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ROLE OF SOME METAL IONS IN ENHANCEMENT OF PHOTOCATALYTIC ACTIVITY OF ZINC OXIDE

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ABSTRACT

Enhanced photocatalytic activity of zinc oxide in presence of some metal ion was investigated through study of photocatalytic bleaching of brilliant blue dye. The progress of the reaction was observed spectrophotometrically. The effect of various operating variables like pH, concentration of dye, amount of semiconductor and light intensity on the rate of reaction was recorded. A comparable study of the effect of addition of some metal ions i.e. Mn^{2+}, Fe^{2+} and Co^{+2} on the rate of photocatalytic activity of ZnO was also observed. It was concluded that added metal ions increase the reaction rate to some extent, however, Co^{2+} was found to be most effective.

INTRODUCTION

Although zinc oxide is an attractive semiconductor for numerous applications because of its hardness, chemical stability, optical transparency, large excitation binding energy and piezoelectric properties[1-4], the efficiency of the process is relatively low. Therefore, it seems necessary to modify the semiconductor to make it more effective. Doping with transition metals has been created a valuable position in photochemistry.

Kurtz et al.[5] invented new synthetic routes for more active Cu/ZnO catalyst for methanol synthesis. Fujita et al.[6] studied the effect of the calcinations and reduction conditions on the Cu/ZnO catalyst for methanol synthesis from CO_2. They prepared Cu/ZnO catalyst using 50:50 molar ratio of Cu : Zn. Mirica et al.[7] described the morphological evolution of ZnO thin films deposited by magnetron sputtering while Okabayashi et al.[8] investigated the electronic structure of $Zn_{1-x}M_xO$ (M : 3d transition metal) and discussed the chemical trends. Wilke and Breuer[9] studied the influence of transition metal doping on the physical and photocatalytic properties of titania. They reported that doping with transition metal ions i.e. Cr^{3+} and Mo^{5+} induced a bathochromic shift of the band gap and doping changes the life time of electron-hole pair and the absorption properties. Radovanovic et al.[10] reported colloidal transition-metal-doped zinc oxide quantum dots. They observed that Co^{2+} is isotropically doped throughout the ZnO nanocrystals. Effect of transition metal ions on the TiO_2-assisted photodegradation of dyes under visible irradiation was studied by Chen et al.[11] They studied the effect of metal ions like Cu^{2+}, Fe^{3+}, Zn^{2+}, Al^{3+} and Cd^{2+} on dyes and found that trace quantities of transition metal ions such as Cu^{2+} and Fe^{3+} having suitable redox potential alter the electron-transfer pathway involving the dye, O_2 and TiO_2 particles and markedly depress the photodegradation under

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visible irradiation. Bhandari et al.[12] observed spectrophotometrically, the photocatalytic bleaching of some dyes (erythrosin-B, congo red FCF and eosin Y), carried out in the presence of semiconducting zinc oxide. The study has been made on Fe^{2+}, Ni^{2+}, Ag^{+}, Cu^{2+}, Co^{2+}, V^{2+} and Mn^{2+} ions and it was found that all the added metal ions increase the reaction rate to some extent. Vaya et al.[13] also reported an enhanced photocatalytic activity of ZnS doped with transition metal ions in case of degradation of eosin Y. The doping was carried out by stirring and microwave exposure methods. Synthesis and characterization of TiO_2 photocatalyst doped by transition metal ions like Fe^{3+}, Cr^{3+} and V^{5+} were investigated by Vu et al.[14] Non-doped TiO_2, V-, Cr-, Fe-doped TiO_2 and N-doped TiO_2 samples exhibited much higher photocatalytic activity using visible light instead of UV. Zhang et al.[15] investigated graphene-metal-oxide composites as a photocatalyst for the degradation of dyes under visible light irradiation.

EXPERIMENTAL

Materials and methods

ZnO as a photocatalyst and brilliant blue dye (CDH) dye (Fig. 1) ($\lambda_{max\,=}$ 628 nm) were used in the present investigation. To study the effect of metal ions on ZnO, sulphates of Mn (II), Fe (II) and Co (II) were used. 1.0 × 10^{-3} M solution of brilliant blue (0.0792 g of brilliant blue in 100 mL of double distilled water) was prepared in volumetric flask and stored as a stock solution. Irradiation was carried out keeping whole assembly exposed to a 200 W tungsten lamp (Philips, Light intensity = 80.0 $mWcm^{-2}$). A cutoff filter was placed outside the beaker (Pyrex) to completely remove any thermal radiation just to ensure illumination by visible light only. The intensity of light was measured with the help of a solarimeter (SM CEL 201). The pH of the solution was measured by the digital pH meter (Systronics Model 335). The desired pH of the solution was adjusted by the addition of previously standardized 0.1 N sulphuric acid and 0.1 N sodium hydroxide solutions. The optical density (O.D.) was measured colourimetrically (Systronics photoelectric colourimeter Model 112) following the necessary conditions that the solutions are free from semiconductor particles and impurity. Therefore, a centrifuge was used for removal of any suspended particles. The progress of the photocatalytic reaction was observed by taking optical density at regular time intervals.

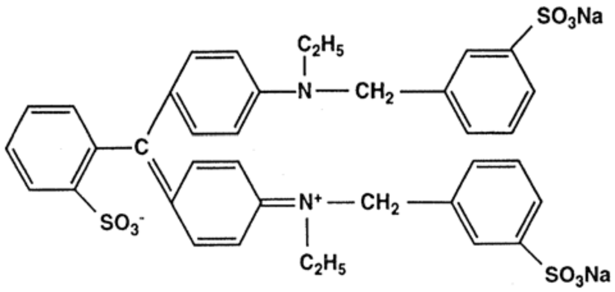

Fig. 1: Brilliant Blue Dye

Enhanced photocatalytic activity test

A 50 mL beaker was filled with 30 mL of dye solution containing photocatalyst. The mixture was sampled to assay at given time intervals by recording variation in the absorbance. The change in the maximum absorption versus irradiation time was obtained. The typical run has been presented in Fig. 2. It was observed that the optical density (O.D.) of brilliant blue solution decreases in presence of the semiconductor and light. The plot of log OD v/s time was linear and hence, this reaction follows pseudo-first order kinetics. The rate constant for this reaction was determined using the expression k = 2.303 × slope. The effect of transition metals Fe^{2+}, Co^{2+} and Ni^{2+} was examined using aqueous solutions of their sulphate ions.

Table 1: A typical run for bleaching of brilliant blue

[Brilliant blue] = 1.0×10^{-5} M pH = 8.5
Light Intensity = 80.0 mW cm^{-2} ZnO = 0.20 g

Time (min.)	2 + log O.D.
0	1.17
20	1.14
40	1.11
60	1.11
80	1.07
100	1.04
120	1.03
140	1.00
160	0.96
180	0.95
200	0.92
220	0.90
240	0.86
260	0.84
	k = 4.76×10^{-5} s^{-1}

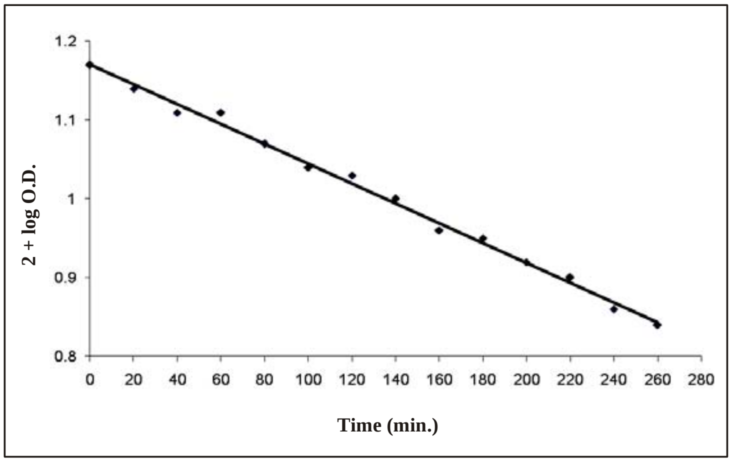

Fig. 2: A typical run for photocatalytic bleaching of brilliant blue

RESULTS AND DISCUSSION

Effect of pH

The effect of pH on photocatalytic bleaching was investigated in the range 6.5 – 10.0. The results are reported in Table 2.

Table 2: Effect of pH

[Brilliant blue] = 1.0 x 10^{-5} M
Light Intensity = 80.0 mW cm^{-2} ZnO = 0.2 g

pH	k x 10^5 (s^{-1})
6.5	2.27
7.0	2.63
7.5	2.78
8.0	2.94
8.5	**4.76**
9.0	3.75
9.5	3.25
10.0	2.84

It is evident from the data that the rate of bleaching of brilliant blue increases with increasing pH of mixture up to 8.5 and above this value of pH, there is a decrease in the rate of photocatalytic bleaching of brilliant blue. It may be explained on the basis that at low pH, anionic dye molecules remain in their protonated form and semiconductor surface also possesses positive charge due to adsorption of H^+ ions. That's why the dye molecules are repelled from the semiconductor surface and rate of photobleaching was low. As the pH increases, repulsion between dye and semiconductor molecules also decreased and hence, the rate of reaction increases. But, after a certain limit (pH = 8.5), the semiconductor surface becomes negative charged and again started repelling the dye molecules and therefore, after this point the rate of photocatalytic bleaching starts decreasing.

Effect of concentration of brilliant blue

The concentration of dye was varied from 0.25 × 10^{-5} M to 2.00 × 10^{-5} M. The results are reported in Table 3.

Table 3: Effect of concentration of brilliant blue

pH = 8.5
Light Intensity = 80.0 mW cm^{-2} ZnO = 0.2 g

[Dye] x 10^5 M	k x 10^5 (s^{-1})
0.25	0.96
0.50	2.84
0.75	4.28
1.00	4.76
1.25	4.34
1.50	4.28
1.75	2.84
2.00	2.67

It has been observed that the rate of photocatalytic bleaching increases with increase in the concentration of the dye up to 1.0 × 10^{-5} M. It may be due to the fact that as the concentration of the brilliant blue was increased, more dye molecules were available for excitation and consecutive bleaching and hence, an increase in the rate was observed. The rate of photocatalytic bleaching was found to decrease with further increase in the concentration of dye. This may be attributed to the fact that the dye starts acting as a filter for the incident light and it does not permit the desired light intensity to reach the semiconductor surface in a limited time domain; thus, decrease in the rate of photocatalytic bleaching of brilliant blue was observed at higher concentrations.

Effect of amount of semiconductor

The effect of amount of semiconductor is also likely to affect the process of dye bleaching and therefore, different amounts of semiconductor were used. The results are reported in Table 4.

Table 4: Effect of amount of semiconductor

[Brilliant blue] = 1.0×10^{-5} M
Light Intensity = 80.0 mW cm^{-2} pH = 8.5

ZnO (g)	k x 10^5 (s^{-1})
0.05	1.48
0.10	2.02
0.15	2.84
0.20	**4.76**
0.25	4.76
0.30	4.76
0.35	4.76
0.40	4.76

It has been observed that as the amount of semiconductor was increased, the rate of photocatalytic bleaching of brilliant blue also increases but ultimately, the rate becomes constant after a certain amount (0.20 g) of semiconductor. This may be due the fact that after a certain limit, if the amount of ZnO was further increased; there is no increase in the exposed surface area of the photocatalyst. It may be considered like a saturation point; after this saturation point, with any increase in amount of semiconductor, the thickness of the layer increases, as the bottom of the reaction vessel is fully covered by the photocatalyst. This was also confirmed by taking reaction vessels of different dimensions.

Effect of light intensity

The effect of the variation of the light intensity on the rate of reaction was also investigated and the observed data are reported in Table 5.

Table 5: Effect of light intensity

[Brilliant blue] = 1.0×10^{-5} M
ZnO = 0.2 g pH = 8.5

Light Intensity (mW cm^{-2})	k x 10^5 (s^{-1})
20.0	1.13
30.0	1.54
40.0	1.72

Cont…

Light Intensity (mW cm^{-2})	k x 10^5 (s^{-1})
50.0	2.45
60.0	3.23
70.0	3.87
80.0	**4.76**

The data indicate that the 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 time per unit area of the semiconductor powder. An almost linear behaviour between light intensity and the rate of reaction was observed. However, higher intensities were avoided due to thermal effects.

Effect of transition metal ions

Effect of transition metal ion was studied by taking different ions like Mn (II), Fe (II) and Co (II) in the form of their sulphate ions. All the transition metal ions enhance the rate of photocatalytic activity of ZnO. As the surface of ZnO particles is negatively charged[16], metal ions get absorbed to the surface and as a consequence, it becomes electroneutral or slightly positively charged. As the dye has anionic nature, it experience less electrostatic repulsion from the cation doped semiconductor surface.

The effect of transition metal ions on the rate of photocatalytic bleaching of dye was studied at various concentrations. The results are tabulated in Table 6 and graphically represented in Fig. 3.

Table 6: Effect of transition metal ions

[Brilliant blue] = 1.0 x 10^{-5} M
Light Intensity = 80.0 mW cm^{-2} pH = 8.5
$[M^{n+}]$ = 1.60 x 10^{-3} M ZnO = 0.2 g

$[M^{n+}]$	k x 10^5 (s^{-1})
Mn (II)	2.56
Fe (II)	5.76
Co (II)	6.48

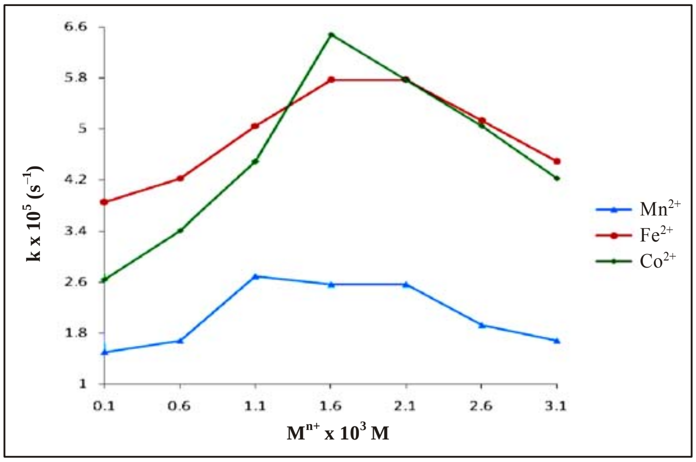

Fig. 3: Effect of metal ion concentration on the photocatalytic behavior of ZnO

It was observed that the concentration of transition metal ion initially increases the rate of the reaction but the photobleaching is suppressed at higher concentrations of all the transition metal ions. However, in some of the cases, the rate decreases initially on addition of transition metal ions.

The effect of metal ions on the photocatalytic bleaching of brilliant blue dye was observed in following order-

$$Co^{2+} > Fe^{2+} > \text{Undoped} > Mn^{2+}$$

Mechanism

On the basis of experimental observations, a tentative mechanism for photocatalytic bleaching (mineralization) of brilliant blue has been proposed as:

$${}^1Dye_0 \xrightarrow{hv} {}^1Dye_1 \quad \text{…(1)}$$

$${}^1Dye_1 \xrightarrow{ISC} {}^3Dye_1 \quad \text{…(2)}$$

$$ZnO \xrightarrow{hv} ZnO^+ (h^+) + e^- (CB) \quad \text{…(3)}$$

$$M^{n+} + e^- \longrightarrow M^{(n-1)+} \quad \text{…(4)}$$

$$M^{(n-1)+} + O_2 \longrightarrow M^{n+} + O_2^{-\bullet} \quad \text{…(5)}$$

$$ZnO\ (h^+) + OH^- \longrightarrow ZnO + {}^\bullet OH \quad \text{…(6)}$$

$${}^3Dye_1 + {}^\bullet OH \longrightarrow \text{Products (Colorless)} \quad \text{…(7)}$$

In the reaction, dye molecules absorb radiations of suitable wavelength and give rise to excited singlet state. Then it undergoes intersystem crossing (ISC) to give the excited triplet state of the dye. Semiconductor ZnO also utilizes the radiant energy to excite its electron from valence band to the conduction band; thus, leaving behind a hole. The electron from ZnO conduction band are transferred to metal ions to convert it into its lower oxidation state, which in turn transfer this electron to oxygen molecule ; thus preventing electron-hole recombination. At the same time, the positively charged vacancies (h^+) remaining in the valence band of ZnO can extract electrons from hydroxyl ions in the solution to produce hydroxyl radicals (${}^\bullet OH$). These (${}^\bullet OH$) radicals oxidize the dye molecule into colorless products. The participation of ${}^\bullet OH$ radicals as an active oxidizing species was confirmed by carrying out the reaction in presence of hydroxyl radical scavenger, where the rate of photocatalytic bleaching was drastically reduced.

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