



AN ECO-FRIENDLY PROCESS FOR REMOVAL OF p-ROSANILINE HYDROCHLORIDE USING A PHOTOCATALYST AND STUDY OF EFFECT OF OPERATIONAL PARAMETERS

**ANKITA VIJAY, SHAMTA NIHALANI, NUPUR TRIPATHI and
SHIPRA BHARDWAJ***

Department of Chemistry, Govt. PG College, KOTA – 324001 (Raj.) INDIA

ABSTRACT

Dyes are one of the major pollution causing agents. A photocatalyst is used to remove the dye in present research work. Effect of various factors like pH, amount of semiconductor, concentration of dye, intensity of light etc. was studied. The reaction was found to follow pseudo first order rate law. Conditions were optimized at pH 8.6, amount of semiconductor 0.18 g/50 mL, concentration of dye 1×10^{-5} M and intensity of light 37 mW/cm². Scavenger study suggested free radical ([•]OH) participation. Formation of nontoxic degraded products like NO₂, CO₂ and H₂O etc. was observed.

Key words: Photo degradation, Pseudo first order, p-rosaniline hydrochloride, Tungsten oxide, Scavenger, Free radical.

INTRODUCTION

Dyes are one of the major pollutants, which are released in environment through various industries like paper, yarn and plastic, cosmetic, paint etc. and pollute it. As use of synthetic dyes started, a new problem drew attention of scientists and it was the removal of these carcinogenic dyes from environment. Pollutants were then removed through various techniques. Elimination of coloured contaminants from waste water was studied by Dipika¹. Decolouration of water², oxidation³, photo catalysis⁴ etc. are some other methods. Semiconductors for the purpose of photocatalysis have been studied extensively. Some semiconductors have less energy difference between conduction and valance band and so an electron can jump by absorbing lower energy, which falls nearly in visible region. Due to

* Author for correspondence; E-mail: sidsidsmart@yahoo.co.in

this hole in valance band and a free electron in conduction band is generated. These holes are responsible for oxidation and electrons are responsible for reduction.

Photocatalytic studies started in 1920's with first catalyst TiO_2 . Hashimoto et al.⁵ extensively studied TiO_2 as photocatalyst. Photobleaching by TiO_2 in vacuum and in presence of oxygen was observed in 1938⁶. Photodegradation of the textile dye reactive black-5 in presence of various semiconducting oxides was carried out by Poulis et al.⁷ In due course of time, researchers realised the need of a faster and quicker process for removal of such pollutants. Then new search introduced some doped semiconductor⁸, nanosized compounds⁹, binary, ternary and quaternary substances¹⁰ etc.

Photocatalysis by phosphorous, nitrogen and molybdenum ternary wide band gap P-block metal semiconductor ZnGa_2O_4 was used by Li et al.¹² for photocatalytic degradation of benzene. Zinc cadmium sulphide was used as photocatalyst by Song et al.¹³ for photocatalytic activity. Ternary indium titanate nanoparticles were used for H_2 generation photocatalytically¹⁴. Photocatalytic decomposition of methyl orange dye on ternary sulphide (CdIn_2S_4) under visible light was studied by Danyu et al.¹⁵ The photocatalyst was prepared by temperature hydrothermal method. It was found much active than the catalyst prepared by simple precipitation method. Effect of method of preparation of ternary $\text{CdS/TiO}_2/\text{Pt}$ on photocatalysis was studied by Park et al.¹⁶ Bi_2WO_6 was synthesized by Zhang et al.¹⁷ Some quaternary and other photocatalyst are now used for degradation studies. Torres-Martinez et al.¹⁸ used $\text{Sm}_2\text{FeTaO}_7$ as photocatalyst. A novel composite photocatalyst for water splitting was used by Yang et al.¹⁹ Dom et al.²⁰ have studied photocatalytic and photoelectrochemical study of ferrites.

It was observed that p-rosaniline chloride dye is carcinogenic and is harmful for human health. An eco-friendly photocatalyst WO_3 is used for degradation of this commercial dye p-rosaniline hydrochloride. It was found to degrade the carcinogenic substance into products, which were not harmful and treated the waste water so that it could be used for some other purpose like cleaning, cooling, printing, agriculture etc.

EXPERIMENTAL

Materials and methods

Tungsten (VI) oxide (WO_3) (Loba Chemie) and p-rosaniline chloride ($\text{C}_{19}\text{H}_{18}\text{N}_3\text{Cl}$) (BDH) were used for studies. It is a dye of tri phenyl methane group and its structure is as shown in Fig. 1. λ_{max} for the dye is 544 nm.

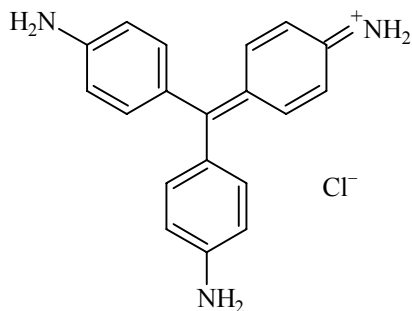


Fig. 1: Structure of p-rosaniline hydrochloride

The stock solution of dye (p-Rosaniline chloride $0.0809 \text{ g}/250 \text{ mL} = 1 \times 10^{-3} \text{ M}$) was prepared in doubly distilled water and diluted as required. The pH of the solution was adjusted by prestandardized HCl and NaOH and was adjusted by pH meter (Henna imported pen type). The dye solution and known amount of semiconductor (WO_3) were taken in a beaker. The beaker was covered with water filter to avoid the thermal reaction. The solution was irradiated with 200 Watt tungsten lamp. Intensity of light was measured by solarimeter (Surya mapi Model 201). Dye sample of about 2-3 mL was taken out at a regular time interval from the test solution and optical density (O.D.) was recorded spectrophotometrically (Systronic Model 106).

The graph was plotted between time and $1 + \log \text{O.D.}$ It was found to be a straight line suggesting the reaction to follow pseudo first order kinetics. The rate constant was determined by-

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

Use of scavenger suggested the participation of OH free radical in the reaction, which is found to be strong enough to break different bonds of dye (C=C, C=N, C-C, C-N etc). Controlled experiment was carried out and it was observed that the dye is bleached in presence of light and semiconductor both. This suggests that the reaction is neither catalytic nor photochemical rather it is a photocatalytic degradation process.

RESULTS AND DISCUSSION

Effect of pH

The most important factor affecting bleaching is pH. The study was carried out by varying pH (5.3 to 9.5). The effect of pH variation on rate of the photodegradation of

p-rosaniline chloride is given in Table 1. It was found that as pH of the reaction mixture is raised, the rate of photocatalytic degradation increases. It attains maximum value at pH 8.6.

Table 1: Effect of pH

[p-rosaniline hydrochloride] = 1×10^{-5} M Light intensity = 37 mW/cm²
Amount of semiconductor = 0.18 g

pH	k x 10 ⁴ (sec ⁻¹)
5.3	0.45
5.8	0.37
6.3	0.45
6.8	1.86
7.3	2.09
7.8	0.98
8.3	3.99
8.6	4.41
8.9	3.63
9.5	3.78

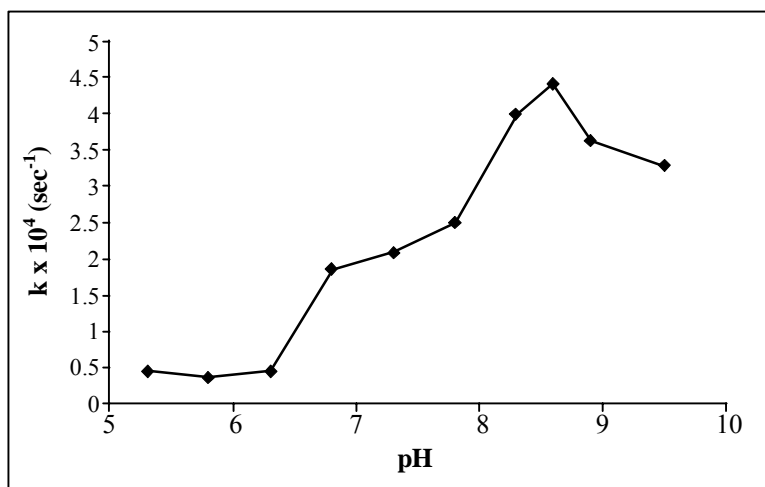


Fig. 2: Effect of pH variation

The pH affects not only the dissociation of dye molecules but also the formation of hydroxyl radical. Increase in pH will increase the number of OH^- ions. A hole is generated on semiconductor surface which abstracts an electron from OH^- ion converting it into OH free radical. This free radical steals an electron from dye degrading it and is responsible for the bleaching of dye as confirmed by use of scavenger. Beyond a particular pH for dye (8.6) if pH is raised further the rate decreases. This is because of repulsion between excessive OH^- ions on photocatalyst surface and electron rich dye surface. The collision reduces the rate. A plot of k versus pH is given in Fig. 2.

Effect of concentration of dye

The concentration of pollutant is a major parameter to be considered in water treatment. Thus the effect of p-rosaniline chloride was studied by varying its concentration from 0.6×10^{-5} M to 3×10^{-5} M keeping the pH constant and it was found that up to an optimum concentration (1×10^{-5} M), the rate of photocatalytic bleaching increases as the rate of reaction is directly proportional to the molar concentration of reacting species. After this limit, if more concentration of dye is taken, it imparts darker colour to the solution and it acts as a filter to the incident light reaching the semiconductor surface. Thereby only fewer photons reach the catalyst surface and therefore, generation of $\cdot\text{OH}$ free radical on the catalyst surface is reduced since the active site of semiconductor gets covered by dye ions. This results in the decrease of the rate of bleaching. The data are given in Table 2. A plot of k and concentration of dye is given in Fig. 3.

Table 2: Effect of concentration of dye

pH = 8.6		Amount of semiconductor = 0.18 g
Intensity of light = 37 mW/cm ²		
Conc. of dye x 10 ⁵ M	k x 10 ⁴ (sec ⁻¹)	
0.6	2.96	
0.7	2.84	
0.8	3.14	
0.9	3.39	
1.0	4.41	
1.5	4.07	
2.0	2.57	
2.5	3.17	
3.0	3.48	

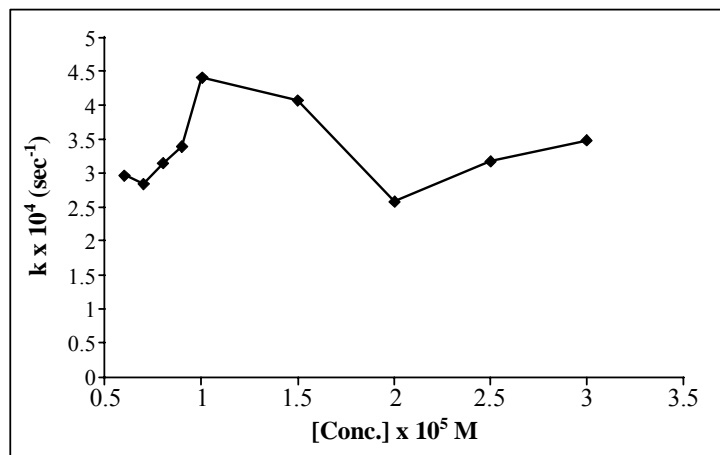


Fig. 3: Effect of concentration of dye solution

Effect of catalyst

Experiments were carried out by taking different amount of WO_3 and keeping other factors constant. It was found that up to a particular amount (0.18 g), the rate of photocatalytic bleaching increases. It is due to the increase in the active site available on the catalyst surface for the reaction which in turn increases the rate of radical formation. After this, the rate of bleaching decreases when the catalyst amount is increased. With a higher catalyst loading the deactivation of activated molecules by collision with ground state molecules dominates, thus reducing the rate of reaction. The data are summarized in Table 3.

Table 3: Effect of amount of semiconductor

[p-rosaniline hydrochloride] = 1×10^{-5} M	
Intensity = 37 mW/cm ²	
Amount of semiconductor (g)	k x 10 ⁴ (sec ⁻¹)
0.04	2.75
0.06	2.84
0.08	2.36
0.12	2.17
0.14	3.12
0.16	3.31
0.18	4.41
0.20	2.97
0.22	1.89

A plot of k and amount of catalyst is given in Fig. 4.

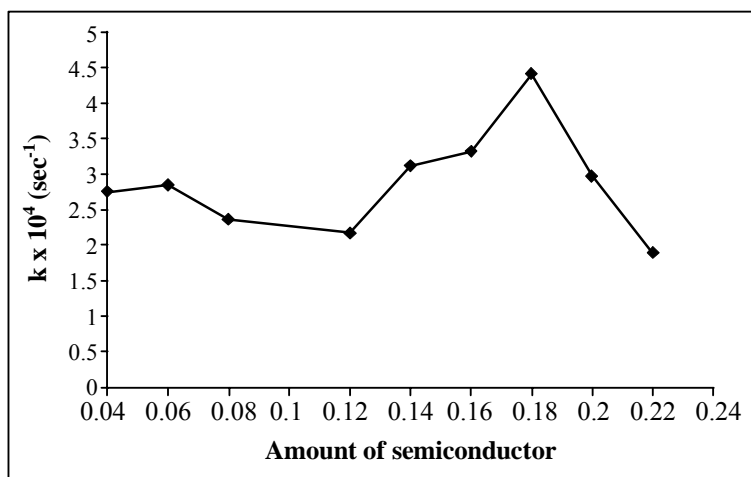


Fig. 4: Amount of semiconductor (g)

Effect of light intensity

Variation of light intensity is one of the major factors affecting the degradation. Thus the experiments were performed by varying it from 23 mW/cm² to 37 mW/cm² with keeping all other factors constant. The rate of photocatalytic bleaching increases as the light intensity was increased. It may be explained on the basis of number of excited molecules. As more intensity of light falls on WO₃ molecules, more number of molecules get excited which in turn may bleach more dye molecules and thus the rate of bleaching was found to increase with increase in intensity of light. The data are given in Table 4 and A plot of k and light intensity is given in Fig. 5.

Table 4: Effect of intensity of light

[p-rosaniline hydrochloride] = 1×10^{-5} M Amount of semiconductor = 0.18 g
pH = 8.6

Light intensity (mW/cm ²)	$k \times 10^4$ (sec ⁻¹)
37	4.41
34	3.18
30	2.98
27	2.50
23	1.86

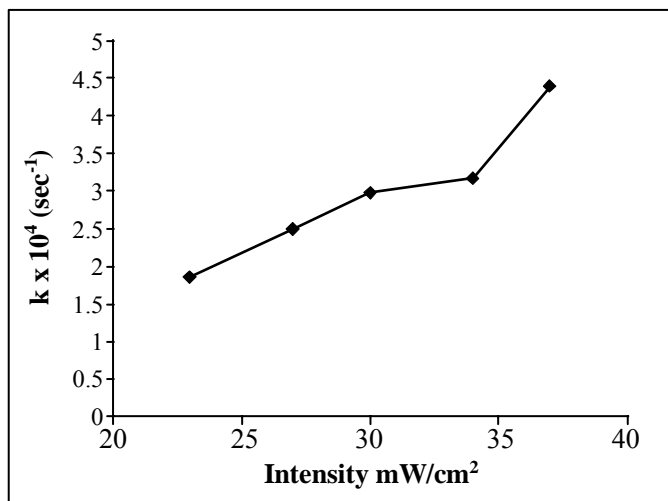


Fig. 5: intensity of light (in mW/cm²)

After carrying out variation of different factors, maximum degradation condition was established which is shown in figure 6. The k value comes out to be $4.41 \times 10^{-4} \text{ sec}^{-1}$.

Table 5: Typical run

Amount of semiconductor = 0.18 g		Light intensity = 37 mW/cm ²	
[P-rosaniline hydrochloride] = 1×10^{-5} M		pH = 8.6	
Time (min.)	O.D.	1 + log O.D.	
0	0.42	0.6304	
2	0.41	0.6222	
4	0.40	0.5820	
6	0.38	0.5611	
8	0.36	0.5327	
10	0.34	0.5185	
12	0.33	0.5010	
16	0.31	0.4913	
18	0.30	0.4871	

$k = 4.41 \times 10^{-4} \text{ sec}^{-1}$

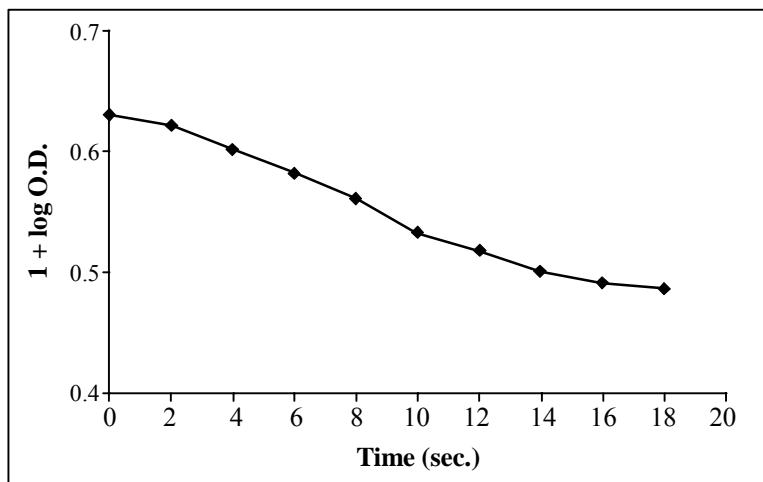
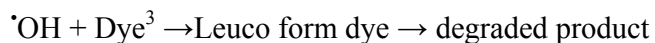
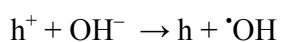
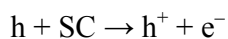
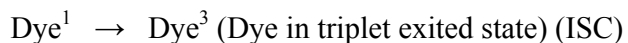


Fig. 6: Typical run

CONCLUSION

It is concluded hereby that dyes are being degraded with the help of photocatalyst and in presence of visible light into fragments and no harmful products are formed. The proposed mechanism is –



Here ISC = Inter system crossing

SC = Semiconductor or photocatalyst

h^+ = Hole generated at the surface of photocatalyst

e^- = Electron generated at the surface of photocatalyst

Thus an eco-friendly and environment protecting process is proposed, which utilizes solar energy and may be used to make the planet clean and pollution free.

REFERENCES

1. J. Dipika, Elimination of Colored Contaminants from Waste Water, *Research J. Chem. Env.*, **16(3)**, 1-4 (2012).
2. P. Hurber and B. Carro, Decolourization of Process Waters in Deinking Mills and Similar Applications—A Review, *Bio Resources*, **7(1)**, 1366-1382 (2012).
3. N. Daneshavar, S. Aber and F. Hossinzadeh, Study of Acid Orange 7 Removal in Contaminated Water by Photocatalytic Oxidation Process, *Proceedings of 9th International Conference on Environmental Science and Technology, Greece* (2005).
4. K. Vinodgopal, D. Wynkoop and P. V. Kamat, Environmental Photochemistry on Semiconductor Surface-Photosensitized Degradation of a Textile Dye Acid Orange on TiO₂ Particles Using Visible Light, *Environ. Sci. Technol.*, **30**, 1660-1666 (1996).
5. K. Hashimoto, H. Irie and A. Fujishima, TiO₂ Photocatalysis – A Historical Overview and Future Properties, *AAPPS Bulletin.*, **17(6)**, 11-28 (2007).
6. C. F. Goodeve and J. A. Kitchener, Photosensitization by Titanium Dioxide, *Trans. Faraday. Soc.*, **34**, 902-908 (1938).
7. I. Poulous and I. Tsachpinis, Photo Degradation of Textile Reactive Black-5 in the Presence of Semiconducting Oxides, *J. Chem. Technol. Biotechnol.*, **74**, 349-357 (1999).
8. P. Arsana, C. Bubpa and W. S. Aroon, Photocatalytic Activity Under Solar Irradiation of Silver and Copper Doped Zinc Oxide-Photodeposition Versus Liquid Impregnation Methods, *J. App. Sci.*, **12(17)**, 1809-1816 (2012).
9. M. J. Pawar, V. B. Nimbalkar and A. K. Khajone, Photocatalytic Degradation of Phenol with Nanosized TiO₂ Synthesized by EDTA-Glycol Method, *Int. J. Adv. Sci. Tech. Res.*, **1(2)**, 422-437 (2001).
10. I. Bhati, P. B. Punjabi and S. C. Ameta, Photocatalytic Degradation of Fast Green using Nanosized CeCrO₃, *Mac. J. Chem. and Chem. Eng.*, **29(2)**, 195-202 (2010).
11. Y. Shen, T. Xiong, H. Du, H. Jin, J. Shang and K. Yang, Phosphorous, Nitrogen and Molybdenum Ternary Co-Doped TiO₂ – Preparation and Photocatalytic Activities Under Visible Light, *J. Sol-gel Sci. Technol.*, **50**, 98-102 (2009).
12. Z. Li, H. Xue, L. Wau, X. Wang and X. Fu, Ternary Wide Band Gap p-Block Metal Semiconductor ZnGa₂O₄ for Photo Catalytic Benzene Degradation, *J. Phy. Chem. C.*, **112(51)**, 20393-20397 (2008).

13. L. Song, S. Zhang, B. Chen, J. Ge and X. Jia, Fabrication of Ternary Zinc Cadmium Sulphide Photocatalysis with Highly Visible Light Photo Catalytic Activity, *Catal. Comm.*, **11(5)**, 387-390 (2010).
14. M. R. Pai, A. M. Singhal, A. M. Banerjee, R. Tiwari, G. K. Dey, A. K. Tyagi and S. R. Bhardwaj, Synthesis Characterization and Photocatalytic H₂ Generation Over Ternary Indium Titanate Nanoparticles, *J. Nanosc. Nanotech.*, **12(3)**, 1957-1966 (2012).
15. X. Danyu, X. S. Qu, Y. H. Guo and C. W. Hu, Photocatalytic Dye Methyl Orange Decomposition on Ternary Sulphide (CdInS₄) Under Visible Light, *Chinese Chem. Lett.*, **16(9)**, 1259-1262 (2005).
16. H. Park, W. Chio and M. R. Hoffmann, Effect of the Preparation Method of the Ternary CdS/TiO₂/Pt Hybrid Photocatalysis on Visible Light Induced Hydrogen Production, *J. Mater. chem.*, **18**, 2379-2385 (2008).
17. L. W. Zhang, Y. J. Wang, H. Y. Cheng, W. Q. Yao and Y. F. Zhu, Synthesis of Porous Bi₂WO₆ Thin Films as Efficient Visible Light Active Photocatalysts, *Adv. Mater.*, **21**, 1286-1290 (2009).
18. L. W. Torres-Martinez, M. A. Rui-Gomez, M. Z. Figueroa-Torres, I. Juarez-Ramirez and E. Moctezuma, Sm₂FeTaO₇ Photocatalytic for Degradation of Indigo Carmine Dye Under Solar Light Irradiation, *Int. J. Photoenergy*, doi:10.1155/2012/939608 (2012).
19. H. Yang, L. Guo, W. Yan and H. Lui, A Novel Composite Photocatalyst for Water Splitting Hydrogen Production, *J. Power Sources.*, **159**, 1305-1309 (2006).
20. R. Dom and P. H. Borse, Photocatalytic and Photoelectrochemical Study of Ferrites for Water Splitting Application-A Comparative Study, *Mat. Sci. forum.*, **734**, 334-348 (2013).

Revised : 10.03.2013

Accepted : 12.03.2013