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Photocatalytic Degradation of Two Commercial Reactive Dyes in Aqueous Phase Using Nanophotocatalysts

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Abstract

This study involves the photocatalytic degradation of Reactive Black 5 (RB5) and Reactive Orange 4 (RO4) dyes, employing heterogeneous photocatalytic process. Photocatalytic activity of different semiconductors such as titanium dioxide (TiO_2) and zinc oxide (ZnO) has been investigated. An attempt has been made to study the effect of process parameters through amount of catalyst, concentration of dye, and pH on photocatalytic degradation of RB5 and RO4. The experiments were carried out by varying pH (3–11), amount of catalyst (0.25–1.5 g/L), and initial concentration of dye (10–100 mg/L). The optimum catalyst dose was found to be 1.25 and 1 g/L for RB5 and RO4, respectively. In the case of RB5, maximum rate of decolorization was observed in acidic medium at pH 4, whereas the decolorization of RO4 reached maximum in basic region at pH 11. The performance of photocatalytic system employing ZnO/UV light was observed to be better than TiO_2/UV system. The complete decolorization of RB5 was observed after 7 min with ZnO, whereas with TiO_2, only 75% dye degraded in 7 min. In the case of RO4, 92 and 62% decolorization was noticed in the same duration.
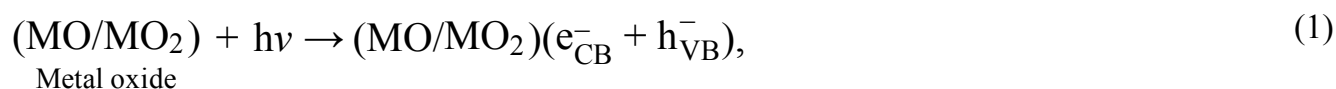

Introduction

Textile industries produce large volume of colored dye effluents which are toxic and non-biodegradable [1]. Among the different types of dyes used in textile industries, 60–70% are azo compounds. These dyes create severe environmental pollution problems by releasing toxic and potential carcinogenic substances into the aqueous phase.

Reactive dyes, one of the prominent and most widely used types of azo dyes, are typically azo-based chromophores combined with different reactive groups. They are extensively used in many textile-based industries because of their favorable characteristics, such as bright color, water-fastness, and simple application [2]. However, up to 50% of reactive dyes are lost through hydrolysis during the dyeing process, and therefore, a large quantity of the dyes appears in wastewater [3]. These dyestuffs are designed to resist biodegradation and are barely removed from effluents using conventional wastewater treatments, such as activated sludge [4].

Recently there has been considerable interest in the utilization of advanced oxidation processes (AOPs) for the complete destruction of dyes. AOPs are based on generation of reactive species such as hydroxyl radicals that oxidizes a broad range of organic pollutants quickly and non-selectively [5, 6]. AOPs include photocatalysis systems such as combination of semiconductors and light, and semiconductor and oxidants. Heterogeneous photocatalysis has emerged as an important destructive technology leading to the total mineralization of most of the organic pollutants including organic reactive dyes [7–16].

The photocatalyzed decolorization of a dye in solution is initiated by the photoexcitation of the semiconductor, followed by the formation of electron–hole pair on the surface of catalyst (Eq. 1). The high oxidative potential of the hole (h_{VB}^+) in the catalyst permits the direct oxidation of the dye to reactive intermediates (Eq. 2).

$$(\underset{\text{Metal oxide}}{MO/MO_2}) + h\nu \rightarrow (MO/MO_2)(e_{CB}^- + h_{VB}^-), \tag{1}$$

$$h_{VB}^+ + dye \rightarrow dye^{\cdot+} \rightarrow \text{oxidation of the dye}. \tag{2}$$

Another reactive intermediate which is responsible for the degradation is hydroxyl radical (OH$^\bullet$). It is either formed by the decomposition of water (Eq. 3) or by reaction of the hole with OH$^-$ (Eq. 4). The hydroxyl radical is an extremely strong, non-selective oxidant (E

$^O = +3.06$ V), which leads to the partial or complete mineralization of several organic chemicals [17].

$$h_{VB}^{+} + H_2O \rightarrow H^{+} + \,^{\cdot}OH, \tag{3}$$

$$h_{VB}^{+} + OH^{-} \rightarrow \,^{\cdot}OH, \tag{4}$$

$$^{\cdot}OH + dye \rightarrow degradation\ of\ the\ dye. \tag{5}$$

Titanium dioxide (TiO$_2$) is generally considered to be the best photocatalyst and has the ability to detoxificate water from a number of organic pollutants [11–13]. However widespread use of TiO$_2$ is uneconomical for large-scale water treatment, thereby interest has been drawn toward the search for suitable alternatives to TiO$_2$. Many attempts have been made to study photocatalytic activity of different semiconductors such as SnO$_2$, ZrO$_2$, CdS, and ZnO [14–16, 18, 19]. Kansal et al. [16] compared the photocatalytic activity of TiO$_2$, ZnO, SnO$_2$, ZnS, and CdS for the decolorization of methyl orange and rhodamine 6G dyes and found ZnO to be the most effective catalyst for the decolorization of dyes. Lizma et al. [18] reported the photocatalytic decolorization of Reactive Blue 19 (RB-19) in aqueous solutions containing TiO$_2$ or ZnO as catalysts and concluded that ZnO is a more efficient catalyst than TiO$_2$ in the color removal of RB-19. Daneshvar et al. [17] reported that zinc oxide (ZnO) is a suitable alternative to TiO$_2$ for the degradation of Acid Red 14, an azo dye, since its photodegradation mechanism has been proven to be similar to that of TiO$_2$.

Azo reactive dyes are among the most commonly used dyes to color cellulosic fibers. Therefore in this study, the photocatalytic decolorization of two commercial reactive dyes through Reactive Black 5 (Remazol Black B) and Reactive Orange 4 has been investigated using different semiconductors through titanium dioxide (TiO$_2$) and zinc oxide (ZnO) in order to select the most effective catalyst for degradation of dyes. Reactive Black 5 is a representative diazo vinyl sulfone reactive dye and reactive orange 4 is a representative monoazo dichlorotrianzinyl reactive dye. Further, the efficacy of different photocatalysts has been compared for the degradation of both the dyes.
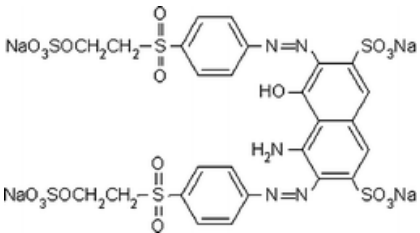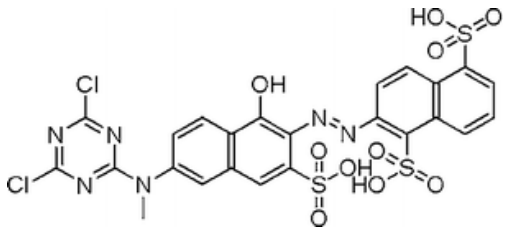
Experimental Details

Materials

Titanium PC-105 was gifted by Millennium Inorganic Chemicals, France, and was used as-received. ZnO (5 m^2/g) was purchased from Merck, India, and were used without further

purification. RB5 dye was obtained from Colortex Dye Company, Surat, and RO4 dye was gifted by Colours India Inc., Ahmedabad, India. The molecular structure and other properties of both dyes are given in Table 1. Double-distilled water was used for preparation of various solutions. pH of the solutions was adjusted with 1 M HCI or 1 M NaOH.

Table 1

Properties of RB5 dye

Name	Reactive Black 5 (RB5)	Reactive Orange 4 (RO4)
Nature	Anionic reactive dye	Anionic reactive dye
λ_{max} (nm)	597	490
Molecular weight (g/mol)	278.78	715.527
Molecular structure		

Photocatalytic Reactor

The photochemical degradation was carried out in specially designed batch reactor with external circulation as shown in Fig. 1. The light source was 20 W UV lamp (Philips) having a wavelength of 365 nm. Measurement of UV light intensity was done by an instaneous solar radiation meter (Eppley 499). The measured intensity was 11.9 W/m^2. The temperature was maintained constant throughout the reaction time. The spectra were taken with UV–Vis spectrophotometer (Shimadzu UV-2401 PC).
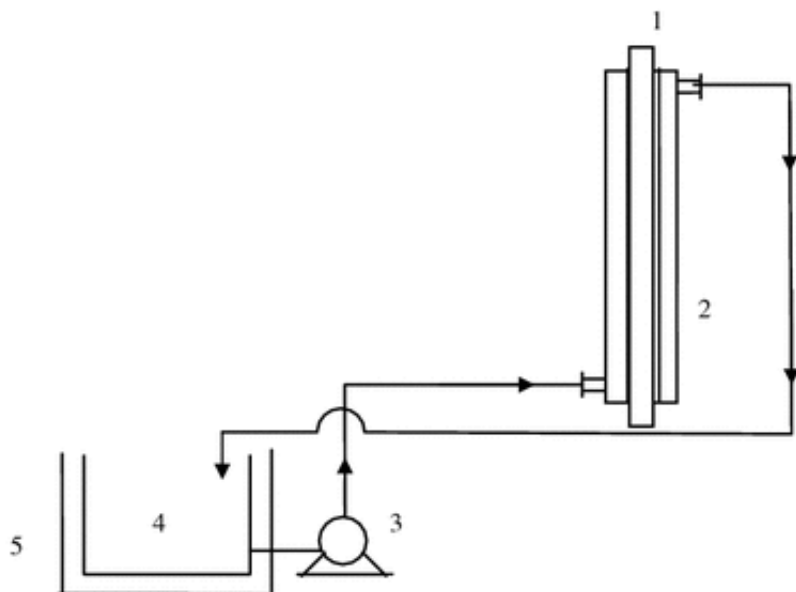
Fig. 1

Experimental set-up (*1* UV source, *2* glass tube, *3* pump, *4* solution reservoir, *5* constant temperature bath)

Procedure

For the degradation experiments, fixed amount of photocatalyst ZnO/TiO_2 was added to 1000 mL of 25 mg/L solution of dye in each trial at definite pH. The suspension was subjected to irradiation under UV light for a fixed interval of time. The aqueous suspension was externally circulated through the reactor with the help of a pump. 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 absorption spectra were recorded and rate of decolorization was observed in terms of change in intensity at λ_{max}, i.e., 597 nm for RB5 and at 490 nm for RO4. The percentage decolorization was calculated as follows:

%Decolorization $= 100 \times (C_0 - C)/C_0$, where $C_0 =$ initial concentration of dye solution, $C =$ concentration of dye solution after photoirradiation. In order to determine the effect of catalyst loading, the experiments were performed by varying catalyst concentration from 0.25 to 1.5 g/L for dye solutions of 25 mg/L at natural pH (6.67 for RB5 and 6.63 for RO4). Similar experiments were carried out by varying the pH of the solution (pH 3–11) and concentration of dye (10–100 mg/L).

Results and Discussion

Reactive Black 5 (RB5) and Reactive Orange 4 (RO4) dyes are two widely used reactive dyes in the textile industry. RB5 is a diazo vinylsulfone reactive dye, whereas RO4 is a monoazo dichlorotrianzinyl reactive dye.

UV–Vis Spectra of Dyes

Figure 2 shows typical time-dependent UV–Vis spectrum of RB5 dye during photoirradiation with ZnO. The rate of decolorization was recorded with respect to the change in the intensity of absorption peak in visible region. The prominent peak was observed at λ_{max}, i.e., 597 nm which decreased gradually and finally disappeared indicating that the dye had been degraded.
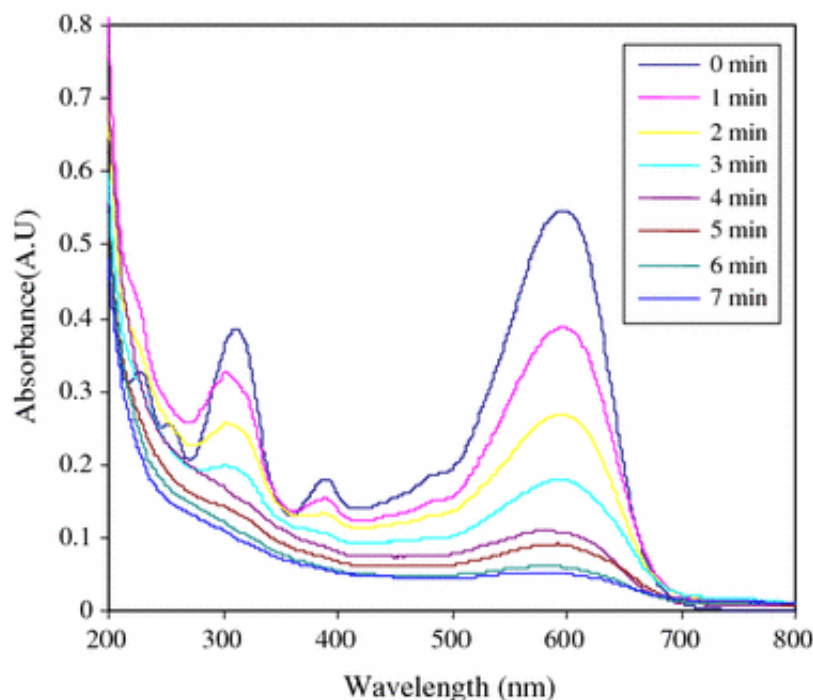
Fig. 2

Time-dependent UV–Vis absorption spectra for decolorization of RB5 using ZnO

The UV–Vis analysis for the decolorization of RO4 is shown in Fig. 3. RO4 showed absorption peak at 490 nm in visible region which diminished and finally disappeared during the reaction, which indicates that the dye had been degraded.
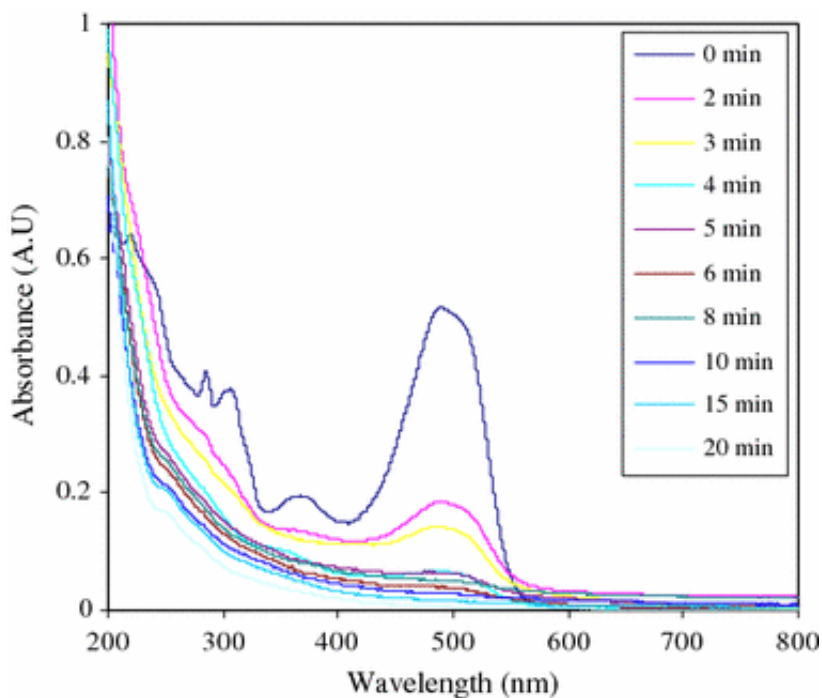
Fig. 3

Time-dependent UV–Vis absorption spectra for decolorization of RO4 using ZnO

Decolorization of RB5 Dye Under Different Experimental Conditions

Decolorization of RB5 was investigated under five different experimental conditions through UV alone, UV + TiO_2, UV + ZnO, Dark + TiO_2, and Dark + ZnO. Figure 4 depicts the photocatalytic decolorization of RB5 under these experimental conditions. Initially blank experiments were performed under UV irradiation without addition of any catalyst (UV alone) and only 17% decolorization was observed.
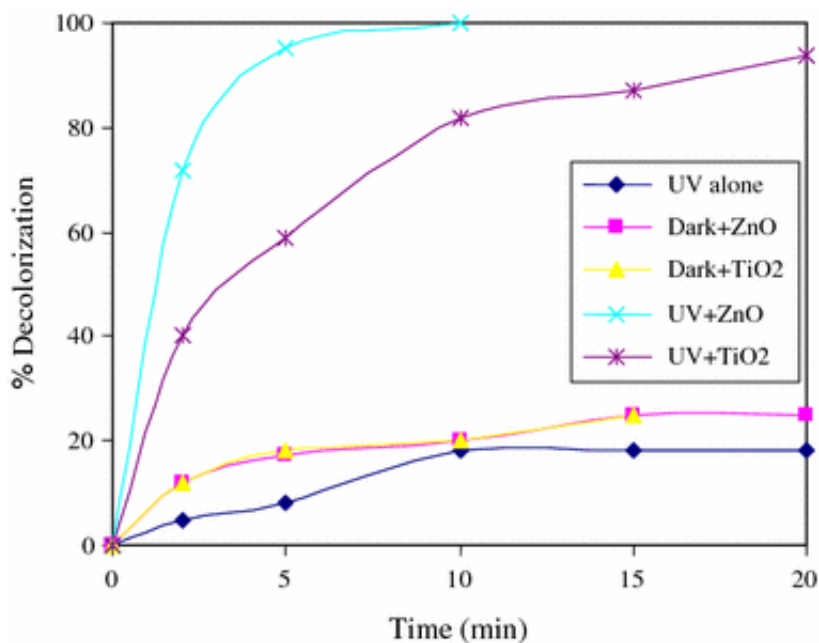
Fig. 4

Photocatalytic decolorization of RB5 dye (dye initial concentration—25 mg/L, pH 4 in the case of ZnO and pH 5 in the case of TiO2)

Then photocatalytic experiments were carried out using both catalysts at fixed dye concentration (25 mg/L) and catalyst loading of 1 g/L. When experiments were performed under UV irradiation with ZnO as photocatalyst (UV + ZnO), the complete decolorization of dye was achieved after 10 min, whereas with TiO_2 as a photocatalyst (UV + TiO_2), only 80% decolorization of RB5 was observed in the same duration. It indicates that ZnO exhibits higher photocatalytic activity than TiO_2 for the decolorization of RB5.

Thereafter the adsorption of the dye was observed with both catalysts, i.e., Dark + TiO_2 and Dark + ZnO. Only 20% adsorption of the dye was seen in the same time with both catalysts under dark conditions.

Decolorization of RO4 Dye Under Different Experimental Conditions

Similarly the decolorization of RO4 was studied under different experimental conditions as that of RB5 and the results are shown in Fig. 5. In the case of RO4 dye, about 15% decolorization was achieved when RO4 was irradiated under UV light alone. Almost 100% decolorization was observed when experiments were carried out under UV light in the presence of ZnO (UV + ZnO) for 15 min, whereas with TiO_2 + UV, 70% decolorization was achieved in the same duration. The adsorption of the dye was found to be 15–18% under dark conditions (Dark + TiO_2, Dark + ZnO) using both catalysts. The results clearly show that ZnO is a better

catalyst for the degradation of RO4 dye also. The same trend was observed in earlier findings with azo reactive dyes [18–20]. This was explained as ZnO is having greater quantum efficiency than TiO₂. Thus subsequent experiments were carried out with ZnO for both the dyes.
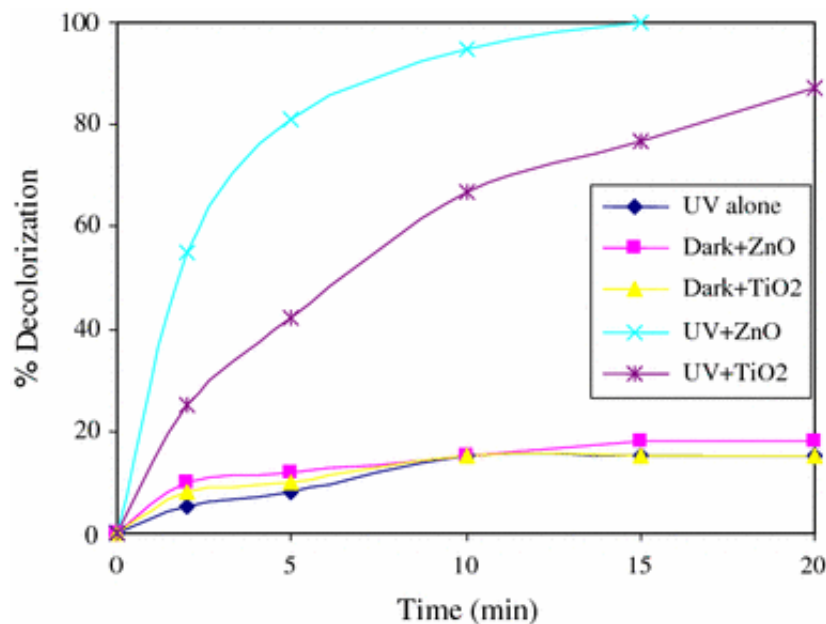

Fig. 5

Photocatalytic decolorization of RO4 dye (dye initial concentration—25 mg/L, pH 11 in the case of ZnO and pH 5 in the case of TiO2)

Decolorization of Dyes by ZnO as Photocatalyst

The experiments were carried out to study the degradation of RB5 and RO4 employing ZnO as catalyst under UV light. Various parameters which affect the decolorization efficiency such as catalyst loading (0.25–1.5 g/L), pH (3–11), initial concentration of dye (10–100 mg/L), and time (0–60 min) of decolorization were assessed under UV light.

Effect of Catalyst Concentration

Figures 6 and 7 show the effect of catalyst loading on the decolorization of RB5 and RO4, respectively, at natural pH. It can be seen that initial slopes of the curves increase greatly by increasing catalyst loading from 0.25 to 1.25 g/L for RB5 and upto 1 g/L for RO4, thereafter the rate of decolorization remains constant or decreases. Further increase in the dose of catalyst had no effect on decolorization of dyes. The photocatalytic destruction of other organic pollutants has also exhibited the same dependency on catalyst dose [19]. This can be explained on the basis that optimum catalyst loading is found to be dependent on initial solute concentration because with the increase in catalyst dosage, total active surface area increases, hence

availability of more active sites on catalyst surface [21]. At the same time, due to an increase in turbidity of the suspension with high dose of photocatalyst, there will be decrease in penetration of UV light and hence photoactivated volume of suspension decreases [17]. 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. Therefore the catalyst doses 1.25 and 1.0 g/L were fixed for RB5 and RO4, respectively, for further studies.
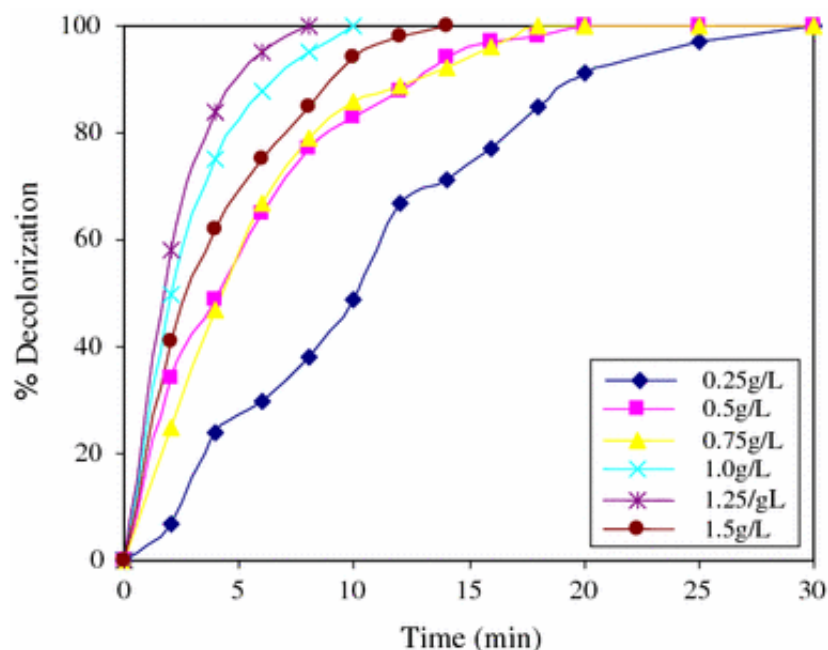
Fig. 6

Effect of ZnO dose on decolorization rate of RB5 dye (pH—natural (6.67), dye initial concentration—25 mg/L)
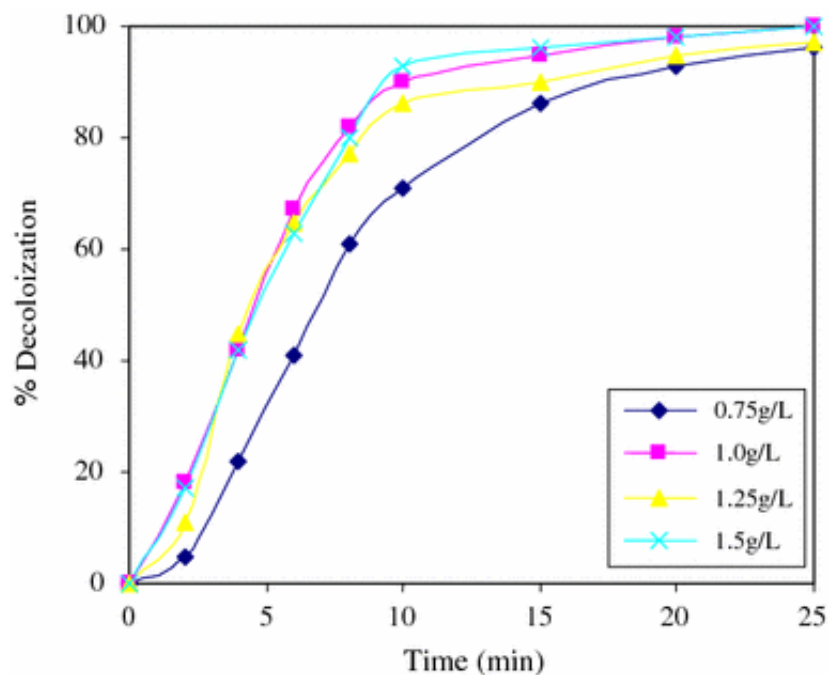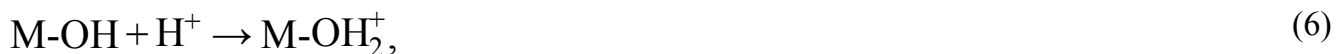
Effect of pH

Wastewater containing dyes is discharged at different pH; therefore it is important to study the role of pH on decolorization of dye. In order to study the effect of pH on the decolorization efficiency, experiments were carried out at various pH values, ranging from 3 to 11 for constant dye concentration (25 mg/L) and catalyst loading (1.25 and 1.0 g/L, respectively, for RB5 and RO4). Figures 8 and 9 show the color removal efficiency of RB5 and RO4 as a function of pH. It has been observed that for RO4, the decolorization efficiency increases with increase in pH exhibiting maximum rate of degradation at pH 11. In the case of RB5, the maximum decolorization was observed at pH 4. Similar behavior has also been reported for the photocatalytic efficiency of ZnO for decolorization of azo dyes [18, 19, 22]. The interpretation of pH effects on the efficiency of the photocatalytic degradation process is a very difficult task, because of its multiple roles. First, it is related to the acid base property of the metal oxide surface and can be explained on the basis of zero point charge. The adsorption of water molecules at surficial metal sites is followed by the dissociation of OH^- charge groups, leading to coverage with chemically equivalent metal hydroxyl groups (M-OH) [23]. Due to amphoteric behavior of most metal hydroxides, the following two equilibrium reactions are considered (Eqs. 6 and 7).
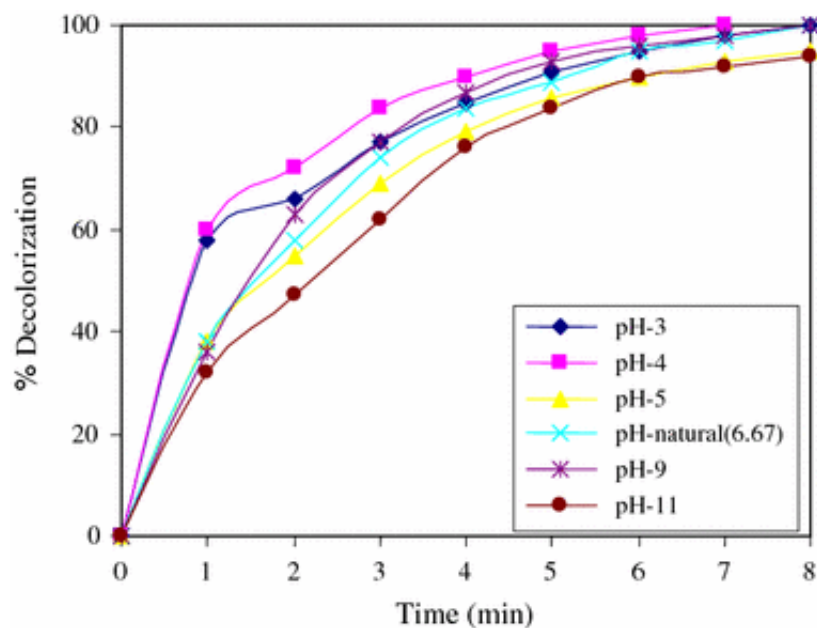
$$\text{M-OH} + \text{H}^+ \rightarrow \text{M-OH}_2^+, \tag{6}$$

$$\text{M−OH} \rightarrow \text{M−O}^- + \text{H}^+. \tag{7}$$

Fig. 8

Effect of pH on decolorization rate of RB5 dye (ZnO dose—1.25 g/L, dye initial concentration—25 mg/L)
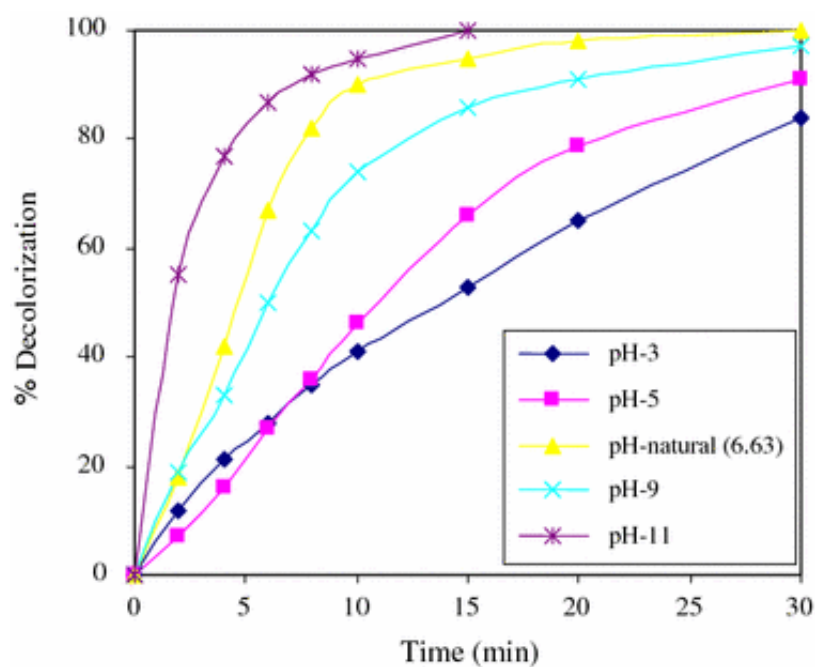

Fig. 9

Effect of pH on decolorization rate of RO4 dye (ZnO dose—1.0 g/L, dye initial concentration—25 mg/L)

The zero point charge (zpc) for ZnO is 9.0 ± 0.3. ZnO surface is positively charged below pH 9 and above this pH, surface is negatively charged by adsorbed OH^- ions. The presence of large quantities of OH^- ions on the particle surface as well as in the reaction medium favors the formation of $OH^\bullet$ radical, which is widely accepted as principal oxidizing species responsible

for decolorization process at neutral or high pH levels, and results in enhancement of the efficiency of the process [19].

The experimental results revealed that higher degradation of RB5 was found to be in acidic conditions. This may be attributed to the electrostatic interactions between the positive catalyst surface and dye anions leading to strong adsorption of the latter on the metal oxide support. In the case of RO4, the rate of photodecolorization increased with increase in pH and reached maximum at pH 11 value. The interpretation for the same could be amphoteric behaviors of the ZnO catalyst. Although the adsorption of dye molecules is low at alkaline pH, the possible reason for this behavior may be the presence of higher proportion of hydrolyzed forms of dye and/or the higher concentration of hydroxide ions leading to the photogeneration of more of the reactive hydroxyl radical species. Gonclaves et al. [24] observed similar behavior in their studies on RO4 dye.

Effect of Concentration of Dye

After optimizing the pH conditions and catalyst dose (pH 11 and catalyst dose 1.25 g/L for RB5, pH 4 and catalyst dose 1 g/L for RO4), the photocatalytic decolorization of both dyes was carried out by varying the initial concentrations of the dye from 10 to 100 mg/L in order to assess the appropriate amount of catalyst dose. As the concentration of the dye was increased, the rate of photodecolorization decreased indicating for either to increase the catalyst dose or time span for the complete removal. Figures 10 and 11 depict the time-dependent graphs of decolorization of RB5 and RO4 at different concentrations of dye solutions (10–100 mg/L). In the case of RB5, for dye solutions of 10 and 25 mg/L, 100% decolorization occurred within 5 and 7 min, respectively, and in the case of 50 mg/L, almost complete degradation was observed in 30 min, and it gets further decreased on increasing the concentration of dye. Similar trend was observed in the case of RO4, where complete decolorization of 25 mg/L dye under optimized conditions was achieved in 15 min (Fig. 11). The possible explanation for this behavior is that as the initial concentration of the dye increases, the path length of the photons entering the solution decreases and in low concentration the reverse effect is observed, thereby increasing the number of photon absorption by the catalyst in lower concentration [25]. The same effect was observed by Neppolian et al. [15] during the photocatalytic degradation of three commercial textile dyes: Reactive Yellow, Reactive Red, and Reactive Blue.
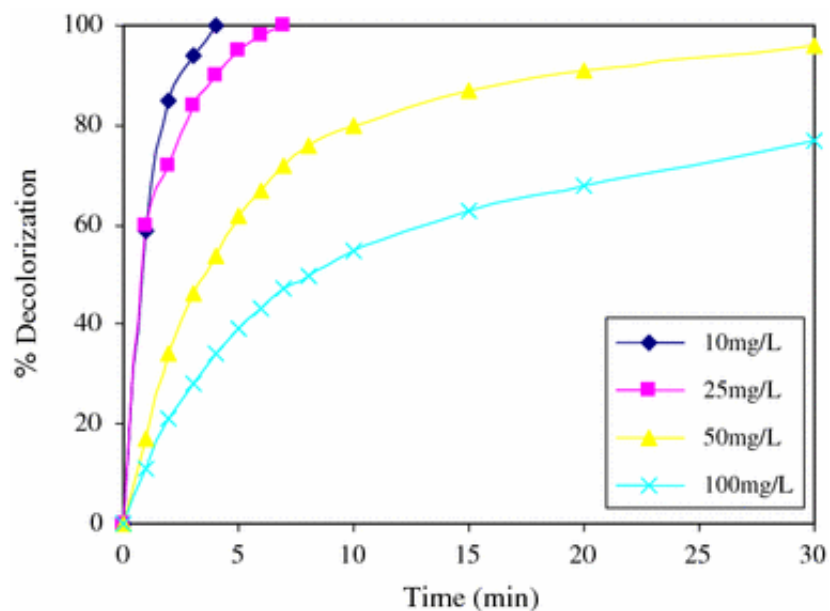
Fig. 10

Effect of initial concentration of RB5 dye on percentage decolorization (ZnO dose—1.25 g/L, pH 4)
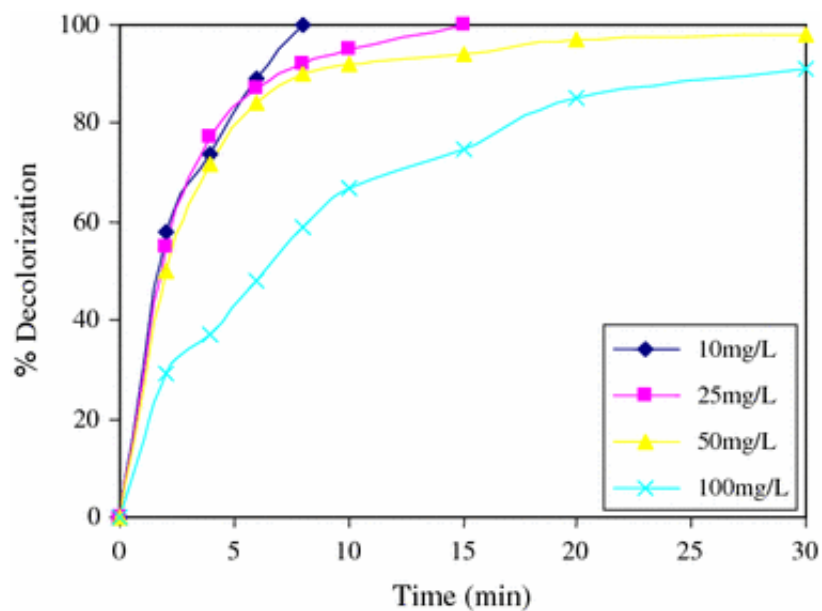

Fig. 11

Effect of initial concentration of RO4 dye on percentage decolorization (ZnO dose—1 g/L, pH 11)

Kinetic Study

Figure 12 shows the kinetics of disappearance of RB5 and RO4 for an initial concentration of 25 mg/L under optimized conditions. The results show that the photocatalytic decolorization of both the dyes in aqueous ZnO can be described by the first-order kinetic model, $\ln(C_0/C) = kt$,

where C_0 is the initial concentration and C is the concentration at any time, t. The semi-logarithmic plots of the concentration data gave a straight line. The correlation constant for the fitted line was calculated to be $R^2 = 0.9833$ and 0.9797 for RB5 and RO4, respectively. The rate constants were calculated to be 0.6271 and 0.3180 min^{-1}.
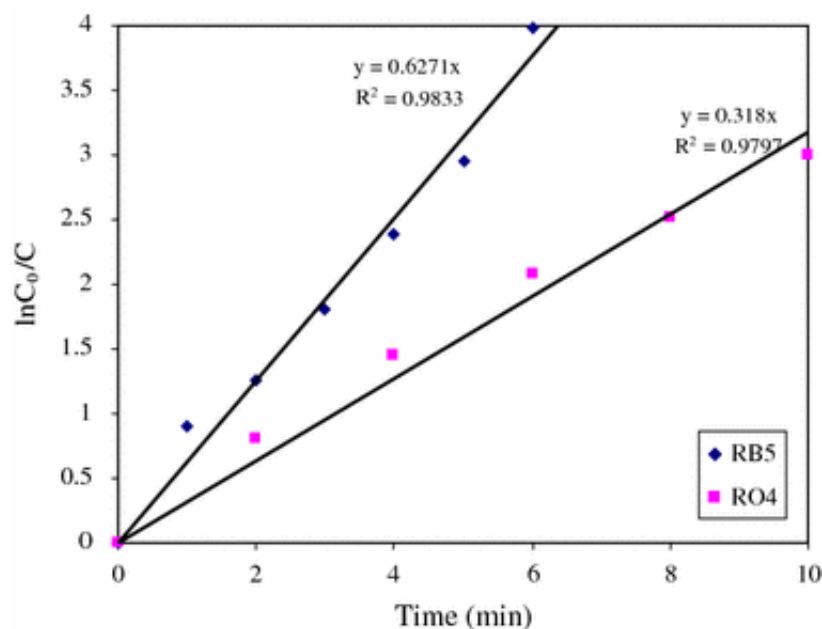

Fig. 12

Kinetics analysis for RB5 and RO4 dye (dye initial concentration—25 mg/L)

Comparison of Photodecolorization of Dyes Using Different Catalysts

The effect of different parameters through catalyst dose, pH, and initial concentration of dye on the decolorization of both dyes was also investigated with TiO_2 as photocatalyst. The optimum catalyst dose was found to be 1 and 0.75 g/L for RB5 and RO4 dyes, respectively, and the rate of decolorization of each dye decreased with increase in initial concentration of the dye. The degradation of both dyes was favored in acidic medium with TiO_2 (results not shown).

The comparative evaluation of TiO_2 and ZnO for the decolorization of both dyes is shown in Fig. 13 in the form of bar graph. The figure clearly indicates ZnO to be a better photocatalyst in both cases. The complete decolorization of RB5 was observed after 7 min with ZnO, whereas with TiO_2, only 75% dye degraded in 7 min. In the case of RO4, 92 and 62% decolorization was noticed in the same duration.
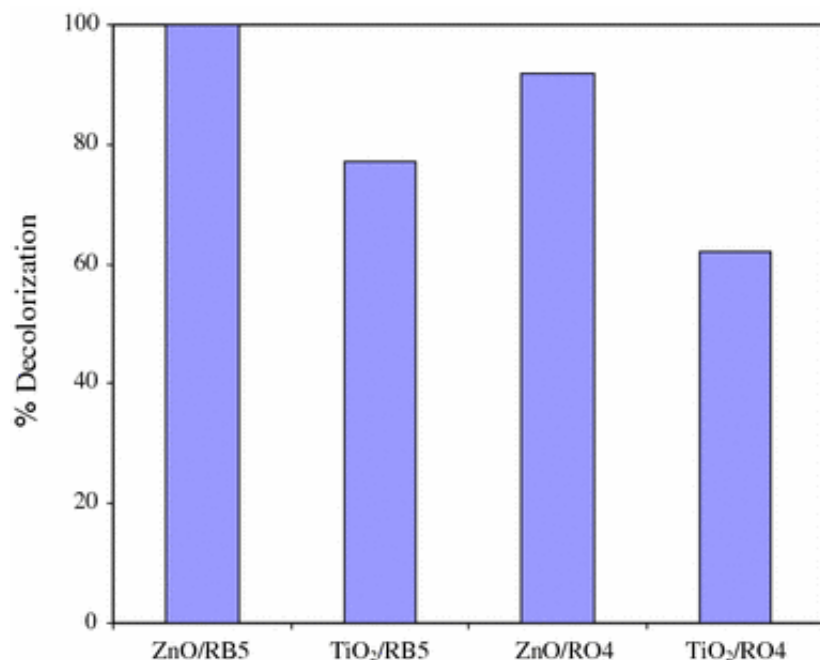
Fig. 13

Comparison between ZnO–TiO2 for RB5 and RO4 dyes under optimized conditions after 7 min of irradiation

Conclusions

Experimental results indicated that the decolorization of dyes is facilitated in the presence of catalyst. Comparison of photocatalytic activity of different semiconductors has clearly indicated that the ZnO is better photocatalyst for decolorization of RB5 and RO4. Besides higher efficiency, the other advantage of ZnO is its low cost. The initial rate of photodecolorization increased with increase in catalyst dose upto an optimum loading. Further increase in catalyst dose showed no effect. As the initial concentration of dyes was increased, the rate of decolorization decreased in each dye. The photocatalytic decolorization followed pseudo-first order kinetics.

References

1. A. Reife, H.S. Fremann, *Environmental Chemistry of Dyes and Pigments* (Wiley, New York, 1996)

2. Z. Aksu, Process. Biochem. **40**, 997 (2005). doi:10.1016/j.procbio.2004.04.008 CrossRef

3. A. Heinfling, M. Bergbauer, U. Szewzyk, Appl. Microbiol. Biotechnol. **48**, 261 (1997). doi:10.1007/s002530051048 CrossRef

4. G.M. Shaul, T.J. Holdsworth, C.R. Dempsey, K.A. Dostal, Chemosphere **22**, 107 (1991). doi:10.1016/0045-6535(91)90269-J CrossRef

5. S. Das, P.V. Kamat, S. Padmaja, V. Au, S.A. Madison, J. Chem. Soc. Perkin Trans. **2**, 1219 (1999). doi:10.1039/a809720h

6. Y. Yang, D.T. Wyatt, M. Bahorsky, Textile Chem. Colorist **30**, 27 (1998)

7. Schiavello (ed.), *Photocatalysis and Environment: Trends and Applications* (Kluwer Academic Publishers, Dordrecht, 1988)

8. C. Guillard, H. Lachheb, A. Honas, M. Ksibi, J.M. Hermann, J. Photochem. Photobiol. Chem. **158**, 27 (2003). doi:10.1016/S1010-6030(03)00016-9 CrossRef

9. C. Galindo, P. Jacques, A. Kalt, J. Photochem, Photobiol. A Chem. **141**, 47 (2001). doi:10.1016/S1010-6030(01)00435-X CrossRef

10. N. Serpone, E. Pelizzetti (eds.), *Photocatalysis Fundamentals and Applications* (Wiley, New York, 1989)

11. M.A. Fox, M.T. Dulay, Chem. Rev. **93**, 341 (1993). doi:10.1021/cr00017a016 CrossRef

12. E. Kusvuran, A. Samil, O.M. Atanur, O. Erbatur, Appl. Catal. B. Environ. **58**, 211 (2005). doi:10.1016/j.apcatb.2004.11.023
CrossRef

13. S.K. Kansal, M. Singh, D. Sud, Chem. Eng. Commun. **194**, 787 (2007). doi:10.1080/009864440701193803
CrossRef

14. S.K. Kansal, M. Singh, D. Sud, Desalination **228**, 183 (2008). doi:10.1016/j.desal.2007.10.007
CrossRef

15. B. Neppolian, H.C. Choi, S. Sakthivel, B. Arabindoo, V. Murugesan, J. Hazard Mater. B **89**, 303 (2002). doi:10.1016/S0304-3894(01)00329-6
CrossRef

16. S.K. Kansal, M. Singh, D. Sud, J. Hazard. Mater. **141**, 581 (2007). doi:10.1016/j.jhazmat.2006.07.035
PubMed   CrossRef

17. N. Daneshvar, D. Salari, A.R. Khataee, J. Photochem, Photobiol. A. Chem. **157**, 111 (2003). doi:10.1016/S1010-6030(03)00015-7
CrossRef

18. C. Lizama, J. Freer, J. Baeza, H.D. Mansilla, Catal. Today **76**, 235 (2002). doi:10.1016/S0920-5861(02)00222-5
CrossRef

19. A. Akyol, H.C. Yatmaz, M. Bayramoglu, Appl. Catal. B Environ. **54**, 19 (2004)

20. C.A.K. Gouvêa, F. Wypych, S.G. Moraes, N. Durán, N. Nagata, P. Peralta-Zamora, Chemosphere **40**, 433 (2000). doi:10.1016/S0045-6535(99)00313-6
PubMed   CrossRef

21. M.S.T. Gonclaves, A.M.F. Oliveira-Campose, E.M.M.S. Pinto, P.M.S. Plasencia, M.J.R.P Queiroz, Chemosphere 39:781 (1999). doi:10.1016/S0045-6535(99)00013-2

22. S. Sakthivel, B. Neppolian, M.V. Shankar, B. Arabindoo, M. Palanichamy, V. Murugesan, Sol. Energy Mater. Sol. Cells **77**, 65 (2003). doi:10.1016/S0927-0248(02)00255-6
CrossRef

23. W. Stumm, J.J. Morgan, *Aquatic Chemistry* (Wiley, New York, 1981)

24. M.S.T. Gonçalves, E.M.S. Pinto, P. Nkeonye, A.M.F. Oliveira-Campos, Dyes Pigments **64**, 135 (2005)
CrossRef

25. R.J. Davis, J.L. Gainer, G.O. Neal, I.W. Wu, Water Environ. Res. **66**, 50 (1994)