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SOLAR NANOPHOTOCATALYTIC DECOLORISATION OF REACTIVE DYES USING TITANIUM DIOXIDE

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ABSTRACT

The discharge of dye-bearing wastewater from textile industries into natural streams and rivers poses several problems. Some dyes are toxic to aquatic life, may damage aesthetic nature of the environment and are difficult to be treated by conventional methods. The present work investigated the photodecolorization of reactive dyes by solar nanophotocatalysis. Nano-TiO_2 was prepared using a sol-gel method and their surface state was analyzed by X-ray diffractometer. Procion Reactive Red (H-E7B) and Procion Reactive Yellow (H-E6G) were used as model compounds. The effects of operational variables such as catalyst type and dose, pH, contact time, H_2O_2, anions ($C1^-$, SO_4^{2-} and CO_3^{2-}), solar light intensity and catalyst reuse were investigated. The complete color removal was achieved at optimum conditions of catalyst dose of 160mg/L, pH=5.5 and contact time = 95 min for dye sample H-E7B and catalyst dose of 500 mg/L, pH=7.4 and contact time = 150 min for dye sample H-E6G, respectively. At optimum conditions, COD reduced from 120 mg/L to 23 mg/L and from 108 mg/L to 17 mg/L for the two types of dye, respectively. Kinetic analyses indicated that photocatalytic decolorization rate a followed a first-order model.

Key words: Reactive dyes; Solar nanophotocatalysis; Catalyst reuse; Sol-gel; Decolorization

INTRODUCTION

Many industries use synthetic dyes to color their products. Textile dyeing industry are first ranked by the consumption of dyes. Discharge of colored wastewaters from such industries create serious problems to the environment. Color removal from textile dyeing effluents has been the target of great attention in the last few years, not only because of its toxicity but mainly due to its aesthetic effect, even at lower concentrations, comparing to many other chemicals found in wastewater (Sreedhar and Kotaiah, 2005). Because of the recalcitrant nature of synthetic dyes, conventional biological treatment processes are ineffective and adsorption and coagulation practices result in secondary pollution (Fang Han, 2009). Consequently, a more promising technology based on advanced oxidation processes (AOPs) has been studied extensively for decolorization and degradation of textile dyes. The heterogeneous photocatalytic oxidation process developed in the 1970s is of special interest especially when solar light is used. The photocatalytic decolorization of a dye is believed to take place according to the following mechanism. When a catalyst is exposed to UV radiation, electrons are promoted from the valence band to conduction band and an electron-hole pair is produced (equation 1).

$$\text{Catalyst} + h\nu \rightarrow e^-_{cb} + h^+_{vb} \qquad (1)$$

where, e^-_{cb} and h^+_{vb} are the electrons in the conduction band and the electron vacancy in the valence band, respectively. Both these entities can migrate to the catalyst surface, where they

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can enter in a redox reaction with other species present on the surface. In most cases, h^+_{vb} can react easily with surface bound H_2O to produce $^{\bullet}OH$ radicals, whereas, e^-_{cb} can react with O_2 to produce superoxide radical anion of oxygen (equations 2 and 3).

$$H_2O + h^+_{vb} \rightarrow {}^{\bullet}OH + H^+ \quad (2)$$

$$O_2 + e^-_{cb} \rightarrow O_2^{-\bullet} \quad (3)$$

This reaction prevents the combination of the electron and the hole which are produced in the first step. $^{\bullet}OH$ and $O_2^{-\bullet}$, can then react with the dye to form other species and is thus responsible for the decolorization of the dye (equations 4 – 7) (Rauf and Salman Ashraf, 2009).

$$O_2^{-\bullet} + H_2O \rightarrow H_2O_2 \quad (4)$$

$$H_2O_2 \rightarrow 2{}^{\bullet}OH \quad (5)$$

$$OH + dye \rightarrow dye_{ox} \; (k = 10^9 – 10^{10} \; 1/M.s) \quad (6)$$

$$dye + e^-_{cb} \rightarrow dye_{red} \quad (7)$$

Among the various semiconductor photocatalysts, TiO_2 has proved to be the most suitable catalyst for widespread environmental application because of its biological and chemical inertness, strong oxidizing power, non-toxicity and long-term stability against photo and chemical corrosion. Commercial Degussa P25 TiO_2 (surface area = 50 m^2/g) has been widely used as a catalyst in photodegradation of dyes. However, the photocatalytic activity of TiO_2 must be further enhanced from the point of view of practical use and commerce.

Nanophotocatalysis using nanostructured semiconductors constitute one of the emerging technologies due to its high catalytic efficiency. A number of methods for preparing Nano TiO_2 have been reported (eg. ultrasonic technique, sol-gel process and hydrothermal process). Khatee *et al.* (2009) reported 100% color removal efficiency of Acid Blue 9 dye with concentration of 20 mg/L at pH = 6.3, catalyst dose = 150 mg/L and contact time = 150 min using UV/Nano-TiO_2. Complete color removal of Acid Blue 25 with concentration of 50 mg/L was reported by Niyaz Mohammad Mahmoodi *et al.* (2006) using Nano-TiO_2 with 600 mg/L H_2O_2 dose after 140 min. Decolorization efficiency of 96% within 120 minutes of Acid Orange 20 was reported by Theodora *et al.* (2007) at catalyst concentration of 250 mg/L. The photocatalytic activity of Nano-TiO_2 was reported to be higher than micron TiO_2 (Degussa P25) in the degradation of active brilliant red X-3B (Liqun *et al.,* 2005), and methylene blue (Zhenling *et al.,* 2006).

Reactive dyes are a class of dyes with high application rate in the textile industry due to their reactivity with fibers and their colour stability. Under typical reactive dyeing conditions (pH > 10, temperature > 65°C and salt:60-100 g/L) as much as 20-50 percent of the initial mass of the reactive dye remains in the spent reactive dye bath in the hydrolyzed form which has no affinity for the fiber (Sreedhar *et al*., 2005). For this reason, they are also one of the dyes most widely reported in the literature (Neppolian *et al*., 2003). It has been extensively demonstrated that the photochemical properties of TiO_2 are strongly dependent on its crystal structure and morphology as well as grain size (Yin *et al*., 2008). This work characterized the decolorization of reactive dyes using nano-TiO_2 in suspension. Solar radiation was also employed in the systems studied. The use of solar energy to start the photochemical degradation of several organic pollutants, such as textile effluents, has been widely reported (Juliana *et al*., 2008). Although solar energy is a free, renewable and environmentally friendly energy source, it is not widely used in tropical countries like India.

In this study nanophotocatalic degradation of reactive dye using TiO_2 and solar energy was investigated.

MATERIALS AND METHODS

Titanium tetra (IV) isopropoxide, isopropyl alcohol, H_2O_2, NaCl, $NaSO_4$ and $NaCO_3$ used in this study were purchased from Merck Chemical Associates, Chennai. The solar photocatalytic decolorization was carried out in 1L glass beakers of 250mm x 150mm x 40mm dimensions. Each beaker was provided with diffuser stones, connected to an aquarium pump

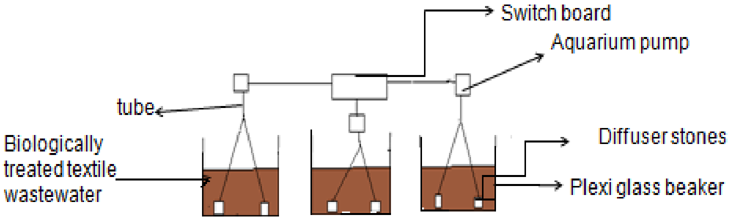

Fig. 1: Experimental set up for solar nanophotocatalysis

for continuous agitation of the sample. The sketch of the experimental set-up used in study is shown in Fig 1. Two Reactive dyes of I:Procion Reactive Red (H-E7B) and II: Procion Reactive Yellow (H-E6G) were used without further purification. Experiments were done with initial dye concentration of 40 mg/L and in the absence of TiO_2 and sunlight individually. The effect of operating variables like catalyst type (nano of micron particles), catalyst dose, pH, contact time, H_2O_2 dose, anions, light intensity and catalyst reuse on decolorization were studied. Decolorization of dye solutions were measured by using a spekol UV-Vis spectrometer. The maximum absorbance of Reactive Red (dye sample I) and Reactive Yellow (dye sample II) in the visible region of UV-Vis spectrum were 545nm and 405nm. Chemical oxygen demand (COD) was measured by open reflux method according to the standard methods (APHA, 2005). The percentage of decolorization and COD removal were calculated using equation 8.

$$\text{Decolorization or COD reduction (\%)} = [1-\frac{C}{C_0}]\times 100 \qquad (8)$$

Where C_0 is initial dye concentration or COD (mg/L) and C is final dye concentration or COD (mg/l) at a given time.

Photooxidation can be fitted reasonably well by an exponential decay curve suggesting a pseudo-first order reaction with respect to dye concentration. Kinetic pathway of color degradation is expressed by equation (9).

$$-\frac{dC}{dt} = kt \qquad (9)$$

where k is the reaction apparent rate constant (1/min); and t, the exposure time (min). This equation, after integration with initial condition $C = C_0$ for t = 0, leads to equation 10.

$$\ln\frac{C}{C_0} = -kt \qquad (10)$$

The Nano-TiO_2 was prepared by sol-gel process and characterised by X-Ray diffractometer. The powder X-ray diffraction patterns of as-synthesized and calcined samples were recorded on a Siemens D5005 diffractometer using CuK_α (λ=0.154nm) radiation. The diffractograms were recorded in the 2θ range of 0.8-10.8° with a 2θ step size of 0.01° and a step time of 10s.

The effect of catalyst dosage on color removal was studied in the range of 100-600 mg/L for Reactive dye samples I & II with 40 mg/L concentration and for a duration of 150 minutes. The effect of pH on color removal for 40 mg/L dye samples I and II was studied at an optimum catalyst dosage of 100 mg/L for dye sample I and 500 mg/L for dye sample II, respectively and for a contact time of 75 minutes. Since real textile dyeing wastewaters contain inorganic salts, in the present study, the effect of inorganic ions on the photocatalytic decolorization of dye samples I and II have been investigated with common inorganic salts such as chloride (1000 – 5000 mg/L), sulphate (500 – 5000 mg/L) and carbonate anions 50 – 400 mg/L). Since the addition of H_2O_2 might play an important role in accelerating the photocatalytic process, experiments were conducted to study the effect of H_2O_2 (dosage in the range of 1 - 4 mL/L) in the decolorization of dye samples I and II under optimum Nano-TiO_2 dosage conditions.

In order to study the effect of solar light intensity, experiments were carried out on 10 different days under varying light intensities at optimum conditions.

RESULTS

Effect of control conditions

Dark adsorption experiments (TiO_2 dosage: 500 mg/L), photolytic experiments (absence of TiO_2) and photocatalytic experiments (TiO_2 dosage = 500 mg/L) were conducted for Samples I and II of 40 mg/L concentration at the actual pH for a duration of 150 minutes. No significant decolorization was observed in dark adsorption and photolytic conditions (Fig. 2).

Comparison of micron and nano photocatalysts

Fig. 3 illustrates the percent of decolorization of dye samples I and II by using micron TiO_2 (0.4µm) and nano-TiO_2 (5.85nm) at experimental conditions (dye:40 mg/L, TiO_2:500 mg/L and 90 minutes duration). The decolorization proceeded nearly two times rapidly in the presence of nano-TiO_2 as compared with micron TiO_2.

Effect of Nano-TiO_2 catalyst dosage

Complete color removal was achieved for a catalyst dosage of 160 mg/L for dye sample I and 500 mg/L for dye sample II (Fig. 4).

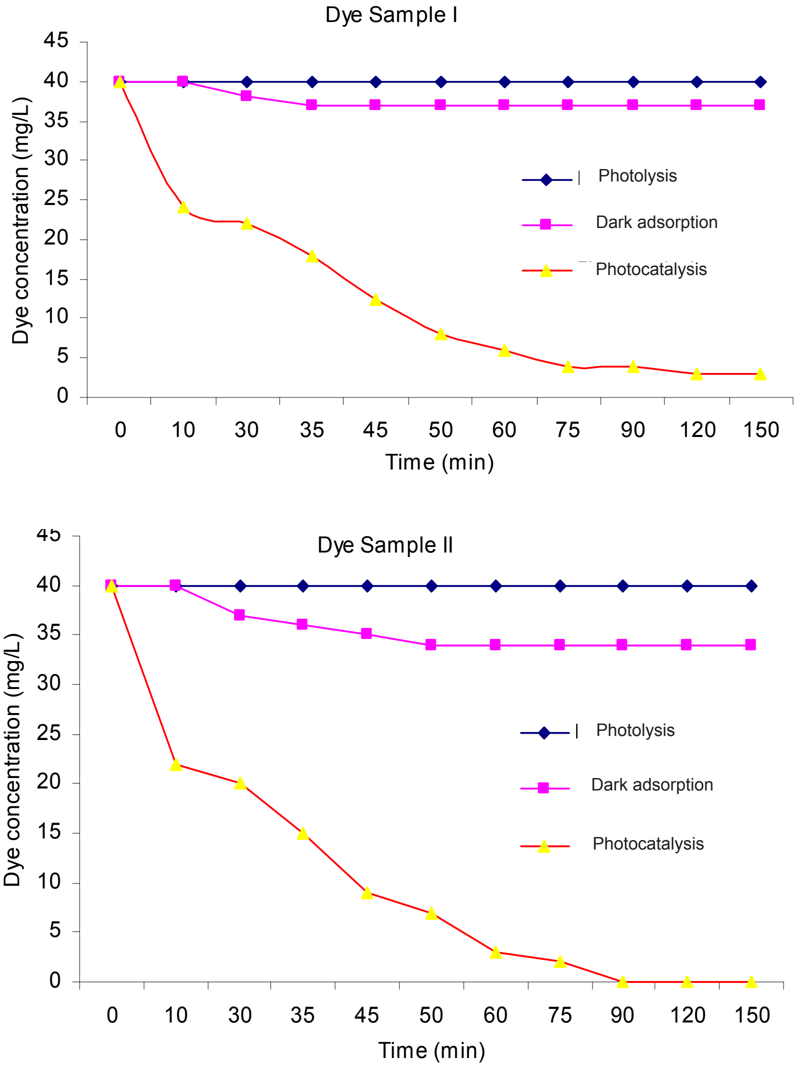

Fig. 2: Effect of control conditions on decolourisation

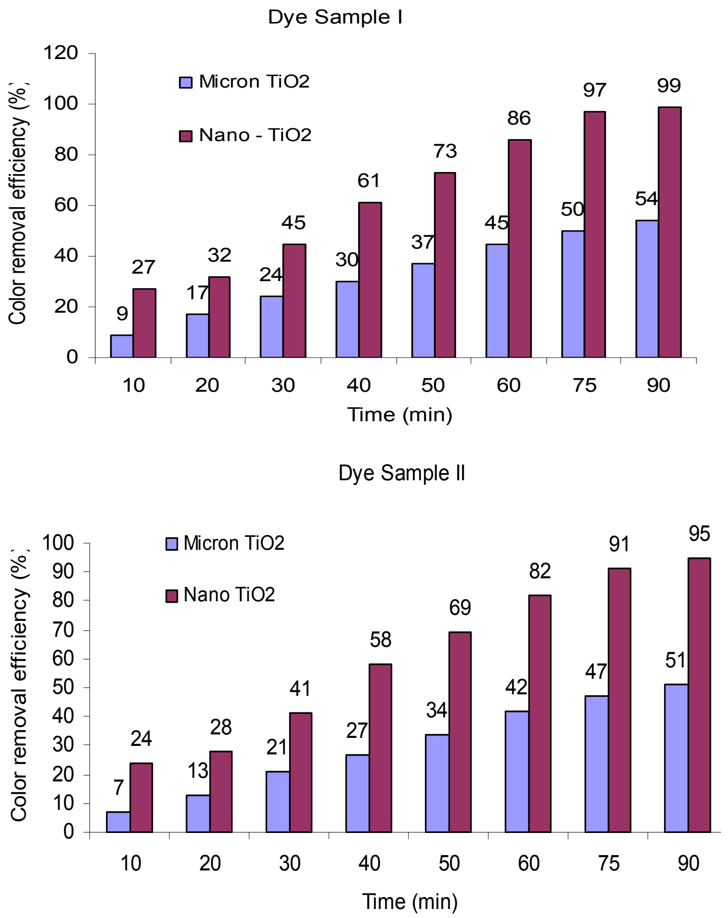

Fig. 3: Effect of catalyst type on decolorisation

Effect of pH

Fig. 5 shows the effect of pH on color removal for dye samples I and II. The maximum decolorization efficiency of dye samples I & II was observed at pH = 5.5.

Effect of inorganic Ions

The results of effect of inorganic ions are presented in Table 1. With the increase of chloride concentration (1000 – 5000 mg/l), the decolorization efficiency decreased from 87%

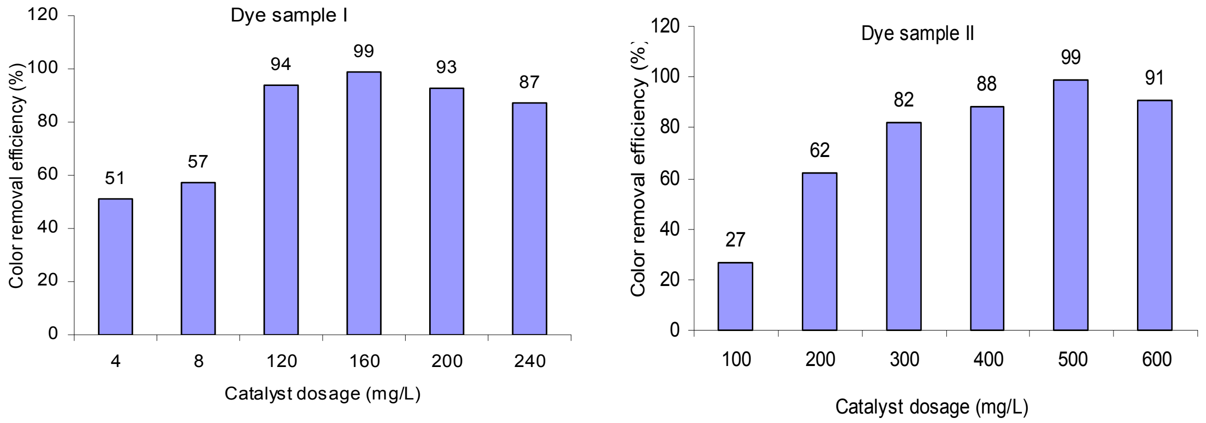

Fig. 4: Effect of catalyst dose on decolourisation

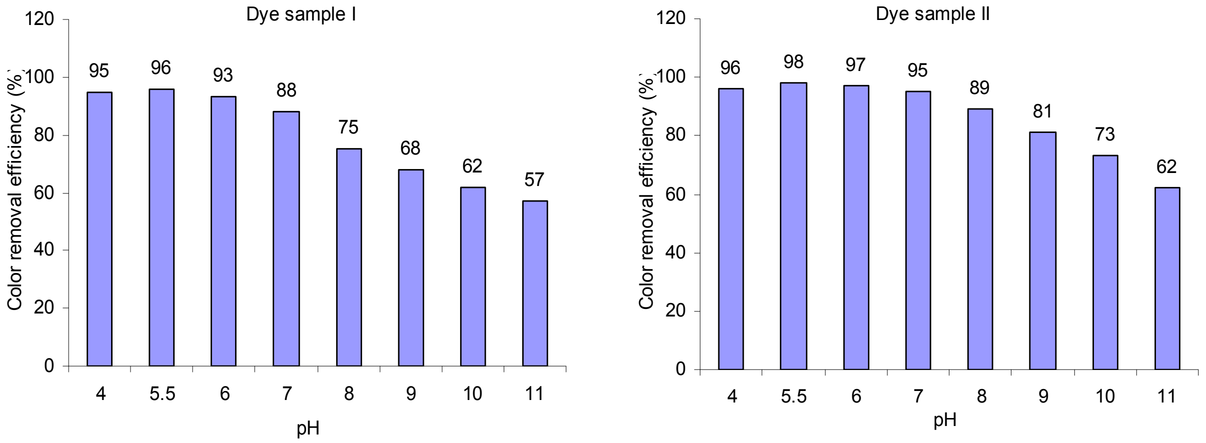

Fig. 5: Effect of pH on decolourisation

Table 1: Effects of inorganic salts

Inorganic salts	Dosage (mg/L)	Color removal efficiency (%)	
		Dye sample I	Dye sample II
Chloride	1000	87	84
	2000	76	72
	3000	67	64
	4000	55	52
	5000	48	44
Sulphate	500	86	85
	1000	79	77
	2000	71	71
	3000	64	66
	4000	51	53
	5000	42	47
Carbonate	50	85	89
	100	79	81
	200	71	76
	300	66	69
	400	53	55

to 48% and from 84% to 44% for dye samples I and II respectively. With the increase of sulphate concentration from 500 mg/L to 5000 mg/L, the decolorization efficiency decreased from 86% to 42% and 85% to 47% for dye samples I and II respectively. With the increase of carbonate concentration from 50 mg/L to 400 mg/L, the decolorization efficiency decreased from 88% to 53% and 89% and 55% for dye samples I and II respectively.

Effect of hydrogen peroxide

In the solar/TiO_2/H_2O_2 system, complete color removal was achieved within 80 min and 120 min. for dye samples I and II, respectively, whereas in solar/TiO_2 system, complete color removal occurred at 90 min and 150 min for dye samples I and II, respectively (Fig. 6).

Effect of solar light intensity

The results of effect of solar light intensity are presented in Table 2. With the increase in solar UV light for both dye samples, maximum color removal of 100% occurred at maximum solar UV light intensity of 31 W/m^2; minimum color removal of 89% for dye sample I and 85% for dye sample II occurred at minimum solar UV light intensity of 21 W/m^2.

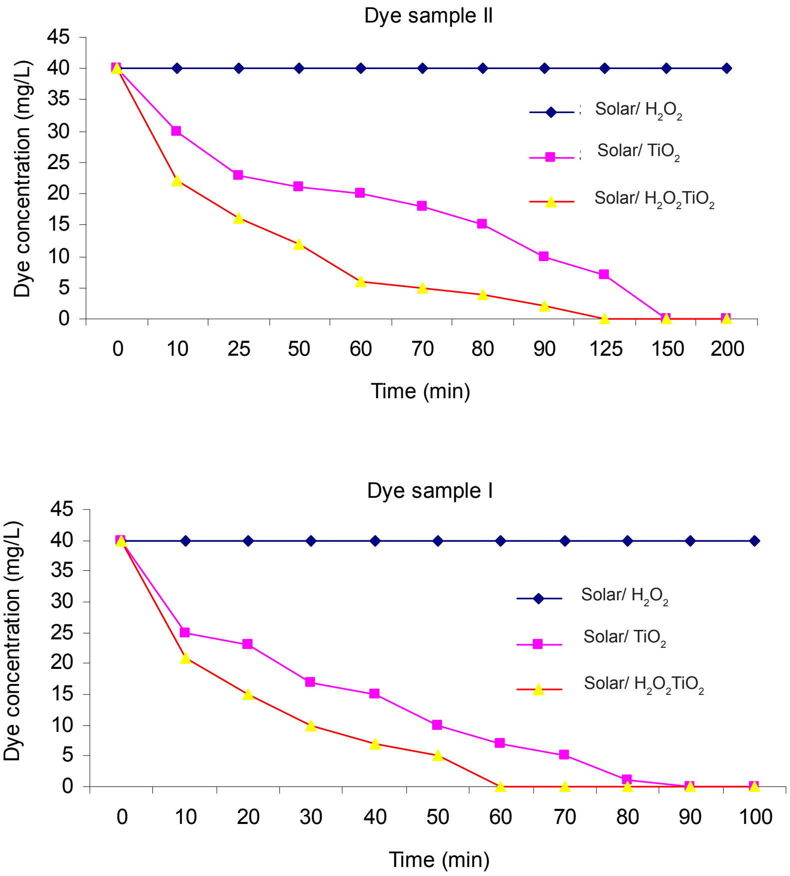

Fig. 6: Effect of hydrogen peroxide on decolorisation

DISCUSSION

This study has shown that the nano-TiO_2 photocatalyst was very effective in the decolorization and degradation (COD removal) of reactive dye samples (Procion Reactive Red (H-E7B) and Procion Reactive Yellow (H-E6G) under solar light. Negligible effect of dark adsorption clearly indicated that the reaction followed photocatalytic process and it is reported

Table 2: Effect of solar light intensity on decolorisation

Solar light intensity (Lux unit)	UV light (W/m^2)	Color removal efficiency (%)	
		Dye sample I	Dye sample II
0	0	0	8
715 x 100	21	89	85
718 x 100	22	92	88
816 x 100	24	94	91
839 x 100	25	95	92
867 x 100	26	92	96
917 x 100	28	97	96
964 x 100	29	99	98
1016 x 100	30	100	100
1023 x 100	31	100	100

that photocatalytic process do not need to occur at the catalyst surface based on the assumption that the reactive hydroxyl radicals and other oxidizing species could diffuse into solution bulk to react with organic pollutants (Arsalan *et al*., 2001).

The photoactivity nano-TiO_2 was found to be almost two times higher than that of micron-TiO_2 in the decolorization of reactive dye samples I & II; similar findings have been reported in the degradation of various dyes viz., methylene blue, Remazol Brill Blue R and Orange G (Nagaveni *et al*., 2004; Lousis, 2005).

The dosage of nano-TiO_2 plays an important role in the photocatalytic decolorization of reactive dye samples I & II. The increase in catalyst dosage beyond the optimum level (160 mg/L for dye sample I and 500 mg/L for dye sample II) in decreasing of dyes due to increase of turbidity which might reduce the light transmission through the solution. Similar findings have been reported in the treatment of Acid Blue 9 dye (Khataee *et al*., 2009), Victoria Blue dye (Mai *et al*., 2008), several organic dyes (Reeves *et al.*, 1992) and also in real textile dyeing rinse wastewaters (Kanmani and Thanasekaran, 2003).

The effect of pH on photocatalytic degradation process is still very much unresolved. In the present study, the percentage of decolorization increased with increase in pH in the acidic conditions and then decreased in alkaline condition. Similar findings were observed in the treatment of Cyanosine (Rajeev *et al*., 2008) and simulated spent reactive dye batch (Sreedhar and Kotaiah, 2005).

The Zero Point Charge (ZPC) of TiO_2 is 6.4 and its The TiO_2 surface is predominantly negatively charged when the pH is higher than the TiO_2 isoelectric point. As the pH decreases, mixture is protonated and the proportion of the positively charged surface increases. Thus, the electrical property of the TiO_2 surface varies with the pH of the dispersion. The surface of TiO_2 would be negatively, charged and adsorb cationic species easily under $pH>pH_{zpc}$ conditions while in the reverse condition it would adsorb anionic ones. However, the adsorption of the substrate onto the TiO_2 surface directly affects the occurrence of electron transfer between the excited dye and TiO_2 and further influences the degradation rate. The surface becomes positively charged, and the number of adsorption sites may decrease above the isoelectric point of TiO_2. A similar observation of the effect of the pH on the adsorption and photocatalytic reaction has been reported for Ag deposition and the degradation of formic acid (Chen *et al*., 2007).

The presence of inorganic ions in the textile dyeing wastewaters is relatively common and thus the effect of these inorganic ions in the photocatalytic decolorization of dye samples I and II was investigated. With the increase in concentration of inorganic ions, gradual decrease in color removal was observed for both the dye samples I and II. This can be explained on the basis that the presence of these ions scavenge the hole and hydroxyl radicals according to the following reactions (equations 2-5) thus causing a decrease in percent decolorization (Rauf & Salman Ashraf, 2009).

$$Cl^{-}+ h_{VB}^{+} \rightarrow Cl^{\bullet} \quad (11)$$

$$Cl^{-}+ Cl^{\bullet} \rightarrow Cl^{\bullet -} \quad (12)$$

$$CO_3^{2-}+ HO^{\bullet} \rightarrow CO_3^{\bullet}+ OH^{-} \quad (13)$$

$$SO_4^{2-}+ HO^{\bullet} \rightarrow SO_4^{\bullet -}+ OH^{-} \quad (14)$$

The hole scavenging property of chloride ion might result in the formation of chlorine atoms (eqn. 1) and might get simultaneously converted into chloride radical anion (eqn. 2) The carbonate and sulphate ions can react with hydroxyl radicals (eqns. 3 and 4) and thus the hydroxyl radical scavenging effect of these ions could result in decrease in color removal of the dye samples I and II. Similar findings have been reported by Neppolian *et al.* (2003) in the treatment of reactive yellow 17 dye and Mahvi *et al.* (2009) in the photocatalytic degradation of reactive Orange 16.

The present study clearly has shown an enhancement in the decolorization of dye samples I and II with the addition of hydrogen peroxide. Similar findings have been reported in the nano-photocatalytic degradation of Reactive textile dyes viz., Reactive Red 152 and reactive orange 107 (Mahmoodi *et al*., 2006) and Methylene blue

(Senthil Kumar *et al*., 2005). The enhancement of decolorization due to addition of H_2O_2 might be due to increase in the formation hydroxyl radicals in two ways. Firstly, the reduction of H_2O_2 at the conduction band would produce hydroxyl radicals and secondly, the self-decomposition by illumination would also produce hydroxyl radicals (Malato *et al*., 1998).

In general, the photocatalytic process is observed to be a function of light intensity. In the present study, it was observed that the increase in the intensity of solar UV light resulted in the increase in the efficiency of color removal of dye samples I and II. In the photocatalytic destruction of 30 mg/l malachite green in water using Degussa P25 TiO_2, Reeves *et al* (1992) have also observed significant increase in reaction rate as the flux increased. In the photocatalytic degradation of dichloroacetic acid (DCA) in a solar pilot plant, the rate was found to be linear with regard to light intensity (0-40 W/m^2) under similar experimental conditions. Kanmani *et al* (2003) have reported the decrease in the reaction time with increase in solar UV light intensity in the simulated textile dyeing rinse wastewaters using micron TiO_2.

The results suggest that the use of solar light irradiation could be a feasible technique for decolorization of textile dye samples and it could also become a cost effective technique at industrial scale application.

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