Photocatalytic degradation of model textile dyes in wastewater using ZnO as semiconductor catalyst

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Abstract

Semiconductor photocatalysis often leads to partial or complete mineralization of organic pollutants. Upon irradiation with UV/visible light, semiconductors catalyze redox reactions in presence of air/O_2 and water. Here, the potential of a common semiconductor, ZnO, has been explored as an effective catalyst for the photodegradation of two model dyes: Methylene Blue and Eosin Y. A 16 W lamp was the source of UV-radiation in a batch reactor. The effects of process parameters like, catalyst loading, initial dye concentration, airflow rate, UV-radiation intensity, and pH on the extent of photo degradation have been investigated. Substantial reduction of COD, besides removal of colour, was also achieved. A rate equation for the degradation based on Langmuir–Hinshelwood model has been proposed.
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1. Introduction

Wastewater from textile, paper, and some other industries contain residual dyes, which are not readily biodegradable. Adsorption and chemical coagulation are the two common techniques of treatment of such wastewater. However, these methods merely transfer dyes from the liquid to the solid phase causing secondary pollution and requiring further treatment [1]. Advanced Oxidation Processes (AOPs) are alternative techniques of destruction of dyes and many other organics in wastewater and effluents. These processes generally, involve UV/H_2O_2, UV/O_3 or UV/Fenton's reagent for the oxidative degradation of contaminants. Semiconductor photocatalysis is a newly developed AOP, which can be conveniently applied to dye pollutants for their degradation.

Semiconductors (such as TiO_2, ZnO, Fe_2O_3, CdS, and ZnS) can act as sensitizers for light-induced redox-processes due to the electronic structure of the metal atoms in chemical combination, which is characterized by a filled valence band, and an empty conduction band [2]. Upon irradiation, valence band electrons are promoted to the conduction band leaving a hole behind. These electron-hole pairs can either recombine or can interact separately with other molecules. The holes may react either with electron donors in the solution, or with hydroxide ions to produce powerful oxidizing species like hydroxyl (oxidation potential 2.8 V) or super oxide radicals [3]. Although, TiO_2 in the anatase form has been used for many environmental applications, ZnO (3.2 eV) is a suitable alternative to TiO_2 so far as band gap energy is concerned. The quantum efficiency of ZnO powder is also significantly larger than that of TiO_2 powder, and higher catalytic efficiencies have been reported for ZnO [4].

A lot of studies have been reported on the photocatalytic degradation (PCD) of refractory organics. Bhatkhande et al. [5] reviewed recent works in this area and listed the compounds degraded by photocatalysis by various researchers. Degussa P-25 TiO_2 has been used for many systems either in suspended or in supported forms [6–8]. Phenolic substrates have been tried upon in a majority of the studies [9–11]. In few studies, other semiconductors, such as ZnO [12–14], CdS [15,16], Fe^0 and Zn^0 [17], and WO_3 [12] have been

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used. The biggest advantage of ZnO is that it absorbs over a larger fraction of solar spectrum than TiO$_2$ [4]. For this reason, ZnO photocatalyst is the most suitable for PCD in presence of sunlight.

Literature reports on PCD of dyes are not many. Sunlight mediated photocatalysis of Reactive Blue 4 was reported by Neppolian et al. [13] in a slurry reactor. Degradation of the dye was facilitated by an alkaline pH and by the presence of persulphate and carbonate ions. Optimum catalyst loading was found to be 400 mg/100 ml solution. Pandurangan et al. [14] carried out the PCD of basic yellow Auramine O in a batch reactor, using ZnO exposed to solar radiation. The process followed a pseudo-first order kinetics. The rate constant decreased with increase in initial dye concentration. A lower pH was more suitable. The presence of Fenton's reagent enhanced the degradation rate. Mineralization was indicated by a reduction of COD of the solution. Degradation of Acid Green 16, was studied by Sakthivel et al. [4], using ZnO irradiated with sunlight. Here also the photodegradation efficiency decreased with an increase in initial dye concentration. Optimum catalyst loading was found to be 250 mg in 100 ml. Poulios and Tsachpinis [12], investigated the PCD of Reactive Black 5, using different semiconducting oxides, viz. P-25 Degussa TiO$_2$, UV-100 TiO$_2$, ZnO, and TiO$_2$/WO$_3$. Four parallel blacklight blue fluorescent tubes were used as the UV-light source. The decolourization process was the slowest with TiO$_2$/WO$_3$ and the fastest with ZnO. Photocatalytic activity reached a maximum at a pH around 6. The rate of degradation followed a pseudo first order kinetics based on the Langmuir–Hinshelwood model. Poulios et al. [18] conducted PCD of Auramine O in aqueous suspension using ZnO and TiO$_2$ separately in a batch reactor. The UV-light source was four parallel 18 W lamps. The mineralization process was faster with ZnO. An increase in pH from 2.6 to 8.2 resulted in a four-fold increase in the initial reaction rate. Therefore, in some cases, rate of degradation of pollutants, proceeds faster with ZnO than with P-25 Degussa TiO$_2$ [12,18].

The aim of the present work, is to investigate the potential of ZnO as a photocatalyst under UV radiation for the oxidation of textile dyes in aqueous solutions. Model dyes used were: Methylene Blue and Eosin Y. Effects of parameters like catalyst-loading, initial dye concentration, airflow rate, pH, and UV radiation intensity on the rate of degradation were studied. These are the major variables governing the efficiency of the process. An irradiation time of 2 h was used. Both the removal of colour and the reduction of COD were monitored, because the former does not always confirm the latter. The initial rates of reaction were calculated for various initial dye concentrations. The Langmuir–Hinshelwood model was found suitable for interpreting the initial rate data and for the development of a rate equation for degradation of the dyes. The efficiency of the reused catalyst was also examined.

2. Materials and methods

2.1. Dyes

The model dyes were Eosin Y and Methylene Blue.

Eosin Y:	C.I. number 45380; formula weight 691.914; λ_{max} 516 nm.
Methylene Blue:	C.I. number 52015; formula weight 319.86; λ_{max} 665 nm.

2.2. Photocatalysts

The ZnO catalyst was a GR grade material of 99% purity (LOBA Chemie, India) and was used without any further treatment.

2.3. Analytical methods

The dye concentrations in a sample were determined, using a Shimadzu-160A UV-Visible spectrophotometer against standard calibration curves at appropriate dilutions.

Chemical Oxygen Demand (COD) was determined by the open reflux method, using standard K$_2$Cr$_2$O$_7$ and Mohr salt (APHA Standard Methods [19]).

Optical intensity was measured by digital optical power meter, Advantest TQ8214.

3. Experimental set up and procedure

The reactor was a borosil glass vessel of 4 in. diameter and 12 in. length. A sintered glass disk was fitted at a height of 2 in. from the bottom to disperse air in the liquid. Four 4 W UV lamps were inserted within glass tubes fitted in the holes of the Bakelite lid of the reactor. The glass tubes acted as sheaths of the lamps. There was an additional opening in the lid for collection of samples of solution from the reactor from time to time. Air was supplied to the reactor by an air-compressor. The flow rate of air was measured by a calibrated capillary flow meter. An oil trap, a humidifier and a demister were fitted between the delivery of the compressor and the reactor. Fig. 1 shows a schematic of the experimental set up. A similar reactor with a single, 6 W UV source was used to study the effect of the intensity of irradiation on photocatalysis.

400 ml of a dye solution was taken in the reactor with a weighed quantity of photocatalyst. Air at a predetermined flow rate was bubbled through the sintered disk into the dye solution with the UV lamps OFF till adsorption equilibrium was reached. After the equilibrium had been attained, the UV lamps were turned on. The reactor was wrapped around by an aluminium foil for reflection of UV light back into the reactor. The UV lamps were kept on for a period of 2-h. Samples of approximately 25 ml aliquots were withdrawn from time to time, centrifuged at 8000 rpm to remove any suspended solid and analysed by a Shimadzu-160A UV-Visible
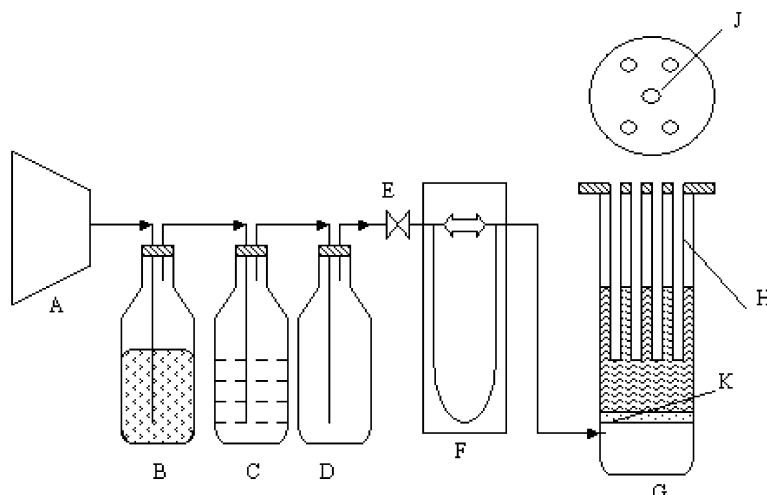
Fig. 1. Experimental set up for PCD of Eosin Y and Methylene Blue, using ZnO. ((A): Air compressor, (B): oil separator, (C): humidifier, (D): demister, (E): needle valve, (F): flow measuring device, (G): photo reactor, (H): UV lamp in glass tube (typ.), (J): sampling port on the lid, (K): sintered glass disk).

spectrophotometer for the undegraded dye in the solution. The COD of the stock and of the degraded solutions were measured following the standard procedure referred to before.

4. Results and discussions

4.1. Characterization of the photocatalyst

The surface area, particle size, morphology, and other characteristics of ZnO catalyst were determined. The BET surface area was found to be $3.23 \, \text{m}^2/\text{g}$. Analysis of particle size distribution was conducted by a dynamic light scattering instrument (Zeta Plus of Brookhaven Instrument Corporation), using a scattering angle of $90°$. The mean particle diameter was 146.7 nm. Fig. 2 shows the surface morphology studied using a scanning electron microscope. The SEM pictures indicate that the particles are non-porous, and form irregular shaped clusters. X-ray diffraction study of the catalyst was done by Philips X'Pert model no. PW 3040/60, using Cu Kα radiation ($\lambda = 1.5060 \, \text{Å}$). The 2θ as well as the d values coincide with those of the standard hexagonal ZnO reported in the literature. FTIR of the ZnO catalyst indicates the presence of water molecule adsorbed on the surface.

4.2. Adsorption of the dyes on ZnO-photocatalyst

Since, the photo-assisted degradation of the dyes occurs predominantly on the photocatalyst surface, studies on the

adsorption of the dyes from aqueous solution onto ZnO particles are relevant and important. The equilibrium concentration of the dye (C_{eq}) in contact with the catalyst, instead of that of the feed dye solution, represents the true dye-concentration in solution at the start of irradiation. For this reason C_{eq} has been used in the kinetic studies of such processes [20].

Adsorption (dark) experiments were carried out for both Methylene Blue and Eosin Y under gentle air agitation in the same experimental set up, taking dye solutions of different initial concentrations. For both the dyes, ZnO loading was 0.4 g in 400 ml solution at a temperature of $30 °C$.

There are quite a few common isotherms used for correlating adsorption equilibrium data [21]. Equilibrium adsorption data collected in this study could be fitted by both Langmuir and Freundlich isotherms. The common forms of these adsorption isotherm equations, respectively, are:

$$q_{eq} = \frac{q_0 C_{eq}}{1 + K_L C_{eq}} \tag{1}$$

$$q_{eq} = K_F C_{eq}^{1/n} \tag{2}$$

where q_{eq} is the dye adsorbed in mg/g of ZnO catalyst surface at equilibrium, C_{eq} the concentration of the solution in mg/l at equilibrium, q_0 the maximum adsorption capacity (Langmuir) in mg/g of ZnO, K_L the Langmuir constant in l/mg, K_F the Freundlich isotherm constant in mg/g of ZnO, n the Freundlich index indicating non-linearity of the system.

The constants of both the isotherms were obtained by least square fitting of the experimental adsorption equilib-

Table 1
Adsorption of dyes on ZnO—Langmuir and Freundlich constants

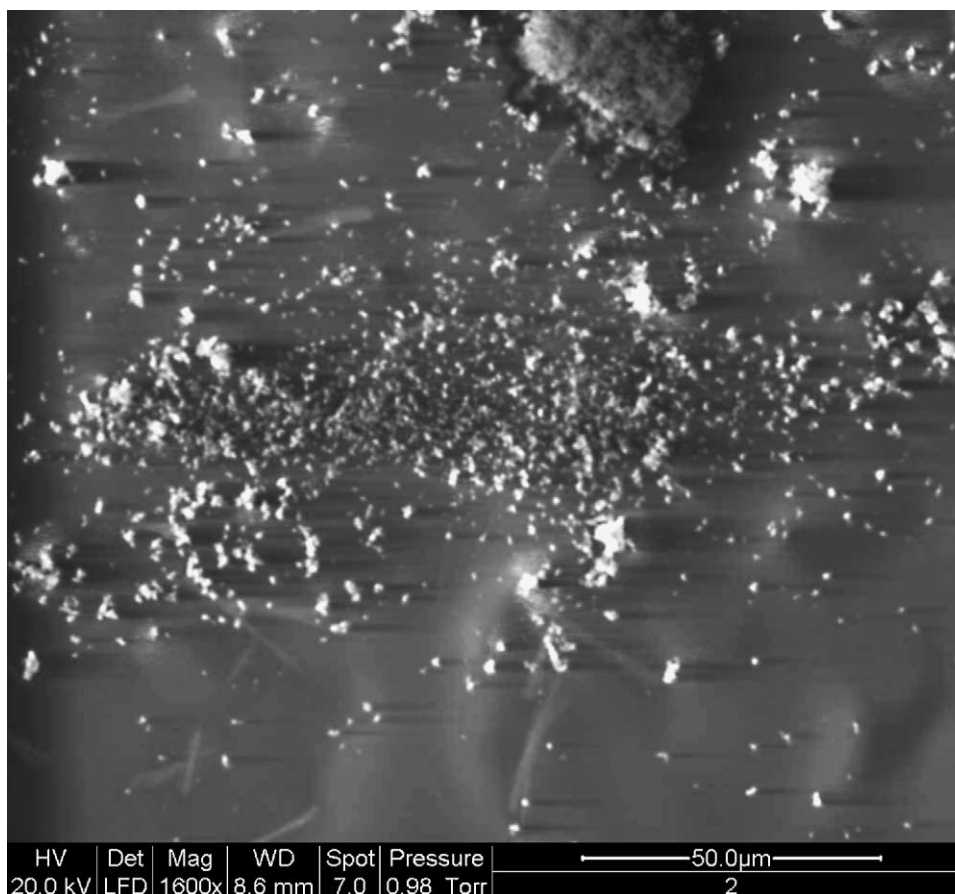| Dye	q_0	K_L	R^2	n	K_F	R^2
Methylene Blue	0.2318	8.62×10^{-3}	0.9797	1.3433	0.4309	0.9587
Eosin Y	0.0539	2.19×10^{-3}	0.8021	1.1111	0.0874	0.7122

Fig. 2. SEM Picture for ZnO Photocatalysts at 1600×.

rium data. Data for Methylene Blue fit better to both the isotherm equations compared to that of Eosin Y. The Langmuir isotherms calculated, using the values of these constants, and the experimental isotherms are shown in Fig. 3.
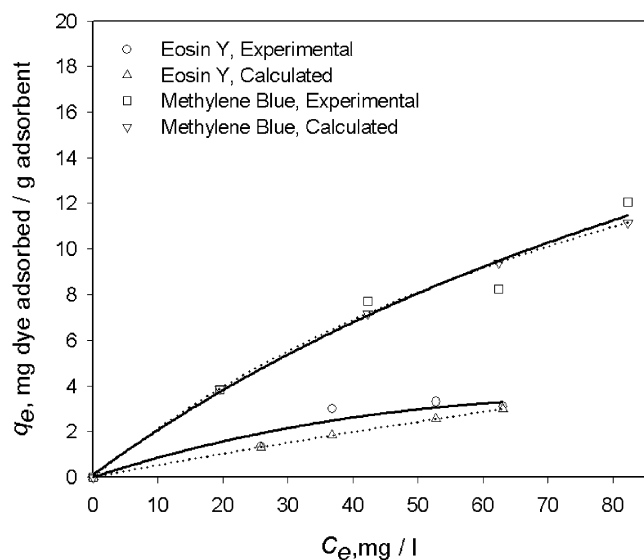
Table 1 gives the constants in Langmuir and Freundlich equations for both the dyes.

4.3. Comparison of degradation of the dyes

The effect of molecular structure and functional groups on PCD was studied by various researchers [5]. Methylene Blue and Eosin Y differ in their molecular structure, and functional group, as well as in the extent of ionization in aqueous solution. Methylene Blue is a cationic/basic dye, whereas, Eosin Y is an anionic/acidic dye and they are expected to behave differently in the photocatalytic process.

Both the dyes were treated at the same experimental conditions, viz. catalyst loading $= 0.4\,g$ in $400\,ml$ solution, wattage of the UV source $= 16\,W$, temperature $= 30\,°C$, airflow rate $= 6.13\,l/min$, initial dye concentration $= 50\,mg/l$, and pH 7.0. Extent of PCD after 2 h was determined by the reduction in absorbance of the solution. It was 58% for Methylene Blue,(a basic dye), compared to 39% for Eosin Y, (an acid dye). Removal of COD for Methylene Blue at the above conditions was 24%, whereas, that for Eosin Y was only 8.1%. This indicates that the dyes were degraded but not completely oxidized.

Fig. 3. Experimental and calculated (Langmuir) adsorption isotherms for Methylene Blue and Eosin Y on ZnO photocatalysts.

As adsorption is a prerequisite for photocatalysis, this may be due to the higher extent of adsorption in case of Methylene Blue than in case of Eosin Y.

4.4. Effect of photocatalyst loading

Some dyes are degraded by direct UV radiation. Therefore, it should be examined to what extent the dyes are 'photolyzed' if no catalyst was used. In other words, it is important to estimate the contribution of direct 'photolysis' in the overall PCD. Blank experiments were carried out for both the dyes without catalyst for this purpose. It is also interesting to determine, the minimum amount of catalyst required to decolorize the maximum amount of dye at a particular experimental condition. For this, experiments were carried out varying the amount of ZnO-photocatalyst for both the dyes.

In the absence of the catalyst, Eosin Y was photolyzed only up to 4% in 2 h. Then with an increased catalyst loading from 0.2 to 1.0 g in 400 ml in a set of runs, the percent of dye degraded after 2 h increased from 47 to 74%. Removal of COD increased from 24.3 to 48.6%. After that, the increase in catalyst loading did not affect the percent degraded significantly. Thus, the catalyst loading for maximum degradation of Eosin Y was 1.0 g in 400 ml solution under the experimental conditions specified in Fig. 4.

In case of Methylene Blue, the experimental conditions were nearly the same as in case of Eosin Y except airflow rate, which was 6.13 l/min. Photolysis in this case was 22% after 2 h without the photocatalyst. Further increase of catalyst loading from 0.4 to 2.4 g in 400 ml solution, increased the photodegradation from 58 to 76% in 2 h. Removal of COD increased from 24 to 32%. Beyond 2.4 g, increase in catalyst loading did not increase the extent of degrada-

tion. Thus, the catalyst loading for maximum degradation of Methylene Blue is 2.4 g in 400 ml solution (Fig. 5).

The increase in the amount of catalyst increased the number of active sites on the photocatalyst surface, which in turn, increased the number of hydroxyl, and superoxide radicals. When the concentration of ZnO catalyst increased above the limiting value, the degradation rate decreased due to the interception of the light by the suspension.

4.5. Effect of initial dye concentration

The influence of initial concentration of the dye solution on the PCD is an important aspect of the study. One can calculate the initial rate of reaction, and thus, the rate constant for the PCD from these data using the Langmuir–Hinshelwood equation. Initial concentrations were varied in the range 25–60 mg/l in case of Eosin Y, and 25–100 mg/l in case of Methylene Blue.

For both the dyes, the PCD decreased with increasing initial concentration of the dye solution. Fig. 6 shows the time–concentration profile for degradation of Methylene Blue at various initial concentrations. Colour-removal decreased from 87 to 40% in 2 h as the approximate initial concentration was increased from 25 to 100 mg/l. Corresponding decrease in COD-removal was from 29 to 9.9%.

In case of Eosin Y, percentage-removal decreased from 93 to 63% in 2 h as the initial concentration of the solution increased from 25 to 50 mg/l, beyond which increase in initial concentration did not affect the removal significantly. A minimum was obtained at approximately 55 mg/l concentration.

With the increase in the concentration of a dye solution, the photons get intercepted before they can reach the catalyst surface, decreasing the absorption of photons by the catalyst. This is what causes reduction in the PCD.
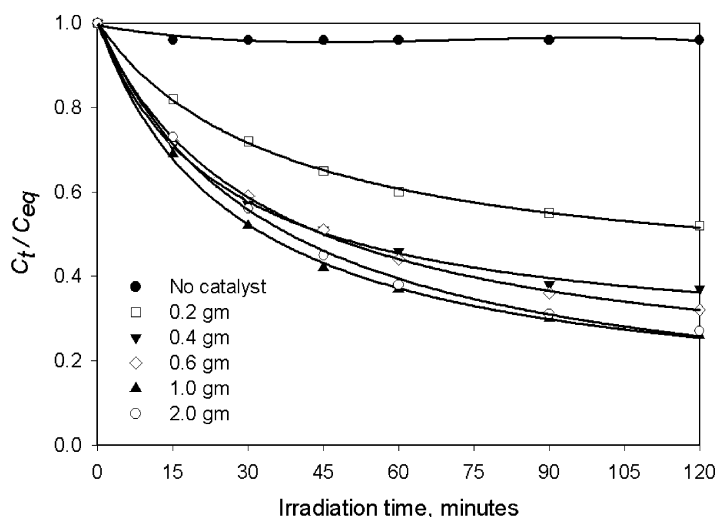

Fig. 4. Effect of catalyst loading on PCD of Eosin Y, using ZnO. (Temperature: 30 °C, solution volume: 400 ml, airflow rate: 11.3 l/min, initial dye concentration: 50 mg/l, pH: 6.9, UV lamp: 16 W).
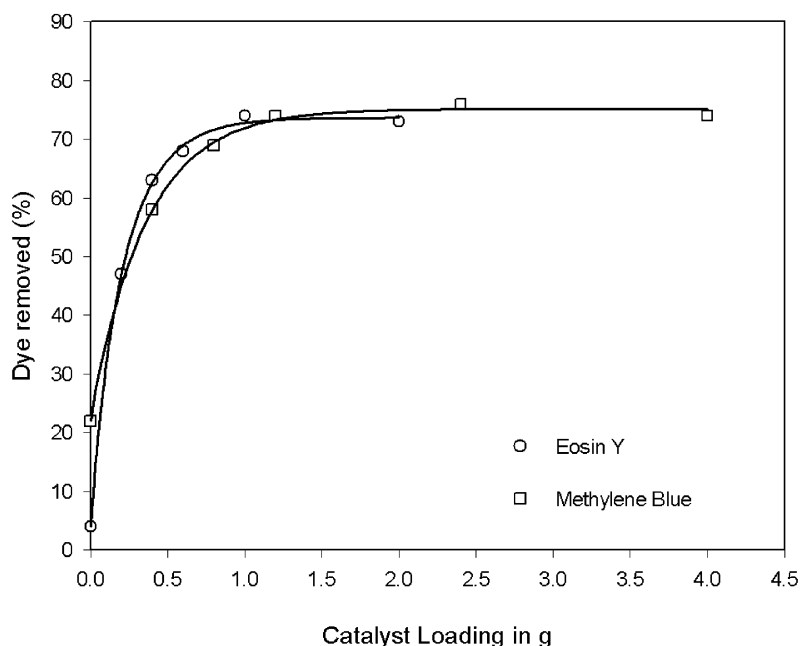
Fig. 5. Limiting catalyst loading for the PCD of Eosin Y and Methylene Blue, using ZnO. (Temperature: 30 °C, solution volume: 400 ml, airflow rate: 11.3 l/min (6.13 l/min for Methylene Blue), initial dye concentration: 50 mg/l, pH: 6.9, UV lamp: 16 W, time: 120 min).

4.6. Effect of airflow rate

Oxygen required for scavenging electrons generated by UV radiation came from the air bubbled through the liquid. The airflow rate was also sufficient to keep the ZnO particles in suspension. It is therefore, pertinent, and useful to study the effect of airflow rate on the rate of PCD.

For both the dyes, the extent of PCD increased with increase in the airflow rate. Fig. 7 shows the fractional-removal of the reaction for Eosin Y at various airflow rates. The percentage degradation increased from 39 to 63% as the airflow rate increased from 0 to 11.3 l/min. Corresponding COD-removal increased from 8.1 to 37.8%. For Methylene Blue, percentage-removal increased from 50 to 58% as the airflow rate increased from 0 to 6.13 l/min. Percentage of COD-removal increased from 20 to 24%.

An increase in the airflow rate increased the supply of oxygen by way of enhanced turbulence, gas holdup, gas–liquid interfacial area, and the mass transfer coefficient. Therefore, the number of hydroxyl and superoxide radicals produced also increased. Hence, the degree of photodegradation increased with an increase in the airflow rate.
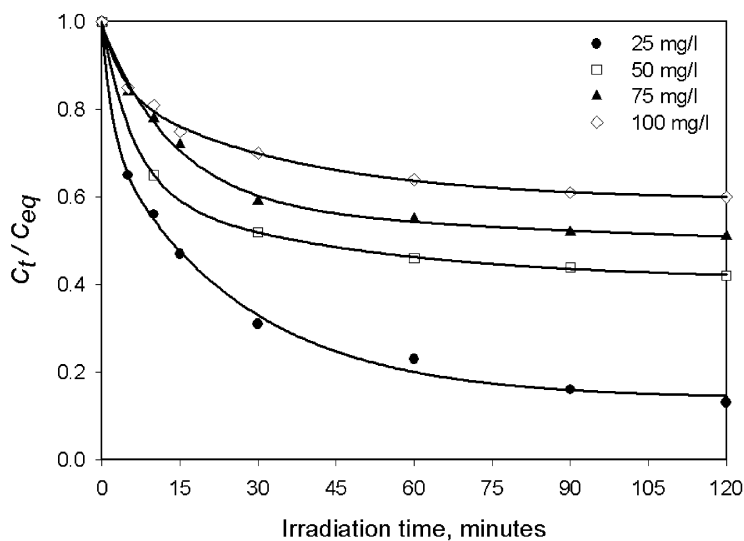

Fig. 6. Effect of initial dye concentration on PCD of Methylene Blue, using ZnO. (Temperature: 30 °C, solution volume: 400 ml, catalyst loading: 0.4 g, airflow rate: 6.13 l/min, pH: 7.5, UV lamp: 16 W).
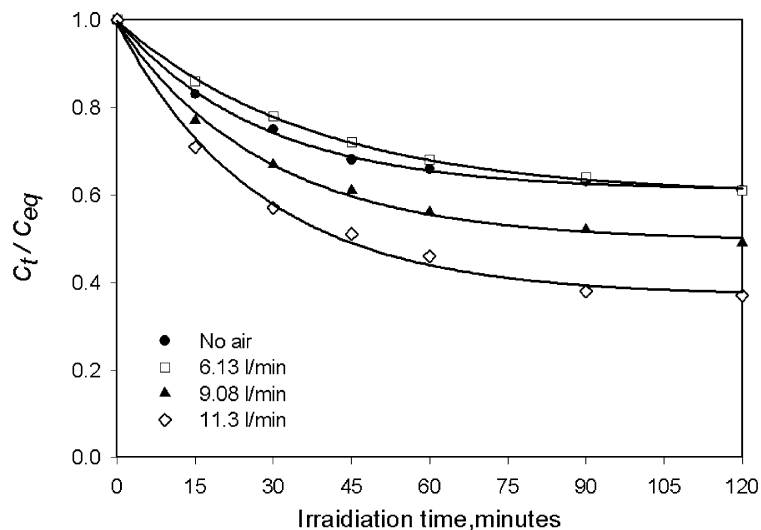
Fig. 7. Effect of airflow rates on PCD of Eosin Y, using ZnO. (Temperature: 30 °C, solution volume: 400 ml, catalyst loading: 0.4 g, initial dye concentration: 50 mg/l, pH: 6.9, UV lamp: 16 W).

Also, possible breakage of the particles because of attrition at a larger airflow rate may generate a larger catalyst surface area, thereby, increasing the rate of degradation. However, we did not check the breakage of catalyst during use.

For both the dyes, the extent of degradation in the absence of air when the catalyst was kept in suspension by magnetic stirrer, was about the same for the case where a low airflow was used to keep the catalyst in suspension. Disintegration of the catalyst by stirring increases the catalyst surface area and simultaneously increases the rate of degradation. But catalyst disintegration is unlikely to occur when kept in suspension by airflow. Also a small air rate does not supply adequate oxygen in solution to generate enough hydroxyl radical to carry out the dye degradation. The above factors together

explain the fact that a low air rate does not enhance the degradation rate above that attained in the absence of air but with magnetic stirrer.

4.7. Effect of pH

Because of the amphoteric behaviour of most semiconductor oxides, an important parameter governing the rate of reaction taking place on semiconductor particle surfaces is the pH of the dispersions, since, it influences the surface-charge-properties of the photocatalysts [20]. Further, industrial effluents may not be neutral. Therefore, the effect of pH on the rate of degradation needs to be considered. Experiments were carried out at pH values of 5.5, 7.5, and 9.7, using 50 mg/l Methylene Blue solutions.
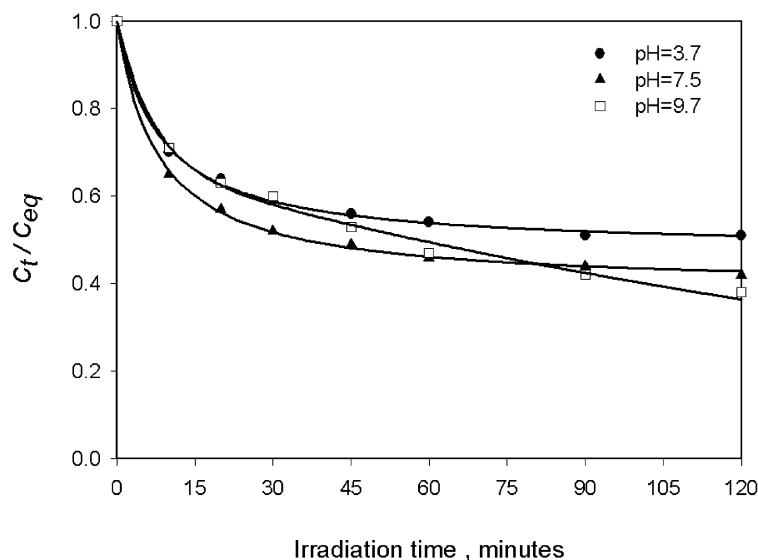

Fig. 8. Effect of pH on Photocatalytic Degradation of Methylene Blue using ZnO. (Temperature: 30 °C, solution volume: 400 ml, catalyst loading: 0.4 g, initial dye concentration: 50 mg/l, airflow rate: 6.13 l/min, UV lamp: 16 W).
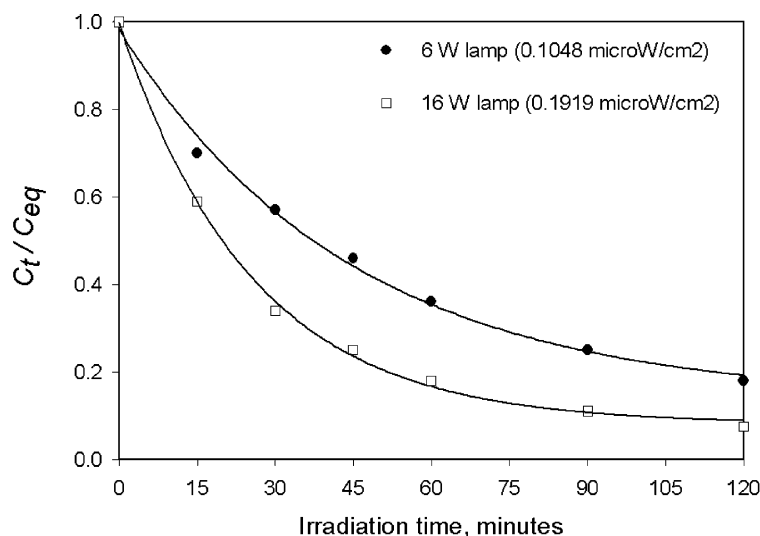
Fig. 9. Effect of UV Lamp Intensity On Photocatalytic Degradation of Eosin Y using ZnO. (Temperature: 30 °C, solution volume: 400 ml, catalyst loading: 0.4 g, initial dye concentration: 25 mg/l, airflow rate: 11.3 l/min, pH: 6.9).

For Methylene Blue, the extent of photocatalysis increased with increase in pH. As the pH increased from 5.5 to 9.7, the percent destruction increased from 49 to 62 in 2 h. Fig. 8 shows the time–concentration profiles of degradation of Methylene Blue at various pH.

The decrease in the PCD at acidic pH may be due to a very high adsorption at low pH. As the catalyst surface was covered by the dye molecules, the absorption of UV radiation on the catalyst surface decreased. At higher pH, there was excess of OH^- anions, which facilitate photogeneration of hydroxyl radicals. Change in pH shifts the redox-potentials of valence and conduction bands, which may affect interfacial charge-transfer.

4.8. Effect of Light intensity

UV irradiation generates the photons required for the electron transfer from the valence band to the conduction band of a semiconductor photocatalyst. The energy of a photon is related to its wavelength and the overall energy input to a photocatalytic process is dependent on the light intensity. Therefore, the effects of both intensity and wavelength are important. Here, we have studied the effect of lamp intensity only keeping the wavelength (356 nm) unaltered.

A 6 W lamp and 4 × 4 W lamps were used in different experiments. Average optical intensities measured inside the reactor were $0.1919 \, \mu W/cm^2$ with the 16 W lamp and $0.1048 \, \mu W/cm^2$ with the 6 W lamp.

For Eosin Y, extent of photo degradation decreased from 93 to 82% as the light intensity decreased from 0.1919 to $0.1048 \, \mu W/cm^2$ under the same experimental conditions. Fig. 9 shows the concentration history of degradation. This is due to the decrease in the number of photons generated with a reduced intensity of the lamp.

But in case of Methylene Blue, the degradation percent increased from 58 to 74 in 2 h as the intensity of the lamp decreased from 0.1919 to $0.1048 \, \mu W/cm^2$. Electron-hole recombination is normally predominant at a higher intensity of irradiation. Moreover, airflow rate was less in case of Methylene Blue leading to the insufficient supply of electron scavenger. The combined effect may be responsible for the reverse trend.

4.9. Efficiency of the recycled catalyst

Photocatalysis is a clean technology, which normally does not involve any waste disposal problem. The catalysts can be recycled. TiO_2 can be used at least twice without significant change in the efficiency [16]. The economy of the photocatalytic process depends upon how many times a catalyst can be reused without sacrificing its efficiency and the type of regeneration it requires.

The photodegradation efficiencies of the two recycled catalysts RC-1 and RC-2 were examined. RC-1 achieved 21% and RC-2 achieved 23% removal of Eosin Y dye compared to 39% obtained with the fresh catalyst under the same experimental conditions. The used catalyst was regenerated to get RC-1 first by treating with boiling distilled water till a colorless wash liquid was obtained and then by drying it in a hot air oven at a temperature of 90 to 100 °C. RC-1 was heated in a muffle furnace at about 600 °C to yield RC-2.

The decrease in the efficiency of the recycled catalyst may be attributed to the deposition of photoinsensitive hydroxides (fouling) on the photocatalysts surface blocking its active sites. This is a major problem of working with photocatalysts like ZnO and CdS.

5. Rate equation for degradation

Turchi and Ollis [22] made a detailed investigation on the reaction mechanism of TiO_2-photocatalysis. It has been re-

ported in the literature that the initial rates of photo degradation of different compounds are pretty close under otherwise identical conditions. This can only be explained by a rate-limiting step consisting of hydroxyl radical formation or attack. Hydrogen peroxide also contributes to the degradation of the substrate by acting as a direct electron acceptor or as a source of the hydroxyl radical. Electron transfer to oxygen may also be the rate-limiting step. In most cases, oxygen gas is present as electron scavenger and it has been observed that hydrogen peroxide originates entirely from it [2]. Hoffman et al. have also shown that ZnO produces H_2O_2 more efficiently than TiO_2. The ZnO photo-assisted degradation, therefore, may have proceeded through either by photo catalytic oxidation or by oxidation with the photo catalytically generated H_2O_2, or by the simultaneous operation of the both pathways [23].

For engineering purposes, it is useful to find out a simple and easy-to-use rate equation that fits the experimental rate data. Since, adsorption is considered critical in the heterogeneous photocatalytic oxidation process, the Langmuir–Hinshelwood model was used to describe the photo-oxidation kinetics of dyes by a few previous researchers [3]. This treatment is subject to the assumptions that sorption of both the oxidant and the reductant is a rapid equilibrium process and that the rate-determining step of the reaction involves both species present in a monolayer at the solid–liquid interface [2].

Langmuir–Hinshelwood pseudo-first order kinetic model, modified to accommodate reactions occurring at a solid-liquid interface is as follows [12]:

$$r_0 = -\frac{dc}{dt} = \frac{k_r K C_{eq}}{1 + K C_{eq}} \qquad (3)$$

where r_0 is the initial rate of reaction in mg/l min, k_r the rate constant for photocatalysis in mg/l min, K the rate constant for adsorption in l/mg, C_{eq} the concentration of bulk solution in mg/l at adsorption equilibrium, c the concentration of bulk solution at any time t, t the time in minutes.

This may be linearized as follows:

$$\frac{C_{eq}}{r_0} = \frac{1}{k_r} C_{eq} + \frac{1}{k_r K} \qquad (4)$$

Experimental data on C_{eq}/r_0 were plotted against C_{eq} for both the dyes in Fig. 10. The initial rate of degradation was obtained from the derivative of the time–concentration curve in first 10 min. Eq. (4) shows an excellent fit for the data on Eosin Y (correlation coefficient 0.98). For Methylene Blue also, a pretty good straight line was obtained although with a slightly smaller correlation coefficient. The rate constants obtained from the plots are given in Table 2.

It is noteworthy that the Langmuir adsorption constants obtained from the dark experiments are significantly different from that determined from the Langmuir–Hinshelwood equation. This is due to the photoadsorption and very rapid photoreaction of the dyes on the catalyst surface [20].
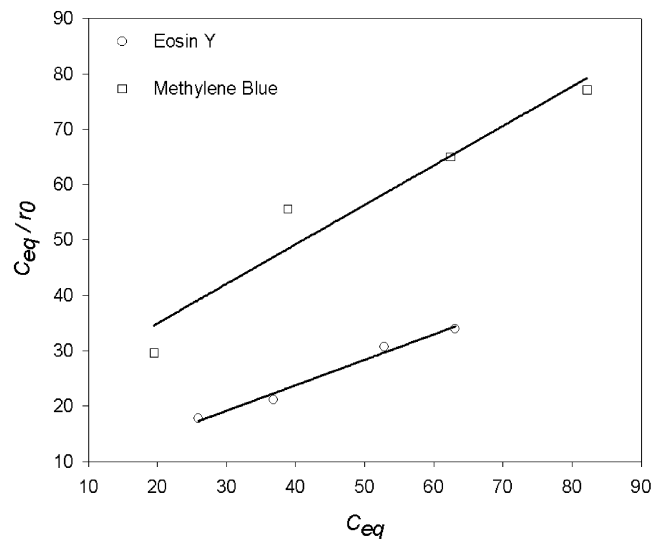

Fig. 10. Initial reaction rate plots.

Table 2
Constants for photocatalysis and adsorption

Constants	Methylene Blue	Eosin Y
Photocatalysis (k_r)	1.4023	2.1743
Adsorption (L–H equation) (K)	0.0345	0.0859
Adsorption (dark) (Langmuir) (K_L)	8.623×10^{-3}	2.193×10^{-3}

6. Conclusions

The PCD of Methylene Blue and Eosin Y with ZnO was effective in the removal of these dyes from aqueous solution. In addition to the removal of colors, the reaction simultaneously reduced the COD suggesting that the dissolved organics were at least partially oxidized. The oxidation process required air, water, a photocatalyst, and UV radiation.

The PCD efficiency has been generally, found to increase with increase in catalyst loading up to a limiting value, decrease in initial concentration, increase in airflow rate, pH, and UV light intensity. Of the two dyes, Methylene Blue was degraded faster.

The rate equation for the PCD followed pseudo-first order kinetics and the rate-constants were determined, using Langmuir–Hinshelwood model. The kinetic model was based on hydroxyl radical attack. The efficiency of the once-recycled catalyst was reduced to 58.9% of the fresh catalyst.

Therefore, this simple technology of PCD of the colored effluents has the potential to improve the quality of the wastewater from textile and other industries. The economy may be further improved using certain modifications.

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