Photocatalytic degradation of Direct Red 23 dye using UV/TiO$_2$: Effect of operational parameters

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Abstract

In this study, the photocatalytic degradation of Direct Red 23 (Scarlet F-4BS) was investigated in UV/TiO$_2$ system. The effect of catalyst loading and pH on the reaction rate was ascertained and optimum conditions for maximum degradation were determined. The results obtained showed that acidic pH is proper for the photocatalytic removal of Direct Red 23. In addition, the effects of several cations (Cu^{2+}, Al^{3+}, Cr^{3+}, and Sn^{4+}) and anions (BiO$_3{}^-$, SO$_4{}^{2-}$, and CN$^-$) and C$_2$H$_5$OH were examined in this photocatalytic process. On the order hand, three types of catalysts (Fe$_2$O$_3$, SnO$_2$, and ZnO) were compared with TiO$_2$. After 90 min reaction, the relative decomposition order established was UV/TiO$_2$ > UV/SnO$_2$ > UV/Fe$_2$O$_3$ > UV/ZnO.
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Keywords: Direct Red 23 dye; UV/TiO$_2$; Photocatalysis; Wastewater treatment

1. Introduction

Dyes are extensively used in the textile industry, photocatalytic industry, coating industry, and photochemical application. Treatment of colored wastewater from textile or other industries is a serious problem that has attracted the attention of many researchers during last decades. In general, the methods for the treatment of wastewater containing dyes can be divided into two main groups [1]: (I) chemical or physical methods of dye removal, which refer to the process called decoloration and (II) dye removal by means of biodegradation. Physical methods of decoloration include different precipitation methods (coagulation, flocculation, and sedimentation), adsorption (on activated carbon, biological sludge, and silica gel), filtration, reverse osmosis and etc. Among chemical methods of dye removal, there are processes such as reduction, oxidation, compleximetric methods, ion exchange and neutralization. Biological treatment can be conducted in the presence or absence of oxygen. Thus it can be differentiated as aerobic process and the anaerobic one [1].

Each of the methods has some disadvantages. Physical methods are usually non-destructive, and the post-treatment of the solid wastes is necessary and expensive. Chemical treatment using strong oxidants such as chlorine or ozone has led to more successful results, but they are not economically feasible due to high dosages needed. Biological treatment does not work efficiently due to high resistance of synthetic dyes to aerobic degradation of organic compounds. UV radiation in presence of heterogeneous photocatalysis has been found promising for the degradation of azoreactive dyes [2,3]. Photocatalysis using a semiconductor is an alternative to conventional methods. Of all the various semiconductors used for the process, titanium dioxide has essentially proved itself to be the best material for environmental purification because of its many desirable properties. TiO$_2$ is a cheap, readily available material, highly stable chemically and the photogenerated holes are highly oxidizing. In addition, TiO$_2$ is capable of oxidation of a wide range of organic compounds into harmless compounds such as CO$_2$ and H$_2$O [4]. Lignin wastewater was decolorized by the use of photochemical UV/TiO$_2$ process [5]. The data obtained in this study demonstrate that the UV/TiO$_2$ process is effective in oxidizing the lignin and the combined UV/TiO$_2$ treatment can achieve better removal of color than the UV treatment alone. It's basic efficiency can be enhanced by doping [6,7].

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In this work, Direct Red 23 (Scarlet F-4BS) was selected for study. The mechanism of decolorization and degradation of this dye by ozonation combined with sonolysis was previously studied by Song et al. [8]. The main objective of our work is photocatalytic degradation of Direct Red 23 by TiO_2, and examining the influence of various parameters on the photocatalytic degradation. A second objective was to examine the effect of common anions as (BiO_3^-, SO_4^{2-}, and CN^-) and cations as (Cu^{2+}, Al^{3+}, Cr^{3+}, and Sn^{4+}) that are present in the real samples. Degradation and decolorization rates versus irradiation time were determined and the possible effects of anions and cations were evaluated. In addition, the effects of C_2H_5OH on the photocatalytic process were examined. On the order hand, three types of catalysts, Fe_2O_3, SnO_2, and ZnO) were evaluated as well.

2. Experimental

2.1. Materials

Direct Red 23 (Scarlet F-4BS) was obtained from Alvan Sabet Co. and was used without further purification. The characteristics of the dye were provided as diazo type. Titanium dioxide (Merck) with a surface area of $4.86\,m^2\,g^{-1}$, was used in all experiments according to the manufacturer's specifications without further treatment. Other photocatalysts such as SnO_2, Fe_2O_3 and ZnO were used from Merck too. $CuCl_2$, $CrCl_3$, $AlCl_3$, $SnCl_4$, NaCN and Na_2SO_4 (Merck) salts and C_2H_5OH (Merck) were used as purchased. Adjustment of pH of the dye solutions prior to degradation was carried out with NaOH or H_2SO_4 from Merck.

Deionized distilled water was used in all experiments.

2.2. Photoreactor

The apparatus employed in the photocatalytic experiments consists of the light source and the photoreactor. The setup consists of a UV chamber of $40\,cm \times 70\,cm \times 70\,cm$ dimensions equipped with a 40 W UV lamp (Philips), fitted on the top of the chamber. An exhaust fan is fitted on the sidewall of the chamber to keep temperature unchanged. The reactor used is cylindrical in shape and made of borosil glass, with an approximate capacity of 125 mL. The reactor is placed on the stirrer.

2.3. Procedure and analysis

The batch experiments were carried out with 100 mL dye solutions prepared in appropriate concentrations with deionized water. Dye solutions were stirred after adding the catalyst. Five milliliter sample suspensions were withdrawn at regular intervals and were immediately centrifuged at 3500 rpm for 10 min to completely remove catalyst particles. The progress of photocatalytic decolorization was monitored through measuring the absorbance of the solution samples by UV-Vis spectrophotometer (Bio-TEK model no. 992), at $\lambda_{max} = 505\,nm$. For exploring the effect of pH, the solution's pH was initially adjusted by adding 0.01 N NaOH or 0.01 N H_2SO_4 and by controlling with a pH meter (Horiba-F12). Before determining optimum pH,

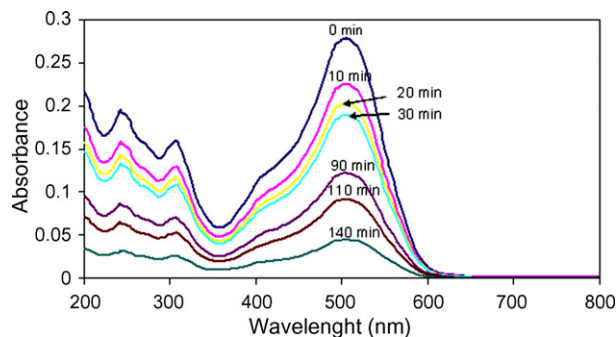
Fig. 1. Spectral changes that occur during the photocatalytic degradation of aqueous solution of Direct Red 23: pH 6.8, $[TiO_2] = 2\,g\,L^{-1}$, $C_0 = 10\,ppm$.

the experiments were carried out at the original pH of the dye solution (pH 6.8).

The percentage of degradation was calculated by using the equation given below:

$$\text{Degradation}\,(\%) = \frac{C_0 - C}{C_0} \times 100 \qquad (1)$$

In which C_0 is the initial dye concentration and C is the dye concentration after the treatments.

3. Results and discussion

3.1. Dye degradation and decolorization – TiO_2 suspensions

The time dependent electronic absorption spectrum of Direct Red 23 dye during photoirradiation was presented in Fig. 1. After 140 min of irradiation under UV light in a TiO_2 aqueous suspension, 83.58% of dye was decomposed and decolorization of solution was observed. Besides, no new bands appear in the UV-Vis region due to the reaction intermediates formed during the degradation process. In order to study the effect of UV/TiO_2 system in elimination dye, two other experiments were also carried out, one in the dark and only in present of TiO_2 and the other in absent of TiO_2 under UV irradiation. Both experiments didn't involve elimination of dye molecules (Fig. 2). It is well documented that the absorption of photons possessing energy equal to or higher than that of the semiconductor (3.2 eV for
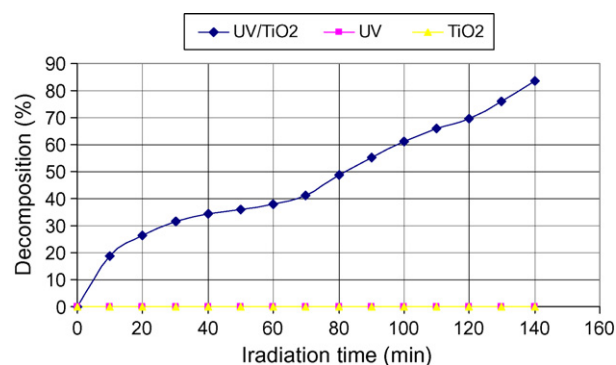

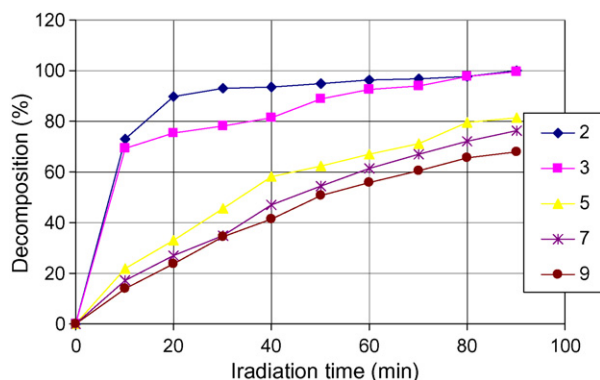Fig. 2. Change in decomposition% of aqueous solution of Direct Red 23 as a function of irradiation time: pH 6.8 $[TiO_2] = 2\,g\,L^{-1}$, $C_0 = 10\,ppm$.

Fig. 3. Change in decomposition% of aqueous solution of Direct Red 23 as a function of pH: $[TiO_2] = 2\,g\,L^{-1}$, $C_0 = 10\,ppm$.

TiO_2) causes charge separation:

$$TiO_2 + h\nu \rightarrow TiO_2(e^-) + TiO_2(h^+) \tag{2}$$

The photogenerated holes may then react with adsorbed dye and oxidize the dye molecule by the formation of hydroxyl radicals. The photo-produced electrons in the conduction band react with the adsorbed oxygen to produce reactive radicals to yield the reactive oxygen species.

3.2. pH effect

The wastewater from textile industries usually has a wide range of pH values. Further, the generation of hydroxyl radicals is also a function of pH. Thus, pH is an important parameter in photocatalytic reactions. Therefore, the degradation of dye was studied at different pH ranging from 2 to 9. In all the experiments, pH was adjusted by adding appropriate amounts of NaOH or H_2SO_4 solutions. The degradation rate for the decomposition of dye as a function of reaction pH was shown in Fig. 3. The degradation rate for the dye decreased with the increase in reaction pH and highest efficiency was observed at pH 2. At this pH, 99.83% of dye was decomposed after 90 min (Fig. 4). The photo-oxidation process can therefore be carried out in acidic medium. Similar observations have been made by other researchers for dyes and several other types of pollutants [2,5,9–11].
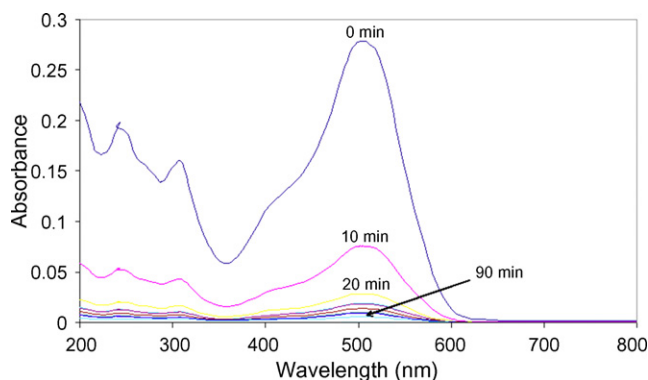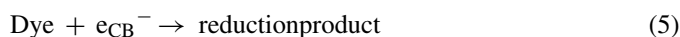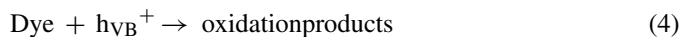

Fig. 4. Spectral changes that occur during the photocatalytic degradation of aqueous solution of Direct Red 23: pH 2, $[TiO_2] = 2\,g\,L^{-1}$, $C_0 = 10\,ppm$.

In reality, the interpretation of pH effects on the efficiency of dye photodegradation process is a very difficult task because three possible reaction mechanisms can contribute to dye degradation, namely, hydroxyl radical attack (3), direct oxidation by the positive hole (4) and direct reduction by the electron in the conducting band (5) [12]. It appears that the effect of pH on degradation of pollutants is variable and controversial since the positive holes are considered as the major oxidation species at low pH whereas hydroxyl radicals are considered as the predominant species at neutral or high pH levels [13].

$$Dye + OH^\bullet \rightarrow degradation product \tag{3}$$

$$Dye + h_{VB}^+ \rightarrow oxidation products \tag{4}$$

$$Dye + e_{CB}^- \rightarrow reduction product \tag{5}$$

Since the influence of pH depends on the type of dye, on the characteristic of textile water and on properties of TiO_2 surface, its effect on the photocatalytic efficiency must be accurately checked before any application.

According to literature reports [14,15], the pH of the solution significantly affects TiO_2 activity, including the charge on the particles, the size of the aggregates it forms and the positions of the conductance and valence bands. The point of zero charge (pzc) of the TiO_2 is widely reported at pH 6 and the TiO_2 surface will remain positively charged in acidic medium (pH < 6.25) and negatively charged in alkaline medium (pH > 6.25), because the photocatalyst can be protonated and deprotonated under acidic and alkaline conditions respectively, as shown in the following equations:

$$TiOH + H^+ \rightarrow TiOH_2^+ \tag{6}$$

$$TiOH + OH^- \rightarrow TiO^- + H_2O \tag{7}$$
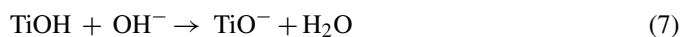
pH changes can thus influence the adsorption of dye molecules onto the TiO_2 surface, an important step for the photo-oxidation to occur. So, at pH 2, a strong adsorption of Red 23 on the TiO_2 particles is observed as a result of the electrostatic attraction of the positively charged TiO_2 with the dye.

3.3. Effect of catalyst loading

In order to determine the optimal amount of photocatalyst, some experiments were performed at pH 2 by varying the amount of catalyst from 2.0 to $5.0\,g\,L^{-1}$. The effect of TiO_2 loading on the rate of degradation is shown in Fig. 5. As seen, the optimum catalyst concentration for degradation of Direct Red 23 dye is $4.0\,g\,L^{-1}$. It is observed that rate increases with increase in catalyst concentration from 2.0 to $4.0\,g\,L^{-1}$. This is probably due to increase in the number of TiO_2 particles, which increases the number of photon absorbed and dye molecule absorbed. Increase of the catalyst concentration more than $4.0\,g\,L^{-1}$ results in the decrease of degradation rate. This phenomenon may be explained by aggregation of TiO_2 particles at high concentrations causing a decrease in the number of surface active sites and increase in opacity and light scattering of TiO_2 particles at high concentration loading to decrease in the passage of irradiation through the sample.
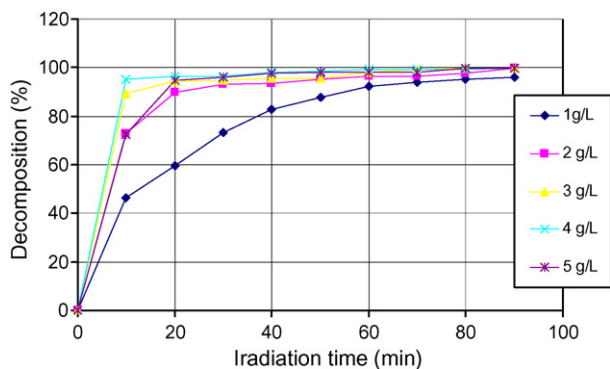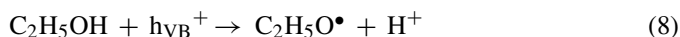
Fig. 5. Change in decomposition% of aqueous solution of Direct Red 23 as a function of catalyst loading: pH 2, $C_0 = 10$ ppm.

3.4. Effects of C_2H_5OH

Experiments were performed to study the variations in the rate of degradation at different C_2H_5OH concentration ranging from 1 to 3% (v/v) at the natural middle pH 2 and $4\,g\,L^{-1}$ of TiO$_2$. It could be seen from Fig. 6 that the degradation rate appeared to decrease with increasing C_2H_5OH concentration. One possible reason for decrease of the reaction rate would be the decrease of the concentration of OH radicals because alcohol accepts a photogenerated hole from a valence band and forms C_2H_5O radical, according to Eq. (8). It also acts as a scavenger as shown in Eqs. (9) and (10):

$$C_2H_5OH + h_{VB}^{+} \rightarrow C_2H_5O^{\bullet} + H^{+} \tag{8}$$

$$C_2H_5O^{\bullet} + 2OH^{\bullet} \rightarrow C_2H_5OH + HO_2^{\bullet} \tag{9}$$

$$HO_2^{\bullet} + OH^{\bullet} \rightarrow H_2O + O_2 \tag{10}$$

3.5. Effects of cations and anions

The effects of several cations (Cu^{2+}, Al^{3+}, Cr^{3+}, Sn^{4+}) and anions (BiO_3^{-}, SO_4^{2-}, CN^{-}) are examined on this photocatalytic process. It could be seen from Fig. 7 (a and b). That the degradation rate appeared to decrease by adding $0.001\,g\,L^{-1}$ of cations and anions but the effect of anions are negligible. The reasons are probably due to redox reactions of ions on the surface of catalyst. As BiO_3^{-} and CN^{-} anions are oxidized at catalyst surface, they compete with dye. However, as the reaction took place
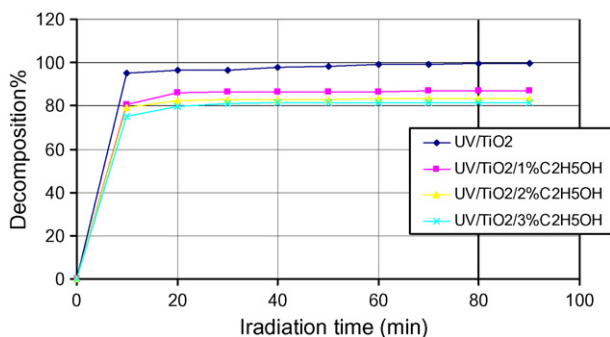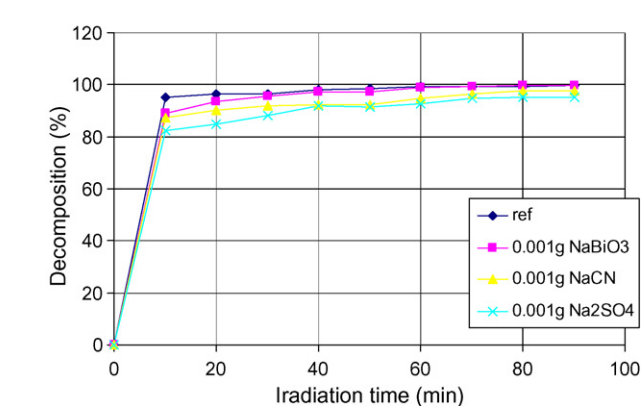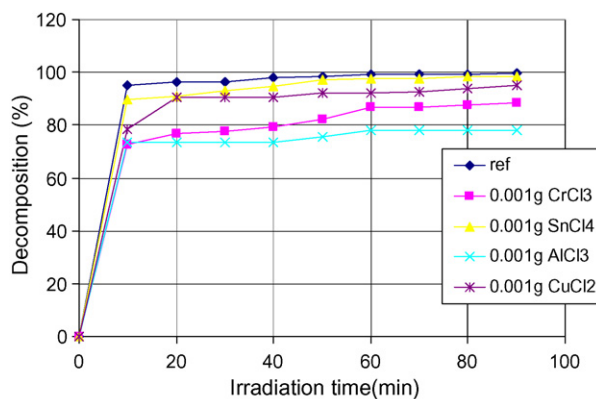

Fig. 7. Comparison of degradation rate for the decomposition of Direct Red 23 in the presence of (a) cations (b) anions: pH 2, [TiO$_2$] = $4\,g\,L^{-1}$, $C_0 = 10$ ppm.

at pH 2, these anions are protonated and neutralized. Therefore, they cannot compete with dye for photocatalytic oxidation.

3.6. Comparison of different photocatalysis

In view of the advantages of titanium dioxide in the heterogeneous photocatalysis, we tested the photocatalytic activity of three different commercially available photocatalysis on the degradation rate of Red 23. The degradation rates for the decomposition of the dye with initial concentrations of $10\,mg\,L^{-1}$ in the presence of different types of photocatalysis are shown in Fig. 8.

The photocatalyst of TiO$_2$ was found to be more efficient in degradation of the dye and ZnO exhibits negligible catalytic

Fig. 6. Change in decomposition% of aqueous solution of Direct Red 23 as a function of C_2H_5OH concentration: pH 2, [TiO$_2$] = $4\,g\,L^{-1}$, $C_0 = 10$ ppm.
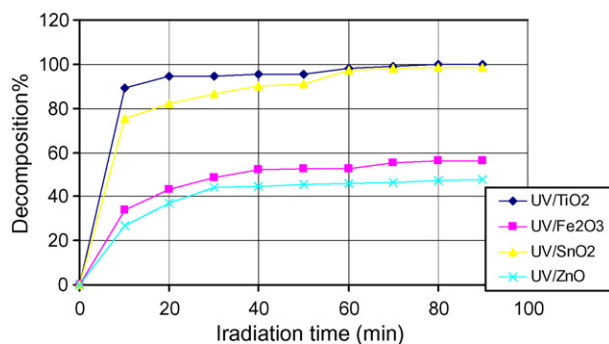

Fig. 8. Comparison of degradation rate for the decomposition of Direct Red 23 in the presence of different photocatalysts: pH 2, catalyst loading = $4\,g\,L^{-1}$, $C_0 = 10$ ppm.

activity compared to the other catalysts used in this study. This phenomenon is attributed to the band gap energy of catalyst, redox potentials and rates of these redox reactions.

For desired reaction, the energy separation (band gap) between e− and h+ must be larger than the energy required and the redox potentials of the e− and h+ (thus the position of CB and VB) must be suitable for inducing redox processes. In addition, the rates of these redox reactions must be faster than or at least fast enough to compete with the e− and h+ recombination [2].

4. Conclusion

In this study, photocatalytic decolorization of an azoreactive textile dye, Direct Red 23, was investigated by the use of TiO_2 powder catalyst. Also, three types of catalysts, Fe_2O_3, SnO_2 and ZnO were compared with TiO_2. The observations clearly demonstrate the importance of choosing the optimum degradation parameters to obtain a high degradation rate. They are affected by the solution pH in a similar manner, exhibiting maxima at pH 2. The dye decomposition rate increases with the TiO_2 suspension concentration up to $4 \, g \, L^{-1}$, and then decreases with increasing TiO_2 suspension concentration. At lower loading levels, photonic adsorption controls the reaction extent due to the limited catalyst surface area, while at higher loading levels; light scattering by catalyst particles predominates over photonic adsorption. The degradation rate decreases with increasing C_2H_5OH concentration. The lower efficiency of degradation in presence of alcohol could be attributed to decrease the concentration of OH radicals. The photocatalyst of TiO_2 was found to be more efficient for the degradation of the dye as compared to other catalysts used in this study. After 90 min reaction, the relative decomposition order established was: $UV/TiO_2 > UV/SnO_2 > UV/Fe_2O_3 > UV/ZnO$.

References

[1] Y.M. Slokar, A. Majcen Le Marechal, Methods of decoloration of textile wastewaters, Dyes Pigments 37 (1998) 335–356.

[2] M. Abu Tariq, M. Faisal, M. Muneer, Semiconductor-mediated photocatalysed degradation of two selected azo dye derivatives, amaranth and bismarck brown in aqueous suspension, J. Hazard. Mater. 127 (2005) 172–179.

[3] E. Bizani, K. Fytianos, I. Poulios, V. Tsiridis, Photocatalytic decolorization and degradation of dye solutions and wastewaters in the presence of titanium dioxide, J. Hazard. Mater. 136 (2006) 85–94.

[4] D. Chatterjee, S. Dasgupta, Visible light induced photocatalytic degradation of organic pollutants, J. Photochem. Photobiol. C 6 (2005) 186–205.

[5] C. Chang, Y. Ma, G. Fang, A. Chao, M. Tsai, H. Sung, Decolorizing of lignin wastewater using the photochemical UV/TiO_2 process, Chemosphere 56 (2004) 1011–1017.

[6] G. Liu, X. Zhang, Y. Xu, X. Niu, L. Zheng, X. Ding, Effect of $ZnFe_2O_4$ doping on the photocatalytic activity of TiO_2, Chemosphere 55 (2004) 1287–1291.

[7] Y. Liu, X. Chen, J. Li, C. Burda, Photocatalytic degradation of azo dyes by nitrogen-doped TiO_2 nanocatalysts, Chemosphere 61 (2005) 11–18.

[8] S. Song, H. Ying, Z. o He, J. Chen, Mechanism of decolorization and degradation of CI Direct Red 23 by ozonation combined with sonolysis, Chemosphere 66 (2007) 1782–1788.

[9] A. Aguedach, S. Brosillon, J. Morvan, E. Kbir Lhadi, Photocatalytic degradation of azo-dyes reactive black 5 and reactive yellow 145 in water over a newly deposited titanium dioxide, Appl. Catal. B Environ. 57 (2005) 55–62.

[10] A. Özkan, M.H. Özkan, R. Gürkan, M. Akçay, M. Sökmen, Photocatalytic degradation of a textile azo dye, Sirius Gelb GC on TiO_2 or Ag-TiO_2 particles in the absence and presence of UV irradiation: the effects of some inorganic anions on the photocatalysis, J. Photochem. Photobiol. A 163 (2004) 29–35.

[11] A. Pal Toor, A. Verma, C.K. Jotshi, P.K. Bajpai, V. Singh, Photocatalytic degradation of Direct Yellow 12 dye using UV/TiO_2 in a shallow pond slurry reactor, Dyes Pigments 68 (2006) 53–60.

[12] W.Z. Tang, A. Zhang, M.O. Quintana, D.F. Torres, TiO_2/UV photodegradation of azo dyes in aqueous solutions, Environ. Technol. 18 (1997) 1–12.

[13] M. Faisal, M. Abu Tariq, M. Muneer, Photocatalysed degradation of two selected dyes in UV-irradiated aqueous suspensions of titania, Dyes Pigments 72 (2007) 233–239.

[14] T. Sauer, G.C. Neto, H.J. Jose, R.F.P.M. Moreira, Kinetics of photocatalytic degradation of reactive dyes in a TiO_2 slurry reactor, J. Photochem. Photobiol. A 149 (2002) 147–154.

[15] B. Neppolian, M.V. Shankar, V. Murugesan, Semiconductor assisted photodegradation of textile dye, J. Sci. Ind. Res. 61 (2002) 224–230.