Research Article

Photocatalytic Degradation of Alizarin Red S, Amaranth, Congo Red, and Rhodamine B Dyes Using UV Light Modified Reactor and ZnO, TiO$_2$, and SnO$_2$ as Catalyst

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The photocatalytic degradation of dyes (alizarin red S, amaranth, congo red, and rhodamine B) present in wastewater was performed with UV lamp. The catalysts employed for this investigation were ZnO, TiO$_2$, and SnO$_2$. The kinetic studies of dyes degradation followed first order reaction. ZnO was found to be most efficient photo-catalyst for degrading these dyes. The optimal result for alizarin red S was $k = 0.2118 \, \text{min}^{-1}$, $t_{1/2} = 3.27 \, \text{min}$, and $R^2 = 0.7998$, for amaranth was $k = 0.146 \, \text{min}^{-1}$, $t_{1/2} = 4.74 \, \text{min}$, and $R^2 = 0.8348$, for congo red was $k = 0.2452 \, \text{min}^{-1}$, $t_{1/2} = 2.8 \, \text{min}$, and $R^2 = 0.8382$, and for rhodamine B was $k = 0.1915 \, \text{min}^{-1}$, $t_{1/2} = 3.6 \, \text{min}$, and $R^2 = 0.76$.

1. Introduction

Textile industries are the major contributor of water pollution due to releasing a large amount of toxic dyes into water bodies [1]. The dyeing industry has been reported as highly polluting industry by board of central pollution control [2]. Almost 15–20% dyes from industries are directly discharged into rivers that affect aquatic life [3]. Fabric industries are heavily dependent on these dyes; however, Pakistan, which is an economically developing nation, does not have a proper disposal system for these dyes effluents; therefore, they are mostly disposed of into land pits or water resources which leads to their contamination and eventually poses health risks for human health and sea life [4]. Therefore, it is highly dangerous to discharge these wasted dyes without properly dismantling them [5].

Dyes such as alizarin red S, amaranth, congo red, and rhodamine B are accounted as extremely dangerous toxicants. Congo red dye can result in genetic mutation [6] and rhodamine B [7] dye can damage skin, eyes, and PNS [8], while amaranth can result in infertility [9] and alizarin red S is a potential allergen [10]. Hence, their removal is necessary

before discharging into the environment. Degradation of dyes is the process in which harmful complex dyes are converted into simple molecules. Several biological and physio-chemical techniques are used for decolorization of dyes [11,12]. Biological methods for treating harmful dyes are ecofriendly but many dyes are not biodegraded due to complex structure [13]. The photocatalytic removal of dyes is an ecofriendly method that involves the exposure of catalyst to UV-visible light [14].

There are a number of operational factors that govern the degradation of dyes [15] including dyes load in water, pH and temperature of the system, catalyst's quantity, and time for degradation. The structure and composition of different dyes respond differently to these factors [16].

The widely used photo-catalysts for removing unwanted dyes are metal oxide semiconductors [17]. The most efficient and cost-effective catalysts are ZnO, TiO$_2$, and SnO$_2$. Their band energy gap and chemical stability make them ideal [18]. For instance, TiO$_2$ has a large band gap, which makes it highly reactive to UV radiations. Some other physical factors such as surface area and zeta potential have huge impact on degradation potential of these catalysts; zeta potential

basically indicates how stable a system is. Greater the value of the zeta potential (either +ve or −ve), stronger are the repulsive forces between the catalyst particles which impart them more stability. The photocatalytic activity of these catalysts can also be studied under Vis region of light if we extend their bang gaps by doping them with certain transition metals or nonmetals. TiO_2 can also be used to improve catalytic potential of other semiconductors by impregnating them on it; it can be done by techniques such as sol-gel and hydrothermal method. So, these factors are really important in obtaining optimal results.

This study aims at the degradation of dyes on feasible economic terms. The present work focuses on photocatalytic degradation of dyes such as Alizarin Red S, Amaranth, Congo Red, and Rhodamine B (Figure 1) performed using various factors such as amount of catalyst and dye load. The tubular UV source is used in this work in such a way that the atmospheric gases, especially oxygen's interference, are removed entirely which is the novelty of the method. The scheme also eliminates the unwanted production of ozone under UV light in an open degradation setup [19].

2. Experimental Work

2.1. Setup Used.
The source of light for degrading dyes was tubular UV lamp (Phillips TUV 11W T5), as shown in Figure 2(a). The dye solution was placed on a hot plate for continuous stirring. Specific wavelength and time absorbance of dye solution were monitored. This is a batch process setup. Tubular UV rod provides better results using simple bulb. Further, for continuous degradation process study, a setup was designed as shown in Figure 2(b). The temperature was 25°C and the dye solution was used as such without the addition of any pH alteration or maintaining reagents.

Preliminary experiments were conducted for comparing the efficiency of both processes, which indicated that the second one is more efficiently removing dyes. So, further working conditions were optimized using the second setup.

2.2. Chemicals.
Amaranth, Alizarin Red S, Congo Red, Rhodamine B, SnO_2, TiO_2, and ZnO all were obtained from Merck (Germany).

2.3. Equipment.
Tubular UV lamp (11 watts, Phillips TUV 11W T5), pH meter, electric balance, UV-visible spectrophotometer with quartz flow cell, hot plate, and magnetic stirrer were used.

2.4. Method Used for Photocatalytic Degradation.
UV lamp and UV-Vis spectrometer were used for this method. Dye solution was stirred on a hot plate. The peristaltic pump takes this dye solution to bottom of the reactor core where the solution was exposed to UV radiations. From its upper part, the dye solution was passed into a second peristaltic pump. Then, it was passed into spectrometer for continuous monitoring of absorbance. Then, that solution was again mixed into starting solution. In spectrometer, the

absorbance of Amaranth (mol. formula: $C_{20}H_{11}N_2Na_3O_{10}S_3$; molar mass: 604.5 g/mol) was monitored at 523 nm wavelength, Alizarin Red S (mol. formula: $C_{14}H_7NaO_7S$; molar mass: 360.28 g/mol) at 507 nm, Congo Red (mol. formula: $C_{32}H_{22}N_6Na_2O_6S_2$; molar mass: 696.665 g/mol) at 497 nm, and Rhodamine B (mol. formula: $C_{28}H_{31}ClN_2O_3$; molar mass: 479.02 g/mol) at 568 nm.

2.5. Degradation of Dyes without Catalyst.
The 0.4 mM solutions of dyes (Amaranth, Alizarin Red S, Congo Red, and Rhodamine B) were prepared and exposed to UV light at room temperature. Then, absorption of solutions was monitored after regular time intervals.

2.6. Degradation of Dyes with Catalyst SnO_2.
In each prepared 0.4 mM dyes solution, 4 mg of SnO_2 was added and placed on a hot plate for proper mixing. Then, solutions were irradiated with UV light for degradation. Absorption of solutions was checked after specific time.

2.7. Degradation of Dyes with Catalyst TiO_2.
The prepared dyes solutions were taken and mixed with 3 mg of catalyst TiO_2. Then, solutions were exposed to UV light and absorption was measured after regular time intervals.

2.8. Degradation of Dyes with Catalyst ZnO.
Sample solutions of dyes were prepared and 4 mg of ZnO was added in them. The solutions were placed under UV light and degradation was observed. Then, absorbance of the solutions which were taken out after regular time was noted by spectrometer.

3. Results and Discussion

The photocatalytic degradation of dyes was experimented using UV lamp and catalysts. The degradation rate and absorbance of dyes were checked and represented graphically. The kinetic studies showed that degradation of dyes follows first order reaction [20]:

$$\ln\left(\frac{C_o}{C_t}\right) = kt, \tag{1}$$

where C_o is the initial dye amount, C_t is the amount of dye at time t, and k is the constant.

The kinetic data results for degradation of alizarin red S, amaranth, congo red, and rhodamine B dyes under different conditions (without catalyst and with catalysts ZnO, TiO_2, and SnO_2) are presented in Table 1.

3.1. Case 1: Photolytic Degradation of Dye Alizarin Red S without Catalyst and with Catalysts ZnO, TiO_2, and SnO_2.
The results for degradation of alizarin red S under different conditions (without catalyst and with catalysts ZnO, TiO_2, and SnO_2) are graphically represented in Figure 3 and Table 1. They indicated that ZnO gives better results among these catalysts for degrading alizarin red S.
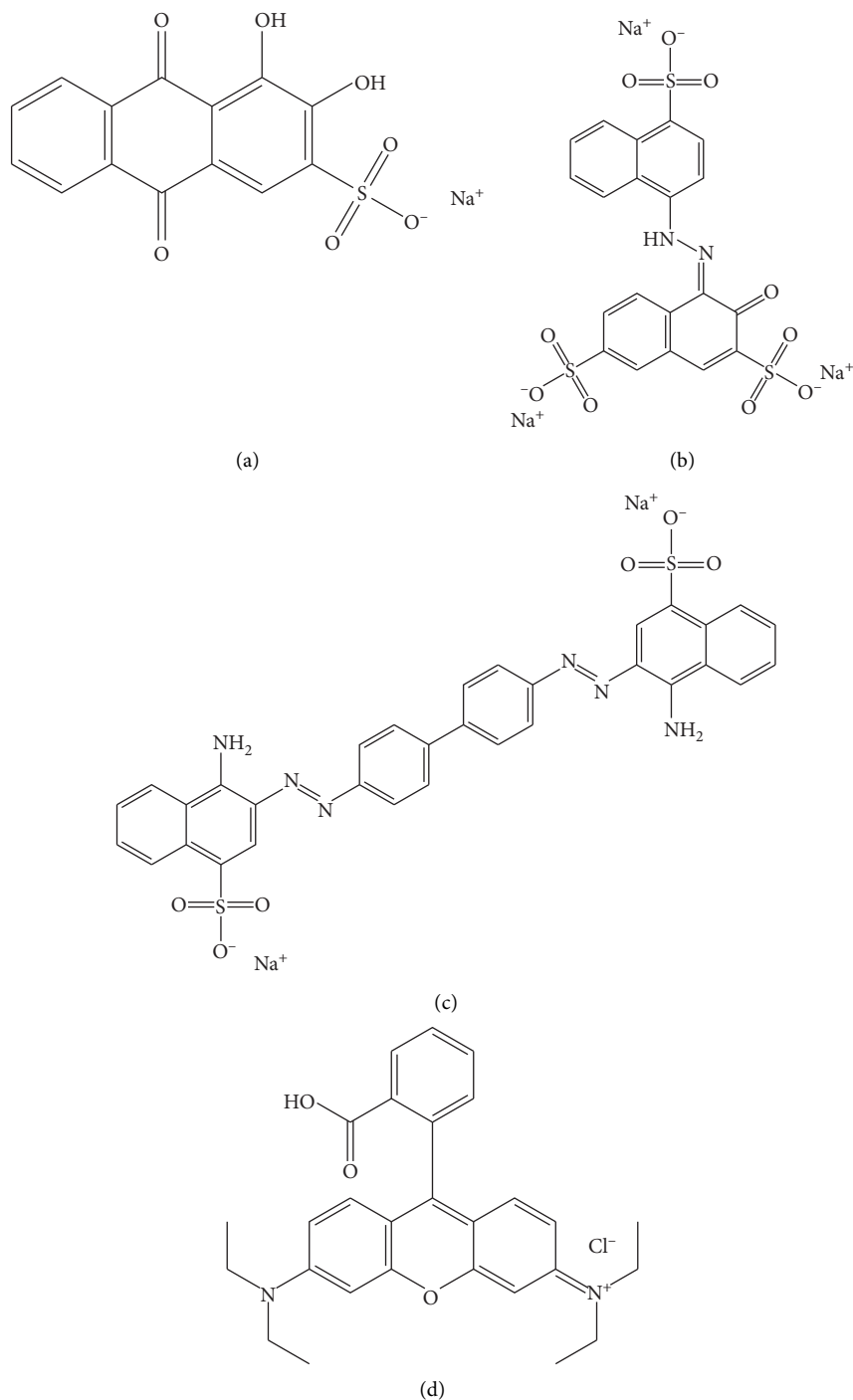
FIGURE 1: Structural formulas of dyes used. (a) Alizarin red S. (b) Amaranth. (c) Congo red. (d) Rhodamine B.

3.2. Case 2: Photolytic Degradation of Dye Amaranth without Catalyst and with Catalysts ZnO, TiO₂, and SnO₂.

3.2. Case 2: Photolytic Degradation of Dye Amaranth without Catalyst and with Catalysts ZnO, TiO$_2$, and SnO$_2$. The graphical representation of amaranth dye degradation at different conditions is given in Figure 4 and Table 1. As in the previous case, ZnO gives better results for amaranth dye also.

3.3. Case 3: Photolytic Degradation of Dye Congo Red without Catalyst and with Catalysts ZnO, TiO$_2$, and SnO$_2$. The degradation rate of congo red at different situations is shown in Figure 5 and Table 1. Same trend is observed here also that ZnO is the best catalyst for its degradation.

3.4. Case 4: Photolytic Degradation of Dye Rhodamine B without Catalyst and with Catalysts ZnO, TiO$_2$, and SnO$_2$. The photolytic decolorization of rhodamine B at various circumstances is illustrated in Figure 6 and Table 1. Again, ZnO gives better results.
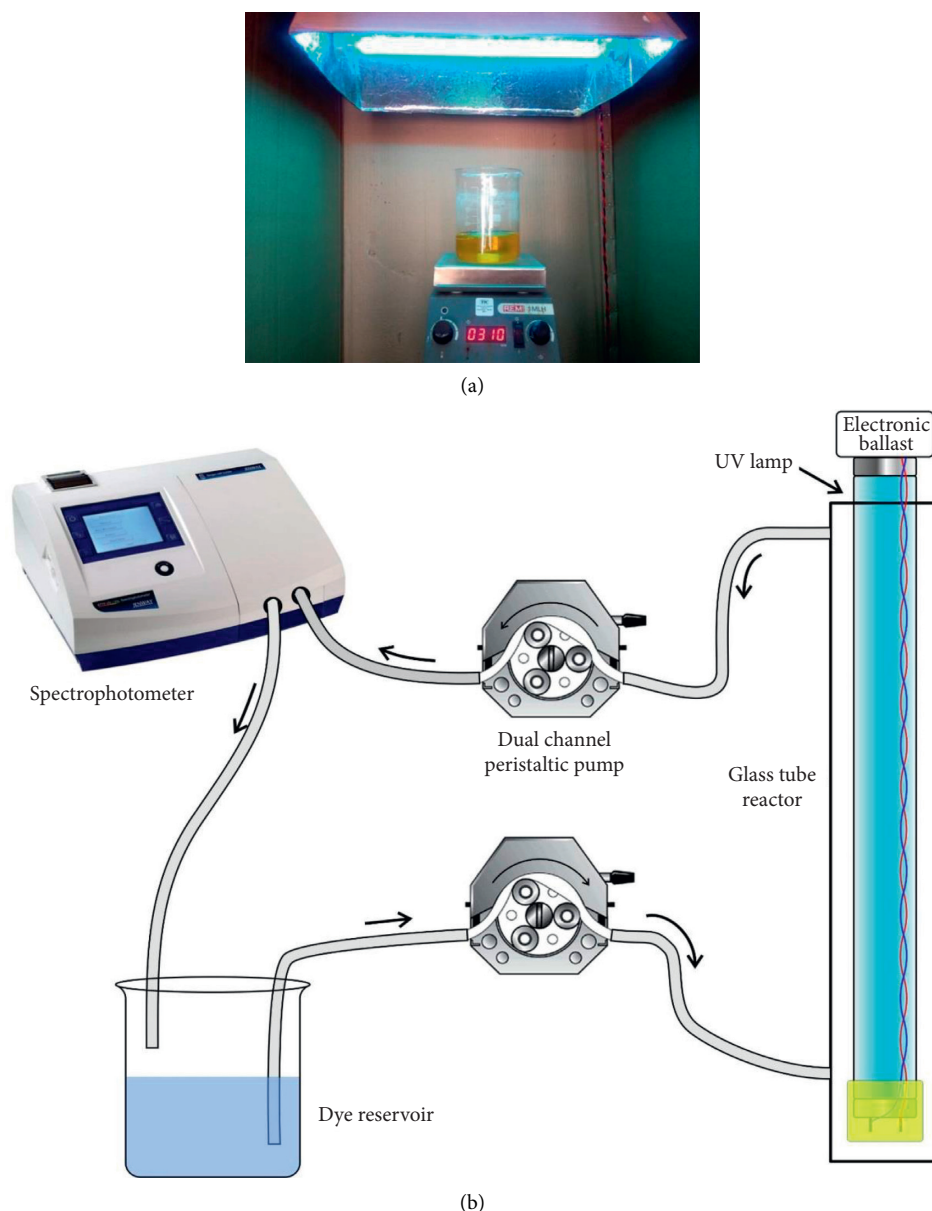
(a)

(b)

FIGURE 2: (a) Batch process arrangements and (b) continuous process setup for photocatalytic degradation of dye.

TABLE 1: Kinetic data of alizarin red S, amaranth, congo red, and rhodamine B dye.

| Dyes | Alizarin red S dye | | | Amaranth dye | | | Congo red dye | | | Rhodamine B dye | | |
Conditions	K (min^{-1})	$t_{1/2}$ (min)	R^2	K (min^{-1})	$t_{1/2}$ (min)	R^2	K (min^{-1})	$t_{1/2}$ (min)	R^2	K (min^{-1})	$t_{1/2}$ (min)	R^2
Without catalyst	0.0261	26.55	0.8611	0.028	24.7	0.7768	0.0548	12.6	0.7464	0.0391	17.7	0.825
ZnO	0.2118	3.27	0.7993	0.146	4.74	0.8348	0.2452	2.8	0.8382	0.1915	3.6	0.76
TiO$_2$	0.1188	5.83	0.8372	0.0671	10.3	0.7678	0.0976	7.1	0.7764	0.0843	8.2	0.837
SnO$_2$	0.0877	7.90	0.7995	0.0447	15.5	0.6976	0.0653	10.6	0.8921	0.0585	11.84	0.816

3.5. Effect of Catalyst Amount on Degradation Rate of Dyes. Degradation efficiency of dyes (alizarin red S, amaranth, congo red and rhodamine B) was investigated by using different amounts of catalysts (ZnO, TiO$_2$, and SnO$_2$). The irradiation time and dye amount were kept constant. It was found that the degradation rate was increased with increase in catalysts amount but decreases after certain point, i.e., optimal point [21], as illustrated graphically in Figure 7.
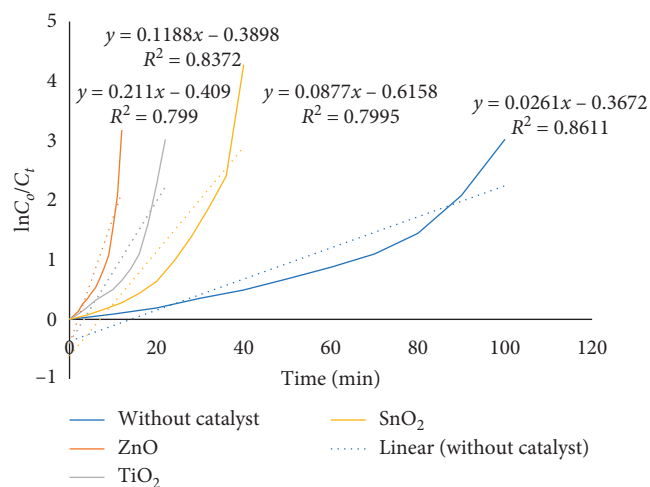
$y = 0.1188x - 0.3898$
$R^2 = 0.8372$

$y = 0.211x - 0.409$
$R^2 = 0.799$

$y = 0.0877x - 0.6158$
$R^2 = 0.7995$

$y = 0.0261x - 0.3672$
$R^2 = 0.8611$

FIGURE 3: Photolytic kinetics of alizarin red S without catalyst and with catalysts ZnO, TiO$_2$, and SnO$_2$.

$y = 0.0671x - 0.4764$
$R^2 = 0.7678$

$y = 0.0447x - 0.6001$
$R^2 = 0.6976$

$y = 0.146x - 0.4608$
$R^2 = 0.8348$

$y = 0.028x - 0.4544$
$R^2 = 0.7768$
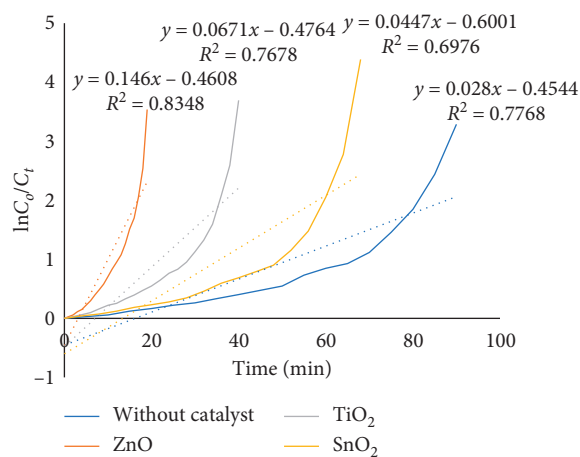
FIGURE 4: Photolytic kinetics of amaranth without catalyst and with catalysts ZnO, TiO$_2$, and SnO$_2$.

$y = 0.2452x - 0.5084$
$R^2 = 0.8382$

$y = 0.0548x - 0.5457$
$R^2 = 0.7464$

$y = 0.0976x - 0.4347$
$R^2 = 0.7764$

$y = 0.0653x - 0.3705$
$R^2 = 0.8921$
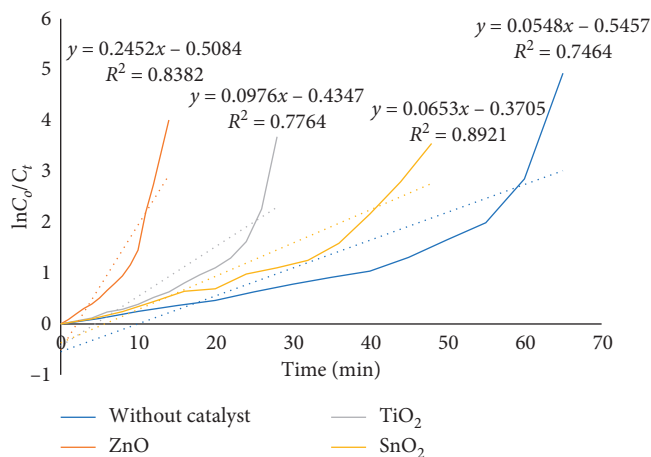
FIGURE 5: Photolytic kinetics of congo red without catalyst and with catalysts ZnO, TiO$_2$, and SnO$_2$.

$y = 0.1915x - 0.5361$
$R^2 = 0.76$

$y = 0.0585x - 0.472$
$R^2 = 0.8161$

$y = 0.0843x - 0.3837$
$R^2 = 0.8371$

$y = 0.0391x - 0.5197$
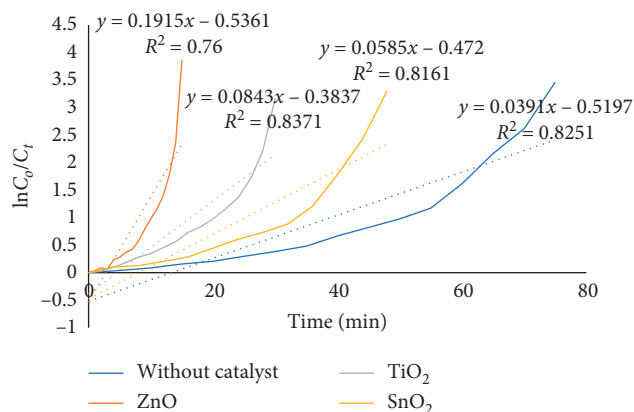$R^2 = 0.8251$

FIGURE 6: Photolytic kinetics of rhodamine B without catalyst and with catalysts ZnO, TiO$_2$, and SnO$_2$.
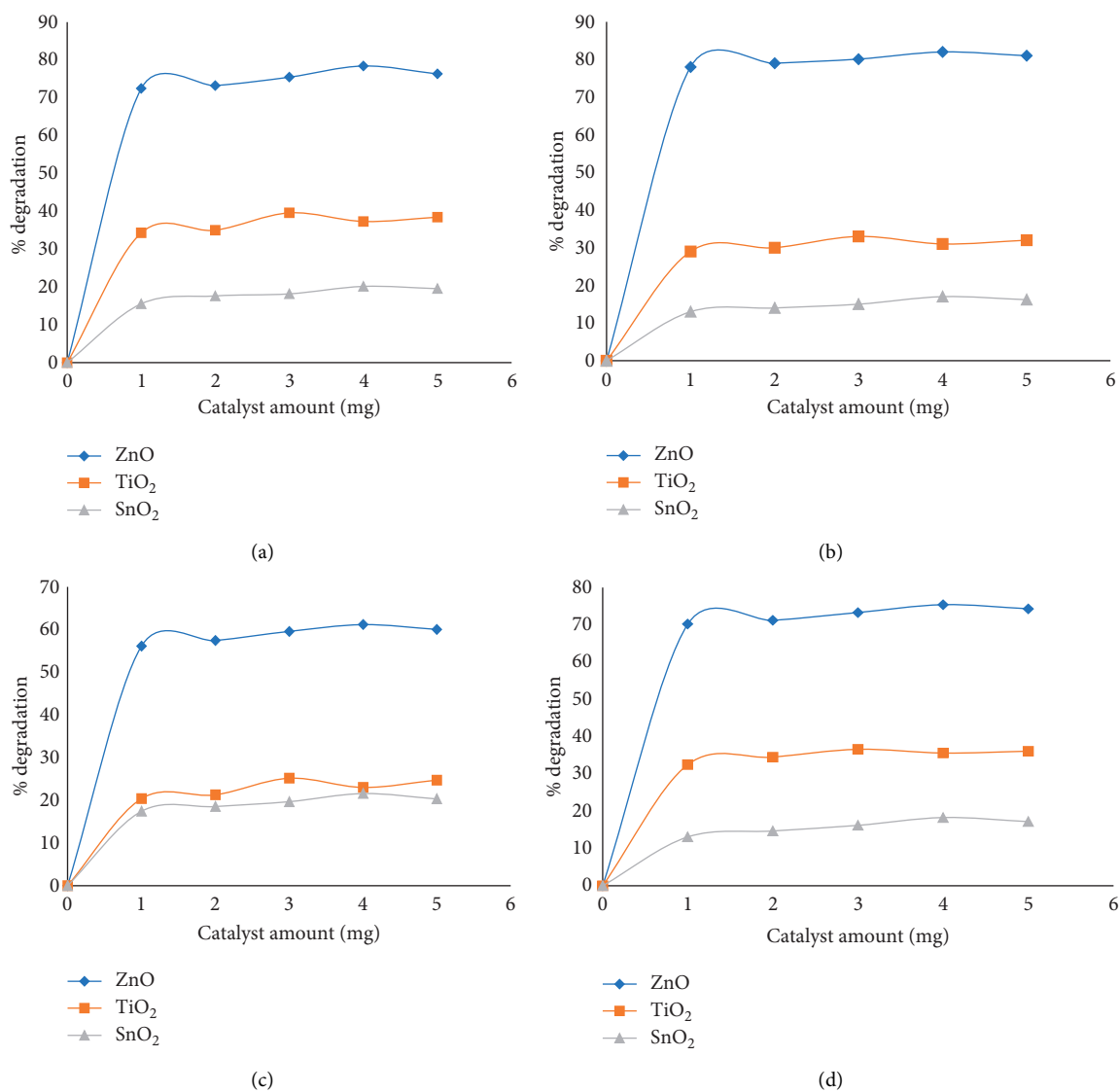

(a)

(b)

(c)

(d)

FIGURE 7: Effect of catalyst amount (ZnO, TiO$_2$, and SnO$_2$) on degradation efficiency of (a) alizarin red S dye, (b) amaranth dye, (c) congo red dye, and (d) rhodamine B dye at the same irradiation time.
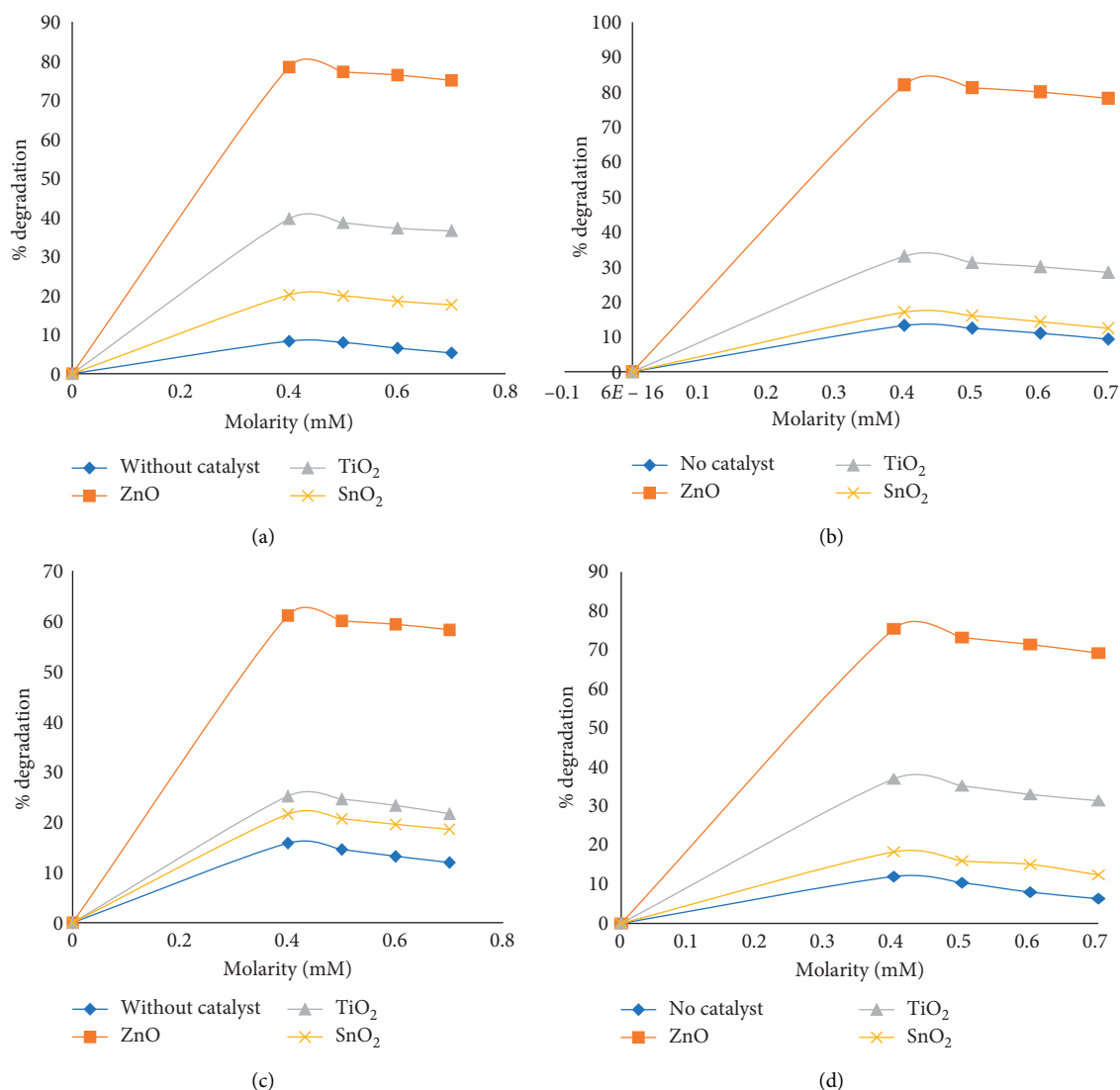
FIGURE 8: Effect of dye amount on degradation efficiency of (a) alizarin red S dye, (b) amaranth dye, (c) congo red dye, and (d) rhodamine B dye at the same irradiation time.

Optimum degradation was obtained at 3 mg/100 mL catalyst amount in all cases; beyond this concentration, the catalyst introduces the opacity and light hindrance. It is also obvious from these results that ZnO gave better results among these catalysts [22].

3.6. Effect of Dye Molarity on Degradation Rate. Effect of dye amount was also studied for each dye by keeping the catalyst amount irradiating time constant. The results indicated in Figure 8 show that degradation efficiency decreases with increase in dye concentration. Optimum concentration

obtained was 0.4 mM in all cases, which is then employed for further experimentations [23].

3.7. Proposed Mechanism of Degradation. When the dye solution was exposed to UV light in the presence of catalyst, the light irradiation promotes electron from valence band to conduction band of the catalyst leaving behind a positive hole in valence band [24]. After that, e^- from the conduction band is transferred to surrounding O_2 and produces O^{2-}. So, the positive hole travels to catalyst surface and reacts with water and produces OH. These hydroxide radicals further result in
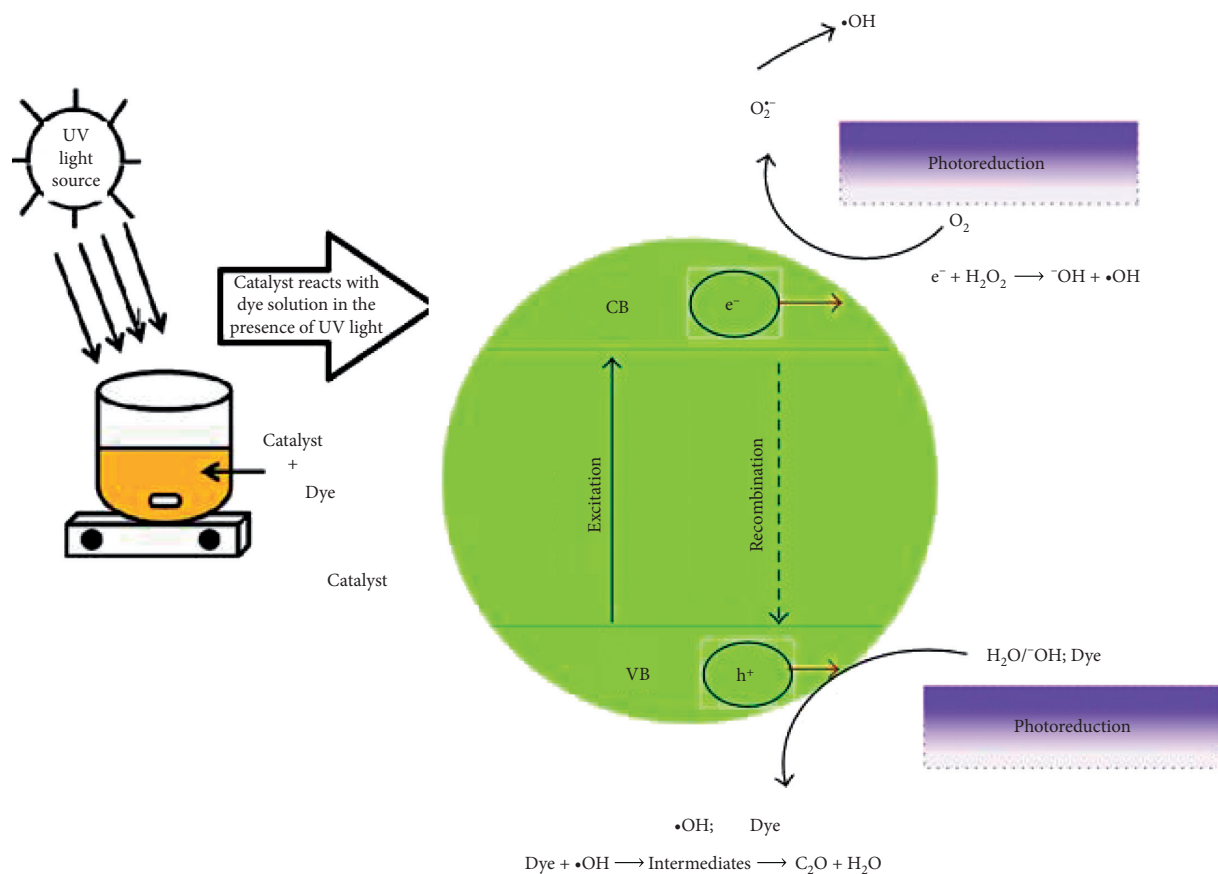
FIGURE 9: Proposed mechanism of photocatalytic degradation of dyes.

decomposition of dye molecules into CO_2 and water [25]. This proposed mechanism has been illustrated in Figure 9.

4. Conclusion

The photocatalytic degradation was carried out by irradiating the dyes solution with UV light. The photocatalytic activity of catalysts ZnO, TiO_2, and SnO_2 was compared. The kinetic results showed that the degradation followed first order reaction. The use of catalysts enhanced the degradation rate as compared to reaction rate without catalyst. Effect of catalyst and dye amount was also investigated. The optimum results were obtained by using zinc oxide catalyst. The optimal results for alizarin S dye were $K = 0.2118 \, min^{-1}$, $t_{1/2} = 3.27 \, min$, and $R^2 = 0.7993$, for amaranth dye were $K = 0.146 \, min^{-1}$, $t_{1/2} = 4.74 \, min$, and $R^2 = 0.8348$, for congo red dye were $K = 0.2452 \, min^{-1}$, $t_{1/2} = 2.8 \, min$, and $R^2 = 0.8382$, and for rhodamine dye were $K = 0.1915 \, min^{-1}$, $t_{1/2} = 3.6 \, min$, and $R^2 = 0.76$ The applied method is cost-effective, harmless, and easily available.

Data Availability

All the relevant data are given in the manuscript along with references.

Conflicts of Interest

The authors have no conflicts of interest.

Acknowledgments

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