

A Comparative Study of Photocatalytic Activity of Some Coloured Semiconducting Oxides

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ABSTRACT: The use of colored semiconductor oxide like copper (II) oxide and nickel (II) oxide for photocatalytic bleaching of rose bengal was investigated in detail. In order to harness the solar energy, the effective wavelength of the photocatalyst is to be expanded into the visible region and that increases the rate of photocatalytic bleaching of the dye. Progress of the reaction was observed spectrophotometrically. The comparative studies of photocatalytic activity of copper (II) oxide (CuO) and nickel (II) oxide (NiO) was made using photocatalytic bleaching of rose bengal as modal system. The effect of various parameters like concentration of dye, pH, amount of semiconductor, light intensity etc. on the rate of photocatalytic bleaching of the dye was also observed. On the basis of rate of the reaction (rate constant) the order of photocatalytic activities of the semiconductor oxides was found to be CuO > NiO. A tentative mechanism for the photocatalytic bleaching of rose bengal has also been proposed.

KEY WORDS: Photocatalysts, Photocatalytic degradation, Rose Bengal, Cupric oxide, Nickel oxide, Photocatalytic activity.

INTRODUCTION

In recent years, the use of semiconducting oxides as photocatalyst for degradation of pollutants has attracted the attention of scientific community all over the world. The commonly used semiconducting oxides are TiO₂ and

ZnO due to their activity and stability. However, the photocatalytic activity of the photocatalyst depends on the band gap of the semiconductor and to harness light energy of visible region, the wavelength of the

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semiconductor is to be expanded. This may be done by using colored semiconductor oxides.

Although a number of photocatalyst have been used by various workers for the treatment of polluted water by dye effluents, no attention has been paid to the use of colored oxides as photocatalyst to expand the wavelength into the visible region and colored oxides like NiO and CuO may have this capability. In the present investigation CuO and NiO were used as photocatalyst for the bleaching of the dye rose bengal (as a model dye) and the effectiveness of these photocatalyst has been compared on the basis of the rate of photocatalytic bleaching of the dye.

TiO₂ sol-gel deposited over glass and its application as a photocatalyst for water decontamination has been reported by *Gelover et al.* [1] while *Schrauzer & Guth* [2] reported that a few micromoles of H₂ and O₂ were produced by the decomposition of gaseous water over TiO₂. *Raber & Rusek* [3] reported co-precipitation of CdS with about 0.5-3 wt.% silver sulphide. *Muradev et al.* [4] reported photocatalytic hydrogen production from the solution. *Nasaka et al.* [5] reported the use of colloidal Pt-CdS photocatalyst (stabilized by pendant viologen polymer) for photoinduced electron transfer and hydrogen evolution. Hydrogen evolution from water on eosin - Y fixed TiO₂ photocatalyst using a silance coupling reagent under visible light irradiation has been observed by *Abe & Hara* [6].

Sharma et al. [7] reported photocatalytic reduction of CO₂ to HCHO and HCOOH using dye-coated TiO₂. *Kako et al.* [8] have suggested some preventive methods against catalytic poisoning of TiO₂ photocatalyst by H₂S. The effect of TiO₂ acidic pre-treatment on the photocatalytic phenol degradation was reported by *Colon et al.* [9] whereas photodegradation of lignin from black liquor using a UV/TiO₂ system was investigated by *Ksibi et al.* [10]. Enhanced efficiency of unsymmetrical versus symmetrical squaraine dyes sensitized nanocrystalline TiO₂ was reported by *Alese et al.* [11].

Morwetz & Selli [12] investigated the effect of iron species in photocatalytic degradation of azo dye in TiO₂ suspension. Photocatalysis provide a promising solution to the problem of wide ranging use and release of volatile organic compounds, many of which pose hazardous environmental threats [13-17]. *Mansoori et al.* [18,19] used zinc oxide and lead oxide (PbO) as photocatalysts

for the photocatalytic bleaching of rhodamine-B and rhodamine-6G.

Photocatalytic degradation of azo dye acid readily in water using ZnO as photocatalytic has been investigated by *Daheshvar et al.* [20]. Whereas photocatalytic bleaching of basic blue-24 in presence of ZnO has been reported by *Ameta et al.* [21]. *Kim et al.* [22] used ZnO coated TiO₂ nanoparticles for the flexible dye-sensitized solar cells. Use of semiconducting iron (II) oxide in photocatalytic bleaching of some dyes (malachite green, crystal violet and methylene blue) has been reported by *Ameta et al.* [23]. Photocatalytic degradation of brilliant red dye and textile waste water has been suggested by *Martins et al.* [24]. The aim of the present study is to investigate the colored semiconductor as photocatalyst to harness solar energy

EXPERIMENTAL SECTION

Rose bengal (CDH), cupric oxide (Reidel) and nickel oxide (Reidel) were used in the present investigations. The dye solution of rose bengal was prepared in doubly distilled water. The photocatalytic degradation of rose bengal was studied in the presence of CuO, NiO and visible light. 0.1050 g of rose bengal was dissolved in 100.0 ml of doubly distilled water (1.0×10^{-3} M). This was used as stock solutions. The photocatalytic degradation of rose bengal was observed taking 30 mL of dye solution (1.50×10^{-5} M) which was prepared in doubly distilled water and 0.15 g of semiconductor was added to it. The pH of the reaction mixture was adjusted to 9.5 and 6.5 for CuO and NiO, respectively. The reaction mixture was exposed to light (intensity 70.0 mWcm^{-2}). A 200 W tungsten lamp was used for irradiation purpose. Sunlight was used for higher intensities of light. The intensity of light was measured by *Suryamapi* (CEL Model SM 201). A water filter was used to cut off thermal radiations. The pH of the solution was measured by a digital pH meter (Systronics Model 106). The desired pH of the solution was adjusted by the addition of previously standardized hydrochloric acid and sodium hydroxide solutions. The necessary conditions for the correct measurement of optical density is that the solution must be free from suspension and therefore centrifuge machine (Remi-1258) and Whatmann filter paper was used to remove the suspension but both were not found suitable. Thus, G-3 sintered glass crucible

Table 1: The experimental observations for the typical run.

Time (min.)	CuO		NiO	
	Optical Density (O.D.)	1 + log O.D.	Optical Density (O.D.)	1 + log O.D.
0.0	0.881	0.9450	0.562	0.7497
15.0	0.733	0.8651	0.513	0.7101
30.0	0.609	0.7846	0.476	0.6776
45.0	0.513	0.7101	0.422	0.6253
60.0	0.404	0.6064	0.393	0.5944
75.0	0.351	0.5450	0.355	0.5502
90.0	0.291	0.4639	0.327	0.5145
105.0	0.237	0.3747	0.295	0.4698
120	-	-	0.272	0.4346
135	-	-	0.248	0.3945

[Rose Bengal] = 1.5×10^{-5} M
 CuO = 0.06 g
 Light Intensity = 70.0 mWcm⁻²
 pH = 9.5

[Rose Bengal] = 3.0×10^{-5} M
 NiO = 0.12 g
 Light Intensity = 70.0 mWcm⁻²
 pH = 6.5

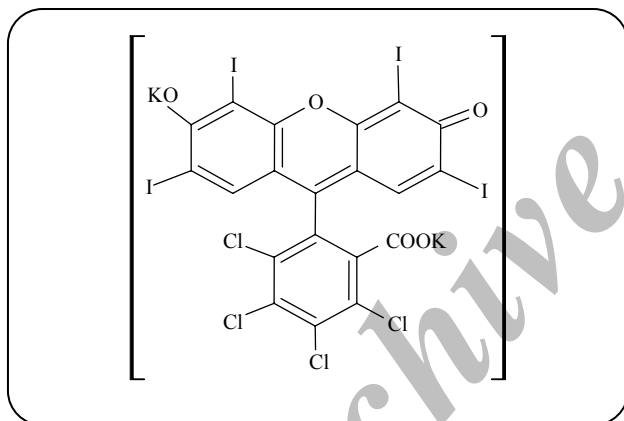


Fig.1: Rose Bengal.

was used for filtration to obtain the desired accuracy in measurement of optical density (O.D.) at different time intervals, whereas λ_{\max} of the dye was determined with the help of ultraviolet-visible recording spectrophotometer (Shimadzu U.V. 240).

RESULTS AND DISCUSSION

The photocatalytic degradation of rose bengal was observed at $\lambda_{\max} = 545$ nm. The results for the typical run are given in Table 1. (structure given in Fig. 1)

It was observed that optical density of rose bengal solution decreases with the increase in the time of

irradiation; thus, indicating that rose bengal is consumed on irradiation. A plot of 1 + log O.D. against time was linear and it followed pseudo-first order kinetics. The optimum rate constant k with CuO and NiO photocatalyst were determined to be $2.09 \times 10^{-4} \text{ s}^{-1}$ and $2.40 \times 10^{-4} \text{ s}^{-1}$, respectively. The experimental observations for the typical run have been presented in Table 1.

Effect of pH

The pH of the solution is likely to affect the bleaching of the rose bengal. The effect of pH on the rate of bleaching of rose bengal was investigated in the pH range 4.5 - 11.0. The results are reported in Table 2.

It is evident from the above data that the rate of photocatalytic bleaching of rose bengal increases with increase in pH up to 9.5 and 6.5 for CuO and NiO, respectively. The further increase in pH after the optimum pH resulted into the decreases the rate of the reaction. The increase in the rate of photocatalytic bleaching with increase in pH may be due to more generations of $\bullet\text{OH}$ radicals which are produced by the interaction of OH^- with hole (h^+) of the semiconductor. But after optimum pH the decrease in the rate of photocatalytic bleaching may be due to the fact that rose bengal in its anionic form will experience a force of repulsion with negatively charged surface of the

semiconductor due to adsorption of more OH^- ions on the surface of the photocatalyst.

Effect of dye concentration

Effect of variation of rose bengal concentration was studied by taking different concentrations of rose bengal. The results are tabulated in Table 3.

It has been observed that the rate of photocatalytic bleaching increases with an increase in the concentration of the rose bengal. It may be due to the fact that as the concentration of rose bengal increases more dye molecules are available for excitation and energy transfer and hence, an increase in the rate of bleaching of the dye was observed. The rate of photocatalytic bleaching was found to decrease with increase in the concentration of the dye further i.e. above 1.5×10^{-5} M and 3.0×10^{-5} M for CuO and NiO, respectively. This may be attributed to the fact that the dye itself will start acting as a filter for the incident light and it will not permit the desired light intensity to reach the semiconductor particles; thus, decreasing the rate of photocatalytic bleaching of rose bengal.

Effect of amount of semiconductor

The amount of semiconductors is also likely to affect the rate of photocatalytic bleaching of rose bengal and hence, different amounts of photocatalysts were used. The results are reported in Table 4.

It has been observed that the rate of photocatalytic bleaching of rose bengal increases with an increase in the amount of semiconductor but ultimately, it becomes almost constant after a certain amount i.e. 0.06 g and 0.12 g for CuO and NiO, respectively. This may be attributed to the fact that as the amount of semiconductors was increased, the exposed surface area also increases, but after a certain limit, if the amount of semiconductors was further increased, then there will be no increase in the exposed surface area of the photocatalysts. It may be considered like a saturation point; above which any increase in the amount of semiconductors has negligible or no effect on the rate of photocatalytic bleaching of rose bengal, as any increase in the amount of semiconductors after this saturation point will only increase the thickness of the layer at the bottom of the reaction vessel. This was confirmed by taking reaction vessels of different dimensions. The saturation point shifts to higher range for larger vessels, while reverse was true for smaller vessels.

Table 2: Effect of pH on the rate of photocatalytic bleaching of Rose Bengal.

pH	$k \times 10^4$ (s^{-1})	
	CuO	NiO
4.5	-	0.55
5.0	-	0.62
5.5	-	0.71
6.0	-	0.74
6.5	-	1.02
7.0	-	0.92
7.5	-	0.85
8.0	1.01	0.75
8.5	1.21	-
9.0	1.36	-
9.5	2.09	-
10.0	1.79	-
10.5	1.24	-
11.0	0.89	-

$[\text{Rose Bengal}] = 1.5 \times 10^{-5}$ M , $[\text{Rose Bengal}] = 3.0 \times 10^{-5}$ M
 $\text{CuO} = 0.06$ g , $\text{NiO} = 0.12$ g
 $\text{Light Intensity} = 70.0$ mWcm $^{-2}$, $\text{Light Intensity} = 70.0$ mWcm $^{-2}$

Table 3: Effect of Rose Bengal concentration on the rate of photocatalytic bleaching of rose Bengal.

[Rose Bengal] $\times 10^5$ M	$k \times 10^4$ (s^{-1})	
	CuO	NiO
0.5	1.74	-
1.0	1.99	-
1.5	2.09	0.81
2.0	1.87	0.87
2.5	1.60	0.98
3.0	1.29	1.02
3.5	-	0.99
4.0	-	0.93
4.5	-	0.83

$\text{CuO} = 0.06$ g , $\text{NiO} = 0.12$ g
 $\text{Light Intensity} = 70.0$ mWcm $^{-2}$, $\text{Light Intensity} = 70.0$ mWcm $^{-2}$
 $\text{pH} = 9.5$, $\text{pH} = 6.5$

Table 4: Effect of amount of semiconductor on the rate of photocatalytic bleaching of Rose Bengal.

Semiconductor (g)	$k \times 10^4$ (s^{-1})	
	CuO	NiO
0.02	1.78	-
0.04	1.94	-
0.06	2.09	0.46
0.08	2.06	0.87
0.10	2.05	0.86
0.12	2.01	1.02
0.14	1.99	1.01
0.16	1.93	0.97
0.18	-	0.95

$[\text{Rose Bengal}] = 1.5 \times 10^{-5}$ M , $[\text{Rose Bengal}] = 3.0 \times 10^{-5}$ M
 $\text{Light Intensity} = 70.0$ mWcm $^{-2}$, $\text{Light Intensity} = 70.0$ mWcm $^{-2}$
 $\text{pH} = 9.5$, $\text{pH} = 6.5$

Table 5: Effect of light intensity on the rate of photocatalytic bleaching of Rose Bengal.

Intensity of Light (mW cm ⁻²)	k × 10 ⁴ (s ⁻¹)	
	CuO	NiO
10.0	0.83	0.47
20.0	1.06	0.59
30.0	1.27	0.72
40.0	1.39	0.89
50.0	1.66	0.93
60.0	1.84	0.98
70.0	2.09	1.02
80.0	1.80	0.98
90.0	1.79	0.98

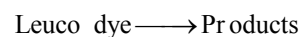
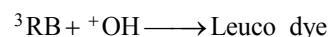
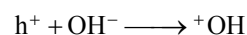
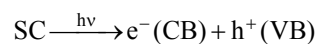
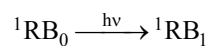
Effect of light intensity

To investigate the effect of light intensity on the photocatalytic bleaching of rose bengal, the distance between the light source and the exposed surface area was varied. The results are summarized in Table 5.

The results given in Table 5 indicate that bleaching action was accelerated as the intensity of light was increased, because any increase in the light intensity will increase the number of photons striking per unit area of semiconductor powder. An almost linear behaviour between light intensity and rate of reaction was observed. However on increasing the intensity above 70.0 mWcm⁻², there was a decrease in the rate. This may be due to some side reactions or thermal effects.

Mechanism

On the basis of experimental observations, a tentative mechanism for photocatalytic degradation of rose bengal (RB) may be proposed as:



Rose Bengal (RB) absorbs radiations of suitable wavelength and gives rise to its excited singlet state.

Then it undergoes intersystem crossing (ISC) to give the triplet state of the dye. On the other hand, the semiconducting oxides (SC) also utilizes the radiant energy to excite its electron from valence band to the conduction band; thus, leaving behind a hole (h⁺). The hole in the valence band of the semiconductor will oxidize the dye to its leuco form, which may ultimately degrade to products. It seems that •OH radicals are the active oxidizing species in the photocatalytic bleaching of rose bengal. This was confirmed by carrying out the same reaction in presence of 2-propanol, where the rate of photocatalytic bleaching of rose bengal was drastically retarded.

CONCLUSIONS

Based on the rate of photocatalytic bleaching of the dye in presence of these semiconducting oxides photocatalytic activities of the semiconductors are compared. The uses of colored semiconductor oxides as photocatalyst in visible region has been established in case of bleaching of bengal. The order of the photocatalytic activity of the semiconductor oxides was found as CuO > NiO. This order of the efficiency of the photocatalyst can be interpreted in terms of the band gap of the semiconductor that is copper (II) oxide (CuO) has less band gap than the nickel (II) oxide (NiO).

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