

Pelagia Research Library

Advances in Applied Science Research, 2012, 3 (2):849-853



Photo catalytic degradation of two commercial dyes in aqueous phase using photo catalyst TiO₂

Meeti Mehra^{*} and T. R. Sharma

K. G. K. Degree College, Moradabad, India

ABSTRACT

The present study involves the photo catalytic degradation of methyl orange and methylene blue by heterogeneous photo catalytic process using TiO2 as semi conductor. An attempt has been made to study the effect of process parameters viz. \rightarrow concentration of dye and pH on photo catalytic degradation of methyl orange and methylene blue. The experiments were carried out by the irradiating the aqueous solution of dyes containing photo catalyst with UV and solar light. The rate of decolorization was estimated from residual concentration spectro- photometrically. The % reduction of methyl orange and methylene blue was estimated under UV / solar system.

Key words: Semicinductors, Photo catalytic degradation, dye decolourization, pH study.

INTRODUCTION

Out of various pollutants contained in industrial waste water, colour is regarded to be very important from the aesthetic point of view also it is a visible pollutant. Almost every industry uses colouring matter to colour their products in order to make them attractive. Unspent colouring materials are discharged in water without any treatment three by increasing aquatic pollution. Dyes are highly coloured polymers but have low bio-degradability, hence persist for long distances in flowing water, retards photosynthetic activity, inhibit the growth of aquatic biota by blocking out sunlight and utilizing dissolved oxygen and also decrease the recreation value of stream.

In the tropical country like India, sunlight is abundantly available natural source of energy which can be conveniently exploited for the irradiation of semi-conductor. Dyes can be degraded in the presence of photo catalyst upon irradiation with visible light because of their absorption in the visible region. Studies have been carried on photo degradation of the dye pre-adsorbed on the surface of TiO_2 particles with visible light[1,2] in which the photo reaction system was almost water free and only the molecules that were in direct contact with the TiO_2 surface underwent photo degradation.

Titanium dioxide is generally considered to be the best photo catalyst and has the ability to de-toxificate water from a number of organic pollutants [3,4]. Many attempts have been made to study photo catalytic activity of different semiconductors such as SnO_2 , ZrO_2 , CdS and ZnO [5, 6]. There are several methods which can be used to treat dye waste water. The technologies can be divided into three categories: biological, chemical and physical [7]. Adsorption is used for its maturity and simplicity. Numerous alternative materials have been investigated to adsorb dyes from aqueous solutions, using Methylene Blue (a basic dye) and Methyl Orange (an azo dye). In the study of adsorption isotherm, linear regression is frequently used to determine the best – fitting isotherm. The linear least – squares method with linearly transformed isotherms has also been widely applied to confirm experimental data, and isotherms using coefficients of determination. The adsorption data were analyzed using langmuir and freundlich isotherms.

Recently Advanced Oxidation process (AOP)[8,9]and Heterogeneous photo catalysis [10,11] has gained a considerable interest for the complete destruction of dyes and other organic pollutants. Use of bio-adsorbant like rice husk [12], coconut coir, banana pith[13], wheat straw, baggase, saw dust [14] used tea leaves, cow-dung [15] have been found to be highly effective, cheap and eco-friendly.

MATERIALS AND METHODS

Methyl Orange is an azo dye with the molecular formula $C_{14}H_{14}N_3NaO_3S$ and molecular mass is 327.34 (gram / mol).



Fig 1: Structure of methyl orange (sodium – 4 – dimethyl amino – azo benzene -4 sulfonate)

Methyl orange is used in textiles, food stuffs, pulp and paper and leather industry. It is most frequently employed acid –base indicator(it changes colour from red to yellow in the pH range 3.1- 4.4)

METHYLENE BLUE

Methylene blue is a basic cationic dye with the molecular formula $C_{16}H_{18}ClN_3S$ and molecular mass is 319.85 [Fig 2].



Fig 2: Structure of Methylene blue:[3,9,bis dimethyl-amino phenazo thiorium chloride]

Basic dyes are the brightest class of dyes[16] and are widely used in small scale industries like textiles, carpets and wool industries.



Fig 3: Absorbance spectra of Methyl Orange during the course of reaction.

METHOD – IRRADIATION EXPERIMENT

To 100 ml of dye solution, photo catalyst TiO₂ was added and suspension was subjected to irradiation. Experiments were carried out under UV light as well as under solar light. The aqueous suspension was magnetically stirred throughout the experiment. At different time intervals a liquot was taken out with the help of a syringe and then filtered through Millipore syringe filter of 0.45 μ m. The absorption spectra were recorded and rate of decolorization was observed in terms of change in intensity at λ_{max} of the dyes as shown in fig 3. The decolorization efficiency % has been calculated as:

Efficiency % = $\frac{Co-C}{Co} \times 100$

Where Co =Initial concentration of dye

C = Concentration of dye after photo irradiation.

Similar experiments were carried out by varying the pH of the solution (pH 2-10), concentration of dye (5-200mg/l) and catalyst loading (0.25-2.0 g/l)

UV VIS SPECTRA OF METHYL ORANGE

The rate of decolorization was recorded with respect to the change in intensity of absorption peaks at 462nm for methyl orange .The absorption peaks, diminished and finally disappeared during reaction, indicating that the dye had been degraded.

DECOLOURIZATION OF DYE USING PHOTO CATALYST TIO2

Investigation was carried out using semi conductor photo catalyst TiO_2 having band gap 3.2 eV, band gap wavelength 387 nm and valence band +3.2. The photocatalysed decolourization of a dye in solution is irradiated by the photo excitation of the semiconductor, followed by the formation of electron – hole pair on the surface of catalyst (Eq-1). The high oxidation potential of the hole (h+_{vb}) in the catalyst permit the direct oxidation of the dye to reactive intermediates (Eq-2).

$$(MO/MO_2) + hv \rightarrow (MO/MO_2) (e_{cb}^- + h_{vb}^+)$$
 Eq-1

Metal oxide

$h^+_{vb} + dye \rightarrow dye^+ \rightarrow oxidation of the dye$	Eq-2
---	------

Another reactive intermediate which is responsible for the degradation is hydroxyl radical (OH*). It is either formed by the decomposition of water (Eq-3) or by reaction of the hole with OH^{-} (Eq-4)

The hydroxyl radicle is an extremely strong and non selective oxidant (E^0 =+3.06V) which leads to the partial or complete mineralization of several organic chemicals[17]

$\mathbf{h^+}_{vb} + \mathbf{H}_2\mathbf{O}_{\rightarrow}\mathbf{H}^+ + \mathbf{O}\mathbf{H}^*$	Eq-3
$h^+_{vb} + OH^- \rightarrow OH^*$	Eq-4
$OH^* + Dye \rightarrow Degradation of the dye$	Eq-5



Fig 4: Photocatlytic efficiency of two catalyst for methyl orange at different pH (dye concentration 25 mg/l: catalyst dose 1g/l:time 4hrs)

Initially blank experiments were performed under UV irradiation without addition of any catalyst and negligible decolorization was observed. Then photo catalytic experiment was carried out using different catalyst at varying pH values 2,4,8,10 at fixed dye concentration of 25 mg/l, and catalyst loading if 1g/l for 4 hours. The results exhibited by TiO₂ photo activity are shown in fig 4.

ADSORPTION BEHAVIOUR OF DYES

In order to study the adsorption behaviour of Methyl Orange at different pH values, the suspension was prepared by mixing 100ml of methyl orange solution(25mg/l) for 60 minutes with fixed catalyst dose (1g/l for MO), the suspension was kept in dark and constant stirring was done, then centrifuged then filtered. The adsorbance of the filtrate was then measured at the maximum band 462nm for methyl orange to determine the concentration of dyes. From the result it was noticed that the adsorption equilibrium at different pH values was reached at about 30 min of equilibrium time. Also the maximum adsorption of Methyl Orange was seen at pH—4.



Fig 5: Adsorption behaviour of Methyl Orange at different pH

Effect of pH

To study the effect of pH on the decolorization of dye experiments were carried out at various pH values, ranging from 2-10 for constant dye concentration (25mg/l) with catalyst loading (1g/l) .It has been observed that the decolorization efficiency increases with increase in pH exhibiting maximum rate of degradation at pH 8. Similar behavior has also been reported for the photo-catalytic efficiency of ZnO for decolorization of azo dyes [18].The experimental results revealed that higher degradation of dye occurred in basic region than in acidic solution. The rate of photo decolorization increased with increase in pH, exhibiting maximum efficiency (98.5%) at pH8, beyond which the rate of degradation remained constant. Although the adsorption of dye molecules are low at alkaline pH, the possible reason for this behavior may be the formation of more *OH radicals, it was earlier also observed similar behavior in their studies on Acid Brown 14 dye [19, 20].

CONCLUSION

The photocatalytic activity of tio₂ is greater in the presence of solar light as compared to UV light. Experimental results indicate that the decolorization of dyes is felicitated in the presence of catalyst. The initial rate of photodecolorization increased with increase in catalyst dose up to an optimum loading after that it did not show any effect. As the initial concentration of the dye was increased, the rate of decolorization decreased in each dye. The rate of photo decolorization was found to increase with increase in pH, exhibiting maximum efficiency (98.5%) at pH8, beyond which the rate of degradation remained constant.

Acknowledgement

Authors are deeply indebted and pleased to acknowledge the sincere efforts of Dr Manish Saxena, Associate Professor, MIT, Moradabad for helping them in finalizing the work for this research article.

REFERENCES

[1] K. Vinodgopal, P.V. Kamat, J. Phys. Chem. 1992, 96, 5053.

[2] P.V.Kamat and K.Vinodgopal, in : P.F.Ollis, H.Al-Ekabi(Eds.), Photocatalytic purification and treatment of water and air, Elsevier Science Publishers, B.V, Amsterdam, **1993**, p. 83.

[3] M.A. Fox, M.T. Dulay, Chem. Rev. 1993, 93, 341.

[4] E. Kusvuran, A. Samil, O.M. Atanur, O. Erbatur, Appl. Catal. B: Env. 2005, 58, 11.

[5] A.A. Khodja, T. Sehili, J.F. Pilichowski, P. Boule, J. Photochem. Photobiol. A: Chem. 2001, 141, 231.

[6] K. Vinod Gopal, P.V. Kamat, Envorn.Sci. Technol. 1995, 29, 841

[7] B. Neppolian, H.C. Choi, S. Sakthivel, B. Arabindoo, V. Murugesan, J.Hazard.Mater., 2002, B 89, 303.

[8] S. Lathasree, R. Nageswara, B. Sivasankar, V. Sadasivam, K. Rengaraj, J. Mole. Catal. A: Chem., 2004, 223, 101.

[9] C. Lizama, J. Freer, J. Baeza, H.D. Mansilla, Catal. Today, 2002, 76(2) 235.

A. Akyol, H.C. Yatmaz, M. Bayramoglu, Appl. Catal. B: Env. 2004, 54,19.

[10] T. Robinson, G. McMullan, R. Marchant, and P. Nigam, Bioresource. Technol. 2001, 77, 247-255.

[11] S. Das, P.V. Kamat, S. Padmaja, V. Au, S.A. Madison, J. Chem. Soc., Perkins Trans. 1999, 2, 1219.

[12] Y. Yang, D. T. Wyatt, M. Bahorsky, Textile Chem. Colorist, 1998, 30, 27.

[13] N. Deo, M. Ali, *Indian J Envtl Prot*, **1993**, 13 (7), pp. 496-508.

[14] C. Namasivayam, K. Kadirvelu, Bioresource Technol. 1997,62 (3), pp.123-127.

[15] R. Singh, COD reduction from the textile wastewaters using bio-adsorbents.- M.Tech Thesis, (2001) Dept of Environmental Sciences & Engg, Guru Jambheshwar University, Hisar, Haryana, India.

[16] S. P. Raghuvanshi,: Decolourisation of Dyes and chromium using bioadsorbents,

[17] from the aqueous solutions. M. Tech Thesis (2001), Dept of Environmental Sciences & Engg, Guru Jambheshwar University, Hisar, Haryana, India.

[18] G. Mckay, M. Elgundi, M. M. Nassar, Water Res 1988, 22(12), 1527-33.

[19] N. Daneshvar, D. Salari, A.R. Khataee, J. Photochem. Photobiol. A: Chem., 2003 157, 111.

[20] S. Sakthivel, B. Neppolian, B.V. Shankar, B. Arabindoo, M. Palanichamy, V. Murugesan, *Sol Ener. Mater. Sol. Cells*, **2003**, 77, 68.