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PHOTOCATALYTIC BLEACHING OF FAST GREEN USING AMMONIUM PHOSPHOMOLYBDATE

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ABSTRACT

The photocatalytic bleaching of fast green was observed spectrophotometrically in the presence of ammonium phosphomolybdate. The effects of variation of different parameters like concentration of dye, light intensity, pH, amount of semiconductor on the rate of photocatalytic bleaching was observed. The tentative mechanism for the photocatalytic bleaching of fast green was observed.

Key words: Photocatalysis, Semiconductor, Ammonium Phosphomolybdate, Fast green.

INTRODUCTION

Water, an essential element for the life of man and organisms, has become polluted as a result of numerous human activities. Obnoxious toxic substances damage the biological activities and kill useful organisms. This poses a serious threat to human life and aquatic biota. Photochemistry plays a significant role in many reactions of biological, synthetic and industrial importance in which energy received from Sun can be better utilized for converting the pollutants into less toxic materials. Generally, a solid semiconductor is employed, whose irradiation promotes generation of radical species, which are capable of mineralizing the organic pollutants present in waste water.

UV light induced photodegradation of malachite green on TiO_2 nanoparticles was studied by Chen et al.[1] Photocatalytic oxidation of organics in water using pure and silver modified TiO_2 particles was observed by Vamatnevan et al.[2] Radeck[3] used TiO_2 for photo-electrocatalytic decomposition of water. Comparison of titanium dioxides in the photocatalytic degradation of benzene sulfonic acids has been done by Rachel et al.[4] Photocatalytic oxidation of remazol brilliant 3R on titanium dioxide thin film electrodes has been investigated by Zanoni et al.[5] Zita et al.[6] have studied correlation of oxidative and reductive

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dye bleaching on TiO_2 photocatalytic film. Sirtori et al.[7] studied the photocatalytic degradation of aqueous solution of camphor using ZnO photocatalyst.

Sharma et al.[8] used ZnO particulate system as a photocatalyst for bleaching of orange G and rose bengal. Photocatalytic properties of alumina supported ZnS-CdS catalyst was investigated by Kobayashi et al.[9] Lair et al.[10] studied naphthalene degradation in water by heterogeneous photocatalysis. Reddy et al.[11] investigated the photocatalytic study of Bi-ZSM-5 and Bi_2O_3/HZSM-5 for the treatment of phenolic waste. Effect of Fe^{3+} ion doping in TiO_2 in the photocatalytic degradation of malachite green dye under UV and visible irradiation was studied by Asilturk et al.[12] Neppolian et al.[13] investigated solar/UV induced photocatalytic degradation of three commercial textile dyes. Heterogeneous photocatalytic degradation of nitrophenol has been reported by Paola et al.[14]

From the literature survey, it is apparent that very little attention has been paid on ammonium phosphomolybdate as semiconductor for photocatalytic bleaching of dye, which is being coloured and able to utilize sunlight efficiently.

EXPERIMENTAL

All solutions were prepared in doublly distilled water. Irradiation has been carried out with a 200W tungsten lamp. The intensity of light was measured with the help of a solarimeter (CEL, Model SM 201). The pH of solution was attained by the addition of 1N H_2SO_4 and 1N NaOH solutions. The progress of photocatalytic reaction was observed by taking optical density at regular intervals using spectrophotometer (Systronic, Model 106).

RESULTS AND DISCUSSION

The absorbance of fast green solution was observed at regular time interval at λ_{max} = 620 nm. It was observed that the absorbance of the solution decreases with increasing time of exposure, which indicates a decrease in concentration of dye. A plot of 1 + log O. D. (optical density) versus time was linear and follows pseudo-first order kinetics. The results of a typical run is represented in Table 1 and Fig. 1. The rate constant (k) of the reaction is measured by the expression –

$$k = 2.303 \text{ x Slope} \qquad ...(1)$$

It was also observed that the absorbance of dye solution in presence of semiconductor was much lower as compared to the solutions without semiconductor or in dark.

Table 1: A typical run

[Ammonium phosphomolybdate] = 0.12 g Intensity of light = 60.0 m W cm^{-2}
[Fast green] = 1.50 x 10^{-5} M Temp. = 308 K pH = 6.0

Time (min)	Optical density (O. D.)	1 + log O. D.
0	0.862	0.935
10	0.749	0.874
20	0.661	0.820
30	0.583	0.765
40	0.512	0.709
50	0.438	0.642
60	0.376	0.575
70	0.335	0.525
80	0.297	0.474
90	0.252	0.401
100	0.225	0.352
110	0.192	0.283
120	0.167	0.222
130	0.147	0.167
140	0.130	0.113
		k = 2.20 x 10^{-4} sec^{-1}

Effect of pH

The effect of pH on the rate of reaction has been observed in the pH range 4.0 – 7.5. The results are reported in Table 2. The rate of photocatalytic bleaching of dye increases with increases in pH till 6.0. But further increase in pH beyond 6.0 results in a decrease in the rate of photocatalytic bleaching. It may be due to the fact that above pH 6.0, the dye will have its major portion in its anionic form. The anionic dye will face a force of repulsion from negatively charged surface of semiconductor and as a consequence, the rate of reaction decreases.

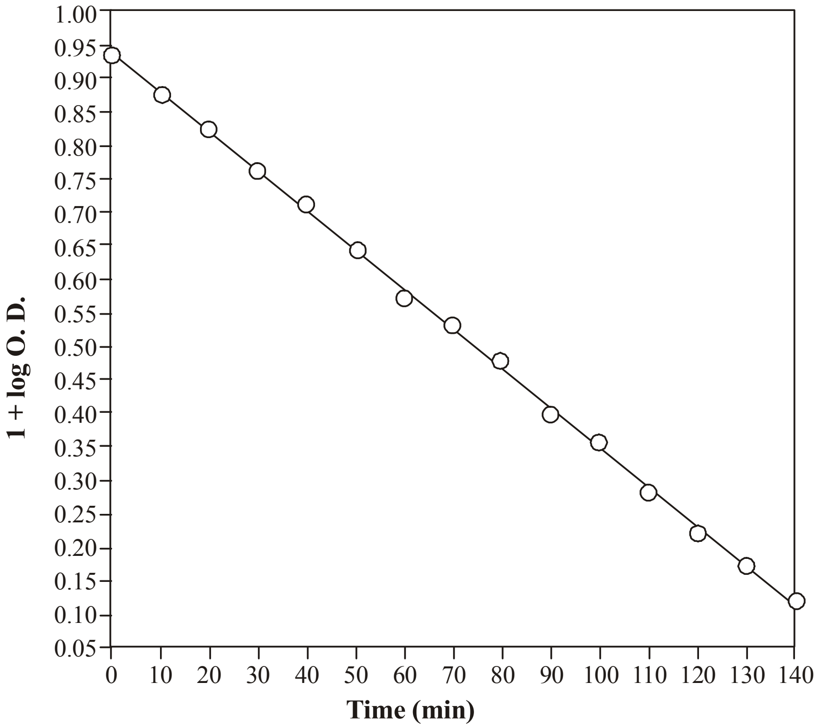

Fig. 1: A typical run

Table 2: Effect of pH

[Ammonium phosphomolybdate] = 0.12 g Intensity of light = 60.0 mW cm^{-2}
[Fast green] = 1.50 x 10^{-5} M Temp. = 308 K

pH	**k x 10^{4} (sec^{-1})**
4.0	1.15
4.5	1.40
5.0	1.68
5.5	1.80
6.0	2.20
6.5	2.00
7.0	1.60
7.5	1.50

Effect of concentration of dye

The concentration of fast green dye was varied from 0.75 x 10^{-5} M to 2.50 x 10^{-5}M. The results are reported in Table 3. It has been observed that the rate of photocatalytic reaction increases with increase in concentration of dye upto 1.50 x 10^{-5} M but further increase in dye concentration beyond this limit results in decrease in rate of degradation. It may be due to the fast that initially when the concentration of dye increases, more number of molecules are available for the degradation but at higher concentration the dye molecules start acting as a filter for incident light and will not permit the desired intensity of light to reach the semiconductor particles. As a consequence, the rate of degradation is decreased.

Table 3: Effect of dye concentration

[Ammonium phosphomolybdate] = 0.12 g
pH = 6.0
Intensity of light = 60.0 mW cm^{-2}
Temp. = 308 K

[Fast green] x 10^5 M	k x 10^4 (sec^{-1})
0.75	1.10
1.00	1.61
1.25	1.83
1.50	2.20
1.75	1.70
2.00	1.24
2.25	1.00
2.50	0.8

Effect of amount of semiconductor

The amount of semiconductor was varied from 0.02 g - 0.16 g. The results are reported in Table 4. It was observed that the rate of reaction increases with increase in amount of semiconductor but after 0.12 g concentration; if the amount of semiconductor was further increased, then there was no increase in the exposed surface area of photocatalyst and a plateau was obtained. It may be considered like a saturation point above which an increase in the amount of semiconductor has negligible or no effect on the rat of photocatalytic degradation. After this point, any increase in the amount of semiconductor will only increase the thickness of the layer at the bottom of the reaction vessel and not the exposed surface area.

Table 4: Effect of amount of semiconductor

[Fast green] = 1.50×10^{-5} M Intensity of light = 60.0 mW cm^{-2}
pH = 6.0 Temp. = 308 K

Ammonium phosphomolybdate (g)	k x 10^4 (sec^{-1})
0.02	0.62
0.04	0.97
0.06	1.40
0.08	1.70
0.10	1.09
0.12	2.20
0.14	2.20
0.16	2.21

Effect of light intensity

The intensity of dye solution was varied between 10-80 mW cm^{-2}. The results are reported in Table 5. It was observed that the rate of reaction was accelerated as the light intensity was increased. This may be due to the increase in the number of photons striking per unit area of the semiconductor powder with increase in the light intensity. However, at higher intensity, the light will also increase the temperature of the dye solution and then thermal reactions may occur in the place of photocatalytic reaction and therefore, higher intensities were avoided.

Mechanism

On the basis of the observed data, the following tentative mechanism may be proposed for the photocatalytic bleaching of fast green. The semiconductor ammonium phosphomolybdate absorbs light to excite an electron to its conduction band leaving behind a hole in the valence band. The dye, fast green, also absorbs radiation of suitable wave length and it is excited from singlet state to first excited state, which is transferred to its triplet state through intersystem crossing. The electron of the semiconductor will reduce the

Table 5: Effect of Intensity of light

[Ammonium phosphomolybdate] = 0.12 g   pH = 6.0

[Fast green] = 1.50×10^{-5} M   Temp. = 308 K

Intensity of light (mW cm^{-2})	k x 10^4 (sec^{-1})
10.0	0.63
20.0	0.89
30.0	1.10
40.0	1.50
50.0	1.80
60.0	2.20
70.0	2.46

dye to its colourless leuco form, which ultimately degrades into products. It was also confirmed that $^{\bullet}$OH radicals do not act as oxidizing species as the reaction rate remains almost unaffected in the presence of $^{\bullet}$OH radical scavenger i.e. isopropanol.

$$\mathrm{SC} \xrightarrow{h\nu} h^{+}\,(\mathrm{VB}) + e^{-}\,(\mathrm{CB}) \quad ...(2)$$

$$^{1}[\mathrm{FCF}]_{0} \xrightarrow{h\nu} {}^{1}[\mathrm{FCF}]_{1} \quad ...(3)$$

$$^{1}[\mathrm{FCF}]_{1} \xrightarrow{\mathrm{ISC}} {}^{3}[\mathrm{FCF}]_{1} \quad ...(4)$$

$$^{1}[\mathrm{FCF}]_{1} + e^{-} \longrightarrow {}^{3}[\mathrm{FCF}]_{1}^{-} + \text{Leuco dye} \quad ...(5)$$

$$\text{Leuco dye} \longrightarrow \text{Products} \quad ...(6)$$

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