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Photocatalytic Degradation of Textile Dye and Wastewater

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Abstract In this study, the photocatalytic degradation of commercial azo dye (Remazol Red 133) in the presence of titanium dioxide (TiO_2) suspensions as photocatalyst was investigated. The effect of various operational parameters, such as pH of dye solution and catalyst concentration on the photocatalytic degradation process, was examined. The mineralization of dye was also evaluated by measuring the chemical oxygen demand of the dye solutions. The extent of photocatalytic degradation was found to increase with increasing TiO_2 concentration. For the Remazol Red dye solutions, a 120-min treatment resulted in 97.9% decolorization and 87.6% degradation at catalyst loading of 3 g/L. Experiments using real textile wastewater were also carried out. Textile wastewater degradation was enhanced at acidic conditions. The decolorization and degradation efficiencies for textile wastewater were 97.8% and 84.9% at pH 3.0, catalyst loading of 3 g/L, and treatment time of 120 min.

Keywords Photocatalysis · Azo dyes · Titanium dioxide · Textile wastewater

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1 Introduction

The textile industry consumes considerable amounts of water during the dyeing and finishing operations. Considering both the volume discharged and effluent composition, the wastewater generated by the textile industry is rated as one of the most polluting among all industrial sectors. Given the great variety of fibers, dyes, process aids, and finishing products in use, the textile industry generates wastewaters of great chemical complexity, diversity, and volume (Bizani et al. 2006; Secula et al. 2008).

Azo dyes are the most important class of synthetic organic dyes used in the textile industry and are therefore common industrial pollutants. They are produced in large amounts and enter the environment during the production and manufacturing processes (Sobana and Swaminathan 2007). They are characterized by the presence of one or more azo group (–N=N–) bound to aromatic rings (Aleboyeh et al. 2008). It has been reported that some of them are toxic, mutagenic, and carcinogenic compounds. Their resistance to biological and even chemical degradation makes them hazardous for the environment even at low concentration (Sahel et al. 2007). They represent about 50% of the worldwide production and correspond to an important source of contamination considering that approximately 15% of the synthetic textile dyes are lost in waste streams during manufacturing or processing operations (Silva and Faria 2003).

Traditional physical techniques (adsorption on activated carbon, coagulation by chemical agents,

ion exchange on synthetic adsorbent resins, etc.) can generally be used efficiently for the removal of dyes. Nevertheless, they are non-destructive since they just transfer organic compounds from water to solid phase, thus causing secondary pollution. Consequently, regeneration of the adsorbent materials and post-treatment of solid wastes, which are expensive operations, are needed. Chemical treatment using strong oxidants such as chlorine or ozone has led to more successful results, but they are not economically feasible due to the high dosages needed. Due to the large degree of aromatics present in dye molecules and the stability of modern dyes, conventional biological treatment methods are ineffective for decolorization and degradation. Furthermore, the majority of dyes is only adsorbed on the sludge and is not degraded (Konstantinou and Albanis 2004; Sohrabi and Ghavami 2008).

Advanced oxidation processes have been described as efficient procedures for obtaining high oxidation yields from several kinds of organic compounds. These methods are based on the generation of very reactive agents such as hydroxyl radicals ($OH^{\bullet}$) that are extremely reactive and strong oxidizing agent (E_o = 2.8 V), capable of mineralizing organic pollutants (Saien and Soleymani 2007). Among these processes, heterogeneous photocatalysis was found as an emerging destructive technology leading to the total mineralization of most of organic pollutants (Guillard et al. 2003).

The following mechanism that accounts for the photodegradation of organic species by oxidation is widely accepted. When a photocatalyst was illuminated with a photon of energy equal to or greater than its band gap width, this leads to the formation of electron/hole (e^-/h^+) pairs with free electrons produced in the empty conduction band (e_{CB}^-), leaving behind an electron vacancy or "hole" in the valence band (h_{VB}^+). If charge separation is maintained, the electron and hole may migrate to the catalyst surface where they participate in redox reactions with adsorbed species. Specially, h_{VB} may react with surface-bound H_2O or OH^- to produce the hydroxyl radical, and e_{CB} is picked up by oxygen to generate superoxide radical anion ($O_2^{\bullet -}$), as indicated in the following equations (Eqs. 1–3; Faisal et al. 2007; Qamar et al. 2005):

$$TiO_2 + h\upsilon \rightarrow e^-{}_{CB} + h^+{}_{VB} \quad (1)$$

$$O_2 + e^-{}_{CB} \rightarrow O_2^{\bullet -} \quad (2)$$

$$H_2O + h^+{}_{VB} \rightarrow OH^{\bullet} + H^+. \quad (3)$$

It has been suggested that the hydroxyl radicals ($OH^{\bullet}$) and superoxide radical anions ($O_2^{\bullet -}$) are the primary oxidizing species in the photocatalytic oxidation processes. These oxidative reactions would result in the bleaching of the dye. Alternatively, direct absorption of light by the dye can lead to charge injection from the excited state of the dye to the conduction band of the semiconductor, as summarized in the following equations (Abu Tariq et al. 2008):

$$Dye_{ads} + h\upsilon \rightarrow Dye_{ads}^{*} \quad (4)$$

$$Dye_{ads}^{*} + TiO_2 \rightarrow Dye_{ads}^{+} + TiO_2(e^-). \quad (5)$$

In the present work, the photocatalytic degradation of a reactive class mono azo dye Remazol Red 133 (RR) and textile wastewater was investigated. The influence of operational parameters on photocatalytic degradation was examined to find out the optimum conditions for efficient decolorization and degradation.

2 Experimental

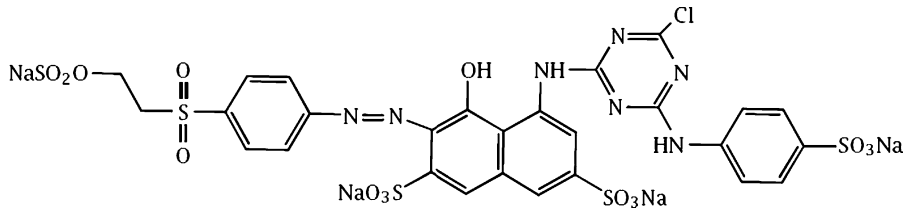
2.1 Chemicals

The commercially available azo dye RR, product of Dystar, was used as received. The chemical structure and characterization of the dye was presented in Fig. 1 and Table 1, respectively. Titanium dioxide (anatase) was used as photocatalyst and obtained from Merck. Single distilled water was used to prepare the dye solutions. Sodium hydroxide and hydrochloric acid were used to adjust the pH of dye solutions. Colored wastewater was obtained from a textile industry located in Denizli, Turkey. The characteristics of the textile wastewater were given in Table 2. It was taken right after the dye bath and was stored at 4°C in glass flasks and used without pretreatment.

2.2 Irradiation Procedure

For irradiation experiment, 150 mL aqueous solution of the dye of desired concentration was taken in the

Fig. 1 Chemical structure of Remazol Red 133 (Dizge et al. 2008)



glass beaker and the required amount of photocatalyst was added. The pH of the reaction mixture was adjusted by adding 0.1 M HCl or 0.1 M NaOH solutions. After stirring, the mixture was irradiated from the top without the glass cover with a 300-W Osram ultraviolet lamp which produces a mix of radiation very similar to that of natural sunlight. Maximum emission peaks in spectral distribution of the used light source are between 300- and 600-nm wavelength. The main emission intensity is approximately 750, 530, 600, and 340 mWm^{-2} per 1,000 lx for 350, 425, 540, and 560 nm, respectively. The aqueous suspension was magnetically stirred throughout the experiment. Samples of 5 mL were taken at different time intervals and centrifuged for 15 min at 4,000 rpm prior to analysis (Baran et al. 2008). Experiments were carried out by varying the pH of the solution (pH 3.0–9.5) and catalyst loading (0.5–3.0 g/L). In order to investigate the effectiveness of photocatalytic treatment, experiments using real textile wastewater were carried out using the same experimental procedure described above.

Table 1 Characterizations of Remazol Red 133 (Dizge et al. 2008)

Parameter	Value
Color index name	Reactive Red 198
Chromophore group	Azo
Reactive anchor systems	Monochlortriazine+ Vinylsulfone
Molar mass (g/mol)	984.2
Max absorbance, λm (nm)	518
Purity (%)	63
Water solubility at 293 K (g/L)	70
pH value (10 g/L water)	7
COD (mg/g)	540
BOD_5 (mg/g)	<10
DOC (mg/g)	120

2.3 Analysis

The decolorization of dye solutions was monitored spectrophotometrically with a UV–vis spectrophotometer (PG Instruments T60U) at 519 nm. The concentrations of the dye were calculated by calibration curve obtained from the absorbance of the dye at different concentrations. The progress of photocatalytic decolorization of textile wastewater was monitored by measuring the absorbance at 500 nm, which is the wavelength that corresponds to the maximum absorbance in the visible region. Percent decolorization was calculated relative to the initial absorbance of the untreated textile effluent. In order to determine the extent of degradation of the dye and textile effluent, chemical oxygen demand (COD) was measured. The COD of the wastewater and dye solutions were determined by the dichromate closed reflux method using Merck Themoreactor TR620 (APHA 1995, method 5220D). Percent COD reduction was calculated relative to the initial COD value of the untreated textile effluent and dye solution. The COD gives a measure of the degradation of dye and generated intermediates during the irradiation and also a measure of the oxygen equivalent of the organic

Table 2 Composition of the textile wastewater used in this study

Component	Concentration
BOD_5 (mg/L)	173
COD (mg/L)	380
pH	9.5
EC (mS/cm)	2.52
Absorbance (at 500 nm)	0.460
SS (mg/L)	37
TKN (mg/L)	19.60
Ammonium nitrogen (mg/L)	3.9
Oil and grease (mg/L)	5.40

content in a sample that is susceptible to oxidation by strong oxidant (Mahmoodi et al. 2006).

3 Results and Discussion

3.1 Photocatalytic Degradation of Remazol Red 133

3.1.1 Effect of pH

To investigate the effect of pH on the decolorization efficiency of RR, experiments were carried out at various pH values, ranging from 3.0 to 9.5, at a constant dye concentration of 100 mg/L and catalyst loading of 1 g/L. The decolorization efficiency of RR at different pH values was shown in Fig. 2. The decolorization efficiencies were 93.8%, 80.9%, and 79.5% after 120 min of irradiation for pH 3.0, 7.0, and 9.5, respectively. The highest decolorization efficiency was found at pH 3.0. The effect of pH on the photocatalytic degradation of RR was shown in Fig. 3. Increase of pH of the dye solution from 3.0 to 9.5 decreases the degradation from 61.9% to 30.9% at 90 min and from 82.5% to 52.6% at 120 min. The pH 3.0 was found to be the optimum pH for the degradation and decolorization of RR.

The pH influences the adsorption of dye molecules on the TiO_2 surface, which is an important step in photodegradation (Neppolian et al. 2002; Akpan and Hameed 2009). The point of zero charge of the TiO_2 is widely reported at pH 6.8, and the TiO_2 surface will

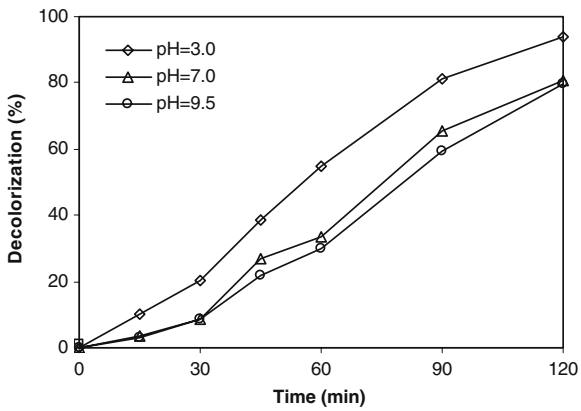


Fig. 2 Effect of pH on photocatalytic decolorization of RR (C_0 = 100 mg/L, TiO_2 = 1 g/L)

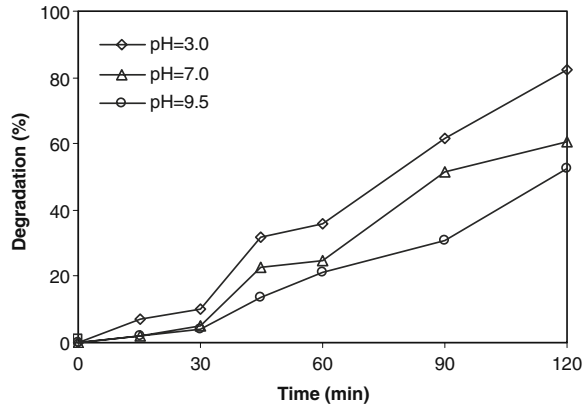


Fig. 3 Effect of pH on photocatalytic degradation of RR (C_0 = 100 mg/L, TiO_2 = 1 g/L)

remain positively charged in acidic medium (pH<6.8) and negatively charged in alkaline medium (pH>6.8), as shown in the following equations (Muruganandham and Swaminathan 2004):

$$\mathrm{pH} < \mathrm{pzc} : \mathrm{Ti-OH} + \mathrm{H^+} \leftrightarrow \mathrm{TiOH_2}^+ \quad (6)$$

$$\mathrm{pH} > \mathrm{pzc} : \mathrm{Ti-OH} + \mathrm{OH^-} \leftrightarrow \mathrm{TiO^-} + \mathrm{H_2O} \quad (7)$$

The pH changes can thus influence the adsorption of dye molecules onto the TiO_2 surface, an important step for the photooxidation to occur (Sohrabi and Ghavami 2008). Since the dye has a sulfonate group in its structure, which is negatively charged, the acidic solution favors the adsorption of the dye onto photocatalyst surface; thus, the photodegradation efficiency increases (Neelavannan et al. 2007).

It can be seen that the decolorization rate of the dye was faster than its degradation rate, identified by COD removal. The color of azo dyes is determined by the azo bonds and their associated chromophores and auxochromes. Azo bonds can be oxidized by positive hole or hydroxyl radical or reduced by electron in the conduction band. The cleavage of –N=N– bonds leads to the decoloration of the dyes (Rauf and Salman Ashraf 2009). Muruganandham and Swaminathan (2006) reported that the fast decolorization of the dye is due to the initial electrophilic cleavage of its chromophoric azo (–N=N–) bonds attached to the naphthalene ring. The degradation of the aromatic part of the dye molecule produced a number of intermediate com-

pounds, and the removal of these intermediates took a longer time.

3.1.2 Effect of Catalyst Concentration

The effect of catalyst concentration on the removal of RR was investigated in the range of 0.5–3 g/L of the catalyst, at 100 mg/L dye concentration, and at pH 3.0. The effect of catalyst concentration on decolorization was shown in Fig. 4. It was found that the increase in the amount of TiO_2 increased the decolorization of the dye, achieving maximum decolorization at the TiO_2 concentration equal to 3 g/L. The decolorization efficiencies were 90.5%, 93.8%, 96.3%, and 97.9% after 120 min of irradiation at catalyst concentrations of 0.5, 1, 2, and 3 g/L. Figure 5 shows the degradation of RR at different catalyst concentrations. After 120 min of irradiation, the COD removal efficiencies were 72.2%, 77.3%, 83.5%, and 87.6% at catalyst concentrations of 0.5, 1, 2, and 3 g/L, respectively. The optimum concentration of the catalyst for efficient decolorization and degradation was found to be 3 g/L.

The observed enhancement in decolorization and degradation is probably due to an increased number of available adsorption and catalytic sites on TiO_2. As the catalyst concentration increases, the number of photons absorbed and the number of dye molecules adsorbed are increased owing to an increase in the number of catalyst particles. The density of particles in the area of illumination also increases, and so the degradation rate is enhanced

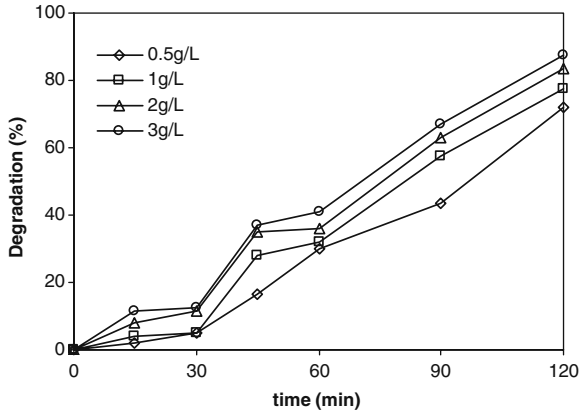


Fig. 5 Effect of catalyst concentration on photocatalytic degradation of RR (C_0 = 100 mg/L, pH = 3.0)

(Akbal 2005; Muruganandham et al. 2006; Ghaly et al. 2007).

3.2 Photocatalytic Degradation of Textile Wastewater

3.2.1 Effect of pH

The effect of pH on decolorization and degradation efficiency of the textile wastewater was investigated at pH 3.0, 7.0, and 9.5. The decolorization of textile wastewater as a function of irradiation time was given in Fig. 6. It can be seen that the decolorization efficiency was higher at low pH. After 120 min of reaction, the decolorization efficiencies were 97.8% at pH 3.0, 85.6% at pH 7.0, and 96.5% at pH 9.5. The decolorization proceeds rapidly at pH 3.0, and 81.3%,

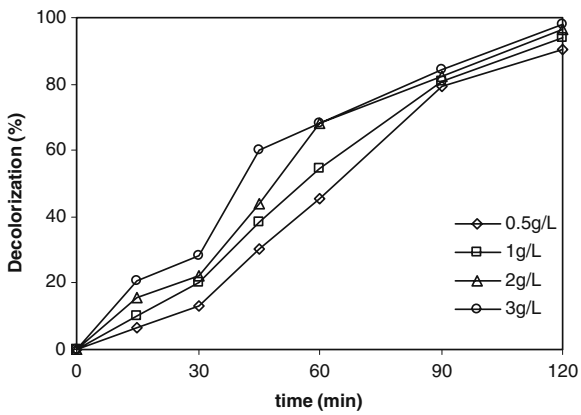


Fig. 4 Effect of catalyst concentration on photocatalytic decolorization of RR (C_0 = 100 mg/L, pH = 3.0)

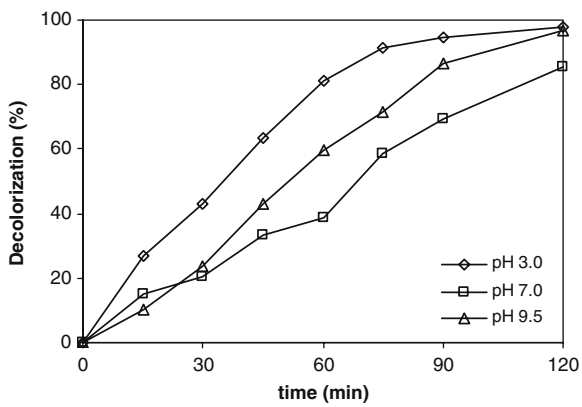


Fig. 6 Effect of pH on photocatalytic decolorization of textile wastewater (TiO_2 = 1 g/L)

94.6%, and 97.8% decolorization were attained after 60, 90, and 120 min of irradiation, respectively.

As the reduction of COD reflects the extent of degradation, the percentage change in COD was determined for textile wastewater. The COD removal as a function of irradiation time was given in Fig. 7. As can be seen, COD removal exhibited a similar trend to the color removal. After 120 min of irradiation, the COD removal at pH 3.0, 7.0, and 9.5 were 75.7%, 64.5%, and 32.9%, respectively. The pH 3.0 was found to be the optimum pH for the degradation and decolorization of textile wastewater. The decolorization rate of the textile wastewater was faster than its degradation rate. After 120 min of irradiation, in the presence of 1 g/L TiO_2 at pH 3.0, 7.0, and 9.5, the decolorization efficiencies were 97.8%, 85.7%, and 96.5%. Corresponding COD removal efficiencies after 120 min of irradiation were 75.7%, 64.5%, and 32.9%.

The higher photocatalytic degradation efficiency under acidic pH can be explained as follows: at pH values lower than about 6.8, which is the point of zero charge for TiO_2, the TiO_2 surface becomes positively charged, while at pH values greater than about 6.8, it becomes negatively charged (Martins et al. 2006). The dyes found in the wastewater have sulfonic groups which are negatively charged. Therefore, acidic conditions would favor the electrostatic attraction between the positively charged TiO_2 surface and the reactive dyes, which would result in increased adsorption and consequently in increased degradation of dyes. Pekakis et al. (2006) reported that both the decolorization and degradation efficiency of textile wastewater were higher in acidic conditions.

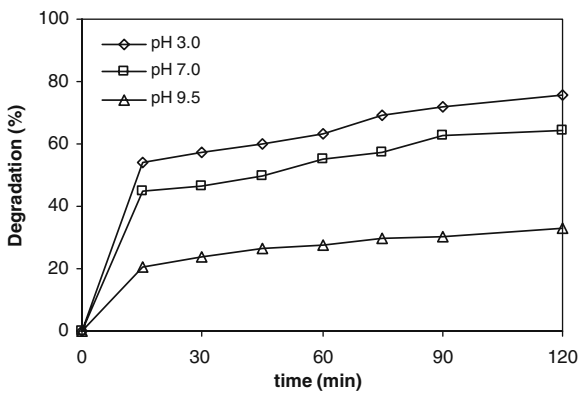


Fig. 7 Effect of pH on photocatalytic degradation of textile wastewater (TiO_2 = 1 g/L)

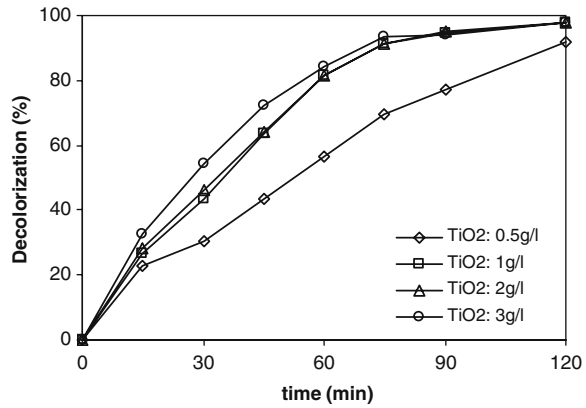


Fig. 8 Effect of catalyst concentration on photocatalytic decolorization of textile wastewater (pH 3.0)

3.2.2 *Effect of Catalyst Concentration*

In order to determine the effect of catalyst loading, the experiments were performed by varying catalyst concentration from 0.5 to 3.0 g/L at pH 3.0. The decolorization efficiency as a function of catalyst loading was shown in Fig. 8. It was found that after 120 min of irradiation, decolorization was 91.7% at a catalyst concentration of 0.5 g/L and increased to 97.8% with increasing catalyst concentration to 1 g/L. Only a slight enhancement was observed when TiO_2 concentration further increased up to 3 g/L. At a catalyst concentration of 1 g/L, the decolorization efficiencies were 81.3%, 94.6%, and 97.8% after 60, 90, and 120 min of irradiation, respectively.

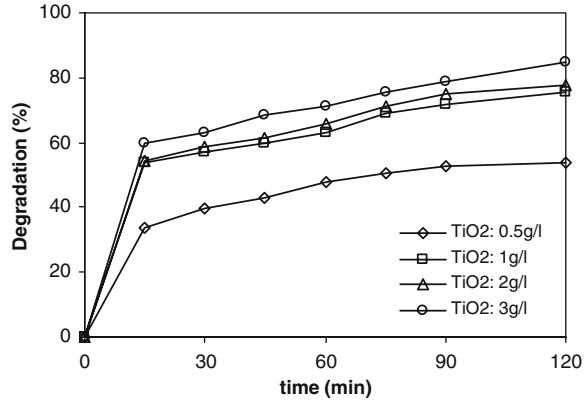


Fig. 9 Effect of catalyst concentration on photocatalytic degradation of textile wastewater (pH 3.0)

Figure 9 shows a decrease in COD values of textile wastewater at catalyst concentrations in the range of 0.5–3 g/L and pH 3.0. The COD removal increased with increasing catalyst concentration and irradiation time. After 120 min of irradiation, the COD removal efficiency was 53.9%, 75.7%, 77.6%, and 84.9% at catalyst concentrations of 0.5, 1, 2, and 3 g/L, respectively. The optimum amount of catalyst loading was found to be 3 g/L for the degradation and decolorization of textile wastewater. At a catalyst concentration of 3 g/L, COD removal efficiencies were 59.9% at 15 min, 71% at 60 min, and 84.9% at 120 min.

The decolorization and degradation rate of textile wastewater was found to increase with the increase in catalyst concentration, which is the characteristic of a heterogeneous photocatalyst, and the results are in agreement with earlier studies (Kansal et al. 2007; Baran et al. 2008). The number of photons absorbed and the number of dye molecules adsorbed are increased with the increase in catalyst concentration, thereby enhancing the rate of degradation. Initially, the degradation is fast and at the end of the photocatalytic process the removal rate is slow. This is due to the formation of intermediate compounds in the dye degradation. The competition of the intermediate compounds with the parent molecules in the photocatalytic degradation process slows down the degradation rate.

4 Conclusion

Photocatalytic degradation using TiO_2 was successfully applied for the degradation of textile dye (RR) and wastewater. The results indicated that the degree of degradation of RR was obviously affected by the catalyst concentration and pH. The decolorization and degradation efficiency was increased significantly by increasing the amount of catalyst. The results indicated that during the photocatalytic degradation of RR and textile wastewater, the decolorization rate was faster than the degradation rate. The decolorization efficiency of RR was 97.9% at 3 g/L of catalyst loading and pH 3.0 during a 120 min irradiation. The COD removal of 87.6% was attained at the same time. About 84.9% of the COD and 97.8% of the color of the textile wastewater were removed after 120 min of irradiation at pH 3.0 and 3 g/L of catalyst loading.

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