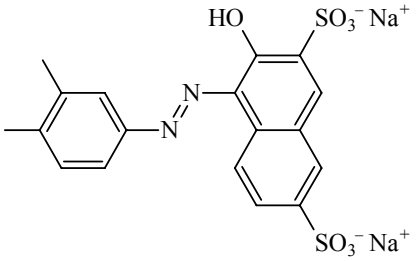

Fig. 1: Chemical formula of xylidine ponceau; Molecular weight: 436.461 g mol^{-1}

Peng et al.[10] carried out stepwise synthesis of two inorganic-organic hybrids, $[H_2bpy][Ag(bpy)][HPMnMo_{11}O_{39}]$ and $[H_2bpy]$ $[H(bpy)]$ $[PMnMo_{11}O_{39}].H_2O$ (bpy = 4,4'-bipyridine). Former compound has shown good activity for photocatalytic degradation of Rh-B based on the manganese mono substituted Keggin polyanion chains. A number of oxides and sulfides have also been used as a photocatalyst for the degradation of contaminants mainly dyes from printing, dyeing and textile industries. The photocatalytic reaction of xylidine ponceau on semiconducting ZnO powder was carried out by Sharma et al.[11] while Alikhani et al.[12] studied the combined action of laccase and cellobiose dehydrogenase for the decolourisation of the azo dye xylidine ponceau R.

The photocatalytic degradation of methylene blue by MoO_3 modified TiO_2 under visible light was carried out by Yang et al.[13] Wang and Wu[14] synthesized TiO_2 nanoparticles by a facile hydrothermal method. TiO_2. Nanoparticles exhibit much better photocatalytic activity towards the photodegradation of benzene. Mirkhani et al.[15] carried out the photocatalytic degradation of some textile azo dyes by using TiO_2 and modified TiO_2 with Ag metal (1% w/w) in aqueous solution under irradiation with a 400 W high pressure mercury lamp. Ternary zinc spinal oxides such as Zn_2SnO_4, $ZnAl_2O_4$ and $ZnFe_2O_4$ were synthesized and characterized, and their activities in the photodegradation of phenol molecules were investigated by Anchieta et al.[16]

Eskan et al.[17] synthesized cadmium sulphide nanostructures via a simple precipitation method. The photocatalytic activities of the synthesized samples were investigated for degradation of methylene blue (MB) under blue LED (3W) and solar light irradiation. Bi_2S_3 nanostructures with different dimensionalities including dots, rods and sheets have been synthesized by Huang et al.[18] for the study of their photocatalytic activities in degradation of organic dyes while Sharma et al.[19] used bismuth sulfide as photocatalyst for the degradation of rose Bengal. The photocatalytic degradation of p-chlorophenol by H_2O_2/TiO_2 hybrid in aqueous suspension under irradiation was reported by Nguyen and Juang[20].

EXPERIMENTAL

0.0436 g of xylidine ponceau was dissolved in 100.0 mL of doubly distilled water (1.0×10^{-3} M). This stock solution was further diluted to 1.0×10^{-5} M. The dye solution was divided in equal amounts in four beakers. The first beaker containing xylidine ponceau solution was kept in dark and the second beaker containing xylidine ponceau solution was exposed to light. The third and fourth beakers containing xylidine ponceau and 0.10 g Well-Dawson polyoxometallate was kept in dark and exposed to light, respectively. After keeping these beakers for 4 hrs, the absorbance (A) of the solution in each beaker was measured with the spectrophotometer at λ_{max} = 507 nm. It was noticed that the absorbance of the solutions of the first three

beakers remained almost constant, while the solution of fourth beaker had a decrease in initial value of absorbance.

A solution of 1.0 x 10^{-5} M xylidine ponceau was prepared in doubly distilled water and 0.10 g of the Well-Dawson catalyst was added to it. The pH of the reaction mixture was adjust to 8.0 by adding sodium hydroxide solution (0.1 M). Then the mixture was exposed to a 200 W tungsten lamp. An aliquot of 5.0 mL was taken out from the reaction mixture and its absorbance was observed at λ_{max} = 507 nm at regular time intervals. The rate constant was measured by the equation (1).

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

A decrease in absorbance of xylidine ponceau solution was observed with increasing time of exposure. A linear plot was obtained with 2 + log A against time was linear, so that one can say that the reaction follows pseudo-first order kinetics. Table 1 represents the data for the typical run. The typical run is shown in Fig. 1.

Table 1: A typical run

[Xylidine ponceau] = 1.0 x 10^{-5} M [Amount of POM] = 0.1 g
Light intensity = 50 mWcm^{-2} λ_{max} = 507 nm
pH = 8.0

Time (min)	Absorbance (A)	2 + log A
0.0	0.963	1.9836
10.0	0.733	1.8651
20.0	0.582	1.7649
30.0	0.489	1.6893
40.0	0.391	1.5921
50.0	0.301	1.4785
60.0	0.232	1.3654
70.0	0.195	1.2903
80.0	0.142	1.1522
90.0	0.115	1.0569
100.0	0.095	0.9777
110.0	0.072	0.8563
120.0	0.053	0.7248
130.0	0.041	0.6127
140.0	0.038	0.5797
150.0	0.026	0.4149
160.0	0.021	0.3222
170.0	0.017	0.2304
		Rate constant (k) = 4.07 x 10^{-4} sec^{-1}

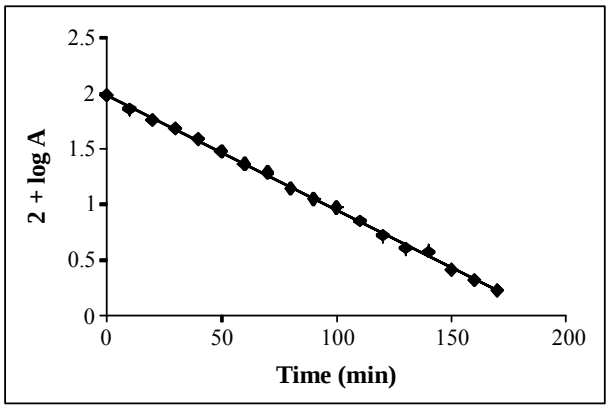

Fig. 1: A typical run

Effect of pH

The effect of pH on photocatalytic degradation of xylidine ponceau was studied at different pH. The data are reported in Table 2 and Fig. 2. The rate of photocatalytic degradation of xylidine ponceau was found to increase up to pH 8.0, and then it starts decreasing. This phenomenon can be explained on the basis that as the value of pH was increased, the generation of $^{\bullet}OH$ radicals was also increased due to the reaction between ^{-}OH ions and holes (h^{+}) of semiconductor.

Table 2: Effect of pH

[Xylidine ponceau] = 1.0 x 10^{-5} M [Amount of POM] = 0.1 g
Light intensity = 50.0 mWcm^{-2}

pH	k × 10^4 (sec^{-1})
6.0	1.18
6.5	1.73
7.0	2.57
7.5	3.15
8.0	**4.07**
8.5	3.95
9.0	3.58

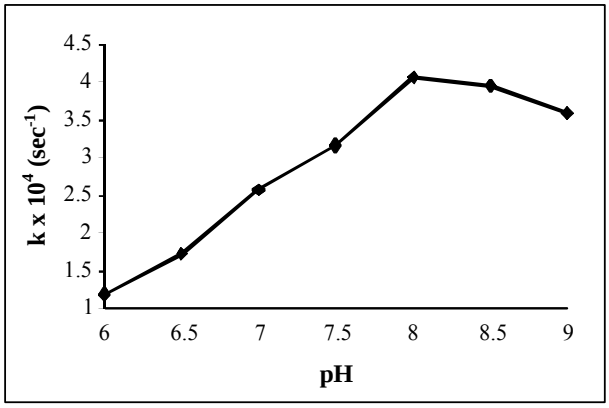

Fig. 2: Effect of pH

At pH > 8.0, the OH^- ions will make the surface of the semiconductor negatively charged and as a consequence of repulsive force between OH^- ions and anionic dye the approach of dye to the semiconductor will be inhibited. Thus, a decrease in the rate of photodegradation of xylidene ponceau dye was observed.

Effect of dye concentration

Effect of dye concentration was studied by using different concentrations of xylidine ponceau. The results are shown in Table 3 and Fig. 3.

Table 3: Effect of dye concentration

pH = 8.0 [Amount of POM] = 0.1 g
Light intensity = 50.0 $mWcm^{-2}$

[Xylidine ponceau] x 10^{-5} M	**k x 10^4 (sec^{-1})**
0.4	1.15
0.6	2.55
0.8	3.75
1.0	**4.07**
1.2	3.88
1.4	2.78
1.6	2.18
1.8	1.13

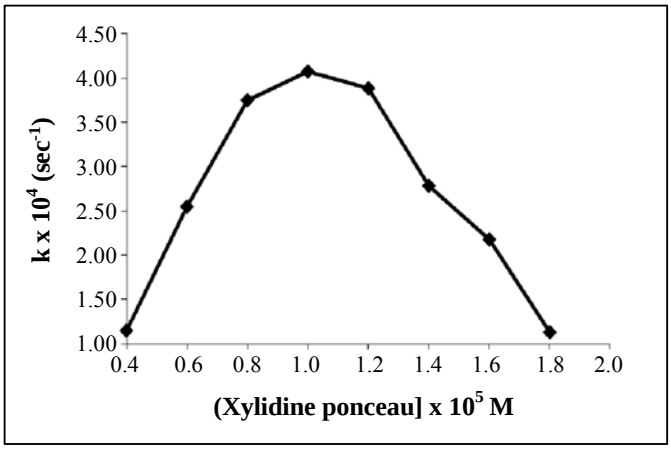

Fig. 3: Effect of dye concentration

As the concentration of dye was increased, the rate of photodegradation reaches a maximum value at 1.0 x 10^{-5} M and after this, increase in the concentration resulted in the decrease of the rate of photodegradation of dye. It was observed due to the fact that as the concentration of the dye was increased, more dye molecules were available for excitation and energy transfer but at concentration above 1.0 x 10^{-5} M, the dye itself may start acting as an internal filter for the incident light causing decrease in the rate of photodegradation of xylidine ponceau dye.

Effect of amount of semiconductor (POM)

The effect of amount of semiconductor on the rate of photodegradation of xylidine ponceau was also observed by using different amounts of semiconductor. The results are tabulated in Table 4 and Fig. 4.

Table 4: Effect of amount of semiconductor (POM)

[Xylidine ponceau] = 1.0 x 10^{-5} M	pH = 8.0
Light intensity = 50.0 mWcm^{-2}	
Amount of POM (g)	**k x 10^4 (sec^{-1})**
0.02	2.16
0.04	2.78
0.06	3.33
0.08	3.79
0.1	**4.07**
0.12	4.07
0.14	4.04
0.16	4.01

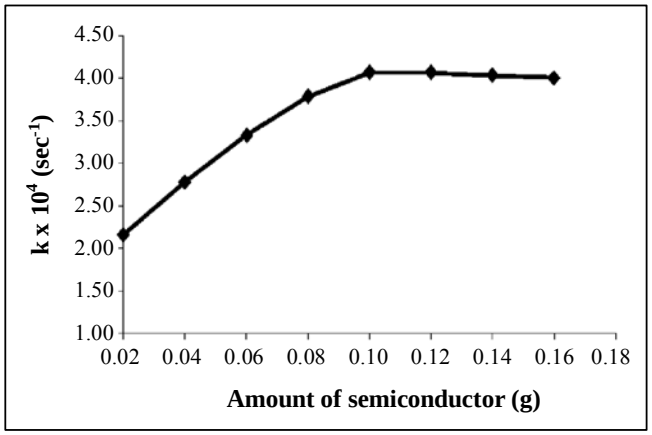

Fig. 4: Effect of semiconductor (POM)

It has been observed that the rate of photocatalytic degradation of dye increases with increase in amount of semiconductor upto 0.1 g and above this, the rate of reaction becomes almost constant. This may be due to the fact that as the amount of semiconductor was increased, exposed surface area of semiconductor increases but after this limiting value of amount of semiconductor (0.1 g) will not increase the exposed surface area and it will only increase the thickness of the layer at the bottom of the reaction vessel. It may be considered like a saturation point. This was confirmed by using reaction vessels of different dimensions.

Effect of light intensity

To study the effect of light intensity on the photodegradation of xylidine ponceau, the distance between the tungsten lamp and the exposed surface area of photocatalyst was varied. The results are reported in Table 5 and Fig. 5. It was observed that an increase in the intensity of light was increased the rate of photodegradation of xylidine ponceau. This may be explained due to the fact that as the intensity of the light

increases, the number of photons striking per unit area of the semiconductor also increases. It can be seen from the Tables that above 50.0 $mWcm^{-2}$ the rate constant decreases, which may be due to some chemical reactions.

Table 5: Effect of light intensity

[Xylidine ponceau] = 1.0×10^{-5} M [Amount of POM] = 0.1 g
pH = 8.0

Light intensity ($mWcm^{-2}$)	**$k \times 10^4$ (sec^{-1})**
10	1.97
20	2.05
30	3.39
40	3.78
50	**4.07**
60	3.65
70	2.99

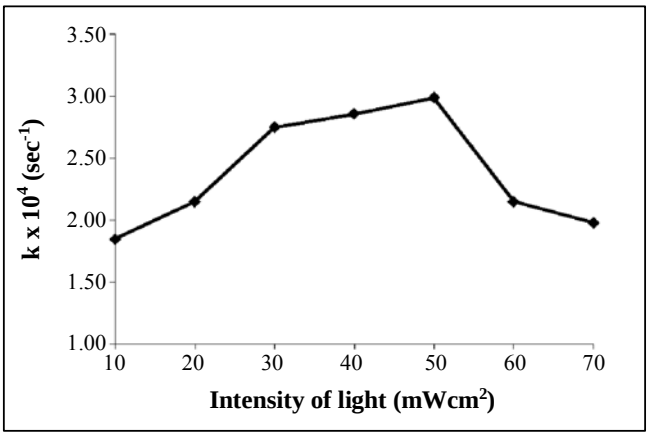

Fig. 5: Effect of light intensity

Mechanism of photocatalytic degradation

The following tentative mechanism can be proposed for the photocatalytic degradation-

^{1}Xylidine ponceau$_0$ $\xrightarrow{h\nu}$ ^{1}Xylidine ponceau$_1$ (singlet excited state) ...(2)

^{1}Xylidine ponceau$_1$ (ISC) $\xrightarrow{ISC}$ ^{3}Xylidine ponceau$_1$ (Triplet excited state) ...(3)

Semiconductor $\xrightarrow{h\nu}$ e^- (CB) + h^+ (VB) or SC* ...(4)

$h^+ + OH^- \longrightarrow {}^{\bullet}HO$ ...(5)

^{3}Xylidine ponceau$_1$ + $^{\bullet}OH$ $\longrightarrow$ Leuco Xylidine ponceau ...(6)

Leuco Xylidine ponceau $\longrightarrow$ Products ...(7)

When the xylidine ponceau is exposed to light, it absorbs radiations of suitable wavelength. Initially the dye molecules are excited to singlet excited state, then it undergoes intersystem crossing (ISC) to give the triplet state of the dye. The semiconductor also absorbs the suitable radiation to excite its electron from valence bond to conduction band, creating a hole (h^+). By accepting the e^- from OH^- ions, the hole (h^+) generate $^{\bullet}OH$ radical, which convert the dye into harmless products. The participation of $^{\bullet}OH$ radical as an active species was confirmed by using hydroxyl radical scavenger like 2-propanol, where the rate of the degradation was drastically reduced.

REFERENCES

1. R. Kannan, S. G. Peera, A. Obadiah and S. Vasanthkumar, MnO_2 Supported POM- A Novel Nanocomposite for Dye Degradation, Digest. J. Nanomater Biostruct., **6(2)**, 829-835 (2011).
2. C. Wang, Y. Hua, J. Liu, B. Wang, C. Wu and X. Lu, Photocatalytic Degradation of Rhodamine-B using Fe (III) Substituted Phototungstic Heteropoly Anion, J. Mol. Catal. A: Chem., **365**, 8-14 (2014).
3. K. C. Deva and V. Sharma, Well-Dawson Type Polyoxometallate of 3d Series and their Industrial use as Ecofriendly and Green Catalysts in Organic Reactions, J. Indian Chem. Soc., **88**, 1047-1050 (2011).
4. A. Troupis, T. Triantis, A. Hiskia and E. Papaconstantinou, Photocatalytic Reductive Oxidative Destruction of Acid Orange-7 by Polyoxometllate, Appl. Catal. B: Environ., **86(1-2)**, 98-107 (2009).
5. M. Cao, J. Lin, J. Lu, Y. You, T. Liu and R. Cao, Development of a Polyoxometallate Based Photocatalyst Assembled with Cucurbit [6] Uril-Via- Hydrogen Bonds for Azo Dyes Degradation, J. Hazard. Mater. **186(1)**, 948- 951 (2010).
6. N. Wu, Y. Quin, X. L. Wang, C. Quin and E. B. Wang, Synthesis and Photocatalytic Activity of Two Layered Copper–Bis (Triazole) with Keggin Polyoxoanion Assemblies, Inorg. Chem. Comm., **37**, 174-177 (2013).
7. W. Wang and S. Yang, Photocatalytic Degradation of Organic Dye Methyl Orange with Phosphotungstic Acid, J. Water Resource Prot., **2(11)**, 979-983 (2010).
8. E. P. Ferreira-Neto, S. Ullah, F. L. S. de Carvalho, A. L. de Souza, M. de Oleveira Jr., F. Schneider et al., Properties, Characterization and Photochromic Behavior of Phosphotungustic Acid-Ormosil Nanocomposites, Mater. Chem. Phys, **153**, 410-421 (2015).
9. C. L. Marchena, R. A. Frenzel, S. Gomez, L. B. Pierella and L. R. Pizzieo Tungstophosphoric Acid (TPA) Immobilized on NH_4Y and ZSM5 Zeolites for the Degradation of 4-Chiorophenol, Appl. Catal. B: Environ., **13-131**, 187-196 (2014).
10. H. J. Peng C. J. Jang, N. N. Huang, D. Y. Huang and Y. G. Chen, Stepwise Synthesis of Two Inorganic-Organic Hybrids for the Photodegradation of Rh-B, Solid State Sci., **35**, 33-38 (2014).
11. A. Sharma, P. Rao, R. P. Mathur and S. C. Ameta, The Photocatalytic Reaction of Xylidine Ponceau on Semiconducting ZnO Powder, J. Photochem. Photobiol. A, **86(1-3)**, 197-200 (1995).
12. R. Alikhani, K. Enayatzamir, F. Tabandeh, B. Yakhehali, L. Mohammadi and S. Rodriguez-Couto, Combined Action of Laccase and Collobiose Dehydrogenase for the Decolourisation of the Azo Dye Xylidine Ponceau R, New Biotechnol., **25**, S152 (2009).
13. H. Yang, X. Li, A. Wang, Y. Wang and Y. Chen, Photocatalytic Degradation of Methylene Blue by MoO_3 Modified TiO_2 Under Visible Light, Chinese J. Catal., **35(1)**, 140-147 (2014).

14. C. Wang and T. Wu, Photodegradation of Benzene by TiO_2 Nanoparticles Ceramics Int., **41(2) B**, 2836-2839 (2015).

15. V. Mirkhani, S. Tangestaninejad, M. Moghadam, M. H. Habibi and A. Rostami-Vartooni, Photocatalytic Degradation of Azo Dyes Catalyzed by Ag Doped TiO_2 Photocatalyst, J. Iran. Chem. Soc., **6(3)**, 578-587 (2009).

16. G. Anchieta, D. Sallet, E. L. Foletto, S. S. da Silva, O. C. Filno and A. O. do Nascimento, Synthesis of Ternary Zinc Spinal Oxides and their Application in the Photodegradation of Organic Pollutant, Ceramics Int., **40(3)**, 4173-4178 (2014).

17. P. Eskan, F. Kazemi and Y. Azizian-Kalandaragh, Preparation of CdS Nanostructures as a Highly Efficient Photocatalyst under Blue LED and Solar Light Irradiation, Separation and Purification Technol., **120**, 180-185 (2015).

18. J. Huang, H. Zhang, X. Zhou and X. Zhang, Dimensionally Dependent Performance of Nanostructured Bi_2S_3 in Photodegradation of Organic Dyes, Mater. Chem. Phys., **138(2-3)**, 755-761 (2013).

19. S. Sharma, R. Ameta, R. K. Malkani and S. C. Ameta, Use of Semi-Conducting Bismuth Sulfide as a Photocatalyst for Degradation of Rose Bengal, Macedonian J. Chem. Chem. Eng., **30(2)**, 229-234 (2011).

20. A. T. Nguyen and R. S. Juang, Photocatalytic Degradation of p-Chlorophenol by Hybrid H_2O_2 and TiO_2 in Aqueous Suspension under U.V. Irradiation, J. Environ. Manage., **147**, 271-277 (2015).