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USE OF SEMICONDUCTING MANGANESE (IV) OXIDE PARTICULATE SYSTEM AS A PHOTOCATALYST : PHOTOASSISTED BLEACHING OF SOME DYES

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ABSTRACT

The most serious polluters of environment are industries like textiles, tannery, electroplating and pulp and paper etc. Photocatalytic degradation has been considered to be an effective process for degradation of organic pollutants, which are present in the effluents released by these industries. The photocatalytic degradation was carried out on some cationic dyes (Methylene blue, azure B and toluidine blue) in the presence of semiconducting manganese (IV) oxide and it was observed spectrophotometrically. The effects of various operating variables like pH, concentration of dyes, amount of semiconductor, light intensity, particle size, stirring etc. were also observed on the rate of the reaction. A tentative mechanism has also been proposed for this photocatalytic bleaching.

Key words: Photodegradation, Photocatalytic bleaching, Manganese (IV) oxide, Methylene blue, Azure B, Toluidine blue.

INTRODUCTION

Photocatalysis has a number of applications like solar energy conversion, synthesis of energy rich products, treatment of industrial effluents and domestic water and recovery of costly metals at very low concentrations. Extensive researches in photocatalysis resulted in various applications based on the use of semiconductors. Photocatalytic bleaching was found to be the most promising process for the waste water treatment in which semiconductor particles act as photocatalyst or short circuited microelectrodes on excitation. This method involves the generation of hydroxyl radicals and using these radicals as the primary oxidant for degrading organic pollutants.

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The visible light induced photodegradation of organic pollutants on dye adsorbed TiO_2 surface has been reported by Chatterjee and Mahata[1]. The solar photochemical detoxification and disinfection for water with TiO_2 has been studied by Cooper et al.[2,3] The photocatalytic degradation of methyl orange by TiO_2 in aqueous phase was studied by Rashed and El Amin[4]. Zinc oxide is an attractive semiconductor for numerous applications[5-10] because of its hardness, chemical stability, optical transparency, large excitation energy and piezoelectric properties. Mansilla and Villasnov[11] investigated photodegradation of Kraft-black liquor using platinum-impregnated ZnO and reported compete discoloration after 60 min UV irradiation. Sharma et al.[12-13] reported the use of zinc oxide particulate system as a photocatalyst in the photobleaching of brilliant green and rose bengal. Ameta et al.[14] have reported the use of semiconducting iron (III) oxide in photocatalytic bleaching of some dyes.

Recently, Mu et al.[15] carried out the photocatalytic degradation of orange II in the presence of Mn^{2+} while Daneshwar et al.[16] carried out the photocatalytic degradation of azo dye acid red-14 in water with ZnO as an alternative to TiO_2. The effect of transition metal ions on the TiO_2 assisted photodegradation of dyes under irradiation with visible light was studied by Chen et al.[17] The photocatalytic degradation of textile azo dye sirius gelb GC on TiO_2 or Ag-TiO_2 particles in absence or presence of UV irradiation effect has been reported by Ozkan et al.[18]

The photocatalytic degradation of various dyes (Orange II, orange G, congo red, indigo carmine, crystal violet, malachite green, ramazol blue and methylene blue) have been reported by Hachem et al.[19] Hydrogen evolution from water on eosin-Y fixed TiO_2 photocatalyst using a silane coupling reagent under visible light irradiation has been observed by Abe and Hara.[20] Kako et al.[21] suggested some preventive methods against catalytic poisoning of TiO_2 photocatalyst by H_2S. Kim et al.[22] used ZnO coated TiO_2 nanoparticles for the flexible dye-sensitized solar cells. Photocatalytic degradation of brilliant red dye and textile waste water treatment has been suggested by Martins et al.[23] The present work describes the use of manganese (IV) oxide as photocatalyst in degradation of some cationic dyes.

EXPERIMENTAL

Cationic dyes (Methylene blue, azure B and toluidine blue) and manganese (IV) oxide were used in the present investigations. All the solutions were prepared in doubly distilled water. The photocatalytic bleaching of the dyes were observed by taking dye solution and manganese (IV) oxide was added to it. Irradiation was carried out keeping the whole assembly exposed to a 200 W tungsten lamp (Philips; light intensity = 40 $mWcm^{-2}$).

The intensity of light at various distances from the lamp was measured with the help of a solarimeter (SM CEL 201). A water filter was used to cut out thermal radiations. The digital pH meter (Systronics-335) was used to measure the pH of the solutions. The desired pH of the solutions was adjusted by the addition of previously standardized sulphuric acid and sodium hydroxide solutions.

The necessary conditions for correct measurement of the optical activity is that the solution must be free from semiconductor particles and impurities and hence, a centrifuge (REM-1258) was used to remove these species. The progress of the photocatalytic reaction was observed by taking absorbance at regular time interval using ultraviolet visible spectrophotometer (JASCO-7800).

RESULTS AND DISCUSSION

The photocatalytic degradation of the dyes were observed at λ_{max} = 660, 625 and 650 nm, respectively for methylene blue, toluidine blue and azure B. The results of the typical run are graphically reported in Fig. 1.

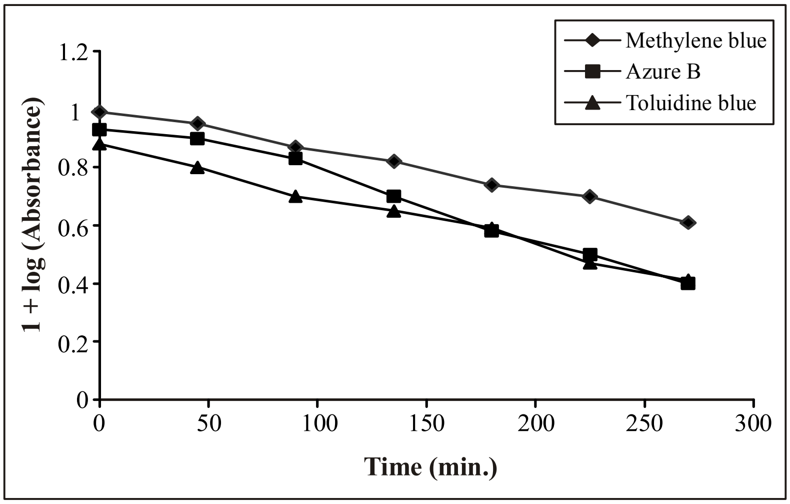

Fig. 1: A typical run

♦ - [Methylene blue] = 1.4 x 10^{-5} M, pH = 7.5, Manganese (IV) oxide = 0.16 g,
Light Intensity = 40.0 mW cm^{-2};   k = 5.53 x 10^{-5} sec^{-1}.

■ - [Azure B] = 5.0 x 10^{-5} M, pH = 6.5, Manganese (IV) oxide = 0.20 g,
Light Intensity = 40.0 mW cm^{-2}; k = 8.52 x 10^{-5} sec^{-1}.

▲- [Toluidine blue] = 4.0 x 10^{-5} M, pH = 8.0, Manganese (IV) oxide = 0.20 g,
Light Intensity = 40.0 mW cm^{-2}; k = 6.73 x 10^{-5} sec^{-1}

It was observed that the absorbance of the dye solutions in presence of semiconductor was much low as compared to sample without semiconductor at the same intervals of time; thus, indicating that rate of this photocatalytic degradation is favorably affected by manganese (IV) oxide in the case of these dyes. A plot of log (absorbance) versus time was linear (Fig. 1) and hence, this reaction follows pseudo-first order kinetics. The rate constants of this reaction were determined by the expression -

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

Effect of pH

The pH of the solution is likely to affect the photobleaching of the dyes and hence, the effect of pH on the rate of bleaching of dye solutions was investigated in the pH range (5.5-9.0). The results are graphically presented in Fig. 2.

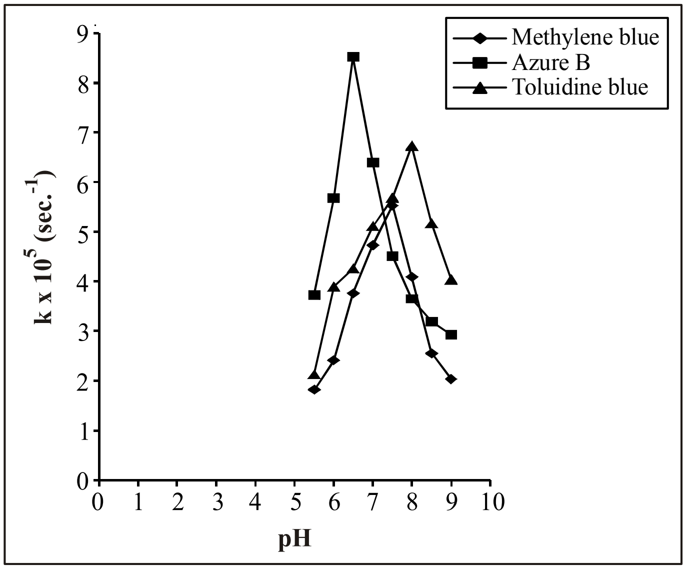

Fig. 2: Effect of pH

♦- [Methylene blue] = 1.4 x 10^{-5} M, Manganese (IV) oxide = 0.16 g,
Light Intensity = 40.0 $mWcm^{-2}$.

■- [Azure B] = 5.0 x 10^{-5} M, Manganese (IV) oxide = 0.20 g,
Light Intensity = 40.0 $mWcm^{-2}$.

▲- [Toluidine blue] = 4.0 x 10^{-5} M, Manganese (IV) oxide = 0.20 g,
Light Intensity = 40.0 $mWcm^{-2}$

Photocatalytic bleaching of methylene blue, azure B and toluidine blue were maximum at pH = 7.5, 6.5 and 8.0, respectively. At low pH, the dyes are in their protonated form, and the semiconductor surface is positively charged due to adsorption of H^+ ions. Thus, the dye molecules are repelled from the surface of the semiconductor and therefore, the rate of photobleaching is slow at lower pH of the medium. Above the respective maximum pH, a further increase in pH will result in a negatively charged semiconductor surface due to adsorption of OH^- ions; the electron rich dye molecules will electrostastically repelled and therefore, the rates decreases. This has also been reported by Mansoori et al.[24]

Effect of dye concentration

The effect of dye concentration was also studied by taking different concentrations of the dyes. The results are presented in Fig. 3.

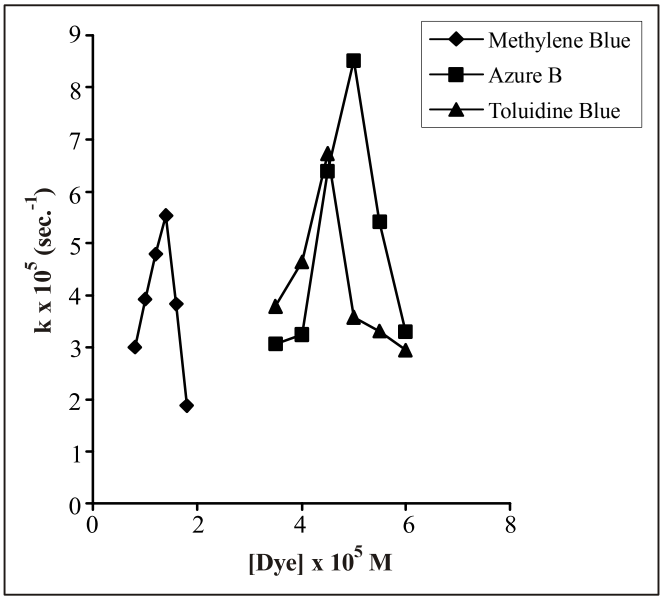

Fig. 3: Effect of dye concentration

♦- [Methylene blue]; pH = 7.5, Manganese (IV) oxide = 0.16 g,
Light Intensity = 40.0 $mWcm^{-2}$.

■- [Azure B]; pH = 6.5, Manganese (IV) oxide = 0.20 g,
Light Intensity = 40.0 $mW\ cm^{-2}$.

▲- [Toluidine blue]; pH = 8.0, Manganese (IV) oxide = 0.20 g,
Light Intensity = 40.0 $mWcm^{-2}$

The rate of photocatalytic bleaching of dyes was found to increase on increasing the concentration up to [Methylene blue] = 1.4 x 10^{-5} M, [Azure B] = 5.0 x 10^{-5} M and [Toluidine blue] = 4.0 x 10 $^{-5}$ M. It may be due to the fact that as the concentration of dye was increased, more dye molecules were available for excitation and consecutive energy transfer. As a result, increase in the rate of bleaching was observed. The rate of photocatalytic bleaching was found to decrease with further increase in the concentration of the dyes, i.e. above their corresponding limits. This decrease may be attributed to the fact that the dye itself will start acting as a filter for the incident light. It will not permit the desired intensity of light to reach the semiconductor particles; thus, decreasing the rate of photocatalytic blaechig of the dyes.

Effect of amount of semiconductor

The amount of semiconductor is also likely to affect the process of dye bleaching and hence, different amounts of photocatalysts were used. The results are summarized in Table 1.

Table 1: Effect of amount of semiconductor

Mn (IV) oxide (g)	[Methylene blue] = 1.4 x 10^{-5} M pH = 7.5	[Azure B] = 5.0 x 10^{-5} M pH = 6.5	[Toluidine blue] = 4.0 x 10^{-5} M pH = 8.0
	k x 10^5 (sec.$^{-1}$)	**k x 10^5 (sec.$^{-1}$)**	**k x 10^5 (sec.$^{-1}$)**
0.05	1.47	3.41	2.32
0.10	2.64	4.51	3.57
0.15	3.41	6.39	4.87
0.20	5.53	8.52	6.73
0.25	5.61	8.50	6.82
0.30	5.48	8.52	6.73

It was observed that initially, the rate of photobleaching of the dyes increases with an increase in the amount of semiconductor but it becomes virtually constant after a certain amount of the photocatalyst. This may be attributed to the fact that as the amount of semiconductor was increased, the exposed surface area of semiconductor also increases. A plateau is then obtained, which may be considered like a saturation point; above which, any increase in the amount of semiconductor has no or negligible effect on the rate of photocatalytic bleaching of the dyes, because any further increase in the amount of semiconductor after this point will only increase the thickness of the layer at the bottom of the vessel and not the exposed surface area. It is also confirmed by taking reaction vessels of different dimensions. It was observed that the point of saturation shifted to a higher value for vessels of larger capacities while it shifted to lower side for vessels of smaller capacities.

Effect of light intensity

To observe the effect of light intensity on the photocatalytic bleaching of the dyes, light sources of different wattage were used or the distance between the light source and the exposed surface area was varied. The results are presented in Table 2. It was observed that the bleaching of the dyes was enhanced on increasing the intensity of light. This may be due to an increase in the number of photons striking per unit area of manganese dioxide powder on increasing the intensity of light. An almost linear behaviour between light intensity and rate of reaction was observed.

Table 2: Effect of light intensity

Light intensity (mW cm^{-2})	[Methylene blue] = 1.4×10^{-5} M Mn (IV) oxide = 0.16 g pH = 7.5	[Azure B] = 5.0×10^{-5} M Mn (IV) oxide = 0.2 g pH = 6.5	[Toluidine blue] = 4.0×10^{-5} M Mn (IV) oxide = 0.2 g pH = 8.0
	k x 10^5 (sec.$^{-1}$)	**k x 10^5 (sec.$^{-1}$)**	**k x 10^5 (sec.$^{-1}$)**
20.0	2.62	2.41	2.55
30.0	3.87	5.48	4.26
40.0	5.53	8.52	6.73
50.0	7.31	9.84	8.52
60.0	9.13	11.37	10.23
70.0	12.79	12.79	10.55

Effect of particle size

The effect of particle size on the rate of photocatalytic bleaching of the dyes was investigated by varying the size of semiconductor (0.8-4.0 μm). The results are summarized in Table 3. The rate of photobleaching of dyes increases with decreasing particle size. This enhancement in the rate may be explained on the basis of the increased surface area of the photocatalyst as the particle size was reduced. The expected increase in the surface area of the semiconductor is four times on reducing the particle size to its half. This should increase the rate of reaction four times, but it has never been achieved. This is due to the fact that the surface area exposed to light may not increase to the extent as expected theoretically.

Table 3: Effect of particle size

Light Intensity = 40.0 mW cm^{-2}

Particle size (μm)	[Methylene blue] = 1.4×10^{-5} M Mn (IV) oxide = 0.16 g. pH = 7.5	[Azure B] = 5.0×10^{-5} M Mn (IV) oxide = 0.2 g pH = 6.5	[Toluidine blue] = 4.0×10^{-5} M Mn (IV) oxide = 0.2 g pH = 8.0
	k x 10^5 ($sec.^{-1}$)	**k x 10^5 ($sec.^{-1}$)**	**k x 10^5 ($sec.^{-1}$)**
0.8	13.75	17.35	16.53
1.6	7.25	10.78	9.93
2.4	6.73	9.47	8.23
3.2	5.53	8.52	6.73
4.0	4.93	6.35	4.95

Effect of stirring

The effect of stirring on the rate of photocatalytic bleaching of the dyes was also investigated and results are reported in Table 4. It has been observed that the rate of degradation of the dyes was higher in the stirred solution as compared to unstirred one. The saturation point is shifted to a higher value of manganese dioxide depending upon the number of revolutions per minute. It may be explained on the basis that as the solutions was stirred; all the particles are better exposed to the light in all directions, while it is not possible in case of unstirred solution as only the upper hemispheres and that too of the particles on the surface are exposed.

Table 4: Effect of stirring

Light Intensity = 40.0 mW cm^{-2}

Rate of stirring (RPM)	[Methylene blue] = 1.4 x 10^{-5} M Mn (IV) oxide = 0.16 g pH = 7.5	[Azure B] = 5.0 x 10^{-5} M Mn (IV) oxide = 0.2 g pH = 6.5	[Toluidine blue] = 4.0 x 10^{-5} M Mn (IV) oxide = 0.2 g pH = 8.0
	k x 10^5 (sec.$^{-1}$)	**k x 10^5 (sec.$^{-1}$)**	**k x 10^5 (sec.$^{-1}$)**
-	5.53	8.52	6.73
400	6.10	9.35	7.23
800	6.73	10.21	8.45
1200	7.43	11.35	9.73
1600	8.23	12.79	10.23
2000	9.97	13.43	11.57

MECHANISM

On the basis of the observed data, the following tentative mechanism may be proposed for the photocatalytic bleaching of dyes.

$$\text{Dye} \xrightarrow{\nu h} \text{Dye}^* \qquad \ldots(2)$$

$$\text{SC} \xrightarrow{\nu h} e^-(\text{CB}) + h^+(\text{VB}) \text{ or } \text{SC}^+ \qquad \ldots(3)$$

$$h^+ + {}^-\text{OH} \longrightarrow {}^\bullet\text{OH} \qquad \ldots(4)$$

$$\text{Dye}^* + {}^\bullet\text{OH} \longrightarrow \text{Leuco (Dye)} \qquad \ldots(5)$$

$$\text{Leuco (Dye)} \longrightarrow \text{Products} \qquad \ldots(6)$$

Dye absorbs radiations of suitable wavelength and it is excited to its higher energy state. The semiconducting manganese dioxide utilizes the incident light energy to excite its electron from valence band to the conduction band; thus, leaving behind a hole. This hole can abtract an electron from hydroxyl ions to generate hydroxyl radicals. These hydroxyl radicals will then oxidize the dye to its leuco form, which may ultimately degrade to products. The involvement of hydroxyl radical ($^{\bullet}OH$) as an active oxidizing species was confirmed by using hydroxyl radical scavenger (2-propanol) where the rate of bleaching was drastically reduced.

CONCLUSION

The field of heterogeneous photocatalysis is quite promising for newer chemical transformations, which are sometimes inaccessible with conventional reagents, reaction conditions, and improved selectivity in multifunctional molecules or with a mixture of reagents. The photocatalytic bleaching of dyes using low cost semiconducting powder like manganese (IV) oxide may open new avenues for the treatment of wastewater from dyeing, printing and textile industries. Not only this, the treated wastewater may be used for cooling, cleaning, wasteland irrigation, etc., which is not possible with colored water. Time is not far-off, when photocatalysis will be firm footed as a promising technology in wastewater treatment.

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