

DECOLOURIZATION OF SAFRANINE O IN AQUEOUS SOLUTION EMPLOYING MANGANESE DIOXIDE SEMICONDUCTOR

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Key words : Safranin O, Manganese dioxide, Photocatalytic degradation.

ABSTRACT

In recent years, array of industrial activities have been disturbing the water quality by release of various contaminants like dyestuff, heavy metal ions and many other organic substances. Discharges containing dyes, in particular, are to be controlled due to their highly toxic nature. These dyes are commercially important chemicals and frequently used in dyeing, printing, textile, photography, food and cosmetic industries. Despite of their importance, dyes are toxic and carcinogenic in nature. Environmental contamination by these toxic chemicals is causing serious global problems. The photocatalytic degradation of safranin O dye was carried out using MnO_2 as semiconductor. Solution was prepared in distilled water and visible light was used as the source of energy. The effect of various parameters like amount of semiconductor, pH, light intensity, dye concentration etc. on the photodegradation is investigated. A tentative mechanism has been proposed.

INTRODUCTION

Photocatalytic reactions have found an important place in green chemical pathways also as there are found very efficient and economic for the treatment of waste water as compared to the conventional methods, without polluting the atmosphere. During the last few years, experimental studies on the photocatalytic role of manganese dioxide and their possible role in chemical evolution have been taken. Photocatalytic degradation is a part of green chemistry where the catalyst utilizes visible light and converts harmful dyes into less harmful products. Much attention has been directed as investigating the photocatalytic degradation of safranin O pollutants mediated by manganese dioxide semiconductor in aqueous solution un-

der visible-light irradiation.

Chen and Chou (1993) reported photodegradation of methyl orange in aqueous solution with suspended titanium dioxide as photocatalyst. Photocatalytic degradation of cetylpyridinium chloride over TiO_2 has been reported by Singhal *et al.* (1997). Similar photocatalytic reaction of orange G dye by ZnO powder has been reported by Sharma *et al.* (1995, 1995). Yoneyama *et al.* (1979) studied the photocatalytic reduction of dichromate ions using WO_3 powder in acidic range. Costa *et al.* (1999) proposed the mechanism of gas phase degradation of cyclohexanol and methylcyclohexanol catalysed by zirconium phosphate and phosphite. Shyama and Arakawa (1992) have used zirconium dioxide as photocatalyst. Photocatalytic degradation of brilliant green over semiconductor ZnO pow-

der suspended in aqueous solution has been reported by Ameta *et al.* (1997).

Various chemical and physical processes such as coagulation, electrocoagulation (2001) and adsorption on activated carbon are not destructive but only transfer dye from one phase to another; hence, there is a need for developing treatment technologies for eliminating contaminants from wastewater. Photocatalytic degradation by semiconductors is a new, effective and rapid technique for the removal of pollutants from water (2001, 2000). The TiO_2 photocatalyst has attracted much interest in recent years for its highly active photocatalytic functions, like the ability to decompose of chemical compounds, as well as super hydrophilic and antibacterial properties (2000-2004). This photocatalyst and most of other semiconductors have poor activity when used alone, but the presence of a metal on the semiconductor markedly increases their efficiency (2004-2007).

Although there are various techniques to remove these pollutants like adsorption, air stripping, biological methods and various oxidation processes but each one has its own advantages and limitations. Due to the high concentration of organics in effluents and higher stability of modern synthetic dyes, these methods are ineffective for the complete colour removal and degradation of organics and dyes.

EXPERIMENTAL

Material

Safranin O (Sigma) and manganese dioxide (Qualigens) were used in present investigations.

Apparatus

Spectrophotometer (Systronics Model-104), solarimeter (CEL Model-SM 201) and digital pH meter (Systronics Model-371) were used for the measurement of absorbance, light intensity and pH, respectively.

Procedure

0.3508 g safranin O was dissolved in 500 mL doubly distilled water so that the concentration of dye solution was 1.00×10^{-3} M. It was used as a stock solution. This solution was further diluted.

The optical density of this dye solution was determined with the help of spectrophotometer at $\lambda_{\text{max.}} = 515$ nm. This dye solution was placed in equal amounts (50.0 mL) in four beakers.

1) The first beaker containing safranin O solution was kept in dark.

2) The second beaker containing safranin O solution was exposed to light.

3) The third beaker containing safranin O solution and 0.50 g MnO_2 was kept in dark, and

4) The fourth beaker containing safranin O solution and 0.50 g MnO_2 was exposed to light.

After keeping these beakers for 4 hours, the optical density of the solution in each beaker was measured with the help of a spectrophotometer. It was found that the solutions of first three beakers had almost the same optical density while the solution of fourth beaker had a decrease in its initial value of optical density. From this observation, it becomes clear that this reaction requires presence of both; the light as well as semiconductor NiO . Hence, this reaction is photocatalytic in nature.

50.0 mL of 3.0×10^{-6} M of safranin O was taken in a beaker and 0.50 g of MnO_2 was added to it. The pH of the reaction mixture was adjusted to 11.0. Then the solution was exposed to a 200 W tungsten lamp and aliquot of 2.0 mL was taken out from the reaction mixture at regular time intervals and its optical density was observed at 515 nm.

It was observed that the concentration of safranin O decreases with increasing time of exposure. A plot of $1 + \log \text{O.D.}$ against time was found to be linear. The rate constant was measured with the expression-

$$k = 2.303 \times \text{slope}$$

A typical run has been presented in Table 1.

RESULTS AND DISCUSSION

Typical Run

The plot of $1 + \log \text{O.D.}$ and time was found to be linear and hence, the reaction followed pseudo-first order kinetics shown in Table 1 and graphically represented in Fig. 1.

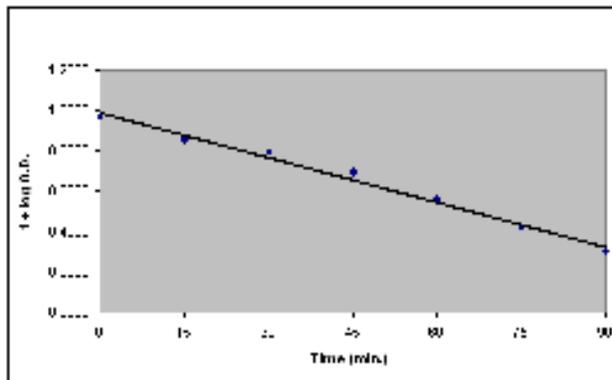


Table 1. A Typical Run

Time (min.)	O.D.	1 + log O.D.
0.0	0.939	0.9730
15.0	0.718	0.8560
30.0	0.623	0.7940
45.0	0.501	0.6990
60.0	0.361	0.5570
75.0	0.265	0.4230
90.0	0.201	0.3030

$$k = 2.91 \times 10^{-4} \text{ (sec}^{-1}\text{)}$$

Effect of pH Variation

The photochemical reaction between manganese dioxide and safranin O may be affected by pH and therefore, the effect of pH on this photochemical reaction has been investigated in the pH range 9.0 to 12.0 keeping all other factors identical. The results are shown in Table 2.

Table 2. Effect of variation of pH

pH	k x 10 ⁴ (sec ⁻¹)
9.0	2.28
9.5	2.37
10.0	2.42
10.5	2.66
11.0	2.91
11.5	2.22
12.0	1.78

It is evident from above data that the rate of photocatalytic degradation of safranin O increases with increase in pH. The increase in rate of photocatalytic degradation may be due to more availability of the OH⁻ at higher pH values. OH⁻ will generate more .OH by combining with the hole and these hydroxyl radicals are responsible for this photocatalytic degradation. As the pH of the solution was increased, more OH⁻ will be available and these will be adsorbed on the surface of the semiconductor making it negatively charged and as a consequence of repulsive force between two negatively charged species (OH⁻ and electron rich dye). The approach of electron rich safranin O to the semiconductor surface will be retarded. This will result into a decrease in the rate of photocatalytic degradation of safranin O.

Effect of dye concentration

Effect of variation of dye concentration was studied by taking different concentrations of safranin O. The results are tabulated in Table 3.

Table 3. Effect of safranin O concentration

[Safranin O] x 10 ⁶ M	k x 10 ⁴ (sec ⁻¹)
2.4	1.71
2.6	2.04
2.8	2.50
3.0	2.91
3.2	2.38
3.4	2.04
3.6	1.71

It has been observed that the rate of photocatalytic degradation increases with an increase in the concentration of the dye upto 3.0 x 10⁻⁶ M. It may be due to the fact that as the concentration of the safranin O was increased, more dye molecules were available for excitation and energy transfer and hence, an increase in the rate was observed. The rate of photocatalytic degradation 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; thus, decreasing the rate of photocatalytic degradation of safranin O.

Effect of Amount of Semiconductor

The amount of semiconductor powder may also effect the rate of photocatalytic degradation of safranin O and therefore, the amount of semiconductor was varied from 0.20 g to 0.80 g keeping all the other factors identical. The result are tabulated in Table 4.

Table 4. Effect of amount of Semiconductor

MnO ₂ (g)	k x 10 ⁴ (sec ⁻¹)
0.20	1.56
0.30	1.86
0.40	2.23
0.50	2.91
0.60	2.90
0.70	2.90
0.80	2.90

As indicated from the data, an increase in the amount of semiconductor also increases the rate of photocatalytic reaction up to a certain amount of semiconductor (saturation point). This can be explained on the basis that with an increase in the amount of semiconductor, the surface area of the semiconductor will increase and hence, the increase in the rate of reaction. But after a certain limiting amount of semiconductor; if the amount of semiconductor is further increased, then it will not contribute to an increase in the exposed surface area. On the contrary, it will increase only the thickness of the layer of semiconductor powder at the bottom of the reaction vessel and thus, the saturation point is reached.

Effect of Light Intensity

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

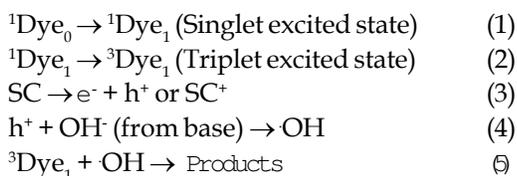
Table 5. Effect of Light Intensity

[Safranin O] = 3.0×10^{-6} M pH = 11.0	MnO ₂ = 0.50 g
Light Intensity (mW cm ⁻²)	k x 104 (sec ⁻¹)
32.0	1.03
35.0	1.12
38.0	1.45
41.0	1.80
44.0	2.03
47.0	2.17
50.0	2.91

The data indicate that the bleaching action is accelerated as the intensity of light was increased, because any increase in light intensity increases the number of photons striking per unit area of the semiconductor. A linear behaviour between light intensity and the rate of reaction was observed. However, higher intensities were avoided due to thermal effects.

MECHANISM

On the basis of above studies, a tentative mechanism has been proposed for the bleaching of dye by nickel oxide semiconductor.



Dye absorbs the light and gets excited to its first singlet state. This gets converted to triplet state through intersystem crossing. On the other hand, the semiconductor gets excited by absorbing light and an electron is excited from its valence band to conduction band leaving behind a hole. This hole abstracts an electron from OH⁻ ions generating .OH free radical. The dye is bleached by this .OH radical. The participation of .OH radical was confirmed by using scavenger (2-propanol), which almost stops the degradation.

ACKNOWLEDGEMENTS

The authors are thankful to Prof. Suresh C. Ameta, Former Professor, Department of Chemistry, M.L. Sukhadia University, Udaipur (Raj.) for helpful discussions and valuable suggestions.

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