



PHOTOCATALYTIC DEGRADATION OF ERIOCHROME BLACK T USING AMMONIUM PHOSPHOMOLYBDATE SEMICONDUCTOR

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ABSTRACT

The photocatalytic degradation of eriochrome black T was investigated using ammonium phosphomolybdate semiconductor, under visible light irradiation. Ammonium phosphomolybdate semiconductor was used as a photocatalyst for degradation of eriochrome black T under different conditions of pH, amount of semiconductor, dye concentration and light intensity. The degradation rate was affected by all these parameters. The degradation of dye followed pseudo-first order kinetics. A maximum degradation of 93.9 % was achieved after irradiation time of 5 hours. The mechanism of photocatalysis has been discussed.

Keywords: Ammonium phosphomolybdate, Eriochrome black T, Photocatalytic degradation.

INTRODUCTION

Dyeing, printing and textile industries throw a lot of effluents in the water resources around; thus, making the water coloured. The removal of colour from waste waters is often more important than the removal of other organic colourless chemicals. Our group has made extensive research in recent years by employing semiconductor in the visible light for the degradation of dye pollutants. Photocatalysis has attracted the attention of photochemists in last two decades¹⁻³. In recent years, many studies have been focussed on the photocatalytic degradation of organic compounds mediated by semiconductor particles acting as photocatalyst⁴⁻⁶. Photocatalytic degradation by semiconductors is a new, effective and rapid technique for the removal of pollutants from water^{7, 8}.

Semiconductors are used to degrade organic pollutants in water to less harmful inorganic materials. The primary event occurring on the illumination of ammonium

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phosphomolybdate by visible light is the generation of photo-induced electron/ hole ($e^- h^+$) pairs. These species play an important role in the photodegradation of dyes.

Photocatalysis has played a pivotal role in many reactions of synthetic, biological and industrial importance. This process may help in combating against the ever increasing water pollution. The overall benefits of the decolorization of textile industrial waste water may be interesting as it may save a huge amount of water, because textile industries are regarded as chemical intensive as well as water intensive.

The commonly used photocatalysts are binary and ternary calcogenides in general, but more explored ones are titanium dioxide, zinc oxide, cadmium sulphide, etc. Among various semiconductors, ammonium phosphomolybdate has been paid negligible attention as a semiconductor. It has been used as an effective photocatalyst, due to its unique photocatalytic efficiency, low cost, non-toxicity and high stability for the reduction of some metal ions in low and as well as high concentrations, but it has not been used for the degradation of dyes so far. Therefore, it has been planned to use ammonium phosphomolybdate for photocatalytic degradation of eriochrome black T.

Eriochrome black T is an azo dye and it is used as a metallochromic indicator. These are the largest group of organic dyes and have widespread applications in many areas of dye-stuff industry, pharmacy and dosimetry due to the presence of azo ($-N=N-$) linkage.⁹⁻¹⁵ Azo dyes are used in dyeing and printing industries. Some of these are toxic and carcinogenic and very little work has been done for their transformation into harmless products. Azo dyes have wide interest of applications in complexometric titrations¹⁶ and in analytical chemistry¹⁷ also.

The present paper describes the study on the interaction of ammonium phosphomolybdate and eriochrome black T dye under visible light irradiation.

EXPERIMENTAL

Material

Eriochrome black T (Loba Chemie) and ammonium phosphomolybdate (Himedia) were used in present investigations.

Apparatus

Digital pH meter : The pH of solution was measured by a digital pH meter (Systronics Model-371).

Solarimeter : The intensity of light was measured by a solarimeter (CEL Model-SM 201) in mWcm^{-2} .

Light source : A 200 watt tungsten lamp was used for irradiation purpose.

Spectrophotometer : Optical density (O.D.) was measured at different time intervals by U.V. -Visible spectrophotometer (Systronics Model -104). The colour fading of the dye was monitored spectrophotometrically at 545 nm. G-3 sintered glass crucible was used for filtration, just to obtain the desired accuracy in the measurement of optical density of dye solutions.

Procedure

0.4613 g of eriochrome black T was dissolved in 1000 mL of doubly distilled water, so that the concentration of dye solution was 1.00×10^{-3} M and 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 a spectrophotometer ($\lambda_{\text{max}} = 545$ nm). 200 mL. of dye solution was taken and divided into 50 mL. in four beakers, each.

- (i) The first beaker containing only eriochrome black T solution was kept in dark.
- (ii) The second beaker containing only eriochrome black T solution was kept in light.
- (iii) 0.30 g ammonium phosphomolybdate semiconductor was added to third beaker containing eriochrome black T solution and it was kept in dark.
- (iv) 0.30 g ammonium phosphomolybdate semiconductor was added to fourth beaker containing eriochrome black T solution and it was kept in light.

These beakers were kept for 4 hours. It was observed that solution of first three beakers had the same optical density and colour, while the solution of fourth beaker showed a decrease in its initial value of optical density.

The above experiment confirms that the reaction between eriochrome black T and ammonium phosphomolybdate is not chemical and photochemical reaction but it is a photocatalytic reaction.

Photocatalytic degradation of eriochrome black T was studied by taking 50 mL of 1.6×10^{-4} M solution in a 100 mL beaker and the pH of the dye solution was adjusted to 11.0

with the help of previously standardized sodium hydroxide and 0.30 g of ammonium phosphomolybdate powder was added to it. The optical density of this dye solution was determined with the help of a spectrophotometer ($\lambda_{\text{max}} = 545 \text{ nm}$). This beaker was exposed to a 200 watt tungsten lamp. A water filter was used to cut off thermal radiations. 2.0 mL of dye solution was taken out at regular intervals, filtered and its optical density was measured.

It was observed that the concentration of eriochrome black T decreases with increasing time of exposure. A plot of $2 + \log \text{O.D.}$ against time was found to be linear.

RESULTS AND DISCUSSION

A typical run

It was observed that optical density decreases with increase in time of irradiation and a plot of $\log \text{O.D.}$ v/s time was a straight line. It indicated that the photocatalytic degradation of eriochrome black T followed a pseudo-first order kinetics. The results of photocatalytic degradation of eriochrome black T are given in Table 1 and graphically represented in Fig. 1. The rate constant of this photocatalytic reaction was determined using the expression-

$$k = 2.303 \times \text{slope} \quad \dots(1)$$

Table 1: A typical run

[Eriochrome Black T] = $1.6 \times 10^{-4} \text{ M}$; pH = 11.0		Ammonium phosphomolybdate = 0.30 g Light Intensity = 51.0 mWcm^{-2}	
Time (min.)	O.D.	2 + log O.D.	
0.0	0.890	1.9493	
20.0	0.630	1.7993	
40.0	0.467	1.6693	
60.0	0.223	1.3483	
80.0	0.116	1.0644	
100.0	0.088	0.9444	
120.0	0.054	0.7323	

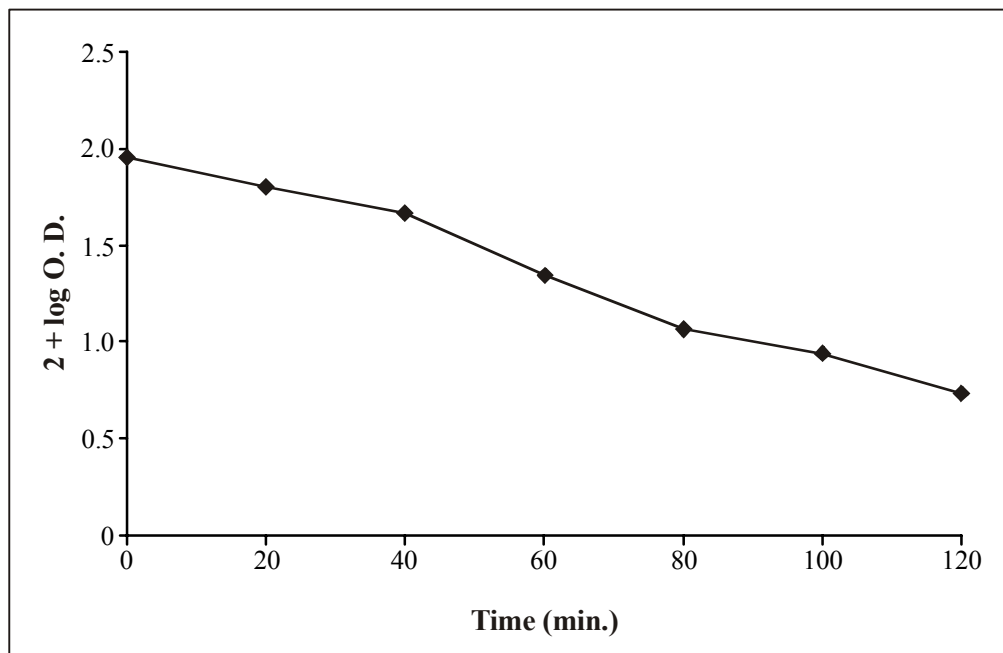


Fig. 1: A typical run

Effect of pH

The variation of pH on the photocatalytic degradation of eriochrome black T was studied in the pH range 10.0 to 12.0 keeping all other factors identical such as concentration of dye, amount of semiconductor and light intensity. Under acidic conditions, eriochrome black T was not degraded but in the basic range, the dye solution was degraded and the colour did not return back even on addition of acid. The value of pH was varied by the addition of NaOH to the dye solution. The results are reported in Table 2.

It is evident from above data that the rate of photocatalytic degradation of eriochrome black T 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 $\cdot\text{OH}$ 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 eriochrome black T to the semiconductor surface will be retarded. This will result into a decrease in the rate of photocatalytic degradation of eriochrome black T.

Table 2: Effect of pH

[Eriochrome Black T] = 1.6×10^{-4} M ; Light intensity = 51.00 mWcm^{-2}
Ammonium phosphomolybdate = 0.30 g

pH	$k \times 10^4 \text{ (sec}^{-1}\text{)}$
10.0	2.26
10.2	2.53
10.5	2.80
10.7	3.35
11.0	3.91
11.2	3.80
11.5	3.68
11.7	3.53
12.0	3.40

Effect of eriochrome black T concentration

The variation of eriochrome black T concentration on the rate of photocatalytic degradation was studied by taking concentrations of eriochrome black T from 1.2×10^{-4} M to 2.0×10^{-4} M keeping all other factors constant. The results are reported in Table 3.

It has been observed that the rate of photocatalytic degradation increases with an increase in the concentration of the dye up to 1.6×10^{-4} M. It may be due to the fact that as the concentration of the eriochrome black T 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 eriochrome black T.

Table 4: Effect of amount of semiconductor

[Eriochrome Black T] = 1.6×10^{-4} M; pH = 11.0
 Light intensity = 51.0 mWcm^{-2}

Amount of semiconductor (g)	$k \times 10^4 \text{ (sec}^{-1}\text{)}$
0.20	2.21
0.22	2.45
0.25	2.70
0.27	3.30
0.30	3.91
0.32	3.90
0.35	3.90
0.37	3.90
0.40	3.90

Effect of light intensity

To observe the effect of light intensity, all other factors were kept constant. The effect of light intensity on the photocatalytic degradation of eriochrome black T was studied by varying it from 41.0 mWcm^{-2} to 51.0 mWcm^{-2} . A 200 W tungsten lamp was used for irradiation purpose, which was located above the surface of the dye solution. The distance of lamp from the solution was changed to vary the light intensity. The intensity was measured by a solarimeter (CEL Model SM-201). The result are reported in Table 5.

The rate of photocatalytic degradation increases as the light intensity was increased. It was found that up to light intensity (51.0 mWcm^{-2}); the rate of photocatalytic degradation increases on increasing light intensity. It may be explained on the basis of number of excited molecules. As more intensity of light falls on ammonium phosphomolybdate semiconductor surface, more number of photons will be available for excitation. Therefore, more electron-hole pairs will be generated on the surface of semiconductor, which in turn, may degrade more dye molecules and thus, the rate of degradation was found to increase with increasing the intensity of light.

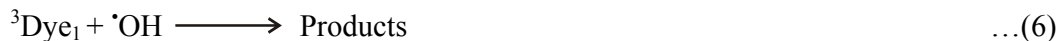
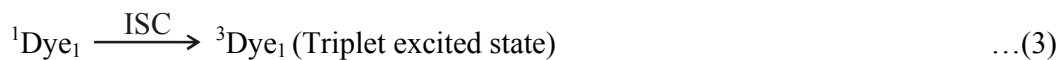
Table 5: Effect of light intensity

[Eriochrome Black T] = 1.6×10^{-4} M; pH = 11.0
 Ammonium phosphomolybdate = 0.30 g

Light Intensity (mWcm ⁻²)	k × 10 ⁴ (sec ⁻¹)
41.00	2.25
42.50	2.38
44.00	2.53
45.50	2.76
47.00	3.01
48.50	3.25
50.00	3.50
50.50	3.70
51.00	3.91

MECHANISM

On the basis of experimental observations, a tentative mechanism has been proposed for the bleaching of dye by ammonium phosphomolybdate semiconductor.



Dye absorbs the light and gets excited to its first excited 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 hydroxyl radical scavenger (2-propanol), which almost stops the degradation reaction.

CONCLUSION

Thus, eriochrome black T dye can be successfully degraded using ammonium phosphomolybdate semiconductor under visible light irradiation. A maximum color removal of 93.9 % was achieved after irradiation time of 4 hours. The easy availability, low cost, and greater efficiency of the ammonium phosphomolybdate semiconductor may provide an alternative way for the rapid degradation of dye in effluents from dyeing, printing and textile industries.

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