

A Comparative Study on Photocatalytic Activity of ZnO, SnO₂ and ZnO-SnO₂ Composites

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Abstract

A comparative study was made on photocatalytic activity of ZnO, SnO₂ and their composite. A simple mechanochemical method was used for preparation of composite. The photocatalytic efficiency of ZnO-SnO₂ composite was compared with pure ZnO and SnO₂. The effect of various parameters such as pH, dye concentration, semiconductor amount and light intensity was observed. The optimum conditions for this degradation were obtained as: Rose Bengal = 6.0×10^{-6} M, pH = 7.5, amount of composite = 0.08 g and light intensity = 60.0 mWcm⁻². It was found that coupled chalcogenide ZnO-SnO₂ show better photocatalytic activity as compared with ZnO and SnO₂ alone for the degradation of rose Bengal in the presence of visible light.

Keywords: ZnO; SnO₂; Composites; Photocatalytic activity; Rose Bengal

Introduction

One of the most essential parts of life is clean water and today, the whole world is facing serious problem of water pollution. Dye effluents of various textile and paper industries are one of the important pollutants. In this era of rapid industrialization, the problem of degradation of pollutants has reached an alarming situation from ecological point of view.

There are many techniques for eliminating these water pollutants. Many researchers have tried to overcome this problem by methods like adsorption by charcoal, precipitation, air stripping, flocculation, thermal dehydration, etc., Photocatalyst may play significant role in solving this problem. Different methods based on it have proved their worth as these are green and affectionate in nature.

Ameta et al. [1,2] have excellently reviewed the field of photocatalysis. Several photocatalysts have been used for the degradation of different dyes from their aqueous solutions. Photocatalytic oxidative degradation of wastewater pollutants in

aqueous suspensions of TiO_2 was observed by Das et al. [3] They observed that certain organic molecules (polynuclear aromatic hydrocarbons) adsorbed on TiO_2 could be reduced with the concomitant oxidation of water. Mansilla and Villasnov [4] investigated the ZnO catalysed photodegradation of Kraft-black liquor, a discharge from the paper and pulp industries. Photocatalytic degradation of amaranth dye on TiO_2/UV in aqueous suspensions has been studied by Gupta et al. [5].

Vidya et al. [6] synthesized nanoparticles of zinc oxide by using leaf extract of jackfruit (*Artocarpus heterophyllus*). These nanoparticles exhibited excellent photodegradation efficiency (>80%, 0.24 g/L, 1 h) against rose Bengal dye, a major water-pollutant discharged by the textile industries. Degradation of rose Bengal and methylene blue dye using $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles as a photocatalyst was reported by Dutta et al. [7] Ag-ZnO catalysts by flame spray pyrolysis (FSP) was prepared by Height et al. [8] Methylene blue was used as model system to evaluate the performance of FSP-made Ag-ZnO. Faisal et al. [9] synthesized SnO_2 doped ZnO nanostructure photocatalyst. As synthesized SnO_2 doped ZnO nanostructures have been used for photodegradation of methylene blue under visible light. Bhattacharjee et al. [10] developed SnO_2 quantum dots by microwave heating method using an amino acid, serine and eosin yellow was degraded by this catalyst. Photodegradation of methyl orange using nanosized coupled ZnO/ SnO_2 photocatalysts investigated by Cun et al. [11].

Mittal et al. [12] studied photocatalytic bleaching of rose Bengal on manganese dioxide powder. Nanostructured semiconductor films of SnO_2 , TiO_2 and $\text{SnO}_2\text{-TiO}_2$ were prepared by Vinodgopal et al. [13] and used for photocatalytic degradation of NBB, a textile azo dye. TiO_2 -assisted photodegradation of eosin has been examined by Zhang et al. [14] ZnS has been used for the photoreduction of carbon dioxide by Kanemoto et al. [15] Anpo et al. [16] gave evidence for the involvement of extrinsic surface sites in the enhancement of the photocatalytic activity of luminescent ZnS catalyst. Ameta et al. [17] used antimony trisulphide for the photodegradation of naphthol green B. A composite polycrystalline ZnO/ TiO_2 system and its photocatalytic activity was reported by Marci et al. [18] Kansal et al. [19] studied photocatalytic degradation of methyl orange and rhodamine 6G using various semiconductors such as titanium dioxide, zinc oxide, stannic oxide, zinc sulphide and cadmium sulphide. Azure B was photocatalytically degraded by Sharma et al. [20] using NiS-ZnS composite in molar ratio 1:5.

Experimental Procedure

Preparation of composite

A composite of ZnO and SnO_2 was prepared by simple solid state mechanochemical method. Composite (ZnO- SnO_2) was prepared by mixing the equal amount of ZnO and SnO_2 (1:1 ratio) and then ground with the help of pestle and mortar and it was used for photocatalytic degradation of rose bengal.

Characterization of composite

X-rays diffraction pattern of the pure ZnO- SnO_2 composite is shown in FIG. 1. Average particle size of the crystalline composite powder was calculated by Debye-Scherrer's equation and it was found 97.25 nm.

The surface morphology and elemental composition were observed out by scanning electron microscope equipped with an energy dispersive X-ray spectrophotometer. The SEM image of ZnO- SnO_2 composite is FIG. 2. It shows that particles have rough surface with irregular size.

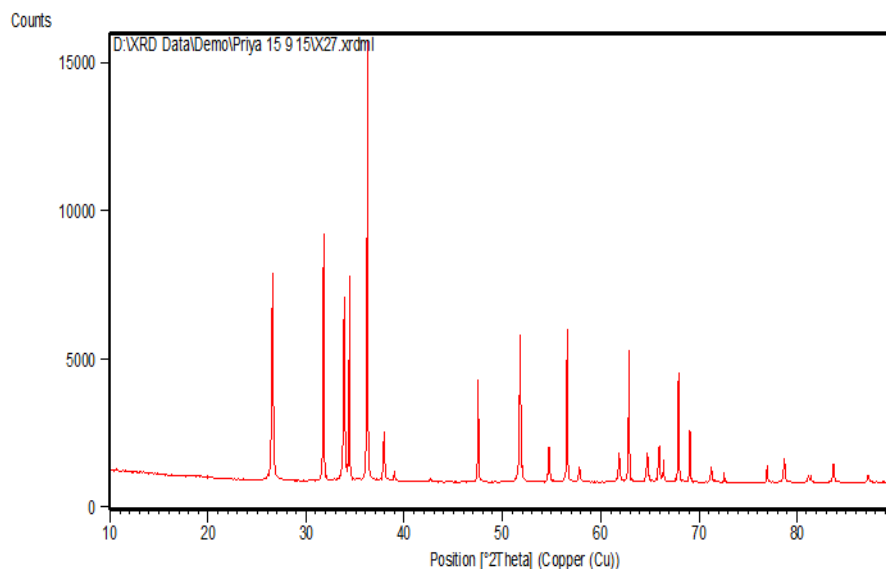


FIG. 1. X- ray diffraction spectrum of composite.

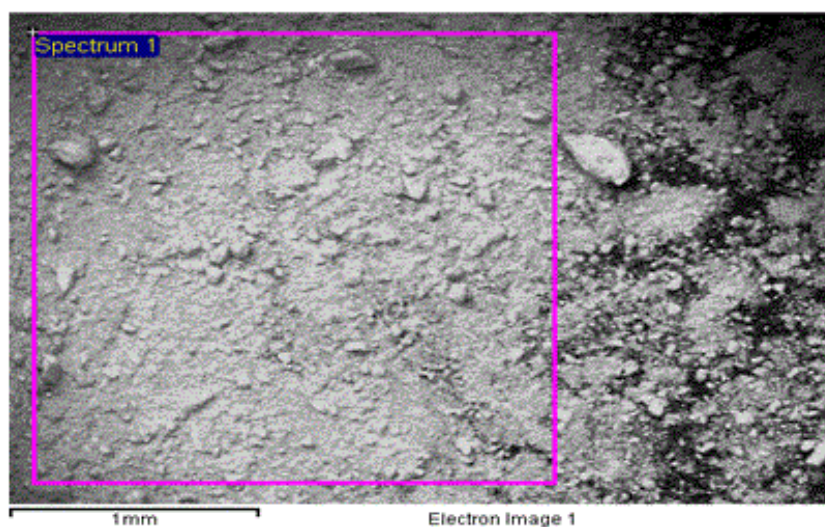


FIG. 2. SEM of composite.

EDX analysis was performed to analyze the elemental constituent of mixed ZnO-SnO₂. It was observed that three elements are present in nanomaterial i.e., Zn, Sn and O (TABLE 1).

TABLE 1. Elemental composition.

Elements	Weight (%)	Atomic (%)
Zn	50.75	28.88
Sn	20.69	8.35
O	50.75	62.75

Photocatalytic degradation

0.1017 g rose Bengal was dissolved in 100.0 mL of doubly distilled water to prepare 1.0×10^{-3} M concentration solution. It was used as a stock solution and further diluted as working solutions when required. The absorbance of rose Bengal solution was observed with the help of spectrophotometer (Systronic model 106) at $\lambda_{\text{max}}=550$ nm. It was irradiated with a 200 W tungsten lamp (CEL, Model SM 201) Reaction solution was exposed to visible light. A water filter between light source and solution was used to cut off the thermal radiation.

Equal amount of dye solution was kept in four beakers.

1. The first beaker of rose Bengal dye solution was placed in dark.
2. The second beaker of rose Bengal dye solution was exposed to visible light.
3. The third beaker of rose Bengal dye solution and 0.10 g ZnO-SnO₂ composite was placed in dark.
4. The fourth beaker of rose Bengal dye solution and 0.10 g ZnO-SnO₂ composite was exposed to visible light.

After 3 hours absorbance of solution was measured by spectrophotometer. The absorbance of first three beaker solution was found almost constant but the absorbance of the solution of fourth beaker had a decrease compared to initial value of absorbance. From all this observation, it is clear that the degradation required the both: light intensity and semiconductor composite.

The photocatalytic degradation of rose Bengal dye was studied, after addition of 0.08 g of composite in 50 mL dye solution (6.0×10^{-6} M) at pH 7.5. A 200 W tungsten lamp was used for irradiation (60.0 mW cm^{-2} light intensity). A glass vessel was used for irradiation. A solarimeter (Suryamapi CEL 201) was used for the measurement of light intensities. Water filter was used to cut thermal effect. pH of the dye solutions was measured using a digital pH meter. pH of the dye solutions was adjusted by addition of previously standardized 0.1N sulphuric acid and 0.1 N sodium hydroxide solution. UV-Visible spectrometer (Systronic Model 106) was used to measure absorbance (A) of the dye solution at regular time intervals. Controlled experiments were also carried out to confirm that the degradation of rose Bengal by ZnO-SnO₂ was photocatalytic in nature. A linear line plot of $1 + \log A$ and time shows that rose Bengal degradation follows pseudo-first order kinetics. The following formula was used to calculate the rate constant.

$$k=2.303 \times \text{slope} \quad (1)$$

Results and Discussion

TABLE 2. A typical run.

[Rose Bengal] = 6.0×10^{-6} M		pH=7.5
Amount of composite=0.08 g		Light intensity= 60.0 mWcm^{-2}
Time (min.)	Absorbance (A)	$1 + \log A$ (ZnO-SnO ₂)
0	0.528	0.7226
10	0.433	0.6365
20	0.395	0.5966
30	0.353	0.5478
40	0.318	0.5024
50	0.285	0.4548

60	0.248	0.3945
70	0.208	0.3181
80	0.184	0.2648
90	0.162	0.2095
100	0.141	0.1492
Rate constant (k) with ZnO= $1.41 \times 10^{-4} \text{ sec}^{-1}$		
Rate constant (k) with SnO ₂ = $1.32 \times 10^{-4} \text{ sec}^{-1}$		
Rate constant (k) with ZnO-SnO ₂ = $2.17 \times 10^{-4} \text{ sec}^{-1}$		

Effect of pH

The pH of the solution always affects the degradation of any dye solution and hence (TABLE 2), pH of the rose Bengal dye solution was varied and the rate of photocatalytic degradation was measured in the pH range 6.0-10.0, as the degradation was found to be reasonably rapid in this range. pH effect results are reported in TABLE 3. It was found that the rate of photocatalytic degradation had an increase with increase in pH up to a certain pH value, the rate constant was found optimum at pH 7.5; more increase in pH, rate of reaction gradually reduced. An increase in the photocatalytic activity with increase in pH may be due to formation of extra $\cdot\text{OH}$ radicals, which are generated from the interaction of OH^- and hole (h^+) of the composite semiconductor. These $\cdot\text{OH}$ radicals are accountable for the oxidative degradation of dye. The rate reduces after certain pH because more hydroxyl ions are available at higher pH and these will be adsorbed on the surface of the semiconductor, which makes it negatively charged so that the approach of anionic form of rose Bengal towards semiconductor surface will be slowed due to repulsion, which results decrease in the rate of degradation.

TABLE 3: Effect of pH.

[Rose Bengal] = $6.0 \times 10^{-6} \text{ M}$	Light intensity = 60.0 mWcm^{-2}
Amount of composite = 0.08 g	
pH	Rate constant (k) $\times 10^4 (\text{sec}^{-1})$
6.0	1.87
6.5	2.00
7.0	2.11
7.5	2.17
8.0	1.80
8.5	1.63
9.0	1.63
9.5	1.50
10.0	1.42

Effect of dye concentration

Different concentrations i.e., $0.2-1.4 \times 10^{-5} \text{ M}$ of rose Bengal dye was used to study the effect on rate of photocatalytic degradation. The results are tabulated in TABLE 4. It was identified that the rate of photocatalytic degradation increases with an increase in dye concentration. The reason behind it, as the concentration of dye was increased additional dye molecules are available for excitation and energy transmission and hence, an upsurge in the rate of photocatalytic degradation of the rose

Bengal dye was observed. The rate of photocatalytic degradation decreased with more increase in the concentration of the dye. The rate constant was found optimum at 6.0×10^{-6} M for rose Bengal. This may be due to the fact that after certain dye concentration, the dye itself starts acting as a filter for the incident light and it will not allow the favoured light intensity to reach the semiconductor particles; thus, decreasing the rate of photocatalytic degradation of dye.

TABLE 4. Effect of dye concentration.

pH =7.5	Light intensity =60.0 mWcm⁻²
Amount of composite=0.08 g	
[Rose Bengal] × 10⁵ M	Rate constant (k) × 10⁴ (sec⁻¹)
0.2	1.91
0.4	1.99
0.5	2.07
0.6	2.17
0.7	1.85
0.8	1.64
1	1.45
1.2	1.24
1.4	0.98

Effect of amount of semiconductor (ZnO-SnO₂) composite

The quantity of semiconductor is also affect the rate of photocatalytic degradation of rose Bengal dye and hence; different amounts i.e., 0.02-0.14 g of semiconducting composite were used. The results are tabulated in TABLE 5. This study showed that the rate of photocatalytic degradation of rose Bengal increases with an increase in the amount of composite but finally, it became almost constant after a certain amount i.e., 0.08 g for ZnO-SnO₂ composite. The possible reason may be as the amount of composite was increased, the exposed surface area is also increased. As a consequence, the rate of photocatalytic degradation of the dyes increased, but after a fix limit, if the amount of semiconductor was more increased, then there was no increase in the exposed surface area of the composite. It can be considered like a saturation point; further increase in the amount of semiconductor has insignificant or no effect on the rate of photocatalytic degradation of the rose Bengal dye, as any increase in the quantity of semiconductor after this saturation point will only increase the thickness of the film at the lowermost of the reaction vessel. This was confirmed by taking reaction vessels of different sizes. The saturation point shifts to higher range for greater vessels, while reverse was true for smaller vessels.

TABLE 5. Effect of photocatalyst.

[Rose Bengal] =6.00 × 10⁻⁶ M	pH=7.5
Light intensity=60.0 mWcm⁻²	
Amount of Composite (g)	Rate constant (k) × 10⁴ (sec⁻¹)
0.02	0.84
0.04	1.18
0.06	1.50
0.08	2.17
0.10	2.14
0.12	2.13
0.14	2.13

Effect of light intensity

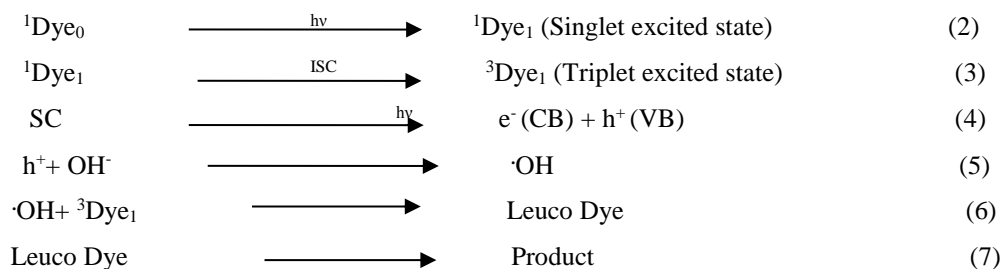
Light intensity was varied to observe the effect of intensity of light on the photocatalytic degradation of the dye. The results are tabulated in TABLE 6. The data shows that an increase in the light intensity increases the rate of reaction and the optimum value was found at 60.0 mWcm⁻². It may be due to the fact as the light intensity was increased, the number of photons striking per unit area also increased, causing higher rate of degradation. Further increase in the light intensity beyond the optimum limit result in decrease in the rate of reaction. It may be probably due to thermal side reactions.

TABLE 6. Effect of light intensity.

[Rose Bengal] = 6.0×10^{-6} M	pH=7.5
Amount of composite=0.08 g	
Light intensity (mW cm ⁻²)	Rate constant (k) $\times 10^4$ (sec ⁻¹)
20.0	0.78
30.0	0.93
40.0	1.09
50.0	1.24
60.0	2.17
70.0	1.54

Mechanism

On the basis of all these observations, a tentative mechanism for degradation of rose Bengal (Dye) is proposed as follows:



Rose Bengal absorbs radiations of appropriate wavelength and converted to its excited singlet state. Then it undergoes intersystem crossing (ISC) to give the triplet state of the dye. Besides, the semiconducting composite ZnO-SnO₂ also used the incident visible light energy to excite its electron from valence band to conduction band; thus, leaving behind a hole. This hole may abstract an electron from OH⁻ ions to generate •OH radicals. These •OH radicals will then oxidize the dye to its leuco form, which may finally degrade to less toxic yields. The participation of hydroxyl radicals as an active oxidizing species was confirmed by using hydroxyl radical scavengers (isopropanol), where the rate of degradation was completely reduced.

Conclusion

A comparative study has been carried out between photocatalytic activity of pure ZnO and SnO₂ and their composite. Rose Bengal dye was used as a model system to compare their photocatalytic performance. The rate constants for photocatalytic degradation of rose Bengal using ZnO, SnO₂ and ZnO-SnO₂ were $1.41 \times 10^{-4} \text{ sec}^{-1}$, $1.32 \times 10^{-4} \text{ sec}^{-1}$ and $2.17 \times 10^{-4} \text{ sec}^{-1}$, respectively. These results clearly show that the composite ZnO-SnO₂ showed better activity as compared to individual ZnO and SnO₂. The observation of present work will explore the use of composites in enhancing photocatalytic performance of a photocatalyst.

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