MAY 2014- JULY 2014, Vol. 4, No. 3; 2669-2675. E- ISSN: 2249 –1929

Journal of Chemical, Biological and Physical Sciences

An International Peer Review E-3 Journal of Sciences

Available online at www.jcbsc.org

Section D: Environmental Sciences

CODEN (USA): JCBPAT Research article

Photocatalytic Degradation of Textile Dye by using Immobilized TiO_2 Nanocatalyst

Santhosh.P[1*] and Revathi.D[2]

[1, 2*]Department of Chemical Engineering, Kongu Engineering College, Perundurai, Erode - 638052, Tamilnadu, India.

Received: 30 March 2014; **Revised:** 14 April 2014; **Accepted:** 06 May 2014

Abstract: This work is to investigate experimentally the removal of organic compounds from textile industrial wastewater by immobilized photocatalytic treatment, for its reuse in the same industry or for domestic purpose and irrigation. Now a day's immobilized photocatalytic technique is used for the treatment of textile wastewater. Due to high photocatalytic activity and stability of titanium dioxide, it is generally used as a photo catalyst for the removal of organic compound. TiO_2 was immobilized by dip-coating technique. When dip-coating technique is applied, the operating region shifted from UV to visible. Sol-gel technique has been taken as one of the adaptable methods for the preparation of metal dipped nanocrystaline TiO_2. In this technique, the wavelength of the UV light and the amount of immobilized TiO_2 were negligible. Photocatalytic oxidation of the combined UV/TiO_2 catalyst excites the particles from the valance band to the conduction band having a forbidden energy zone value of 3.3eV. The free hydroxyl radicals produced due to this excitation removes the organic compounds present in the dye wastewater by degradation. In the present work we investigate in the operating conditions of catalyst concentration 100mg/L, pH of 7 and at room temperature. Under these conditions, the degradation of about 80.5% of Congo red dye and 77.4% of T.blue SBL dye were achievable in 480 minutes.

Keywords: Photocatalytic treatment, Ultraviolet visible light, Industrial wastewater, Titanium dioxide.

INTRODUCTION

Dye wastewater pollutants are the major sources of environmental pollution. Textile wastewater introduces intensive color and toxicity to aquatic systems. Dyes possess complex aromatic structure. Hence conventional biological treatment methods are ineffective for decolourisation and degradation [1-4]. Advanced oxidation process (AOPs) have been successfully used as pretreatment methods to reduce the concentrations of toxic organic compounds that inhibit biological wastewater treatment process. Different types of homogeneous and heterogeneous AOPs have effectively degraded colored aromatic compounds by the destructive oxidation of the dyes. Among heterogeneous AOPs, titanium dioxide (TiO_2) mediated photocatalytic oxidation appears to be a promising alternative, since the optical absorption of TiO_2 is the major advantage than other AOPs. Photo degradation involves the oxidation of organic pollutants where absorption of light is the driving force[5-8]. TiO_2 has proved to be the best material for purification because it is readily available, cheap and chemically stable. TiO_2 semiconductor exists in three crystalline forms-anatase, rutile and brookite. Among this anatase form of TiO_2 was found to be most effective for wastewater treatment. The combination of catalyst is also a very strong oxidizing agent. The combination of TiO_2, UV can create a very fast and efficient process for wastewater treatment by producing hydroxyl radicals. These electrons may form hydroxyl radicals, which can decompose organic compounds. With the use of dipping techniques, thin layer of TiO_2 were coated onto glass slides for testing the possibility of destroying benzoic acid and caffeine. Further testing on greater thickness and light positions needed to be performed to further optimize the use of the catalyst and the reaction kinetics[9-14].

1.1 Mechanism of TiO_2

Photocatalytic oxidation by UV/TiO_2 or ZnO involves the oxidation of TiO_2/ZnO particles by UV light from valence band of the solid to the conduction band.

$$TiO_{2+} h\upsilon \rightarrow e^-_{CB+} h^+_{VB}$$

$$TiO_2(OH^\bullet) + H_2O + H^+ \rightarrow TiO_2(OH^\bullet) + H^+$$

$$TiO_2(OH^\bullet) + R \rightarrow TiO_2(OH^\bullet) + RO + H^- + e^-$$

$$ZnO + h\upsilon \rightarrow e^-_{CB+} h^+_{VB}$$

When a semiconductor such as catalyst absorbs photons the valence band electrons are excited to the conduction band. For this to occur, the energy of photon must exceed the band gap energy of the semiconductor. This excitation results in the formation of an electronic vacancy or positive hole at the valence band edge. This hole has a positive charge and reacts with the adsorbed water molecules on the surface of the solid producing the radical OH^- which has great potential oxidation of organic molecules. TiO_2 is a catalyst in the photo catalytic degradation of organic compounds due to its suitable band gap energy of 3.3 eV over a wide range of pH (Omprakash Shau and Karthikeyan.M.R. 2013). See **Fig. 1**.

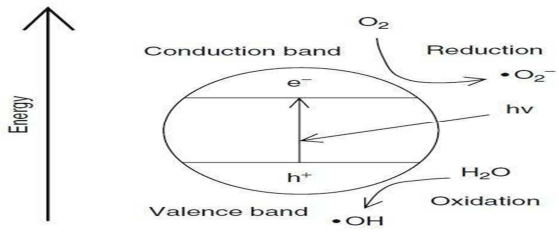

Fig.1: Distribution of energy in bands

TiO_2 Immobilization: Titanium (IV) isopropoxide mixed with glacial acetic acid in a beaker at 0°C. 1gm $MgNO_3$ is dissolved in water and was added drop wise and vigorously stirred for 1 hour using magnetic stirrer. The solution undergoes continuously stirring for another 1 hour to form a clear solution. The resulting solution was kept in dark for overnight and then solution was placed in an oven at a temperature of 70°C for gelation process for 12 hours. Later the gel was dried and calcined at 600°C. The prepared dipped TiO_2 nanoparticle is mixed with deionized water and poly vinyl alcohol (PVA) was subsequently added into the TiO_2 suspension, followed by mechanical stirring at 95°C for 1 hour. Then PVA/TiO_2/H_2O solution mixture rested in air to eliminate air bubbles and to cool the solution to room temperature. The obtained viscous solution mixture was coated onto a clean glass column and was allowed to evaporate overnight at room temperature.

MATERIAL AND METHODS

Collection of sample: The sample of textile dye wastewater was collected from dyeing industry located at SIPCOT, Perundurai, Erode District, and Tamil Nadu.

Reagents and chemicals: The Congo red dye, T.blue SBL dye, Poly Vinyl Alcohol (PVA), Glacial acetic acid and titanium dioxide (TiO_2) were procured from S.D Fine Chemical industry, Mumbai, India. All the chemicals are used for analytical reagent grade and employed directly without further purification. Distilled water was used in all experiments.

Experiment: Experimental studies were carried out in batch photocatalytic reactor of 1L capacity at room temperature which comprises of reactor vessel and UV lamp assembly See **Fig. 2**. In this setup UV lamp was placed in an immersion tube, which is positioned in the reactor vessel containing the liquid to be irradiated. An electrical magnetic stirrer with magnetic bar was used continuously so that catalyst can be uniformly dispersed in the solution when the sample was degraded by UV light. The entire reactor was kept inside the UV inoculation chamber in order to guarantee maximum use of the radiation, to prevent the effect of external radiation and to maintain the temperature of the system. The reactor system temperature was maintained periodically and kept constant. The collected industrial sample is making up and ensured that the complete hydrolysis is takes place. The concentration of sample dye before and after irradiation was determined using UV visible spectrophotometer. The experimental setup of photocatalytic reactor can be found elsewhere. In order to determine the concentration of the dye after treatment, a calibration curve was drawn by measuring the absorbance of dye solution of known concentrations. The calibration curve for the dye is shown below see Fig.3.

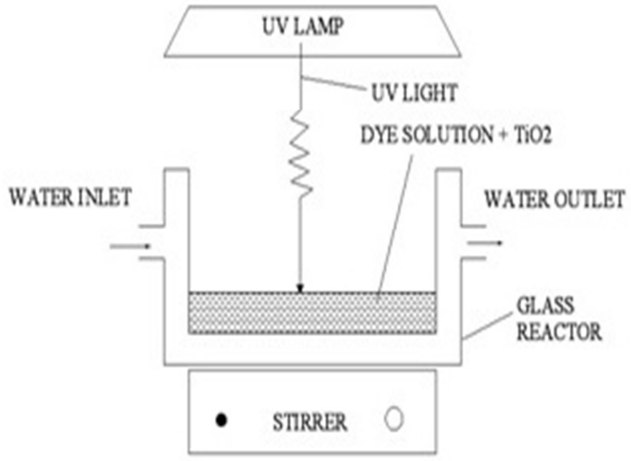

Fig.2: Experiment of photocatalytic reactor

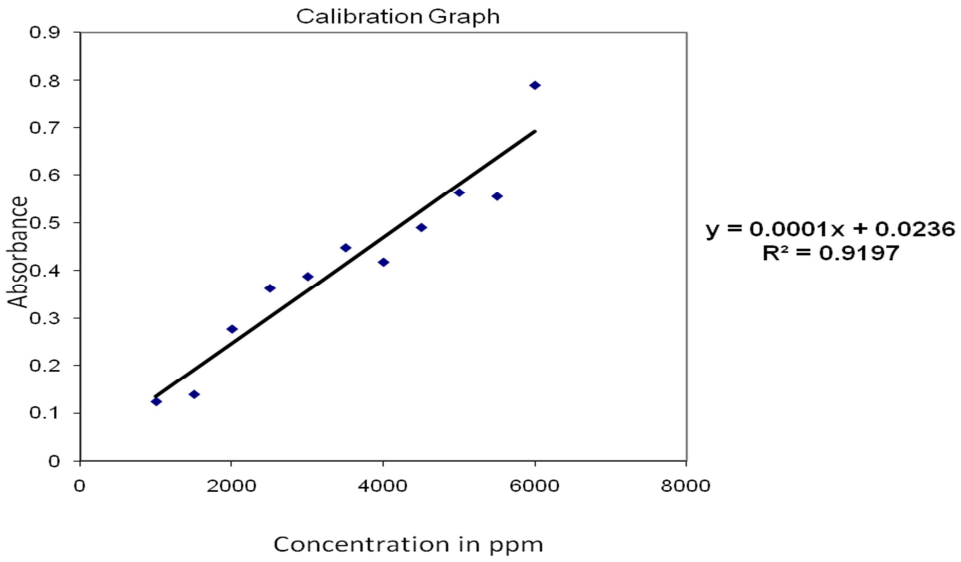

Fig.3: Calibration Curve

The operating conditions of experiments are given in **Table 1**:

Table-1: Operating conditions of experiments

S. No	Parameters	Value
1.	Initial dye concentration	100 mg/l
2.	TiO_2 amount	0 -120 mg/l
3.	Ph	2 - 10
4.	Temperature	20-40·C
5.	Irradiation time	up to 240min

Decolorization efficiency: Decolorization efficiency (DE) was calculated from a mathematical equation adapted from measurements of decolorization used before

$$DE = \frac{(Absorbance)_o - (Absorbance)_t}{(Absorbance)_o} \times 100$$

Where,

$(Absorbance)_o$ = Absorbance before irradiation

$(Absorbance)_t$ = Absorbance at time t

To check the validity of the previous equation for used textile industrial wastewater, the photodegradation percentage of the dye was followed spectrophotometrically, by a comparison of the absorbance at specified interval of times, with a calibration curve accomplished by measuring the absorbance, at known wavelengths, with different concentrations of the dye solution.

RESULTS AND DISCUSSION

3.1 Effect of dye concentration: Experiments were conducted at initial dye concentration as 100mg/l constant both Congo red dye and T.blue SBL dye. The degradation of organic compounds reduction with process time is increase shown in **Fig.3, 4 and 5**. When the time is increased to dye concentration decrease extremely. The rate of degradation depends on the formation of OH radicals. There occurs the replacement of adsorbed OH positions by dye ions which results in reduced generation of OH radicals. On account of the fact these OH radicals react with the dye containing aromatic compounds in the textile wastewater.

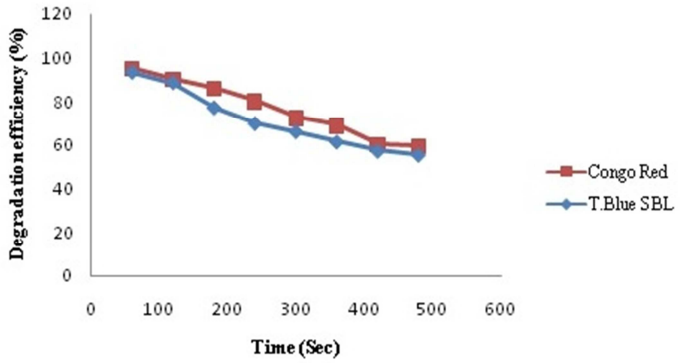

Fig.3: Effect of dye concentration (AOPs)

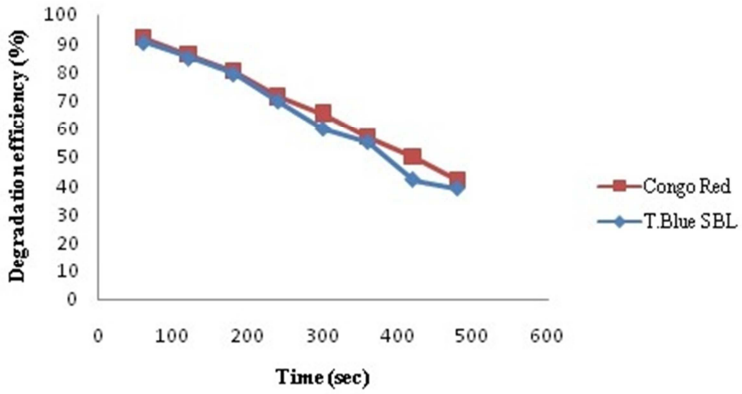

Fig.4: Effect of dye concentration (with TiO_2)

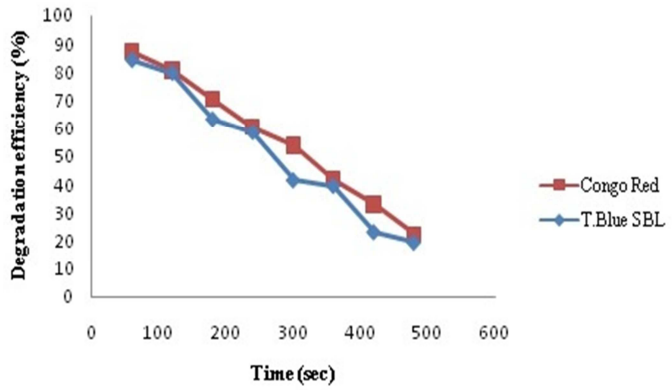

Fig.5: Effect of dye concentration (without TiO_2)

Effect of catalyst dosage: The dosage of catalyst (anatase) was varied with the concentration of dye as constant to find the optimum dosage. The photocatalytic degradation experiments were carried out under the UV light by varying the amount of anatase dosage from 40mg to 95mg and the irradiation time was fixed for 8 hours when the amount of anatase dosage was increased in the wastewater, degradation efficiency was slightly increased up to photocatalyst dosage of 70mg. The photodegradation rate was slightly reduced beyond the 70mg of photo catalyst dosage. Excess catalyst reduces the amount of photo energy being transferred in the medium due to opacity offered by catalyst particles. An amount of 70mg/100ml of photocatalyst was used for the subsequent photocatalytic degradation experiments.

Effect of irradiation time: The required duration for the complete photocatalytic treatment of organic compounds in the textile wastewater was studied based on the duration of catalyst irradiation to the light source. The catalyst irradiation time was varied from 1 to 8 hours under the UV light source for the dosage of 45mg of photocatalyst into 100ml of textile wastewater. In the present study highest degradation efficiency was observed. When the irradiation of photocatalyst was continued till 8 hours under UV light source and the organic compound removal efficiency as 80.5% of Congo red dye and 77.4% of T.blue SBL dye. The photocatalytic degradation efficiency increased with respect to irradiation time of photocatalyst and the result obtained are shown in **Table 2**.

Table-2: Percentage of textile dye degradation.

Time (Sec)	AOPs with UV/ TiO_2		UV Degradation with TiO_2		UV Degradation without TiO_2	
	Congo Red	T.blue SBL	Congo Red	T.blue SBL	Congo Red	T.blue SBL
60	95.25	93.47	91.6	90.25	87.0	84.32
120	90.5	88.75	85.8	84.8	80.5	79.8
180	86.42	77.25	80.0	79.31	70.24	63.41
240	80.27	70.0	71.2	69.8	60.5	58.75
300	72.51	66.25	65.3	60.0	53.9	41.6
360	69.0	61.5	56.8	55.3	42.0	39.62
420	60.31	57.29	50.15	42.1	33.21	23.25
480	59.52	55.5	42.0	39.1	22.6	19.5

Effect of UV light intensity: The absorption spectra of Congo red dye and T.blue SBL dye were studied at different times of irradiation. The effect of variation of light intensity on the degradation efficiency was also investigated. The result indicates that degradation efficiency increases in the light intensity will increase the number of photons striking per unit area of photo catalyst.

CONCLUSION

This work is terminates that the overall degradation percentage of Congo red dye and T.blue SBL dye in textile wastewater by photocatalytic treatment on using TiO_2 as catalyst is 80.5% and 77.4%. The TiO_2 catalyst is immobilized by dip-coating method. The problem of this work is degradation with TiO_2 as photo catalyst is that of being slow compared with conventional treatment methods but it has benefit not leaving toxic by sludge. The percentage degradation is measured for the different concentration of sample solution. Since the photocatalytic reactor is used for the treatment process the UV light is submerged inside the reactor. The percentage removal of the dye is directly proportional to the intensity of the UV light radiation. In this process the combination of TiO_2 catalyst and UV visible radiation is the best oxidizing agent. And it produces free hydroxyl radicals for the effective decomposition of pollutants present in the dye wastewater.

REFERENCES

1. E. Chatzisymeon, C. Petrou, D. Mantzavinos "Photocatalytic treatment of textile dye house effluents with simulated and natural solar light" *Global NEST Journal*, 2013,**15,** 1, 21-28.
2. Omprakash Shan, M.R. Karthikeyan "Reduction of textile dye by using heterogeneous photocatalysis" *American J Envir. Pro*. 2013, **2**(3), 90-94.
3. Harshal Nagpure, Vikram Banakar, Rahul Dhanda and Dr. K.S. Vani "Degradation of paper mill wastewater using batch (photocatalytic) reactor" *Int. J Green Chemistry and Bioprocess*,2013, 277-7199.
4. Jan Sima, Pavel Hasal "Photocatalytic degradation of textile dyes in a TiO_2/UV system" *Chemical Engineering Transactions*, 2013, **32,** 1974-9791.
5. Anoop Verma, Poonam, Divya Dixit "Photocatalytic degradability of insecticide chlorpyritos over UV irradiated Titanium Dioxide in aqueous Phase" *Int.J. Envi.Sci*. 2012, **3**, 2.
6. Munesh, Swathi, R.S. Sindal and R.C. Meena "Degradation of Textile dye from aqueous solution by using MBIR DOWEX photocatalyst" *Int. J. of Basic and Applied Chemical Sciences*,2012, **2,** 23-30.
7. Chhotu Ram, Ravi Kant Pareek and Varineder Singh "Photocatalytic degradation of textile dye by using TiO_2 nanocatalyst" *Int. J. Theo. and Appl.Sci*., 2012, **4**(2), 82-88.
8. Manoj A. Lazar, Shaji Varghese and Santhosh. S. Nair "Photocatalytic water treatment by TiO_2: Recent updates" *Catalysts*, 2012, **2**, 572-601.
9. Rohini Singh, A.D.Kulkarni "Application of immobilized photocatalyst for the degradation of Textile wastewater" *Int.J. Engineering Research and Applications*, 2012, **2**,460-472
10. C. Singara Vadivel, M. Vanitha and N. Balasubramanian "Photo and Electrocatalytic treatment of textile wastewater and its comparison" *J. Electrochemical Science and Technology*, 2012**, 3,** 1, 44-49.
11. H. Falah, Hussein and A. Thekra Abass "Photocatalytic treatment of textile industrial wastewater" *Int. J Chem. Sci*, 2010, **8**(3), 1353-1364.
12. R.C. Meena, Ram Badu Pachnwarya, Vijay Kumar Meena and Shakuntla Arya "Degradation of textile dyes Ponceau-S and Sudan IV using recently developed photocatalyst, Immobilized resin Dowex-11" *American J Envir. Sci*. 2009, **5**(3), 444-450.
13. M.M. Haque, M. Muneer "TiO_2 mediated photocatalytic degradation of a textile dye derivative, bromothymol blue, in aqueous suspensions", Dyes and Pigments, 2007, **75**, 443-448.
14. Amrit Pal Toor, Anoop Verma, C.K. Jotshi, P.K. Bajpai, Vasundhara Singh "Photo catalytic degradation of Direct Yellow 12 dye using UV/TiO_2 in a shallow pond slurry reactor", Dyes and Pigments, 2006, **68**, 53-60.

***Corresponding Author: P. Santhosh;** PG Scholar, Department of Chemical Engineering, Kongu Engineering College, Perundurai, Erode - 638052, Tamilnadu, India.