*International Journal of Theoretical & Applied Sciences,* **4**(2): 82-88(2012)
**ISSN No. (Print) : 0975-1718**
**ISSN No. (Online) : 2249-3247**

# Photocatalytic Degradation of Textile Dye by Using Titanium Dioxide Nanocatalyst

***Chhotu Ram*, Ravi Kant Pareek**and Varinder Singh*****
** Department of Applied Science & Engineering,*
*Indian Institute of Technology, Roorkee, Saharanpur Campus, Saharanpur- (U.P.) India*
*** Department of Civil Engineering,*
*Jan Nayak Ch. Devi Lal College of Engneering, Sirsa (Haryana) India*

*(Received 21 September, 2012, Accepted 12 October, 2012)*

**ABSTRACT: In the present work, degradation of commercial reactive Procion Yellow (PY) dye was studied using photocatalyst combinations ($TiO_2$/UV/Solar/pH). For degradation of PY dye, batch experiments were carried out by irradiating the aqueous solution of dye, in the presence of semiconductors as titanium dioxide ($TiO_2$). The effect of various parameters such as catalyst loading, pH, oxidant dose, intensity variations and initial concentration of the dye on degradation has been investigated. The effect of process parameters viz. pH (2–10), irradiation time, initial concentration of dye (50-200 ppm), UV intensity and photocatalyst loading (0.62–1.5 g/L) on degradation of dye has also been assessed. The experimental results indicated that 83.6% degradation occurred at optimized conditions (Dye concentration 100 ppm, pH 7.8, $TiO_2$ dose 0.5g/L, UV intensity 25 W/m$^2$ and time 3.5h). The performance of the solar photocatalytic system appears to be a suitable alternative to $TiO_2$ in the presence of UV light at natural pH.**

**Keywords:** Photocatalysis; Procion yellow dye; Titanium dioxide; Oxidants

## I. INTRODUCTION

Dyes are introduced into the environment as a result of several man-made activities. Over 70000 tons (about 10000 types) of dyes and pigments are produced annually worldwide, of which about 20% are assumed to be discharged as industrial effluent during the textile dyeing processes. Thus, it was believed that dye molecules are non-biodegradable, intense color and some of them are toxic to environment [1, 2]. Various chemical and physical processes such as precipitation, adsorption, air stripping, flocculation, reverse osmosis and ultrafiltration can be used for color removal from textile effluents [3, 4]. However these techniques are non-destructive, since they only transfer the non-biodegradable matter into sludge, giving rise to new type of pollution, which needs further treatment [5, 6]. Recently there has been considerable interest in the utilization of advanced oxidation processes (AOP,s) for the complete degradation of dyes used in textile industry. The heterogeneous photocatalytic oxidation processes has been extensively used in the literature for the degradation of dyes [7, 8]. Photocatalytic treatments are based on in situ generation of highly reactive hydroxyl radicals. These radicals are high oxidant species; they attack the most of organic molecules. They are also characterized by low selectivity of attack which is useful characteristic for an oxidant used in wastewater treatment. In the last decade, most attention has been given to $TiO_2$ due to its high photocatalytic activity, low cost, nontoxicity and high stability in aqueous solution [9]. $TiO_2$ is generally considered to be the best photocatalyst and has the ability to detoxificate water from a number of organic pollutants [10]. Many studies have been reported related with textile dye and textile wastewater degradation using $TiO_2$ as a catalyst [11, 12, 13, 14]. Only a handful studies have been attempted which compare the efficiency of different catalysts for a particular dye under identical conditions. Adsorption and photodegradation of Procion yellow H-EXL dye in textile wastewater over $TiO_2$ suspension [15].

Procion Yellow (PY) dye is a basic dye used to dye wool, cotton and silk required in textile industry. The release dyes and their products in the environment cause toxicity problems. So an attempt has been made to study the degradation of PY. In this study, semiconductor photocatalysts $TiO_2$ was used for the degradation efficiency of aqueous solution of these dyes. Photocatalyst experiments were conducted to investigate the effects of various process parameters (catalyst loading, pH, initial dye concentration and oxidants dose) on the process performance. The efficiency was also compared with the solar and UV photocatalysis.

## B. EXPERIMENTAL

### *A. Materials*

Titanium dioxide (P-25, surface area 50 $m^2/g$) was used as-received and purchased from Merck, India and were used without further purification. Procion Yellow (PY) MX-R dye was obtained from textile industry. The molecular structure of dye is given in Fig. 1. Single distilled water was used for preparation of dye solutions (100 ppm). pH of the solutions was adjusted with 1 M HCI/NaOH.

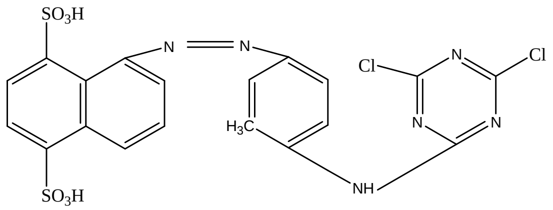

**Fig. 1.** Structure of Procion Yellow MX-R.

### *B. Photocatalytic Reactor*

The photochemical reactions were carried out in specially designed batch reactor as shown in Fig. .2. For photocatalytic UV reactor was used which was rectangular having dimensions of 4.5 feet length, 3 feet width and 3.5 feet height and made up of iron. Roof of the reactor was made up of wooden; seven UV tubes (36 Watt each) were attached with the roof. Temperature inside the reactor was maintained by an exhaust fan. Measurement of UV light intensity was done by an instaneous solar radiation meter (Eppley 499). The measured intensity was 15 $W/m^2$.

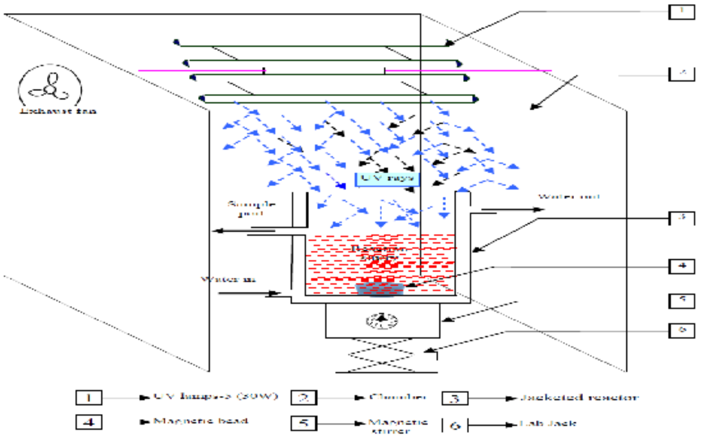

**Fig. 2.** Photocatalytic reactor.

### *C. Experimental Procedure*

For the degradation experiments, fixed amount of photocatalyst $TiO_2$ was added dye solution (100 ppm). The suspension was subjected to irradiation under UV light for a fixed interval of time. At different time intervals, an aliquot was taken out with the help of a syringe and then filtered through a Millipore syringe filter of 0.45 µm. Then wavelength was recorded with the help of spectrophotometer and rate of degradation was observed in terms of decrease in wavelength at $\text{У}_{max}$, i.e. 402 nm for PY dye.

The percentage (%) degradation was calculated as follows: % Degradation = $100*(C_0 - C)/C_0$ where $C_0$ = initial concentration of dye solution, C = concentration of dye solution after irradiation. Chemical oxygen demand (COD) of dye solution was analyzed according to the standard methods for the examination of water and wastewater [16]. In order to determine the effect of catalyst loading, the experiments were performed by varying catalyst concentration, pH variation, UV intensity, initial dye concentration and effect of oxidants viz. $H_2O_2$/NaOCl have been analysed.

## III. RESULTS AND DISCUSSION

The procion yellow dye solution was subjected to photocatalytic treatment and the efficiency of treatment was investigated by altering parameters like pH, catalyst dose, UV intensity and variation of dye concentration as well as effect of UV /Solar light. Firstly dye sample was analyzed for some initial parameters. The values of various initial parameters of procion yellow dye before treatment are shown in Table.1 and earlier also studied [12].

**Table 1. Characteristics of Procion yellow dye (100 ppm).**

| S. No. | Parameter | Value |
|---|---|---|
| 1. | pH | 7.80 |
| 2. | COD (mg/L) | 63 |

### *A. Effect of UV and Solar light (Photolysis)*

Photodegradation of Procion yellow dye (100 ppm) at natural pH (7.80) was carried out under UV and Solar radiation without catalyst to assess the effect of irradiation. After 3.5 h of treatment with UV and Solar radiation 16.5 and 11.5% degradation, respectively, was achieved (Fig. 3). Similar findings have been reported earlier for the degradation of azo dyes such as Congo red and Benzopurpurine 4B in the direct photolysis [13, 17].

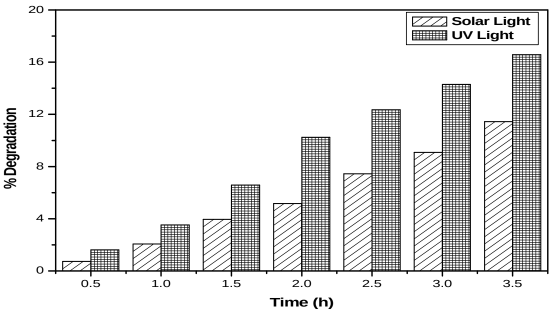

**Fig. 3.** Effect of UV/ Solar light without catalyst, pH = 7.80, Time = 3.5 h.

### *B. Effect of catalyst loading*

In order to determine the optimal catalyst dose, a series of experiments were carried out using different concentrations of $TiO_2$ (0.25 to 1.5g $L^{-1}$), Fig. 4. It was observed that as $TiO_2$ dose increased from 0.25 to 0.5g $L^{-1}$, the percentage degradation increased from 64.9 to 83.7%, Fig. 4. Above 0.5 g $L^{-1}$ of $TiO_2$ dose, there is no significant increase in the degradation of dye. So, 0.5 g $L^{-1}$ of $TiO_2$ has been considered as an optimized dose of $TiO_2$ for degradation of PY dye for subsequent experiments. The increase in degradation rate with increase in the catalyst loading is due to increase in total active surface area i.e. availability of more active sites on catalyst surface [18].

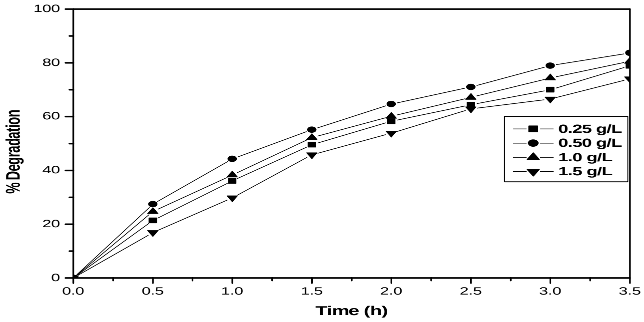

**Fig. 4.** Effect of $TiO_2$ dose on photocatalytic degradation of PY dye (100 ppm), pH = 7.80, Time = 3.5 h.

But higher dose of catalyst results in increase in turbidity of the suspension which decreases the penetration of UV light and hence photoactivated volume of suspension [19]. Thus it can be concluded that higher dose of catalyst may not be useful both in view of aggregation as well as reduced irradiation field due to light scattering. Various studies have also reported the similar observations for degradation of dyes [16, 20].

### *C. Effect of pH*

Textile dyeing wastewater is discharged at different pH; therefore it is important to study the role of pH on degradation of dye. In order to study the effect of pH, experiments were carried out at various pH values (2 to 10) at constant dye concentration (100 ppm) with $TiO_2$ ($0.5gL^{-1}$). It was observed that the degradation efficiency increases with increase in pH and maximum degradation i.e. 94.7% and 93.7% for $TiO_2$ respectively was observed at pH 10. When changing pH 8 to10 there is no significant increase in degradation. Since natural pH of dye solution is 7.80 and the maximum degradation efficiency was almost at pH 10. So, natural pH has been considered as an optimum for degradation. This shows the colour removal efficiency of photocatalysts as a function of pH. The results reveal that the lesser degradation of dye occurs in basic solution and higher in acidic region with $TiO_2$. The interpretation of pH factor on the efficiency of photocatalytic degradation process can be explained on the basis of acid base property of metal oxide surface and the ionization state of ionisable organic molecule [20]. The point zero charge (pzc) for $TiO_2$ (Degussa P25) is 6.8 and for ZnO is 9.0 ± 0.3 [22]. $TiO_2$ surface is positively charged in acidic media (pH < 6.8) whereas it is negatively charged under alkaline condition (Ph > 6.8). Final pH after photocatalytic treatment was 7.4 which is suitable for biological treatment as well as discharge of wastewater into the water bodies (Fig. 5).

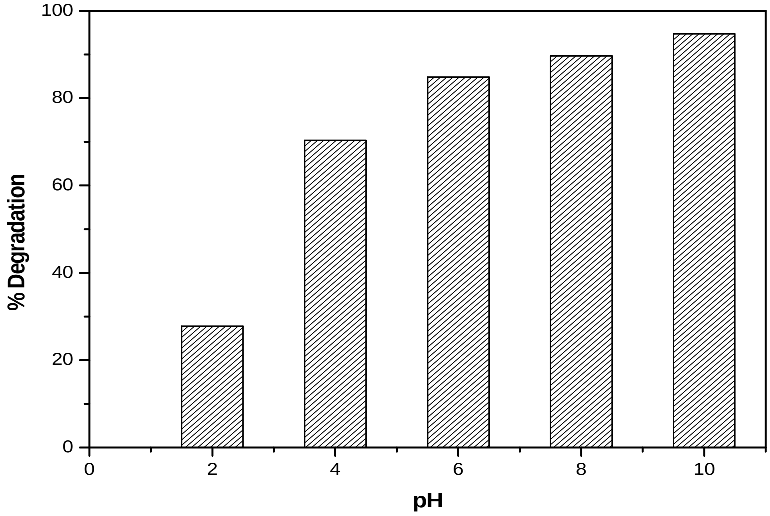

**Fig. 5.** Effect of initial pH on Photocatalytic degradation of dye $[TiO_2] = 0.5\ g\ L^{-1}$, Time = 3.5 h.

### *D. Effect of initial dye concentration*

The influence of initial concentration of dye solution has been investigated on the photocatalytic degradation at optimum of pH (7.80) and catalyst dose ($TiO_2 = 0.5\ g\ L^{-1}$). The dye concentration was varied from 50 to 150 ppm. The reason behind this behavior may be due to the increase in the extent of adsorption on the catalytic surface which reduces the catalytic activity [15]. It has been observed from the Fig. 6.

The degradation was decreases with increases in dye concentration with both the catalyst. The increases in the PY dye solution concentration also decrease the path length of photon entering into the dye solution. At high dye concentration a significant amount of UV-light may be absorbed by the dye molecule rather than the catalyst and this may also reduce the catalytic efficiency. The same trends have been observed by many researchers for dye degradation [17, 20, 21].

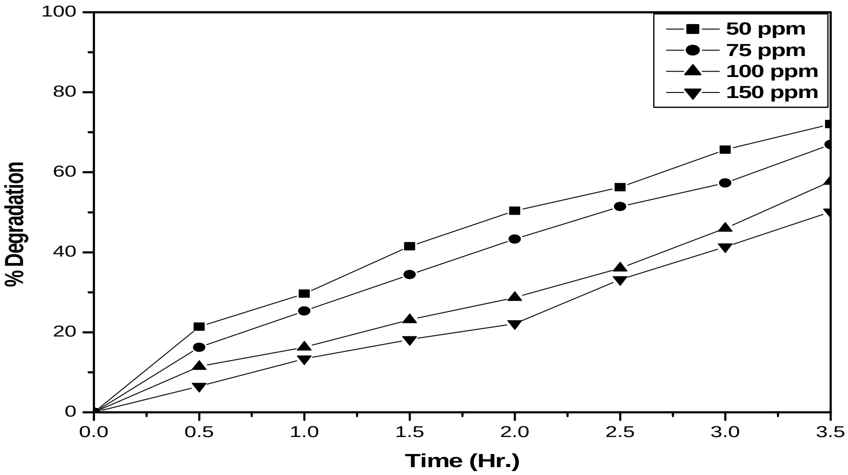

**Fig.6.** Effect of dye concentration on photocatalytic degradation of PY dye at [$TiO_2$] = 0.5 g $L^{-1}$ and Time = 3.5 h.

*E. Effect of UV intensity*

The influence of UV light intensity on the degradation efficiency has been examined on PY dye solution (100 ppm) at a pH 7.8 and $TiO_2$ loading of 0.5 g $L^{-1}$. It is evident from the results that the percentage degradation increases with increase in the light intensity (Fig. 7). The UV irradiation generates the photons required for the electron transfer from the valence band to the conduction band of a semiconductor photo catalyst and the energy of a photon is related to its wavelength and the overall energy input to a photocatalytic process is dependent on light intensity. The rate of degradation increases when more radiation falls on the catalyst surface and hence more hydroxyl radicals are produced. The degradation efficiency is found to be maximum (i.e. 25 $W/m^2$) in the middle area of the photoreactor.

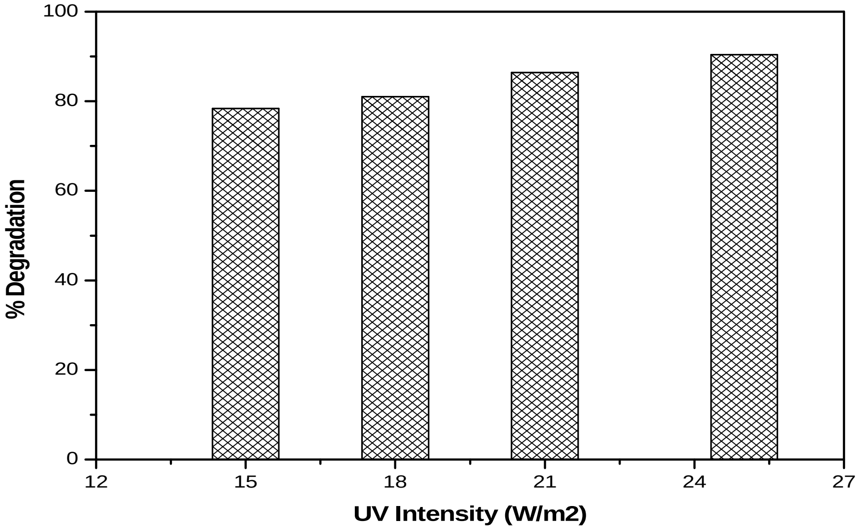

**Fig. 7.** Effect of UV intensity on photocatalytic degradation of PY dye [$TiO_2$] = 0.5 g $L^{-1}$, pH = 7.8, Time = 3.5 h.

### *F. Comparison of UV/Solar light*

The effect of UV/Solar light on the degradation of PY dye solution by photocatalytic process has been investigated. The comparative study has been carried out for the degradation of dye solution in Solar/UV light with $TiO_2$ catalysts. In case of $TiO_2$, the PY dye (100 ppm) solution containing $TiO_2$ (0.5 g $L^{-1}$) was exposed to Solar and UV light at pH 7.8. Fig. 8 shows that the more degradation was observed in UV light (83.5%) as compared to solar light (76.8%). It is evident from the graph that percentage degradation with solar light is very close to UV light so solar light can be efficiently used for the photocatalytic degradation of dye effluent. The efficiency of photooxidation was compared by using hydrogen peroxide, solar and UV radiation for the degradation of PY dyes (4 dyes) and a mixture of dyes either by solar or UV radiation the complete degradation of blue dye and a mixture of dyes was achieved after 3 h [23].

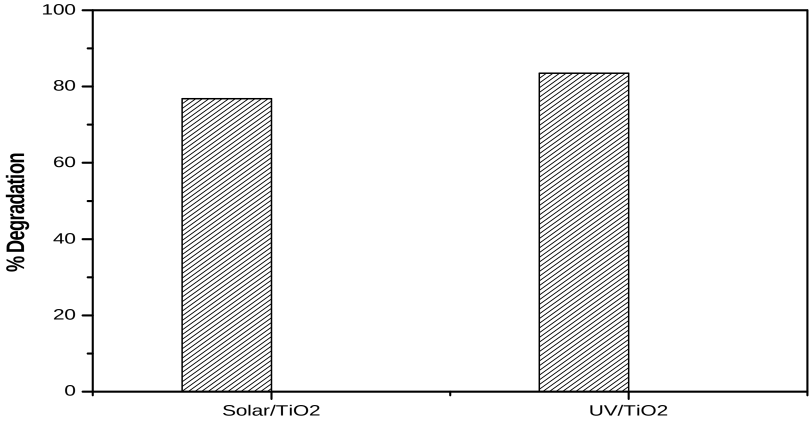

**Fig. 8.** Effect of UV/Solar light on photodegradation of PY dye (100 ppm), pH (7.80), $[TiO_2]$ = 0.5 g $L^{-1}$, Time = 3.5 h.

### *G. Dye characteristics after photocatalytic treatment*

The photocatalytic treatment of PY dye was studied under optimized conditions (pH 7.80, $TiO_2$,) with UV/$TiO_2$, Solar/$TiO_2$.Table 2 shows the parameters analyzed after 3.5 h with $TiO_2$ treatment of PY dye solution which depicts a major reduction in pollution load. These results show that percentage complete degradation of dye solution has occurred.

**Table 2. Characteristics of PY dye after photocatalytic treatment under optimized condition.**

| **S. No.** | **Parameter** | **Value** | **UV/$TiO_2$** | **Solar/$TiO_2$** |
|---|---|---|---|---|
| 1. | pH | 7.80 | 7.40 | 7.50 |
| 2. | COD (mg/L) | 65±5 | 14±483.5% | 76.8% |

## IV. CONCLUSION

The degradation rate of dyes was obviously affected by the operating parameters (illumination time, initial dye concentration, and amount of photocatalyst, light intensity, pH). Moreover, COD reduction and degradation effectively in case of ZnO over used early in 75 min where as in case of $TiO_2$ 3.5 h of reaction time required for the degradation of dye. PY dye has been successfully degraded in the presence of $TiO_2$ degradation was achieved in UV light and 87.9% degradation was achieved in solar light. Hence, it can be concluded from the observations that solar photocatalysis can be suitably and cost effectively employed for the degradation of industrial wastewater. The photocatalytic degradation followed pseudo-first order kinetics. The COD analysis revealed that complete mineralization of dyes could be achieved in longer irradiation times.

## ACKNOWLEDGMENTS

We greatly acknowledge the support obtained from Thapar University, Patiala, India and also from Nahar fabrics limited (India) for providing sample of dyes is also sincerely acknowledged.

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