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Role of Some Metal Ions in Enhancement of Photocatalytic Bleaching of Orange-G Dye

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ABSTRACT

Photocatalytic bleaching of orange G dye was investigated in presence of zinc oxide and some metal ion. The progress of the reaction was observed photocolourimetrically. 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+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} on the rate of photocatalytic bleaching was also observed. It was concluded that added metal ions increase the reaction rate to some extent, however, Cu^{2+} was found to be most effective.

Keywords: Photocatalytic bleaching, orange-G dye, semiconductor, zinc oxide etc.

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INTRODUCTION

The textile, dyeing and printing industries have been recognized as one of the most polluting industries in developing countries. The effluents are discharged from these industries into the water, which can cause severe contamination of surface and underground water. There is an urgent need to treat and remove harmful substances from effluents before letting them into the river. However, this is often not practiced because of the high cost. Such untreated effluents may cause poison in fish, other animals and plants living in water and creates various environmental hazards [1].

The removal of colour from waste water is often more important than the removal of other organic colourless chemicals [2]. The overall benefits of the decolourization of textile industrial wastewater may include subject of saving huge amount of water as they are chemical and water intensive units [3].

Photocatalytic degradation seems to be the most promising technique, in which energy received from sun can be better utilized for converting the pollutants into less toxic materials. In this process the semiconductor particles act as photocatalyst or short circuited microelectrodes on excitation. This involves the generation of hydroxyl radicals used as the primary oxidant for degrading organic pollutants.

Because of having properties (like hardness, chemical stability, optical transparency, large excitation energy and piezoelectric properties) Zinc oxide is an attractive semiconductor for numerous applications. In various photocatalytic activities ZnO proved itself as best suitable semiconductor [4-7].

It has been used for the bleaching of rose Bengal [8], alizarin red and nigrosin [9], methyl orange [10], crystal violet [11], arylmethane, azo and anthraquinone dyestuff [12]. Masuda et al.[13] studied photoelectrochemical reactions at n-type polycrystalline ZnO electrode using photoacoustic detection technique whereas, Claire et al.[14] reported the oxidizing species involved in photocatalytic transformation of ZnO.

Although zinc oxide has been successfully used as photocatalyst for waste water treatment, 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. [15] invented new synthetic routes for more active Cu/ZnO catalyst used for methanol synthesis. Fujita et al.[16] studied the effect of the calcinations and reduction conditions on the Cu/ZnO catalyst for methanol synthesis from CO_2.

Radovanovic et al. [17] reported colloidal transition-metal-doped zinc oxide quantum dots. They observed that Co^{2+} is isotropically doped throughout the ZnO nanocrystals. S.

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Bhandari et al.[18] observed the enhanced photocatalytic bleaching of some dyes (erythrosin-B, Orange G FCF and eosin Y), carried in the presence of Fe^{2+}, Ni^{2+}, Ag^{+}, Cu^{2+}, Co^{2+}, V^{2+} and Mn^{2+} ions doped zinc oxide and it was found that all the added metal ions increase the reaction rate to some extent.

Shaoguang et al. [19] reported the preparation and characterization of Co- doped zinc oxide and titanium dioxide. Choi et al. [20] showed that doping with Fe^{3+} increased the photoactivity significantly for CH_4 oxidation and $CHCl_3$ reduction. Iron proved to be the best dopant as compared to Mo^{5+}, Ru^{3+}, Os^{3+}, Re^{5+}, V^{4+} and Rh^{3+}.

MATERIALS AND METHODS

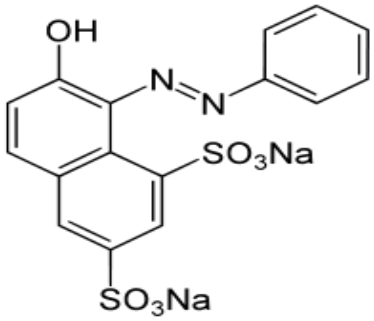

Figure 1: Orange G Dye

Orange G dye (s. d. fine-chem.) (Fig. 1) and ZnO as a photocatalyst were used in the present investigation. 1.0×10^{-3} M solution of orange G was prepared in volumetric flask with doubly distilled water 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 $mWcm^{-2}$). The intensity of light was measured with the help of 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 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. The effect of transition metals Fe^{2+}, Co^{2+},Ni^{2+}, Cu^{2+}, Zn^{2+} and Mn^{+2} was examined using aqueous solutions of the ions.

PHOTOCATALYTIC ACTIVITY TEST

The photocatalytic activity of the ZnO under visible light was investigated using the photocatalytic bleaching of Orange G dye λ_{max} = 475 nm. A cutoff filter was placed outside the beaker (Pyrex) to completely remove any thermal radiation just to ensure illumination by visible light. A 50 mL beaker was filled with 30 mL of dye solution containing photocatalyst. The

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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 orange G 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.

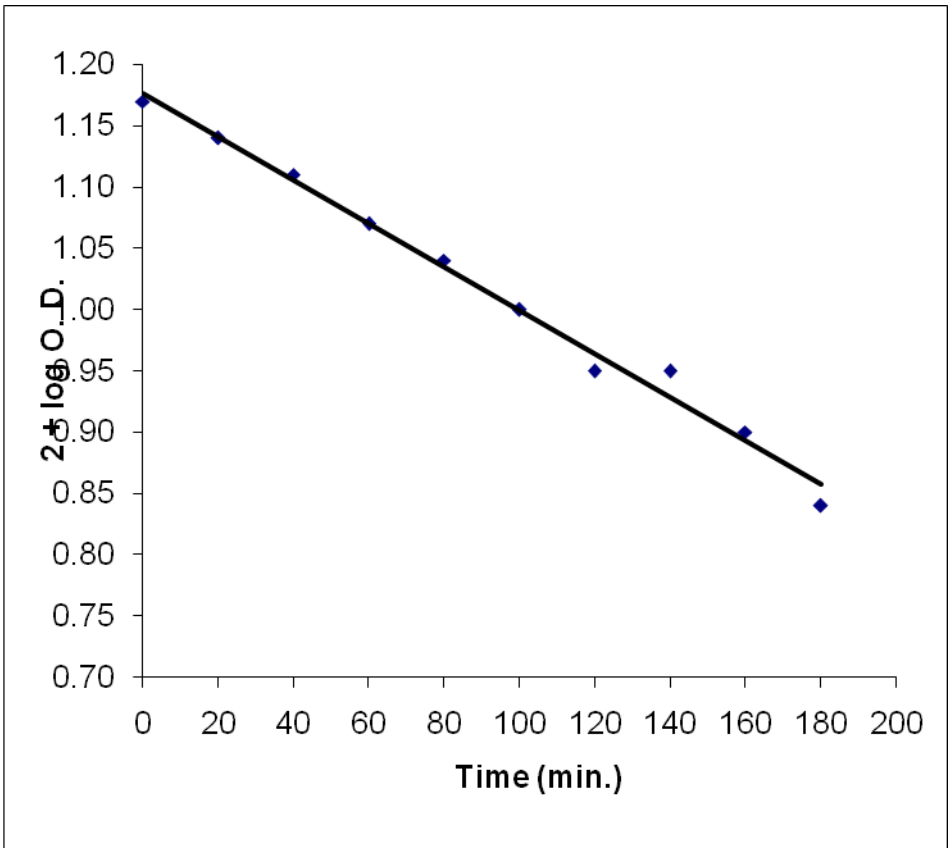

Figure 2: A typical run for photocatalytic bleaching of Orange G

Table 1: A typical run for bleaching of Orange G

[Orange G] = 1.0×10^{-5} M ZnO = 0.15 g
Light intensity = 80.0 mW cm^{-2} pH = 8.0

S. No.	Time (Min.)	Absorbance (O. D.)	2 + Log O.D.
1	0.00	0.15	1.176
2	20.0	0.14	1.146
3	40.0	0.13	1.113
4	60.0	0.12	1.079
5	80.0	0.11	1.041
6	100.0	0.10	1.00
7	120.0	0.09	0.954

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8	140.0	0.09	0.954
9	160.0	0.08	0.903
10	180.0	0.07	.0845

$k = 6.52 \times 10^{-5}\ s^{-1}$

RESULTS AND DISCUSSION

EFFECT OF PH

The effect of pH on photocatalytic bleaching was investigated in the range 5.5 – 9.0. The results are reported in Table 2.

Table 2: Effect of pH

[Orange G] = 1.0×10^{-5} M ZnO = 0.15 g
Light intensity = 80.0 mW cm^{-2}

pH	k x 10^5 (s^{-1})
5.5	3.56
6.0	4.66
6.5	4.80
7.0	5.48
7.5	5.76
8.0	**6.52**
8.5	4.08
9.0	2.40

It is evident from the data that the rate of bleaching of orange G increases with increasing pH of mixture up to 8.0 and above this value of pH, there is a decrease in the rate of photocatalytic bleaching of Orange G. 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 decreased and hence the rate of reaction increases. But, after a certain limit (pH = 8.0), 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 ORANGE G

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.

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Table 3: Effect of concentration of Orange G

pH = 8.0 ZnO = 0.15 g

Light intensity = 80.0 mW cm^{-2}

[Dye] x10^5 M	k x10^5 (s^{-1})
0.25	4.15
0.50	4.79
0.75	5.27
1.00	**6.52**
1.25	4.47
1.50	4.31
1.75	3.45
2.00	2.74

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 orange G 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 orange G was observed at higher concentration.

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

[Orange G] = 1.0 × 10^{-5} M

Light intensity = 80.0 mW cm^{-2} pH = 8.0

ZnO (g)	k x 10^5 (s^{-1})
0.05	4.10
0.10	5.43
0.15	**6.52**
0.20	6.52
0.25	6.52
0.30	6.52
0.35	6.52
0.40	6.52

It has been observed that as the amount of semiconductor was increased, the rate of photocatalytic bleaching of orange G also increases but ultimately the rate becomes constant after a certain amount (0.15 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

[Orange G] = 1.0×10^{-5} M ZnO = 0.15 g
pH = 8.0

Light Intensity (mW cm^{-2})	k x 10^5 s^{-1}
20.0	1.92
30.0	2.30
40.0	2.74
50.0	3.56
60.0	4.99
70.0	6.40
80.0	**6.52**

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 because it may cause thermal effects.

EFFECT OF TRANSITION METAL IONS

Effect of transition metal ion was studied by taking different ions like Co(II), Fe(II),Ni(II), Cu(II), Zn(II) and Mn(II). All the transition metal ions enhanced the rate of photocatalytic bleaching. As the surface of ZnO particles is negatively charged metal ion get absorbed to the surface and as a consequence, it becomes electro neutral or slightly positively charged. As the dye is of anionic nature, it experience less electrostatic repulsion from the cation doped semiconductor surface.

The effect of some dissolve transition metal ions on the rate of bleaching of dyes was studied at various concentrations. The results are tabulated in Table 6.

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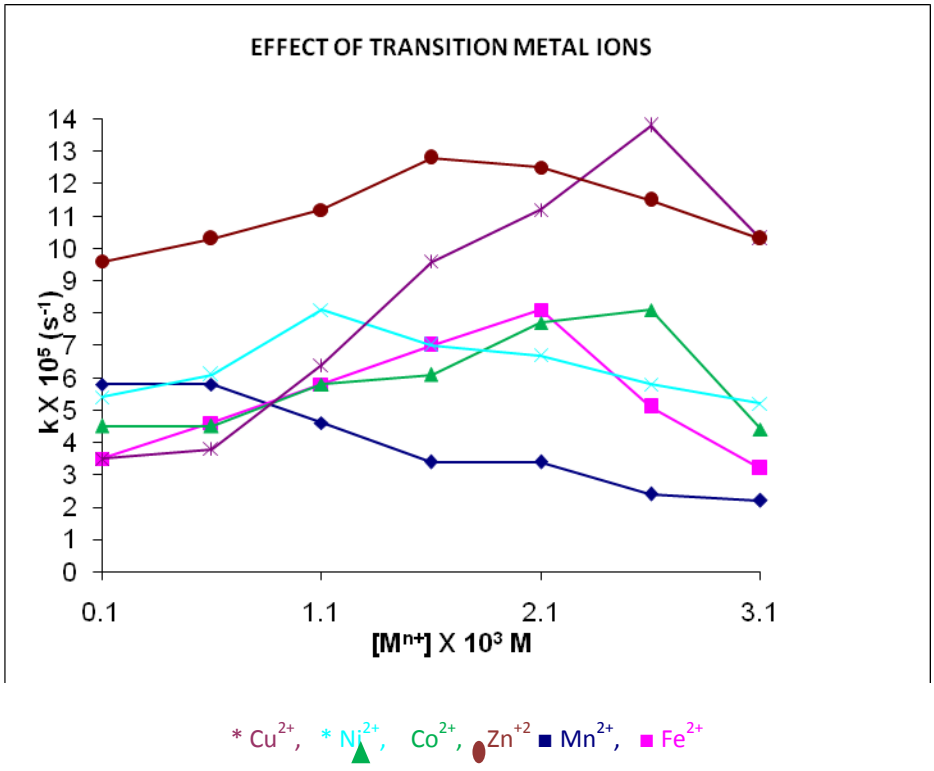
Table 6: Effect of metal ion concentration

[Orange G] = 1.0 x 10^{-5} M pH = 8.0
Light intensity = 80 mW cm^{-1} ZnO = 0.15 g

k x10^5 (s^{-1})							
S. No.	**Concentration $[M^{n+}]$ x 10^3M**	**Mn^{2+}**	**Fe^{2+}**	**Co^{2+}**	**Ni^{2+}**	**Cu^{2+}**	**Zn^{2+}**
1	0.00	**6.52**	**6.52**	**6.52**	**6.52**	**6.52**	**6.52**
2	0.10	**5.76**	3.45	4.48	5.43	3.45	9.60
3	0.60	5.76	4.61	4.48	6.08	3.84	10.31
4	1.10	4.56	5.76	5.78	**8.16**	6.40	11.19
5	1.60	3.36	7.04	6.14	7.03	9.60	**12.79**
6	2.10	3.36	**8.16**	7.68	6.72	11.19	12.47
7	2.60	2.40	5.12	**8.32**	5.75	**13.75**	11.51
8	3.10	2.24	3.20	4.38	5.23	10.31	10.31

Figure 3: Effect of metal ion concentration



It has been observed that as the concentration of transition metal ion increased the rate of the reaction increases by their adsorption on semiconductor surface and consequently increasing the attraction between dye molecules (anionic) towards semiconductor surface but the photobleaching was suppressed at higher concentration of all the transition metal ions. However, in some of the cases, the rate decreases initially on addition of transition metal ions.

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

$$Cu^{+2} > Zn^{+2} > Ni^{+2} = Fe^{+2} > Co^{+2} > Mn^{+2}$$

The above order may be explained on the basis that metal ions reduce the extent of electron-hole recombination by trapping photogenerated electrons.

$$M^{+2} + e^- \longleftrightarrow M^+ + e^- \longleftrightarrow M$$

The reduced form, in turn, prevents the recombination by trapping holes.

It has been observed that such short circuiting plays an important role in cases of Mn(II), Zn(II), Cu(II) and Co(II) as evident form decrease in rate of photocatalytic bleaching of orange G in presence of small amount of these metal ions. However increasing the concentration of these metal ions, these short circuiting become less dominant, and therefore an increasing in the rate of reaction has been observed. However, if there is much difference in the redox potentials of the dye as compared to metal ions (M^{2+}) the short circuiting reactions will not take places.

MECHANISM

On the basis of experimental observations, a tentative mechanism for photocatalytic bleaching of orange G has been proposed as:

$$^1OG_0 \xrightarrow{h\nu} {}^1OG_1$$

$$^1OG_1 \xrightarrow{ISC} {}^3OG_1$$

$$ZnO \xrightarrow{h\nu} ZnO^+ (h^+) + e^- (CB)$$

$$M^{n+} + e^- \longrightarrow M^{(n-1)+}$$

$$M^{(n-1)+} + O_2 \longrightarrow M^{n+} + O_2^{-\bullet}$$

$$ZnO\ (h^+) + OH^- \longrightarrow ZnO + {}^{\bullet}OH$$

$$^3OG_1 + {}^{\bullet}OH \longrightarrow \text{Products (colorless)}$$

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 also utilizes the radiant energy to excite its electron from valence band to the conduction band; thus, leaving behind a hole. The electron present in

conduction band is scavenged by metal ions and later on transferred to dissolved oxygen. Thus it prevents electron hole recombination. The holes presented on the zinc oxide particles will abstract an electron from hydroxyl ion to form $^{\bullet}$OH radicals. These $^{\bullet}$OH radicals will oxidize the dye molecules in to colorless product. 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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