

Studies on photodegradation of two commercial dyes in aqueous phase using different photocatalysts

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Abstract

The present study involves the photocatalytic degradation of Methyl Orange (MO) and Rhodamine 6G (R6G), employing heterogeneous photocatalytic process. Photocatalytic activity of various semiconductors such as titanium dioxide (TiO₂), zinc oxide (ZnO), stannic oxide (SnO₂), zinc sulphide (ZnS) and cadmium sulphide (CdS) has been investigated. An attempt has been made to study the effect of process parameters viz., amount of catalyst, concentration of dye and pH on photocatalytic degradation of MO and R6G. The experiments were carried out by irradiating the aqueous solutions of dyes containing photocatalysts with UV and solar light. The rate of decolorization was estimated from residual concentration spectrophotometrically. Similar experiments were carried out by varying pH (2–10), amount of catalyst (0.25–2.0 g/l) and initial concentration of dye (5–200 mg/l). The experimental results indicated that the maximum decolorization (more than 90%) of dyes occurred with ZnO catalyst and at basic pH and the maximum adsorption of MO was noticed at pH 4 and of R6G at pH 10. The percentage reduction of MO and R6G was estimated under UV/solar system and it was found that COD reduction takes place at a faster rate under solar light as compared to UV light. In case of R6G, highest decolorizing efficiency was achieved with lower dose of catalyst (0.5 g/l) than MO (1 g/l) under similar conditions. The performance of photocatalytic system employing ZnO/solar light was observed to be better than ZnO/UV system.

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1. Introduction

Textile industries produce large volume of colored dye effluents which are toxic and non-biodegradable [1]. These dyes create severe environmental pollution problems by releasing toxic and potential carcinogenic substances into the aqueous phase. Various chemical and physical processes such as precipitation, adsorption, air stripping, flocculation, reverse osmosis and ultra-filtration can be used for color removal from textile effluents [2–5]. However these techniques are non-destructive, since they only transfer the non-biodegradable matter into sludge, giving rise to new type of pollution, which needs further treatment [6–8].

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 [9,10]. 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 [11–20].

Titanium dioxide (TiO₂) is generally considered to be the best photocatalyst and has the ability to detoxify water from a number of organic pollutants [15–17]. However widespread use of TiO₂ is uneconomical for large scale water treatment, thereby interest has been drawn towards the search for suitable alternatives to TiO₂. Many attempts have been made to study photocatalytic activity of different semiconductors such as SnO₂, ZrO₂, CdS and ZnO [18–22]. Lizama et al. [21] reported the photocatalytic decolorization of Reactive Blue 19 (RB-19) in aqueous solutions containing TiO₂ or ZnO as catalysts and concluded that ZnO is a more efficient catalyst than TiO₂ in the

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color removal of RB-19. Daneshvar et al. [23] 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 . The biggest advantage of ZnO is that it absorbs over a larger fraction of solar spectrum than TiO_2 . For this reason, ZnO photocatalyst is the most suitable for photocatalytic degradation in the presence of sunlight [24]. Only a handful studies have been attempted which compare the efficiency of different catalysts for a particular dye under identical conditions.

In India being a tropical country, sunlight is abundantly available natural energy source, which can be conveniently exploited for the irradiation of semiconductor. Dyes can be degraded in the presence of photocatalyst upon irradiation with visible light because of their absorption in the visible region. Studies have been carried on photodegradation of the dyes preadsorbed on the surface of TiO_2 particles with visible light [25,26] in which the photoreaction system was almost water free and only the molecules that were in direct contact with the TiO_2 surface underwent photodegradation. The photoassisted degradation of erythrosine and Rhodamine B has been investigated in an aque-

ous TiO_2 dispersion under irradiation by visible light [27]. Wang [28] investigated the photocatalytic degradation of eight commercial dyes including MO in TiO_2 suspension under solar light. The possibility of using solar irradiation for detoxification of MO as a model compound was also explored by other workers [29]. Wang et al. [30] prepared and investigated the photocatalytic activity of ZnO/ TiO_2 / SnO_2 mixture for decolorization of MO under UV light and found that this mixture was photocatalytically more active than TiO_2 and SnO_2 but slightly less active ZnO. Chen et al. [31] studied the photocatalytic degradation of R6G by electrochemically assisted TiO_2 photocatalytic system.

Rhodamine 6G (R6G) is a basic dye used to dye wool, cotton, silk and papers where brilliant shades of fluorescent effects are required. Methyl Orange (MO) is an azo dye and also has a variety of uses in textiles, foodstuffs, pulp and paper, and leather industry. The release of these complex dyes and their products in the environment cause toxicity problems [32–34]. So an attempt has been made to study the decolorization of these dyes.

In this study, various semiconductor photocatalysts (TiO_2 , ZnO, SnO_2 , ZnS and CdS) were compared for the decolorization efficiency of aqueous solution of these dyes, MO and R6G. After

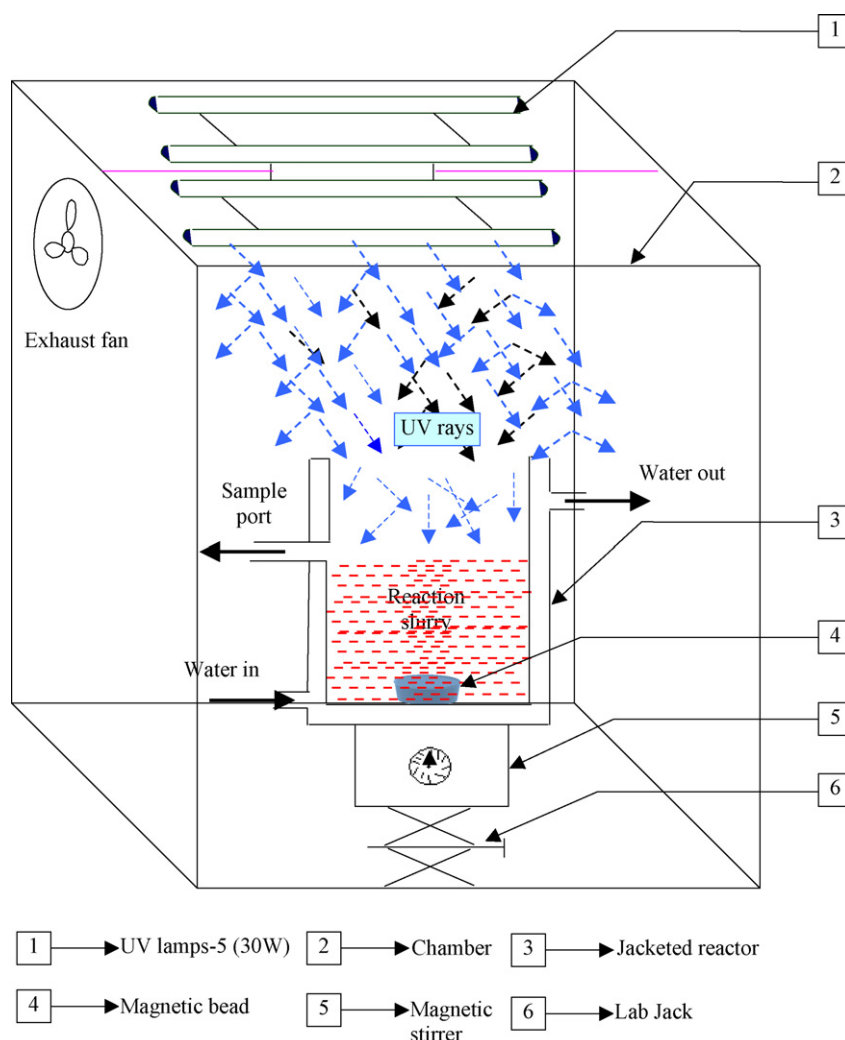


Fig. 1. Experimental setup for photocatalytic process.

the selection of the most active catalyst, subsequent experiments were conducted to investigate the effects of various process parameters (catalyst loading, pH, and initial dye concentration) on the process performance. The decolorization efficiencies of MO and R6G have also been studied by using ZnO/solar light photocatalytic system.

2. Experimental methods

2.1. Materials

Titania P-25 (surface area 50 m²/g) was obtained from Degussa, SnO₂ and CdS were obtained from S.D. Fine Chemicals, India. ZnO (5 m²/g), ZnS, Methyl Orange and Rhodamine 6G were purchased from Merck and were used without further purification. Double distilled water was used for preparation of various solutions. pH of the solutions was adjusted with 1 M HCl or 1 M NaOH. COD (open reflux) was estimated by using standard methods [35].

2.2. Instruments

Photochemical degradation was carried out in specially designed double walled reaction vessels (volume 500 ml) in the UV chamber equipped with five UV tubes each of 30 W (Philips) having wavelength 365 nm (Fig. 1). Constant stirring of solution was insured by using magnetic stirrers. The temperature was maintained constant throughout the reaction time by circulating the water in the jacketed wall reactor. For solar experiments, the borosilicate glass reactors of diameter 0.17 m and 800 ml capacity were made with ports at the top for sampling, gas purge and gas outlet. The solar experiments were performed in daytime between 10 a.m. and 4 p.m. The spectra were taken with UV–vis spectrophotometer (Systronics 119); pH meter (Thermo Orion 920A) was used to adjust the pH of the solution.

2.3. Irradiation experiments

To 100 ml of dye solution, photocatalyst was added and suspension was subjected to irradiation. Experiments were carried out under UV light as well as under solar light. The aqueous suspension was magnetically stirred throughout the experiment. At different time intervals aliquot was taken out with the help of a syringe and then filtered through 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} of the dyes. The decolorization efficiency (%) has been calculated as:

$$\text{efficiency (\%)} = \frac{C_0 - C}{C_0} \times 100$$

where C₀ is the initial concentration of dye and C is the concentration of dye after photoirradiation. Similar experiments were carried out by varying the pH of the solution (pH 2–10), concentration of dye (5–200 mg/l) and catalyst loading (0.25–2.0 g/l).

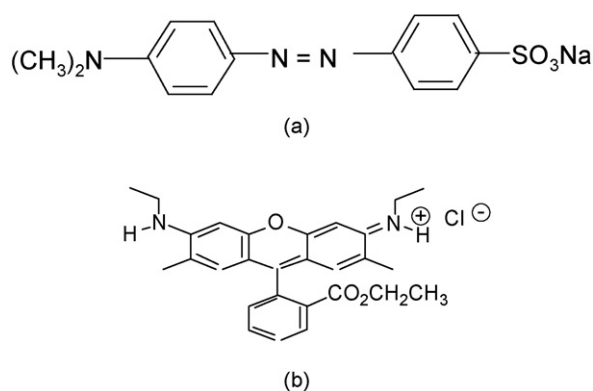


Fig. 2. (a) Structure of Methyl Orange; (b) structure of Rhodamine 6G.

3. Results and discussion

Methyl Orange and Rhodamine 6G dyes have different molecular structure and different functional groups (Fig. 2a and b). MO is an azo dye having sulphonate (SO₃⁻) and azo groups. R6G has xanthene group, showing absorption peak at 523 nm. The photodegradation experiments were carried out under UV light and solar light. Different catalysts viz., TiO₂, ZnO, SnO₂, ZnS and CdS were investigated for their decolorization efficiency. The rate of decolorization was recorded in terms of change in intensity of characteristic peaks.

3.1. UV–vis spectra of dyes

Figs. 3 and 4 show typical time dependent UV–vis spectrum of MO and R6G, respectively, during photoirradiation with ZnO catalyst. MO shows absorption peaks at 272 and 462 nm and R6G show main absorption peaks at 523 nm in visible region and 276 and 343 nm in UV region.

The rate of decolorization was recorded with respect to the change in intensity of absorption peaks at 462 and 523 nm for MO and R6G, respectively. The absorption peaks, corresponding to dyes diminished and finally disappeared during reaction, which indicated that the dyes had been degraded.

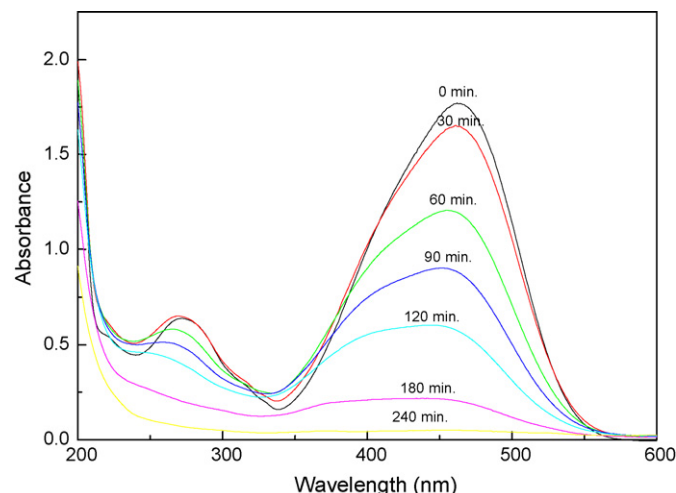


Fig. 3. Absorbance spectra of Methyl Orange during the course of reaction.

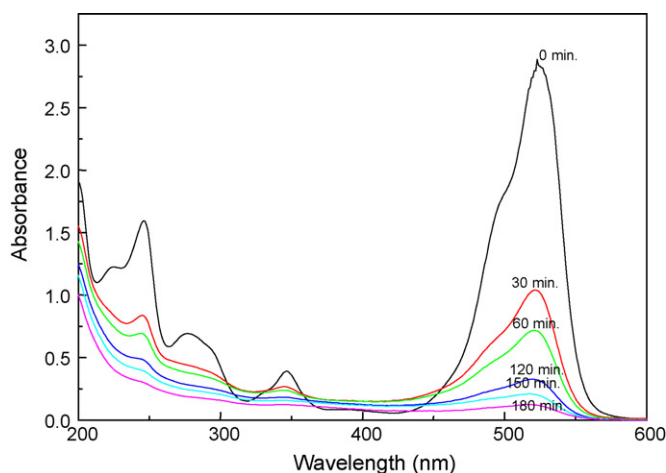
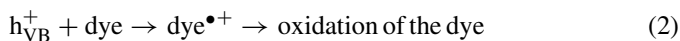
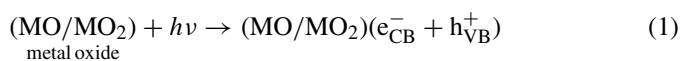


Fig. 4. Absorbance spectra of Rhodamine 6G during the course of reaction.

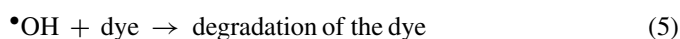
3.2. Decolorization of dyes using various photocatalysts

Investigations were carried out with different semiconductors viz., TiO_2 , ZnO , SnO_2 , ZnS and CdS in order to select the most effective catalyst for degradation of dyes. Band positions of these semiconductors are listed in Table 1.

The photocatalysed 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)):



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 ($E^0 = +3.06 \text{ V}$) which leads to the partial or complete mineralization of several organic chemicals [23]:



Initially blank experiments were performed under UV irradiation without addition of any catalyst and negligible decol-

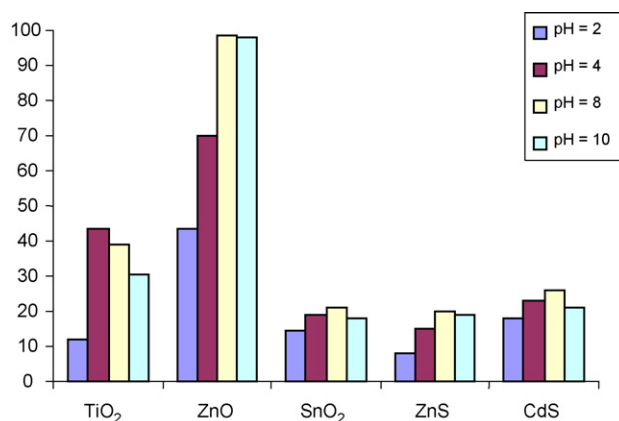


Fig. 5. Photocatalytic efficiency of various catalysts for Methyl Orange at different pH (dye concentration 25 mg/l; catalyst dose 1 g/l; time 4 h).

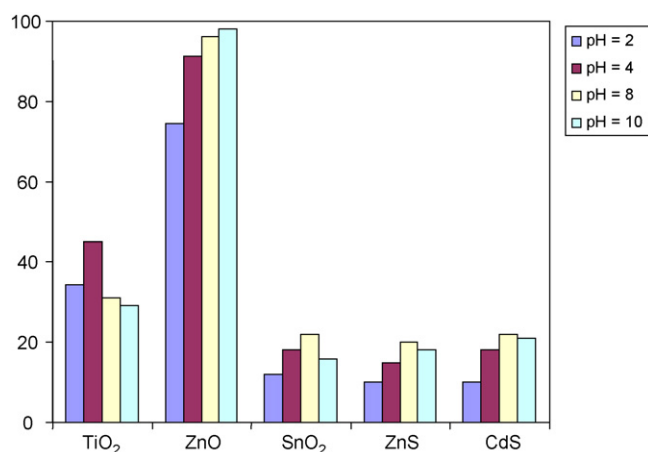


Fig. 6. Photocatalytic efficiency of various catalysts for Rhodamine 6G at different pH (dye concentration 25 mg/l; catalyst dose 0.5 g/l; time 3 h).

orization was observed. Then photocatalytic experiments were carried out using different catalysts, various pH values (2, 4, 8, and 10) at fixed dye concentration (25 mg/l), and catalyst loading of 1 g/l for 4 and 3 h for MO and R6G dyes, respectively. The results indicated that ZnO exhibits higher photocatalytic activity than the others, especially TiO_2 for both the dyes. Figs. 5 and 6 depict the photocatalytic efficiency of various catalysts for MO and R6G at different pH values. The same trend was observed in earlier findings with azo reactive dyes [21,22]. This was explained as ZnO is having greater quantum efficiency than TiO_2 and others. CdS with smaller band gap in which the electrons (CB) in this semiconductor rapidly fall into hole, shows reduced

Table 1
Band positions of some common semiconductor photocatalysts in aqueous solution at pH 1

Semiconductor	Valence band (V vs. NHE)	Conductance band (V vs. NHE)	Band gap (eV)	Band gap wavelength (nm)
TiO_2	+3.1	−0.1	3.2	387
SnO_2	+4.1	+0.3	3.9	318
ZnO	+3.0	−0.2	3.2	387
ZnS	+1.4	−2.3	3.7	335
CdS	+2.1	−0.4	2.5	496

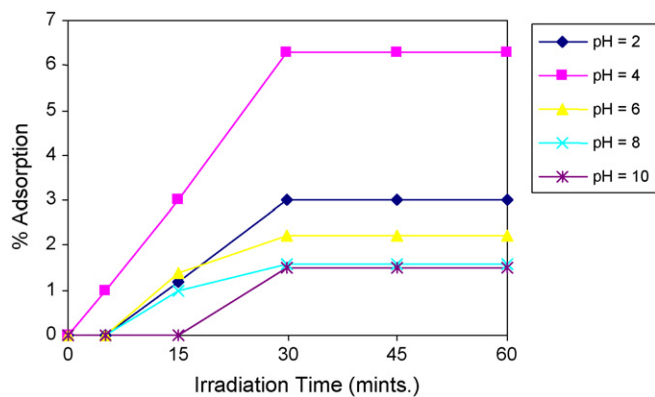


Fig. 7. Adsorption behavior of MO at different pH.

activity. On the other hand SnO_2 exhibits less activity because their wide band gap and light energy is not sufficient to excite this catalyst [24]. The metal sulphide semiconductors are unsuitable based on the stability requirements in that they readily undergo photoanodic corrosion. The order of decolorization efficiency of various photocatalysts is $\text{ZnO} > \text{TiO}_2 > \text{CdS} > \text{SnO}_2 > \text{ZnS}$ for decolorization of MO and R6G. Besides higher efficiency, the other advantage of ZnO is its low cost. Thus subsequent experiments were carried out with ZnO.

3.3. Adsorption behavior of dyes

In order to investigate the adsorption/desorption behavior of MO and R6G at different pH values, the suspension were prepared by mixing 100 ml of dye solutions (25 mg/l) for 60 min with fixed catalyst dose (1 g/l for MO and 0.5 g/l for R6G). The suspensions were kept for given times in the dark under the condition of stirring, and then filtered after being centrifuged. The absorbance of the filtrate was then measured at the maximum band 462 nm of MO and 523 nm of R6G to determine the concentration of dyes. The experimental results are shown in Figs. 7 and 8 for MO and R6G, respectively. From the results, it was noticed that the adsorption/desorption equilibrium of MO and R6G at different pH values under 25 mg/l initial concentration was reached at about 30 min of equilibration time and could not be degraded in the experimental conditions with catalyst but without light irradiation. The maximum adsorption of

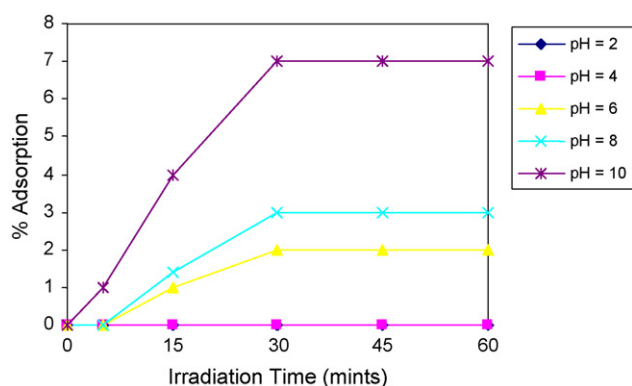


Fig. 8. Adsorption behavior of R6G at different pH.

MO (anionic dye) was seen at pH 4 and of R6G (cationic dye) at pH 10. Hasnat et al. [36] reported similar findings during comparative photocatalytic studies of decolorization of an anionic and a cationic dye.

3.4. Decolorization of dyes by ZnO as photocatalyst under UV light

The experiments were carried out to study the degradation of MO and R6G employing ZnO as catalyst under UV light. Various parameters which effect the decolorization efficiency such as catalyst loading (0.25–2.0 g/l), pH (2–10), initial concentration of dye (5–200 mg/l) and time (0–240 min) of decolorization were assessed under UV light.

3.4.1. Effect of catalyst concentration

In order to determine the effect of catalyst loading, the experiments were performed by varying catalyst concentration from 0.25 to 2.0 g/l for dye solutions of 25 mg/l at natural pH (6.4 for MO and 5.97 for R6G). The decolorization efficiency for various catalysts loading for MO and R6G has been depicted in Fig. 9. Fig. 9 reveals that initial slopes of the curves increase greatly by increasing catalyst loading from 0.25 to 1.0 g/l for MO thereafter the rate of decolorization remains almost constant. In case of MO maximum decolorization is observed with 1.0 g/l and for R6G maximum decolorization was possible with merely 0.5 g/l dose and thereafter increase in the dose of catalyst had no effect. The photocatalytic destruction of other organic pollutants has also exhibited the same dependency on catalyst dose [22]. This can be explained on the basis that optimum catalyst loading is found to be dependent on initial solute concentration because with the increase of catalyst dosage, total active surface area increases, hence availability of more active sites on catalyst surface [37]. 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 [23]. 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 dose 1 and 0.5 g/l were fixed for MO and R6G, respectively, for further studies.

3.4.2. 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. To study the effect of pH on the decolorization efficiency, experiments were carried out at various pH values, ranging from 2 to 10 for constant dye concentration (25 mg/l) and catalyst loading (1 and 0.5 g/l, respectively, for MO and R6G). Fig. 10 shows the color removal efficiency of MO and R6G as a function of pH. It has been observed that the decolorization efficiency increases with increase in pH exhibiting maximum rate of degradation at pH 10 for R6G and pH 8 for MO. Similar behavior has also been reported for the photocatalytic efficiency of ZnO for decolorization of azo dyes [21,22,24]. The interpretation of pH effects on the efficiency of the photocatalytic degradation process is a very difficult

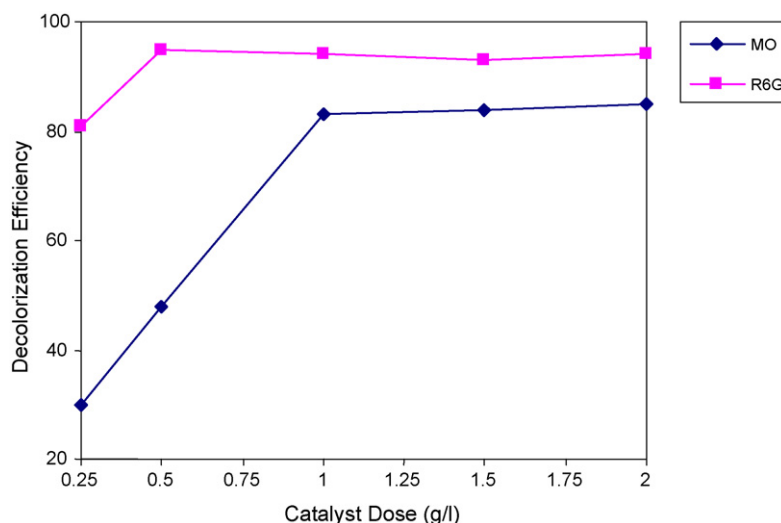
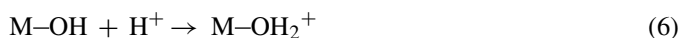


Fig. 9. Effect of catalyst dose on decolorization efficiency of Methyl Orange and Rhodamine 6G (dye concentration 25 mg/l; pH neutral).

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) [38]. Due to amphoteric behavior of most metal hydroxides, the following two equilibrium reactions are considered (Eqs. (6) and (7)):



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 [22].

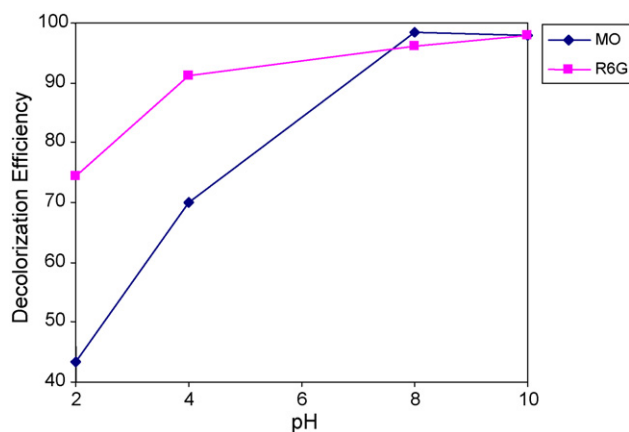


Fig. 10. Effect of pH on decolorization efficiency of Methyl Orange and Rhodamine 6G (dye concentration 25 mg/l).

The experimental results revealed that higher degradation of the dyes occurred in basic region than in case of acidic solution. For MO, rate of photodecolorization increased with increase in pH, exhibiting maximum efficiency (98.5%) at pH 8, beyond which the rate of degradation remained constant. 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. Also 97.9% decolorization was observed at pH value 10. Although the adsorption of dye molecules are low at alkaline pH, the possible reason for this behavior may be the formation of more $\bullet\text{OH}$ radicals. Sakthivel et al. [24] observed similar behavior in their studies on Acid Brown 14 dye. In case of R6G, the rate of photodecolorization increased with increase in pH and reached maximum at pH 10 value. The interpretation for the same could be amphoteric behaviors of the ZnO catalyst.

3.4.3. Effect of concentration of dye

After optimizing the pH conditions and catalyst dose (pH 8.0 and catalyst dose 1 g/l for MO, pH 10 and catalyst dose 0.5 g/l for R6G), the photocatalytic decolorization of both dyes was carried out by varying the initial concentrations of the dye from 5 to 200 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. Figs. 11 and 12 depict the time dependent graphs of decolorization of MO and R6G at different concentrations of dye solutions (5–200 mg/l). In case of MO, for dye solutions of 5 and 10 mg/l, almost 100% degradation occurred within 60 and 120 min, respectively, and in case of 25 mg/l, almost complete degradation was observed in 4 h. For 50 mg/l of the dye solution degradation was 75% in 4 h and it gets further decreased on increasing the concentration of dye. Similar trend was observed in case of R6G, where complete decolorization of 25 mg/l dye under optimized conditions was achieved in 3 h (Fig. 12). The possible explanation for this behavior is that as the initial concentration of the dye increases, the path length of the photons

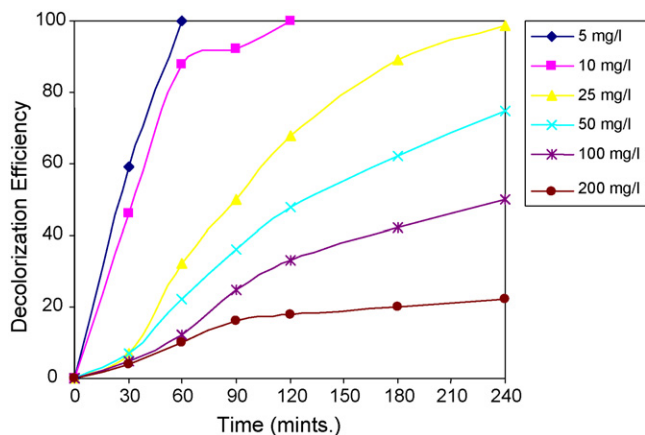


Fig. 11. Effect of concentration of Methyl Orange on decolorization efficiency under UV (dye concentration 25 mg/l; catalyst dose 1 g/l; time 4 h; pH 8).

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 [39]. The same effect was observed by Neppolian et al. [19] during the photocatalytic degradation of three commercial textile dyes (Reactive Yellow, Reactive Red and Reactive Blue) using TiO_2 as photocatalyst under solar light.

3.4.4. Kinetic study

Figs. 13 and 14 show the kinetics of disappearance of MO and R6G 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 $R^2 = 0.9836$ and 0.9880 for MO and R6G, respectively. The rate constants were calculated to be 2.9×10^{-4} and $2.7 \times 10^{-4} \text{ s}^{-1}$.

3.5. Decolorization of dyes under solar light

The photoassisted decolorization of MO and R6G was also carried out using ZnO as photocatalyst and solar irradiation as

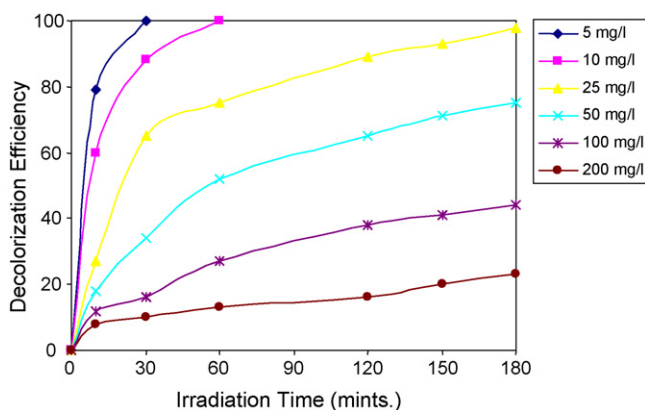


Fig. 12. Effect of concentration of Rhodamine 6G on decolorization efficiency under UV (dye concentration 25 mg/l; catalyst dose 0.5 g/l; time 3 h; pH 10).

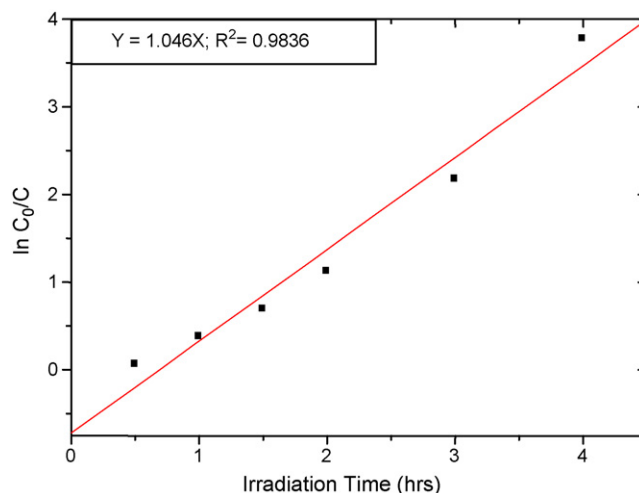


Fig. 13. Kinetic analysis of Methyl Orange under optimized conditions.

light source. Figs. 15 and 16 illustrate the results of photodecolorization of the respective dyes using optimized conditions as a function of irradiation time under solar light. The results indicate that decolorization of MO and R6G occur at a faster rate with solar light in comparison to UV light. In case of MO, 98.92% decolorization efficiency was observed in 90 min irradiation time under solar light, whereas in the presence of UV irradiation for the same duration, only 50% decolorization efficiency was recorded (Fig. 17). For R6G similar trend was observed, as shown in Fig. 18 where 91% decolorization was achieved in first 30 min under solar light in comparison to 65% decolorization under UV light. The results are in agreement with the earlier findings [24], that ZnO can harvest maximum solar energy by utilizing visible light for degradation of water bound organics.

Although sunlight has only 5% of optimum energy for photocatalytic excitation and ultimately for degradation of pollutants, it could be safe and cost effective source. UV source is not only hazardous but also expensive because of large input of electric

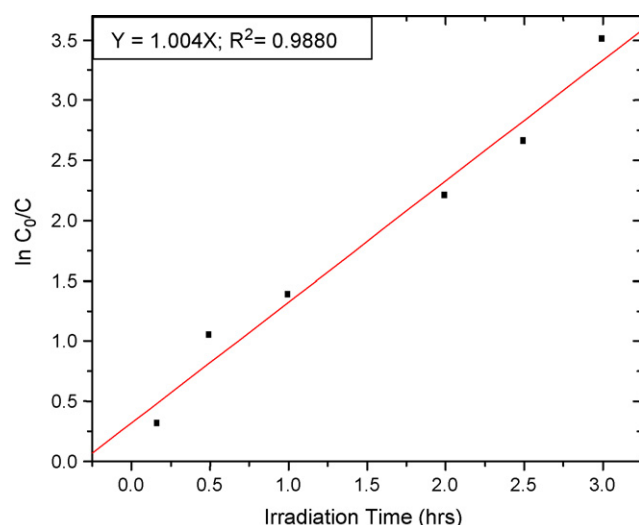


Fig. 14. Kinetic analysis of Rhodamine 6G under optimized conditions.

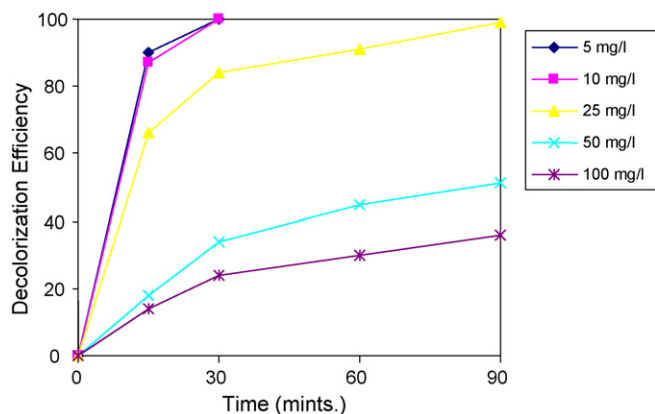


Fig. 15. Effect of initial concentration of Methyl Orange on decolorization efficiency under solar light (dye concentration 25 mg/l; catalyst dose 1g/l; time 1.5 h; pH-8).

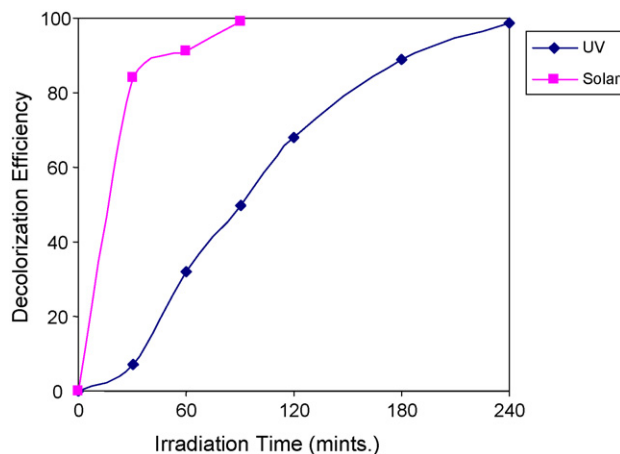


Fig. 17. Comparison of solar/UV irradiation on photocatalytic activity for Methyl Orange.

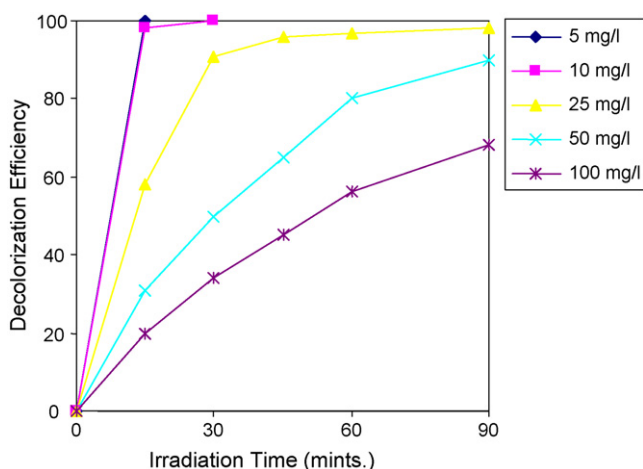


Fig. 16. Effect of initial concentration of Rhodamine 6G on decolorization efficiency under solar light (dye concentration 25 mg/l; catalyst dose 0.5 g/l; time 1.5 h; pH-10).

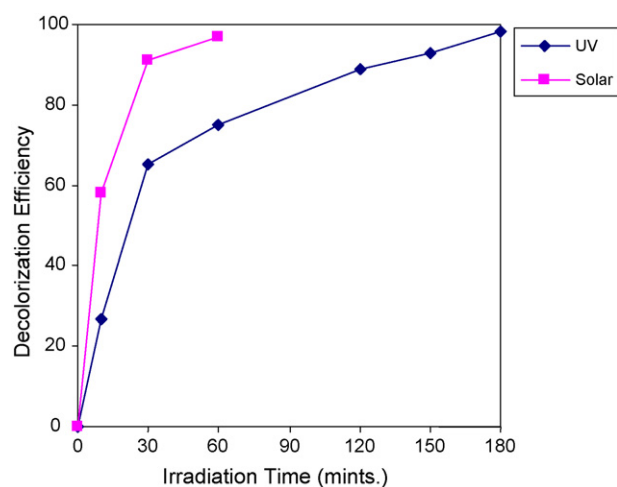


Fig. 18. Comparison of solar/UV irradiation on photocatalytic activity for Rhodamine 6G.

power to generate UV irradiation. In tropical countries like India, intense sunlight is available throughout the year and, hence it could be effectively used for photocatalytic degradation of pollutants in wastewater. Moreover there is no material deterioration in case when sunlight is used as a radiation source.

3.6. Mineralization studies of dyes

As the reduction of chemical oxygen demand (COD) reflects the extent of degradation or mineralization of an organic species, the percentage change in COD was studied for dye samples

Table 2
Percentage COD reduction studies of dyes

Time of irradiation (min)	MO		R6G	
	COD reduction under UV light (%)	COD reduction under solar light (%)	COD reduction under UV light (%)	COD reduction under solar light (%)
0	0	0	0	0
10	7	20	8	20
30	20	36	18	38
60	32	58	29	58
90		80		77
120	49		45	
150	65		60	
180	80		75	
240	89			

(initial concentration 25 mg/l) under optimized conditions (catalysts dose 1 g/l, pH 8 for MO and catalyst dose 0.5 g/l, pH 10 for R6G) as a function of irradiation time using UV and solar light. The results are depicted in Table 2. It can be seen that under UV light, the percentage COD reduction was 89% in 4 h for MO and 75% in 3 h irradiation times for R6G. Whereas under solar irradiation, 80% and 77% COD reduction was achieved in 90 min for MO and R6G. The COD reduction is lesser than percentage decolorization which may be due to the formation of smaller uncolored products. Therefore, it seems that to achieve complete mineralization of dyes, longer irradiation time is required.

4. Conclusions

Comparison of photocatalytic activity of different semiconductors has clearly indicated that the ZnO is the most active photocatalyst for decolorization of MO and R6G. Moreover, photocatalytic activity of ZnO is greater in the presence of solar light as compared to UV light. Experimental results indicated that the decolorization of dyes is facilitated in the presence of catalyst and were favorable in basic region. 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. The COD analysis revealed that complete mineralization of dyes could be achieved in longer irradiation times.

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