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Reserch Article

USE OF AMMONIUM PHOSPHOMOLYBDATE AS PHOTOCATALYST FOR DEGRADATION OF CELESTINE BLUE B

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ABSTRACT

A study on photocatalytic degradation of celestine blue B in aqueous solution has been made in presence of ammonium phosphomolybdate semiconductor. The extent of bleaching was monitored spectrophotometrically by measuring the absorbance at λ_{max} = 555 nm. A maximum colour fading of 97.7 % was achieved after irradiation time of 4 hours. The effect of various parameters such as the concentration of dye, pH of medium, light intensity, and amount of semiconductor on the degradation rates were observed. Maximum degradation was observed in basic conditions. The rate of bleaching of celestine blue B was found to follow pseudo-first order kinetics. A tentative mechanism of photocatalysis has been proposed.

Keywords: Degradation; ammonium phosphomolybdate; celestine blue B.

INTRODUCTION

The water resources continue to the contaminated with run off water from agricultural fields, containing pesticides, fertilizers, soil particles, waste chemicals and several kinds of synthetic dye stuffs. Dye stuffs represent a class of organic pollutants that absorb visible light. A substantial amount of dyestuff is lost during the dyeing process in the textile industry[1] which possess a major problem for the industry as well as a threat to the environment[2-5].

If the water is to be reused, it must be purified. There are several treatments for the degradation and removal of dyes from effluents like coagulation, flocculation, ion–exchange, activated carbon absorption, oxidation, reduction, biological methods etc. The photocatalytic degradation of organic pollutants is having a direct relevance in water remediation treatments. In recent years, many studies have been focussed on the photocatalytic degradation of organic compounds mediated by semiconductor particles acting as photocatalysts[6-8]. A Photocatalysis by semiconductor particles is a promising technology for water treatment.

The removal of colour from process or waste effluents becomes of fundamental importance to the environment[9,10]. Photocatalytic degradation of model textile dyes in waste water using ZnO as semiconductor has been reported by Chakrabati and Dutta[11]. Photodegradation of basic blue – 24 over ZnO particulate system has been reported by Ameta *et al*[12]. Few dyes have been degraded photocatalytically[13-16]. Although a lot of work has been carried out in the field of photocatalysis using TiO_2, ZnO, CdS, ZnS etc. but negligible attention has been paid to ammonium phosphomolybdate as a semiconductor. Ammonium phosphomolybdate is yellow in colour and absorbs visible radiations. Ammonium phosphomolybdate serves as an excellent candidate as a photocatalyst, because of its optical properties, which include a high refractive index, chemical stability, low cost, ready availability, greater efficiency, selectivity and convenient way of treating several undesirable chemicals.

It has been used as a photocatalyst 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 bleaching of some dyes. For the present investigation, celestine blue B has been selected.

Celestine blue B is used in solution with an iron alum mordant as a hematoxylin substitute in the H & E stain. Additionally, the optimum conditions were established by varying the parameters (pH of medium, amount of semiconductor, concentration of dye, and light intensity) one at a time, keeping the others fixed and observing the effect on colour fading.

The main goal of the present study is to investigate the photocatalytic activity of ammonium phosphomolybdate semiconductor for degradation of celestine blue B

EXPERIMENTAL

Material

Safranine 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

0.0363 g of celestine blue B was dissolved in 1000 ml of doubly distilled water, so that the concentration of dye solution was 1.00×10^{-4} 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 (λ_{max} = 555 nm). 200 ml. of dye solution was taken and divided into 50 ml. of this dye solution was taken in four beakers, each.

(1) The first beaker containing only celestine blue B solution was kept in dark.
(2) The second beaker containing only celestine blue B solution was kept in light.
(3) 0.25 g ammonium phosphomolybdate semiconductor was added to third beaker containing celestine blue B solution and was kept in dark.
(4) 0.25 g ammonium phosphomolybdate semiconductor was added to third beaker containing celestine blue B solution and 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 celestine blue B and ammoniumphosphomolybdate is not chemical and photochemical reaction but it is a photocatalytic reaction.

Photocatalytic degradation of celestine blue B was studied by taking 50 ml of 8.8×10^{-5} M solution in a 100 ml beaker and the pH = 10.0 of the dye solution was adjusted with the help of previously standardized sulphuric acid and sodium hydroxide and 0.25 g of ammonium phosphomolybdate powder was added to it. The optical density of this dye solution was determined with the help of a spectrophotometer (λ_{max} = 555 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 celestine blue B decreases with increasing time of exposure. A plot of 2 + log O.D. against time was found to be linear.

RESULT AND DISCUSSION

Typical Run

It was observed that optical density decreases with increase in time of irradiation and a plot of log O.D. v/s time was a straight line. It indicated that the photocatalytic degradation of celestine blue B follows a pseudo-first order kinetics. The results of photo catalytic degradation of celestine blue B are given in Table I and graphically represented in Fig.1. The rate constant of this photocatalytic reaction was determined using the expression-

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

Table 1: A typical run

Time (Min.)	Optical Density (OD)	2 + log OD
0.0	0.967	1.9854
20.0	0.630	1.7993
40.0	0.217	1.3364
60.0	0.144	1.1583
80.0	0.063	0.7993
100.0	0.051	0.7075
120.0	0.022	0.3424

[Celestine blue B] = 8.8 x 10^{-5} M; pH = 10.0; Light intensity = 50.0 mWcm^{-2} ; Ammonium phosphomolybdate = 0.25 g; k = 5.25 x 10^{-4} sec^{-1}

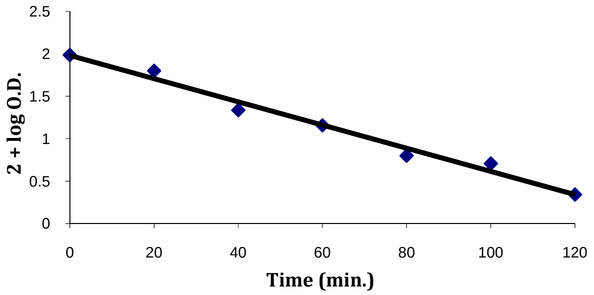

Fig. 1: Photocatalytic Degradation of Celestine blue B

Effect of pH variation

The variation of pH on the photocatalytic degradation of celestine blue B was studied in the pH range 9.0 to 11.0 keeping all other factors identical such as concentratin of dye, amount of semiconductor and light intensity. Under acidic conditions, celestine blue B was not degraded, but in 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 H_2SO_4 (for acidic range) and NaOH (for basic range) to the dye solution. The results are reported in Table 2 .

It is evident from above data that the rate of photo catalytic degradation of celestine blue B 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 celestine blue B to the semiconductor surface will be retarded. This will result into a decrease in the rate of photocatalytic degradation of celestine blue B.

Table 2: Effect of pH variation

pH	Rate Constant k x 10^4 (sec^{-1})
9.0	4.25
9.2	4.46
9.5	4.70
9.7	4.96
10.0	5.25
10.2	5.15
10.5	5.05
10.7	4.73
11.0	4.41

[Celestine blue B] = 8.8 x 10^{-5} M; Light intensity = 50.0 mWcm^{-2}; Ammonium phosphomolybdate = 0.25 g;

Effect of Celestine blue B concentration variation

The variation of celestine blue B concentration on the rate of photocatalytic degradation was studied by taking the concentration of celestine blue B from 8.0 x 10^{-5} M to 9.6 x 10^{-5} M keeping all other factors constant. The result are reported in Table 3.

Table 3: Effect of Celestine blue B concentration variation

[Celestine blue B] x 10^5 M	Rate Constant k x 10^4 (sec^{-1})
8.0	4.18
8.2	4.43
8.4	4.70
8.6	4.96
8.8	5.25
9.0	4.85
9.2	4.46
9.4	4.30
9.6	4.15

Light intensity = 50.0 mWcm^{-2}; pH = 10.0; Ammonium phosphomolybdate = 0.25 g;

It has been observed that the rate of photocatalytic degradation increases with an increase in the concentration of the dye upto 8.8 x 10^{-5} M. It may be due to the fact that as the concentration of the celestine blue B 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 celestine blue B.

Effect of semiconductor amount variation

The amount of semiconductor powder may also effect the rate of photocatalytic degradation of celestine blue B and therefore, the amount of semiconductor was varied from 0.15 g to 0.35 g keeping all the other factors identical. The result are reported in Table 4.

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.

Table 4: Effect of semiconductor amount variation

Amount of semiconductor (g)	Rate Constant k x 10^4 (sec^{-1})
0.15	3.75
0.17	4.08
0.20	4.41
0.22	4.83
0.25	5.25
0.27	5.20
0.30	5.15
0.32	5.15
0.35	5.15

[Celestine blue B] = 8.8 x 10^{-5} M; pH = 10.0; Light intensity = 50.0 $mWcm^{-2}$;

Effect of light intensity variation

To observe the effect of light intensity all other factors were kept constant. The effect of light intensity on the photocatalytic degradation of celestine blue B was studied by varying from 38.0 $mWcm^{-2}$ to 50.0 $mWcm^{-2}$. A 200 W tungsten lamp was used for irradiation purpose, which was located 20 cm above the surface of the dye solution. The solutions were positioned at circles of different diameters such as 4, 6, 8, 10 and 12 cm from to center of the light source. The intensity was measured by solarimeter (CEL Model SM-201). The result are reported in Table 5.

Table 5: Effect of light intensity variation

Light intensity ($mWcm^{-2}$)	Rate Constant k x 10^4 (sec^{-1})
38.00	1.88
39.50	2.10
41.00	2.31
42.50	2.75
44.00	3.20
45.50	3.55
47.00	3.91
48.50	4.58
50.00	5.25

[Celestine blue B] = 8.8 x 10^{-5} M; pH = 10.0; Ammonium phosphomolybdate = 0.25 g;

The rate of photocatalytic degradation increases as the light intensity was increased. It was found that up to light intensity (50.0 $mWcm^{-2}$); 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 and, 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.

MECHANISM

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

$${}^{1}\mathrm{Dye}_{0} \rightarrow {}^{1}\mathrm{Dye}_{1}\ \text{(Singlet excited state)} \qquad (1)$$

$${}^{1}\mathrm{Dye}_{1} \rightarrow {}^{3}\mathrm{Dye}_{1}\ \text{(Triplet excited state)} \qquad (2)$$

$$\mathrm{SC} \rightarrow e^{-} + h^{+}\ \text{or}\ \mathrm{SC}^{+} \qquad (3)$$

$$h^{+} + \mathrm{OH}^{-}\ \text{(from base)} \rightarrow {}^{\cdot}\mathrm{OH} \qquad (4)$$

$${}^{3}\mathrm{Dye}_{1} + {}^{\cdot}\mathrm{OH} \rightarrow \text{Products} \qquad (5)$$

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.

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