Photocatalytic decolorization of reactive black 5 dye in aqueous TiO_2/ZnO suspension under UV light

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Abstract

The release of colored wastewaters in the ecosystem is a dramatic source of aesthetic pollution, eutrophication, and perturbations in aquatic life. Research devoted to the ill-effects caused by chemicals have acquired importance as a result of the increased care and attention paid to the environment and human health by international, socio-political, and legislative authorities. Compliance with strict quality standards is especially called for, in the case of handling and using toxic substances that affect the environment and health. Growing concern about environmental issues has prompted the industries to investigate appropriate and eco-friendly treatment technologies. The prime need of these industries is to have a simple but effective inexpensive technology for the treatment of wastewater. Photocatalysis is considered as an important part of emerging greener technology as it uses environmentally friendly oxidants (oxygen, hydrogen peroxide or ozone), photocatalysts (titanium dioxide, ferrous ions or its complexes), and ultraviolet (UV) radiation to degrade and mineralize the toxic organic pollutants. In this study, the photodecolorization of Reactive Black 5 dye has been performed using titanium dioxide (TiO_2 P-25 Degussa) and zinc oxide (ZnO) using a mixed batch reactor. The rate of degradation was studied in terms of changes in absorption spectra and reduction in chemical oxygen demand (COD). Various process parameters such as catalyst dose, pH, and dye initial concentration have been varied and their effect on the decolorization efficiency has been studied. The photocatalyst zinc oxide was found to be more efficient as compared with titanium dioxide.

Keywords: heterogeneous photocatalysis, reactive black 5 dye, zinc oxide, titanium dioxide, UV light.

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1 Introduction

The coast represents a mosaic of rich and diverse ecosystems and resources and is important to the economic and social well-being and development of countries of the region. But nowadays, the coastal zones are highly affected by problems related to population growth, industrial, and tourism activities. Pollutants that enter the marine and coastal environment originate on land in the form of runoff from industrial, agricultural, and municipal wastes. These pollutants include nutrients (nitrogen and phosphorous), various kinds of dyes and heavy metals and sediments. All these pollutants reduce the levels of dissolved oxygen in the water, thereby deteriorating the water quality, which has a great impact on the marine biodiversity. The most important way to combat coastal environmental pollution is to prevent it in the first instance. Pollution in the textile industry should focus on reducing water use and on more efficient technology for treating wastewater.

Textile industries have shown a significant increase in the use of synthetic complex organic dyes as the coloring material. Dyeing and finishing processes are two important steps in the textile manufacturing process. These steps involve the dyeing of man-made or natural fibers to the desired permanent color and processing of these fabrics into final commercial products. The disposal of large quantities of aqueous waste generated by the textile industries causes significant environmental problem [1–3].

Usually the conventional biological treatment processes do not readily remove dyes from textile wastewaters because of their resistance to biological degradation [4–6]. Although some treatment processes, like chemical coagulation and active carbon adsorption, may remove certain categories of dye to about 90%, the main drawback of these processes is the generation of a large amount of sludge or solid waste, resulting in high operational costs for sludge treatment and disposal [7,8].

Heterogeneous photocatalysis is a promising technology valuable for environmental cleaning and remediation. Titanium dioxide (TiO_2) and zinc oxide (ZnO) have been extensively investigated as heterogeneous semiconductor photocatalysts [9–19], since they offer several advantages such as, the use of oxygen as the only required oxidant, and its capability to simultaneously carry out oxidative and reductive reactions. They also offer low costs, mild reaction conditions, high photochemical reactivity, low environmental toxicity, and stability to photocorrosion.

Heterogeneous photocatalysis is based on the irradiation of a photocatalyst with light energy equal to or greater than the band gap energy. This causes a valence-band electron to be excited to the conduction band, causing charge separation. The conduction band electrons and valence band holes can then migrate to the surface and participate in interfacial oxidation-reduction reactions. The oxidative degradation of an organic pollutant is attributed to indirect reaction at the positive hole where adsorbed water or hydroxyl radicals ($^{\bullet}OH$), which then react with the pollutant molecule.

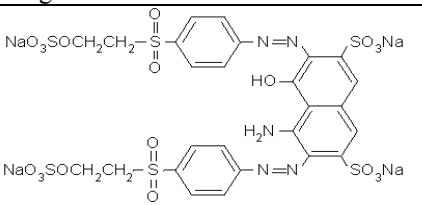
The aim of the present study is to investigate the photocatalytic degradation of Reactive Black 5 dye over semiconductive, TiO_2 and ZnO based, photocatalysts irradiated with a UV source. The effects of doping of TiO_2 and ZnO as well as the effects of operational parameters, such as catalyst dose, pH of the solution and initial dye concentration, on the degradation rate of aqueous dye solutions are examined.

2 Experimental

2.1 Materials

Vinyl sulphone reactive black 5 dye (RB5) was taken from Colourtex Dye Company, Surat, India and its properties are given in Table 1. Titanium P-25 (surface area: 50 m^2/g) was obtained from Degussa, Germany and was used as received. Zinc Oxide was obtained from Qualigen, India. Double-distilled and deionized water was used for preparation of various solutions. The pH of the solutions was adjusted with 1M HCI or 1M NaOH. Chemicals used for chemical oxygen demand (COD) determination like potassium dichromate, sulfuric acid, ferrous ammonium sulfate, silver sulfate, mercuric sulfate, and ferroin indicator were purchased from S.D. Fine Chemicals, India.

Table 1: Properties of RB5 dye.

Nature	Anionic reactive dye
Molecular weight	278.78 g/mol
Molecular structure	
λ_{max}	597 nm
Spectral range	800-200 nm

2.2 Photocatalytic reactor

Irradiation was performed in a double walled mixed batch photoreactor with a UV tube of 20W, both for UV/TiO_2 and UV/ZnO processes. The temperature was maintained constant throughout the reaction by circulating water in jacketed wall reactor.

2.3 Procedure

For the decolorization experiments, fixed amount of photocatalyst (TiO_2 or ZnO) was added to 1000 ml of sample solution. The suspension was subjected to irradiation under UV light. At different time intervals, aliquot was taken out with the help of syringe and then filtered through Millipore syringe filter of 0.45 μm.

Then absorption spectra of sample solution were recorded at λ_{max} with UV-vis spectrophotometer (UV 2401 PC, Shimadzu, Singapore). The rate of degradation was studied in terms of changes in absorbance and reduction in COD.

Similar experiments were carried out by varying the dose of photocatalysts, the pH of the solution and the initial concentration of substrate.

3 Results and discussion

3.1 Photolysis/photocatalytic decolorization of RB5 dye

Photocatalytic decolorization of RB5 dye has been studied under three different experimental conditions: (i) UV alone (ii) Dark+TiO_2/ZnO (iii) UV+TiO_2/ZnO. The degradation experiments were performed with 25 mg/l of dye using 1 g/l of catalyst dose for TiO_2 and 1.25 g/l catalyst dose for ZnO at natural pH. The results of decolorization experiments are depicted in Figure 1 and Figure 2. It is clear from the Figure 1 that the irradiation of TiO_2 suspension along with UV light leads to almost total decolorization of the dye. About 19% decolorization was achieved when dye solution was irradiated under UV alone and 12% adsorption was observed in the same time using TiO_2 and dark conditions.

In the case of ZnO (Figure 2), about 19% decolorization of dye was achieved when irradiated under UV alone and about 100% decolorization was observed when decolorization was carried out using ZnO and UV for 15 minutes. Only 7% adsorption of dye solution was observed in the same time using natural pH, 25 mg/l initial dye concentration and catalyst dose 1.25 g/l.

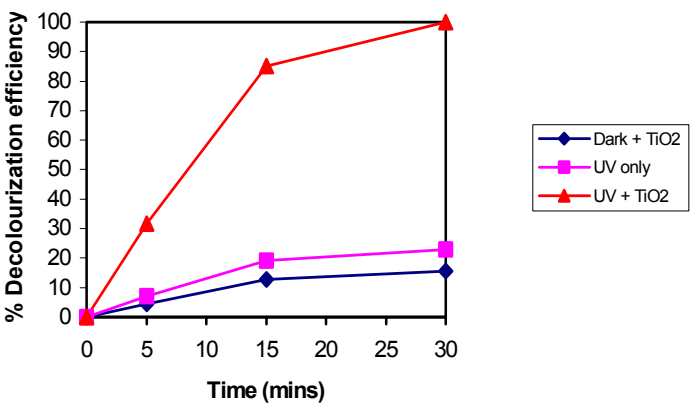


Figure 1: Photocatalytic decolorization of dye solution (dye concentration – 25 mg/l, pH-5.85, TiO_2 dose – 1.0 g/l).

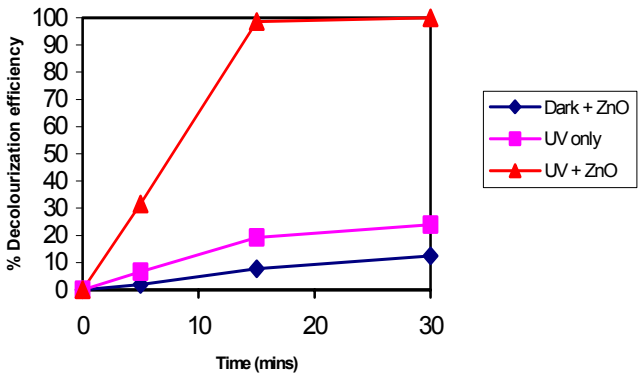


Figure 2: Photocatalytic decolorization of dye solution (dye – 25 mg/l, pH-5.85, ZnO dose – 1.25 g/l).

3.2 Effect of catalyst dose

In heterogeneous catalysis, the catalyst concentration plays an important role in the chemical reactions and has a significant effect on the process efficiency. The increase of catalyst dose increases the total active surface area, hence the ability of more active sites on the catalyst surface for adsorption and reaction. It can be seen from Figure 3 that degree of decolorization of dye increased with increasing amount of photocatalyst TiO_2, reaching highest value at catalyst loading 1.0 g/l and then decreased. This behavior was caused by the so called shielding effect at higher concentration of catalyst where the suspended TiO_2 reduces the penetration of light in solution [20]. Even though more catalyst surface was available for dye adsorption, certain part of the catalyst was not exposed to photons as interfacial area between the reaction solution and the photocatalyst got reduced. The same pattern of decolorization of dye was observed in case of ZnO. The maximum decolorization was achieved at a catalyst dose of 1.25 g/l, as shown in Figure 4.

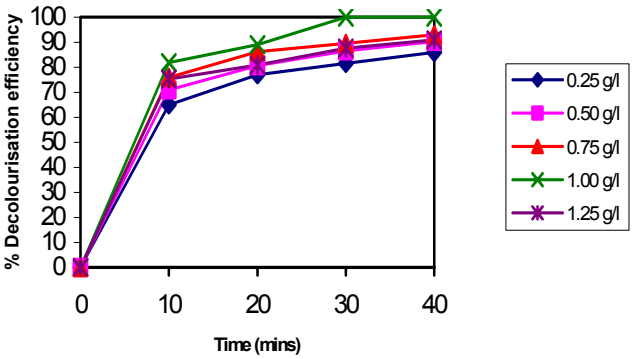


Figure 3: Effect of TiO_2 dose on the photocatalytic decolorization of (dye concentration – 25 mg/l, pH-natural (5.85)).

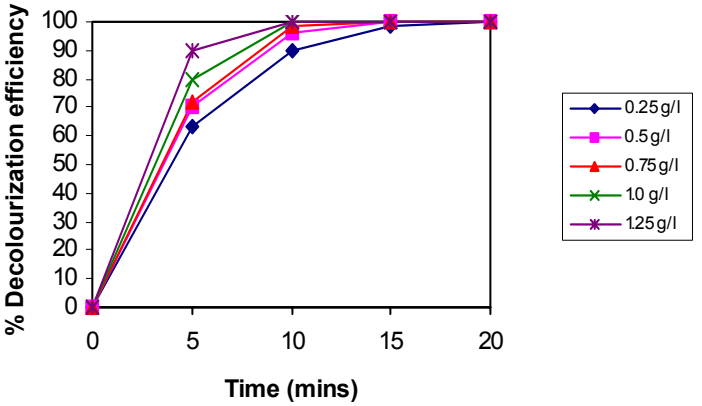


Figure 4: Effect of ZnO dose on the photocatalytic decolorization of (dye concentration – 25 mg/l, pH-natural (5.85)).

3.3 Effect of pH

The pH value is an important parameter in photodecolorization that takes place on the surface of photocatalyst. The pH of solution affects the surface charged properties of the catalyst and therefore, the adsorption behavior of the compound. The decolorization of dye was studied at different pH values (pH 3 to pH 11) under UV light source and at an optimum dose of photocatalyst TiO_2 (1 g/l). The decolorization was found to be highest at pH 3 as shown in Figure 5. The point of zero charge for TiO_2 is at pH-6.8 [21]. TiO_2 surface is thus positively charged in acidic pH (pH<6.8) and negatively charged in alkaline pH (pH>6.8). At more acidic pH values (pH<6.8), electrostatic interactions between the positive TiO_2 surface and RB5 anions lead to strong adsorption and enhancing degradation rate. In the basic pH (pH>6.8), there was a poor adsorption, because the TiO_2 surface and RB5 are both negatively charged in the basic media. Therefore increase in pH causes decrease in degradation rate. Similar results have been obtained when decolorization study was undertaken in the case of ZnO photocatalyst as shown in Figure 6.

3.4 Effect of dye initial concentration

Initial concentration of dye also plays an important role in determining the rate of most of the chemical and photochemical reactions. This is evident in the color pattern given in Figure 7 and Figure 8. The photocatalytic degradation of dye at different initial concentrations in the range 5 mg/l to 100 mg/l was investigated under optimized conditions (1 g/l catalyst dose in case of TiO_2 and 1.25 g/l for ZnO and pH-3). The decolorization rate was found to be highest at 5 mg/l for both the photocatalysts. The extent of degradation decreased with the increase in initial concentration of dye. This may be attributed to several factors. At higher dye concentrations, there would be more adsorption of dye on TiO_2 and ZnO

resulting in a lesser availability of catalyst surface for hydroxyl radical generations. A similar result was observed by Jonna and Morawski [22], and they suggested the formation of several layers of adsorbed dye on photocatalyst surface, at higher dye concentrations. Similarly more photons would be adsorbed by the dye at higher concentrations, which also reduces the energy available for hydroxyl radical generation.

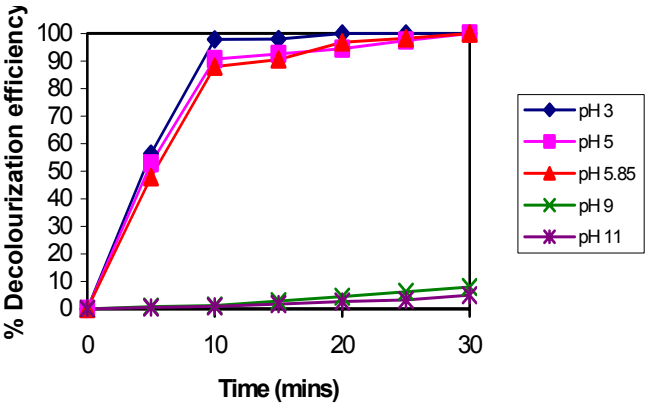


Figure 5: Effect of pH on photocatalytic decolorization of dye (TiO_2 – 1.0 g/l, dye initial concentration – 25 mg/l).

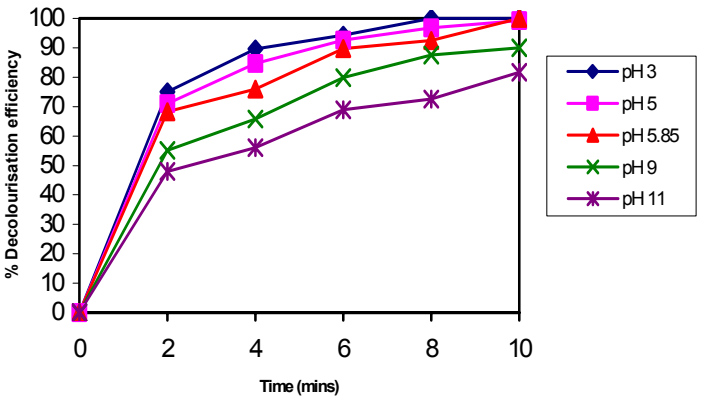


Figure 6: Effect of pH on photocatalytic decolorization of dye (ZnO – 1.25 g/l, dye initial concentration – 25 mg/l).

3.5 COD reduction of dye solution

The dye solution was irradiated under optimized conditions obtained from above studies, and the COD reduction was observed. The results are given in Table 2. From the results, it can be seen that 82% COD reduction was achieved using ZnO photocatalyst whereas 76% COD reduction was achieved in case of TiO_2.

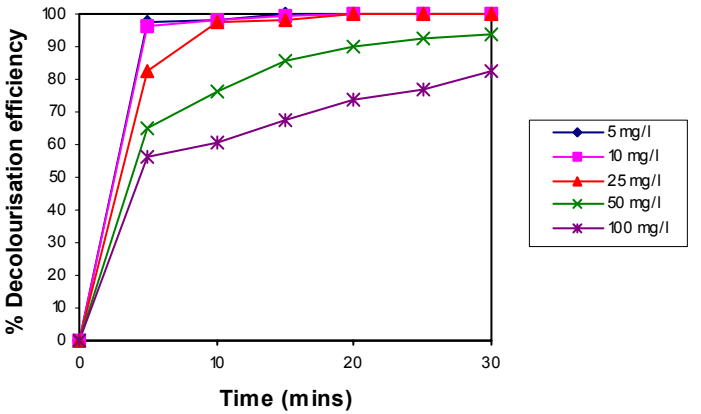


Figure 7: Effect of initial concentration of dye on decolorization efficiency (TiO_2 dose – 1.0 g/l, pH-3).

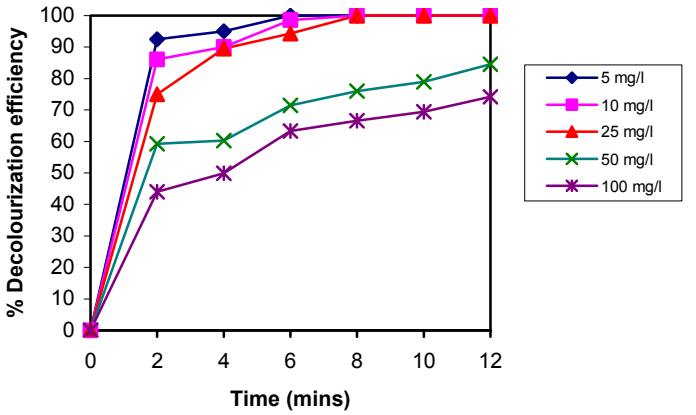


Figure 8: Effect of initial concentration of dye on decolorization efficiency (ZnO dose – 1.25 g/l, pH-3).

Table 2: COD reduction of dye after photocatalytic treatment.

Process	COD before treatment (mg/l)	COD after treatment (mg/l)	% COD reduction
UV/ TiO_2	55.2	12.8	76.8
UV/ZnO	55.2	9.6	82.0

4 Conclusions

The photocatalyst ZnO showed superior photocatalytic activity as compared to TiO_2 for the degradation of dye under investigation. The highest photodegradation efficiency for both the photocatalysts was observed at pH 3 and the most appropriate initial concentration for the maximum degradation rate of dye for both the photocatalysts was found to be 5g/l. An inhibition in the degradation rate was observed from lower substrate concentration to higher substrate concentration. The maximum decolorization was achieved at a catalyst loading of 1.0 g/l for TiO_2 and 1.25 g/l for ZnO. More COD reduction was achieved in case of ZnO. The observations of these investigations clearly demonstrate the importance of choosing the optimum degradation parameters to obtain a high degradation rate, which is essential for any practical application of photocatalytic processes.

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