Available online at www.derpharmachemica.com

Scholars Research Library

Der Pharma Chemica, 2010, 2(1): 38-45
(http://derpharmachemica.com/archive.html)

ISSN 0975-413X

Kinetic study of application of various photo catalysts

Vikesh Kumar, Masihur Rahman*, Naseema Khatoon, Manish Kumar

Chemistry Division, Integral University, Dasauli, Lucknow (U.P.), India

---

Abstract

The photo catalytic degradation of methyl blue dye, over TiO_2 and ZnO were carried out in the presence of light to observe good semi conducting property. The photo catalytic degradation of methyl blue was observed in the presence of both photo catalysts. Parameters like amount, band gap, intensity, sensitizer etc were also studied. Studies show that TiO_2 shows more photo catalytic activity than ZnO.

Keywords: Photo catalytic degradation, Methyl blue, Zinc oxide, Titanium dioxide

---

Introduction

Last few decades numerous research effect in the field of heterogeneous and homogeneous photo catalyst by semi conducting through particular system has been studied [1, 2].However, synthesized degradation of o-nitro phenol that has been studied in the presence of semi conducting oxide [3].Kinetic study of application of ZnO as photo catalyst in heterogeneous medium analyzed recently [4]. In case of zinc oxide the pure white compound turn yellow on heating because of deficit of oxygen has various uses, of which the most important is as co – catalyst , with CuO for low pressure synthesis of methanol by oxidation of methane [5].When a semiconductor is irradiated with light having energy (E= hv) equal to or more than band gap energy, a heterogeneous photo catalyst reaction occur at the solid solution contact surface .The semi conducting forms a pair of volume band (VB) hole and conduction band (CB) electron as in case of zinc oxide and titanium dioxide .

The titanium dioxide is used as white pigment [6] .It also reacts with glycol in the presence of alkali metal hydroxide to yield soluble titanium glaciates [7]. The dioxide impregnated with some metal complexes has been much studied as a catalyst for photodecomposition of water [8]. Ultraviolet irradiation of a gas / solid interface of microcrystalline TiO_2 in the presence of H_2O and CO_2 leads to formation of CO ,H_2 and CH_4 [9]. Many other uses are known; example is found in catalysis [10].Titanium dioxide (TiO_2) shows its unique photo catalytic activity at an excellent choice of photo catalysis application [11-16]. TiO_2 are also using full self cleaning [13], self sterilizing [17].Titanium dioxide work effectively under low UV light intensities and also applicable to indoor and outdoor environments. Titanium dioxide having band gap (3.23eV) semiconductor, is transport to visible light.

However, production of synthetic dyes in India about 25000 metric tons every year [18], which are industrial health hazards to people [19].Dyestuff industries have occupied a prominent place in the industrial organization of the modern world. One of the major routes to incorporate dyestuffs in our biological system is by absorption through skin. Some dyes have different degrees of binding ability with protein, collagen and lipid [20- 21]. Study shows that toxic effects of these synthetic dyes are observed in the presence of the ultraviolet component of sunlight (285-400 nm) [22].Photosensitization reactions in various analysis is oxygen dependent in which a photo excited dye transfers energy to molecular oxygen to produce activated oxygen species like singlet oxygen ($^1O_2$), super oxide radical (HO_2 or $\left(O_2^-\right)$), hydroxyl radical (OH) and hydrogen peroxide. The activated oxygen species contribute to oxidative degradation of proteins, enzymes, lipids and other target molecules of cellular systems [23-25] and are also responsible to act as tumor promoters in the development of cancer [26].Although, photosensitization studies and chemical property of singlet oxygen and super oxide radical was analyzed in recent years by the author [27-28].

Result and Discussion

Effect of sensitizers

Certain dye complexes shows the tendency to increase the rate of degradation by sensitization .The sensitization route are follows from equation no 1 to 4.

The photochemical route proceeds as follows, where sense represents the photo sensitizer

$$^{1}\text{Sens} \xrightarrow{hv} {}^{1}\text{sens}^{*} \quad (1)$$

$$^{1}\text{Sens}^{*} \longrightarrow {}^{3}\text{sens}^{*} \quad (2)$$

$$^{3}\text{Sens}^{*} + {}^{3}O_2 \longrightarrow {}^{1}\text{sens} + {}^{1}O_2 \quad (3)$$

$$^{1}O_2 + \text{substrate} \longrightarrow \text{products} \quad (4)$$

Energy transfer from triplet excited ^{3}sens* to $^{3}O_2$ to give $^{1}O_2$ is a spin allowed process .A representative example is the use of excited azo alkane with O_2.

Effect of band gap of semiconductor

The usual exited semiconductor has separated the hole and electron pairs that induced the photo catalytic reaction and hence the band gap energy has important role to play. The band gaps of different photo catalysts are summarized in Table 1.

$$ZnO + hv \rightarrow h+ (VB) + e^{-} (CB)$$

The hole generated is capable of oxidizing the substrate and the electron of CB is capable of reducing the substrate. Further more, the solution contains species *e.g.* $^{\cdot}OH$, H^{+}, $^{\cdot}O^{-}_{2}$, $^{\cdot}HO_2$, H_2O_2, O_2, which are due to the semiconductor light-water-oxygen interactions. These species are also capable of carrying out redox reactions [4]. The generation of super oxide radical anion $.O_2^{-}$ and .OH radical can be shown as under.

$$h+ (VB) + H_2O \rightarrow {}^{\cdot}OH\ ads + H^{+}$$

$$h+ (VB) + OH\ –ads \rightarrow {}^{\cdot}OH\ ads$$

$$e^- (CB) + O_2\,ads \rightarrow {}^{\cdot}O_2^-$$

Subscript “ads” refers to species adsorbed on the surface of semiconductor.

Table 1.Band gap of different photo catalysts

S.No.	Semiconductor	Band Gap
1	PbS	0.30
2	CdS	2.50
3	ZnO	3.20
4	ZnS	3.80
5	TiO_2	3.23

Photo catalytic activity of TiO_2 and ZnO

To evolve the TiO_2 and ZnO photo catalytic activity six Petri dishes (10 cm diameter) each containing 25 ml of a 10^{-4} M solution of methyl blue were used. To four of them (two of TiO_2 and ZnO); 1.25 gram of TiO_2 and ZnO were added .One of these suspension put was wrapped in a black plastic bag before experiment to the sun. In this way two types of controlled were used .One Petri dishes of each photo catalyst with just the MB solution were used balance MB is a sensitizers. Some degradation caused by UV-visible light –absorption was observed .A second suspension of TiO_2 and ZnO in the MB solution left in the dark acted as control to capture adsorption losses of MB on to TiO_2 and ZnO.

Under the experimental condition it was observed that evaporation losses can reach up to 12 % in just one hour .In order to correct the data obtained in the MB photometric reading, the petri dishes were weight immediately before and after exposure. The suspensions were filtered using 0.22µm membranes and measured absorbances at 555 nm .The results obtained are shown in the Table 1 and 2.

The results shows as in Fig.1 and 2 that the photo catalytic activity of TiO_2 can be seen more than ZnO by the fact that extent of degradation reaches 98.3 % in just one hour while extent of degradation of ZnO reaches 96.9 % in one hour .As shown from both the Table 1 and 2 the net values of degradation includes the contribution of some adsorption as well as direct destruction of organic dyes. When plotting In C/Co to as a function of time a structural line yield K= 0.0799 min^{-1} (slope) and $t_{½}$

8.67 min for TiO_2 and K= 0.0732 min^{-1} (slope) and t $_{½}$ 9.47 min for ZnO. These values are in good agreement to the same parameter determined by 0.070min $^{-1}$ and t $_{½}$ 9.90 min to the same concentration MB used in this experiment [29].

Kinetics of Methylene blue photo degradation:

$$C_{16}H_{18}N_3SCL + 5\,½\,O_2 \rightarrow HCl + H_2SO_4 + 3HNO_3 + 16\,CO_2 + 6\,H_2O$$

Table 2: Photo degrading of methyl blue exposed to Sunlight in presence of TiO_2

Condition	C_0(mM)	C_{60}(mM)	Losses (%)
MB solution	1.0	0.0823	17.7
MB solution + TiO_2 (light)	1.0	0.00174	98.3
MB solution + TiO_2 (dark)	1.0	0.0832	16.8

Table 3: Photo degrading of methyl blue exposed to Sunlight in presence of ZnO

Condition	C_0(mM)	C_{60}(mM)	Losses (%)
MB solution	1.0	0.0823	17.7
MB solution + ZnO (light)	1.0	0.00310	96.9
MB solution + ZnO (dark)	1.0	0.0841	15.9

C_o = initial concentration
C_{60} = concentration after 60 min exposure

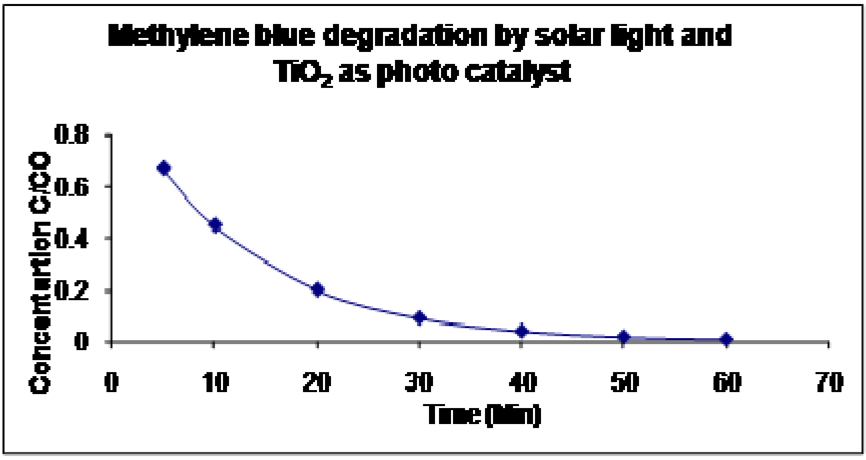

Fig.1.Methylene blue degradation by solar light and TiO_2 as photo catalyst

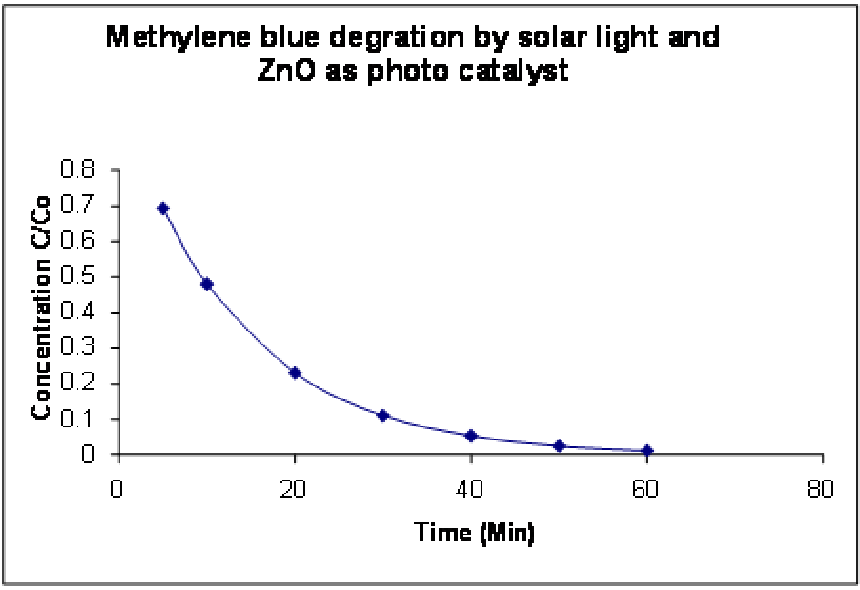

Fig. 2.Methylene blue degradation by solar light and ZnO as photo catalyst

Materials and Methods

Experimental:

Reagents:

Titanium dioxide (TiO_2) and Zinc oxide (ZnO) were used to as 1.0 g/lit suspension. Methyl blue was supplied by Merck and used in a concentration of 10^{-4} M.

Instrumentation:

Ultraviolet and visible spectra were recorded on a Shimadzu 450 UV / visible spectrophotometer using quartz cells of 5 cm path length. Irradiation experiments were done as follow: 10-ml solution was taken in a Petri dish (6cm diameter) and irradiated with direct sunlight. The temperature was maintained at $20\underline{+}2^0$C by using a constant temperature water bath. Irradiation experiments were done in Kanpur, U.P. on sunny days preferably between 9:00 and 11.00 am. The irradiance of emitted light was measured by an International Light IL-730 UV Actinic Radiometer (International Light Company, Newburyport, Mass., U.S.A.) equipped with a calibrated and cosine – corrected ultraviolet radiation detecting probe. Sunlight produced an average ultraviolet radiation of approx.

References

[1] S. Yoon, J. Roh, Park, S. Lee and Hanguk chaely, *Hackhoechi.*, **2000**,10(5), 328-334.
[2] **[**O. Heintz, D. Robert and J. V. Weber , *J Photo Chem. Photobiol. A.*, **2000,**135 (1), 77-80.
[3] J. D. Joshi, J. J. Vora. S. Sharma, C. Patel and A Patel, *Ultra* Science.,**2004** ,16(1), 123-128.
[4] J. J. Vora et al., *E - Journal of Chemistry.*,**2009,** 6(2), 531-536.
[5] K. Klier. et.al., *I & EC Researc.*, **1991,** 29, 61.
[6] A. Baidins. et al., *Progr. Org. Coating.*, **1992**, 20, 105.
[7] **[**L. Lensink. et al., *Inorg .Chem .*, 1995, 34, 746.
[8] J.T. Yates, Jr. et al., *Chem.Rev.*, **1995,95**, 735.
[9] I. Kamber et al., *J.Chem.Soc., Chem.Commun.*, **1995**,533.
[10] K.I. Hadjiivanov and D.G.Klissurski , *Chem. Soc. Rev.*, **1996,**61.
[11] A Fujishima, K .Honda, *Nature.*, **1972,** 238, 37.

[12] Watanabe,T ; A. Kitamura , Kojima , C. Nakayama,; K.Hashimoto, A. Fujishima .,In Photocatalytic Purificatio and treatment of water and air; Ollis ,D.E.,Al-Ekabi,H.,Eds; Elseveir;New York , pp 767. **1993.**

[13] A Fujishima, K Hashimoto, T Watanabe,. TiO_2 Photo catalysis: Fundamental and application; BKC, Inc; Tokyo, Japan, **1999**.

[14] A Fujishima,; Tata N., Rao; Tryk, D.A. *J.Photochem., Photobiology.*, **2000,**C, 1, 1.

[15] S.N Frank,. A. J Bard, *J. Phys Chem*., **1977,** 81; 1484.

[16] A Heller, Acc, *Chem.RES*., **1995,** 28,503-508,.

[17] K Kikuchi, K Sunada, T Lyoda, K Hashimoto, A Fujishima , *Photochem. Photobiol.,A* ., **1997,**106 ,51.

[18] A.C Fernando, Kothari's Economic & Industrial Guide of India, 34the edition, Chemicals & Pharm., Kothari & Sons, Madras, India. 6- 7. **1982 / 3**.

[19] A Munn, and G. Smagghe, Encyclopedia of Occupational Health and Safe (Parmeggiani, L.,ed.), International Labour Organization, Geneva III. Ed. 1, 699,**1983**.

[20] A Joshi, S.K. Khanna, G.B.Singh and C.R. Krishnamutri, *Industrial Health*., **1982,** 20, 305-313.

[21] A Joshi, S.K. Khanna, G.B.Singh and C.R. Krishnamutri, *J. Biosci.*, **1981,** 3, 379 -388.

[22] J.A Parrish,., R.R. Anderson, F. Urbach and D. Pitts UV-A, Biological Effects of Ultraviolet Radiations with Emphasis on Human Responses to Longwave Ultraviolet, Plenum Press, New York. **1978.**

[23] W.A Prayer, Free Radicals in Biology, Academic Press, New York, 2, 85-133, **1976**.

[24] N.I Krinsky, Singlet Oxygen (H.H. Wasserman and R.W. Murray, Eds.)Academic Press, New York. 597- 667, **1979.**

[25] P.C. Joshi, *Toxicol. Lett*., **1985,** 26, 211-217.

[26] J.L. Marx, *Science*., **1983,** 219, 158-159.

[27] Vikesh Kumar, M.R.Tripathi., *E - Journal of Chemistry*., **2009,** 6(3), 659-664.

[28] Vikesh Kumar, M.R.Tripathi., *E - Journal of Chemistry*., **2009, 6** (S1), S79 – S 86,

[29] R. W. Matthews, *J. Chem. Soc. Faraday Trans*., **1989,** 85, 1291-1302,