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Photocatalytic degradation of reactive black-5 dye using TiO_2 impregnated ZSM-5

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Abstract. In the present study, photocatalytic degradation of reactive black-5 (RB-5) dye was investigated using supported TiO_2 photocatalyst based adsorbent as a semiconductor photocatalyst in a batch reactor. The synthesized photocatalyst composition was developed using TiO_2 as photoactive component and zeolite (ZSM-5) as the adsorbents. Attempts were also made to optimize the composition of the supported catalyst and to study the reliability of prepared catalyst. The optimum formulation of supported catalyst was found to be (TiO_2: ZSM-5 = 0·15:1) which gave the highest efficiency with 98% degradation of 50 mg/L RB-5 solution in 90 min. Effect of different parameters such as initial concentration of dye solution, catalyst amount on the rate of photodegradation was also studied. The reduction in the chemical oxygen demand (COD, 88%) proves the mineralization of the RB-5 dye along with the colour removal. The supported TiO_2 was found to be stable for repeated use.

Keywords. Photocatalysis; reactive black-5; TiO_2; adsorbent; ZSM-5.

1. Introduction

The release of this textile effluent in the environment is an ever increasing problem of global concern. Due to their high solubility and stability in water, it is an onerous process to treat coloured water to innocuous levels for many biological and chemical processes. Conventional water treatment technologies such as solvent extraction, activated carbon adsorption, and chemical treatment process such as oxidation by ozone (O_3) often produce hazardous by-products and generate large amount of solid wastes, which require costly disposal or regeneration method (Philippe *et al* 1998; Slokar and Le Marechal 1998; Panduranga *et al* 2001). Due to these reasons, considerable attention has been focused on complete oxidation of organic compounds to harmless products such as CO_2 and H_2O by the advanced oxidation process (AOP) and appears as one of the most emerging promising technologies. Most of the previous studies illustrate the use of pure TiO_2 particulates; however, poor adsorption and low surface area properties lead to great limitations in exploiting the photocatalyst to the best of its photoefficiency. One strategy to enhance the rate of photodegradation efficiency of TiO_2 is the use of adsorbent-like zeolite (ZSM-5) as the support for TiO_2, which provides high concentration of target substances around the catalyst particulate (Crittender *et al* 1997; Poulios and Aetopoulon 1999).

Titanium atoms incorporated into the zeolite framework and particle attached on the external surface of zeolite serve as catalytic sites, and thus the content of framework titanium in a zeolite has presented higher activity in performing some catalytic reactions. Supporting TiO_2 is commonly reported to be less photoactive due to the interaction of TiO_2 with support during thermal treatments (Poulios and Tsachpinis 1999; Ding *et al* 2000). Several attempts have been made to improve the photoefficiency of titania by changing the composition of adsorbent (ZSM-5).

In the present work we have used an environmental free and most effective sol–gel technology to impregnate TiO_2 onto zeolite catalyst (ZSM-5) and studied the photodegradation efficiency of reactive black-5 (RB-5) dye by this prepared catalysts. Removal of colour and organics by photocatalytic degradation is emerging as an effective treatment technique.

2. Materials and methods

Titanium tetraisopropoxide (TTIP, 97%) was procured from Aldrich, USA. The Reactive Black 5 (RB 5) dye was selected as a model compound in this study, which was purchased from the Jasani Dyes and Chemicals Limited, Rajkot, India. Titanium dioxide (TiO_2 P25) obtained from Degusa, was about 70% anatase 30% rutile. Powdered particles of zeolite ZSM-5 (425 m^2/g and Si/Al = 23) was purchased from Zeolyst International, Valley Forge, USA). All solutions

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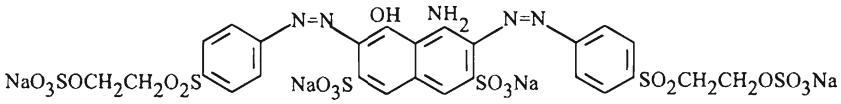

Figure 1. Molecular structure of the RB-5 dye (Reactive black 5 (RB 5) dye: molecular weight: 991·8 g mol^{-1}, maximum absorbance: λ_{max} = 597 nm, colour index = 20505 (azo type)).

were prepared using purified water. The molecular structure and chemical properties of this commercially used dye is given in figure 1.

2.1 *Synthesis of TiO_2: ZSM-5 catalyst by impregnation method*

A TiO_2 sol was synthesized by an acid-catalyzed sol–gel formation procedure which is explained below. The reactant composition was 200 mL of water, 1 mL of nitric acid, and 28·1 g of titanium–(IV) tetraisopropoxide dissolved in 10 mL of ethanol. The resulting slurry was stirred for 3 h. The gel obtained was dried at 80°C for 24 h. The modified sol–gel solution was prepared by addition of a calculated amount of TiO_2 Degussa P25 to the sol solution before drying in the oven at 80°C for 24 h. The powder was added slowly with vigorous stirring to prevent the formation of agglomerates. The TiO_2 obtained then was immobilized according to literature method (Matos *et al* 1998; Neppolian *et al* 2002; Tsumura *et al* 2002). Our preferred method for composite photocatalyst preparation was to bind titanium dioxide thermally onto the surface of the ZSM-5 zeolite. ZSM-5, saturated with water for 90 min, was mixed with TiO_2 sol and stirred for 1 h. Then, this mixture was dried by evaporation at 50°C for 2–3 h. This was followed by heating at 120°C overnight. Finally, the solid was calcined at 450°C for 11–12 h. By this procedure, a series of samples with 15 and 30 wt % of titanium oxide on ZSM-5 were prepared. Thermally loaded TiO_2 displaces surface -OH and is chemisorbed on the surface of the zeolite (Thangaraj *et al* 1991; Millini *et al* 1992; Sulikowski and Klinowski 1992).

3. Properties of catalyst (TiO_2: ZSM-5)

3.1 *XRD analysis*

The X-ray powder diffraction patterns of TiO_2: ZSM-5 and TiO_2 as shown in figure 2, was obtained using Phillips X'pert MPD system using CuKα radiation (λ = 0·15405 nm) in a 2θ range of 0–100° at a scan speed of 0·2° s^{-1}. XRD patterns were compared with the standard anatase and rutile diffractograms. The identification of crystalline phase of TiO_2 as anatase at 2θ = 25·31 (101) and rutile at 2θ = 27·41 (110) was accomplished by comparison with a TiO_2 (P25) prominent (101) plane (Anpo *et al* 1986; Carlos *et al* 2000; Tayade *et al* 2006; Yahiro *et al* 2007). The crystallite size was determined from XRD pattern, using Scherrer formula, $t = 0{\cdot}9\lambda/\beta\cos\theta$, where t is in nm, λ the wavelength of X-ray in Å (1·5418 Å), β the FWHM in radians and θ the Bragg angle. Surface area (table 1) measurements were performed on an ASDI-RXM 100 system representing liquid nitrogen adsorption isotherms at −196°C. Prior to experiments, samples were degassed at 250°C for at least 3 h until a pressure of 10^{-7} Torr was obtained. The volume of adsorbed N_2 was normalized to standard temperature and pressure. The results

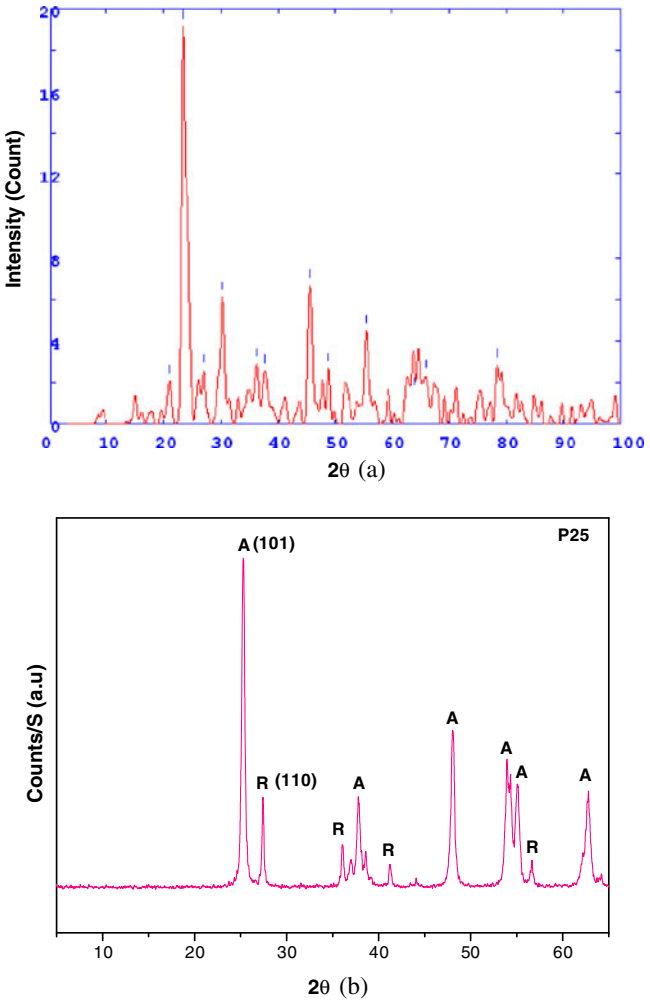

Figure 2. XRD patterns of (**a**) 15% TiO_2: ZSM-5 and (**b**) TiO_2 (P25).

Table 1. Crystalline size and surface area of all supported catalysts.

Catalysts	Crystallite size (nm)[a]	Surface area (m^2/g)
ZSM-5 –	–	400
15% TiO_2–ZSM-5	38·8	180
30% TiO_2–ZSM-5	–	62
TiO_2 (P25)	28·4	56

[a]Calculated from the (1 0 1) diffraction peak of anatase using the Scherrer equation.

were calculated using four points BET method (Lepore *et al* 1993; Haque *et al* 2005; Sindorf and Maciel 1982).

3.2 *SEM analysis*

SEM micrographs of 15% TiO_2–ZSM–5 and TiO_2 (P25) are shown in figure 3. High-resolution SEM studies have shown the impregnation of the TiO_2 particulates onto the ZSM-5 surface. Figures clearly demonstrated irregularly localized, distinct edged, bright aggregates within the regular geometry of raw ZSM-5.

4. Experimental

Experiments were performed in an annular cylindrical glass tube of 500 ml capacity with dimensions of 25 × 8 cm (height × inside diameter) as shown in figure 4. At the top portion of the glass tube side port was provided for the sampling. UV-125 W low pressure mercury lamp (Philips) was used as the radiation source and located inside the annular quartz tube at the centre of the reactor. The light intensity in the region 340–400 nm was obtained. The reactor was placed on a magnetic stirrer for thorough mixing and to make the catalyst particle suspended. In order to conduct experiments at the controlled temperature and protect the lamp from overheating, the reactor was surrounded with a cooling jacket. An aqueous solution of dye containing the required quantity of supported photocatalyst was stirred for about 30 min in the dark in order to achieve the maximum adsorption of the dye onto the semiconductor surface, followed by UV lamp illumination for specified time. All the experiments were carried out at room temperature and atmospheric pressure. In all cases, during the experiments 250 ml of dye solution containing appropriate quantity of the semiconductor power was magnetically stirred before and during the illumination. At specific time intervals samples of 10 ml were withdrawn for the analysis. To remove the catalyst particles, the solution was centrifuged for 20–30 min. Changes in the concentration of the dyes were observed from its characteristic absorption at the optimum wavelength by using UV-visible spectrophotometer.

5. Results and discussion

5.1 *Effect of TiO_2 impregnation on ZSM-5*

The adsorption of reactive black (RB-5) dye by ZSM-5 and 15% TiO_2: ZSM-5 was studied, in order to determine the effect of TiO_2 impregnation on the physical properties such as adsorption capacity of ZSM-5. To the known concentration of dye solution, untreated ZSM-5, TiO_2:ZSM-5 and TiO_2 were added and kept in a small closed dark chamber without any light source for a period of 30 min. Figure 5 shows the adsorption of reactive black dye vs weight of catalyst added. It can be seen that there is no prominent change in the adsorption capacity between TiO_2: ZSM-5 and ZSM-5. This indicates TiO_2 impregnation has no much influence on the adsorption capacity of ZSM-5. Adsorption capacity of the photocatalyst TiO_2 is very low in comparison with the TiO_2: ZSM-5, which may lead to the photocatalytic degradation rate.

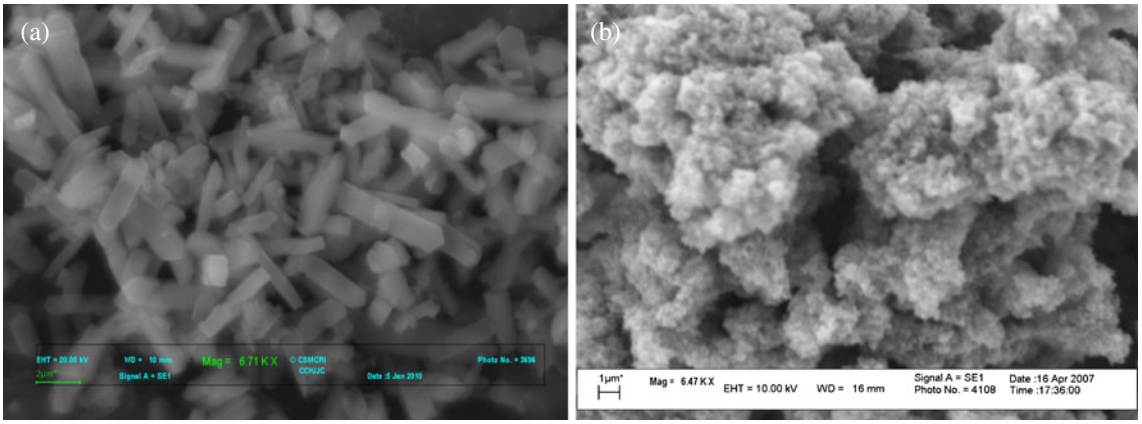

Figure 3. SEM photographs of (**a**) 15% TiO_2: ZSM-5 and (**b**) TiO_2 (P25).

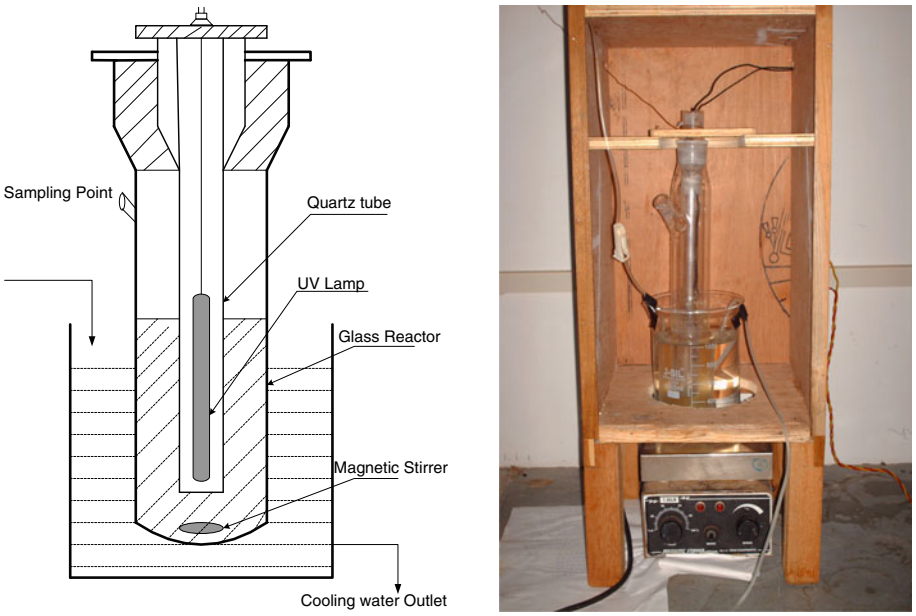

Figure 4. Photocatalytic reactor used for degradation of textile dyes.

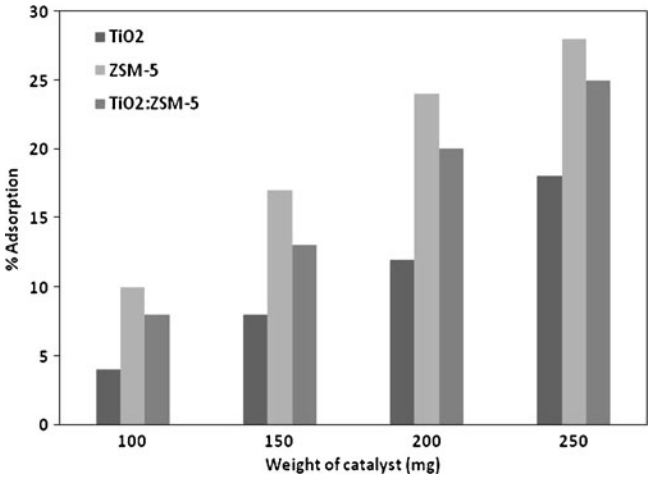

Figure 5. Percentage adsorption of RB-5 on TiO_2, ZSM-5 and 15% TiO_2:ZSM-5.

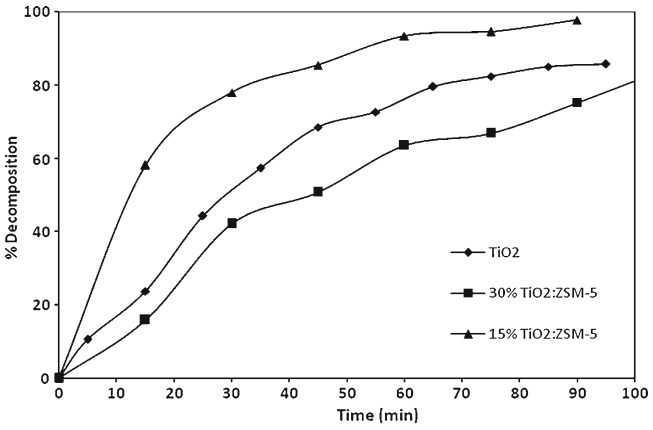

Figure 6. Comparison of photo-degradation efficiency of 15% and 30% TiO_2: ZSM-5 with commercial TiO_2 (P25) with different exposure durations.

5.2 *Efficiency of TiO_2: ZSM-5 over untreated commercial TiO_2*

The efficiency of these prepared catalysts was studied by comparing the decomposition rate of reactive black-5 dye with commercially available TiO_2 (P25). It was found that hydrothermally prepared 15% TiO_2: ZSM-5 shows very high efficiency compared with the untreated commercial TiO_2 and 30% TiO_2: ZSM-5. This result may be because of large active surface area available of the catalyst for low impregnation of TiO_2. As more TiO_2 impregnated on the support that builds surface layers and reduces the active surface available for the decomposition. Figure 6 shows the plot of decomposition vs irradiation time for untreated TiO_2 (P25) and TiO_2: ZSM-5. In this experiment a known concentration of RB-5 (50 ppm) solution was prepared and 150 mg of the catalyst was used with 250 ml of the samples.

5.3 *Effect of catalyst (TiO_2: ZSM-5) loading on photodegradation of RB-5 dye*

Experiments were carried out taking different amounts of 15% TiO_2: ZSM-5, keeping the dye concentration constant (50 ppm), in order to obtain an optimum condition with

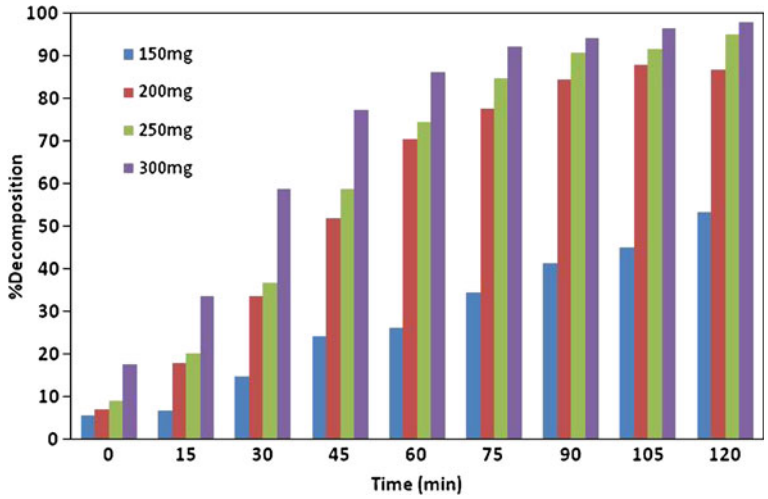

Figure 7. Effect of catalyst (TiO_2: ZSM-5) amount on photodegradation efficiency with different exposure durations of RB-5 at 50 ppm.

respect to the amount of catalyst used at which the photodegradation efficiency was maximum that can save unnecessary use of excess photocatalyst quantity-wise. Figure 7 illustrates the effect of different amounts (150–300 mg) of catalyst on the decomposition of the dye molecules. It was clearly visualized from figure 7 that percentage decomposition of RB-5 was increasing with increase in amount of catalyst but the final decomposition (after 120 min) was nearly same for the catalyst amount >200 mg. At the same time there was also a drastic difference in the rate of decomposition RB-5 for the 150 and 200 mg of catalyst.

An increase in the efficiency was due to an increase in the number of active sites on TiO_2: ZSM-5 available for the reaction, which in turn increases the rate of radical formation. The reduction in the rate may be due to the reduction in the penetration of light with surplus amount of catalyst. The surplus addition of the catalyst makes the solution more turbid and light penetration was retarded. The addition of surplus catalyst also results in the deactivation of activated molecules by collision with ground state molecules. The optimum condition for treatment was found to be 200 mg of catalyst amount for the treatment of 250 ml of the dye solution, which shows maximum photodegradation efficiency (Chen *et al* 2003).

5.4 *Effect of initial dye concentration*

Figure 8 shows the plot of decomposition vs time with respect to different initial concentrations of the RB-5 dye. It shows a high efficiency at low initial concentration of the dye (16 ppm), which was due to the adsorption of dye molecules onto the zeolite surface and immediate degradation of the same. As the initial concentration of the dye increases, the degradation efficiency reduces (Baetz and Iangphasuk 1997;

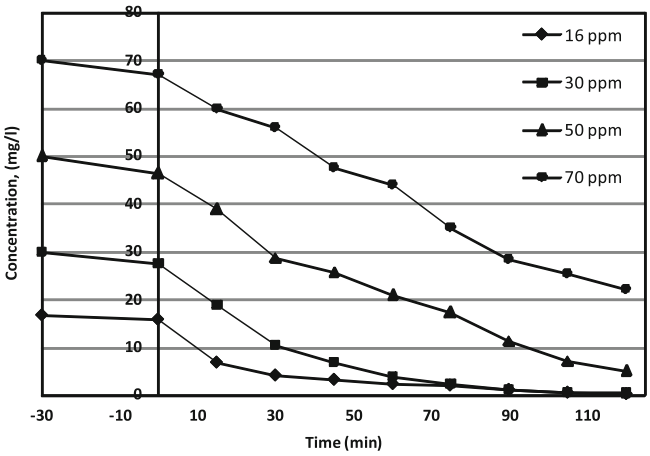

Figure 8. Effect of initial dye concentration on photodegradation efficiency with different exposure durations at 200 mg of TiO_2: ZSM-5.

Neppolian *et al* 2002). The possible reason was that, as the initial concentration of the dye was increased, more dye molecules were adsorbed onto the surface of catalysts. But the adsorbed dye molecules are not degraded immediately because the intensity of light and the catalyst amount was constant and also the light penetration was less. Also with an increase in the dye concentration, the solution becomes more intense coloured and the path length of the photons entering the solution was decreased thereby fewer photons reached the catalyst surface. Hence, the production of hydroxyl and superoxide radicals are limited or reduced. Therefore, the photodegradation efficiency was reduced. Still at higher concentration of the dye, the path length was further reduced and

Table 2. COD values of initial and treated reactive black 5 dye solution.

Catalyst (mg/l)	Initial COD (mg/l)	Final COD (mg/l)	Photodegradation efficiency (%)
TiO_2	97·3	14·56	85·04
15% TiO_2–ZSM-5	97·3	10·32	89·39
30% TiO_2–ZSM-5	97·3	20·86	78·56

the photodegradation was found to be negligible (Poulios and Tsachpinis 1999; Watson *et al* 2004).

$$\text{Photodegradation efficiency (\%)} = (\text{COD}_{\text{initial}} - \text{COD}_{\text{final}}) \times 100/\text{COD}_{\text{initial}} \quad (1)$$

5.5 *Estimation of chemical oxygen demand (COD)*

The chemical oxygen demand (COD) is widely used as an effective technique to measure the organic strength of wastewater. The test allows measurement of waste in terms of the total quantity of oxygen required for oxidation of organic matter to CO_2 and water. The COD of the RB-5 dye solution was estimated before and after treatment using the $K_2Cr_2O_7$ oxidation method. The reduction in the COD values of the treated dye solution indicates the mineralization of dye molecules along with colour removal. Table 2 gives the COD values of blank and treated dye solutions. The photodegradation efficiency is calculated from (1). A maximum of 89·39% of degradation efficiency was obtained in the present study.

6. Conclusions

Impregnation of TiO_2 onto ZSM-5 surface was carried out under mild hydrothermal conditions. The crystal structure and surface morphology was revealed by XRD and SEM studies, respectively. Impregnation of TiO_2 on 15% TiO_2: ZSM-5 shows high adsorption capacity of the catalyst with increase in degradation rate.

A comparative study of the degradation efficiency of commercial TiO_2 (P25), and (15% and 30%) TiO_2: ZSM-5 has shown the efficiency of prepared catalyst. When the loading of TiO_2 exceeds 15 wt % for ZSM-5, the rate of decomposition of RB-5 decreases. The optimization studies revealed dependence of the degradation of reactive black on initial concentration and amount of the catalyst used. This study highlights that the TiO_2: ZSM-5 can be used as an alternative for the conventional isolated use of the TiO_2 photocatalyst.

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