PHOTODEGRADATION OF TWO COMMERCIAL DYES IN AQUEOUS PHASE USING COPPER OXIDE AS PHOTOCATALYST

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ABSTRACT

The present study involves the photocatalytic degradation of dyes [Rhodamine B and methylene blue], employing heterogeneous catalysis. The photocatalytic activity of copper oxide (CuO) has been investigated. An attempt has been made to study the effect of different parameters such as amount of catalyst, concentration of dye, pH and intensity of light. The rate of decolourization was estimated from residual concentration spectrophometrically. The experimental results indicated that the maximum decolourization (near about 80%) of dyes occurred at basic pH, (10.0 and 8.5). It was observed that photocatalytic degradation of dyes follows pseudo first order kinetics. A tentative mechanism has also been proposed for the photocatalytic degradation of dyes in presence of copper oxide semiconductor.

Key words: Photocatalytic degradation, Rhodamine B, Methylene blue, Semiconductor, Copper oxide.

INTRODUCTION

Water, which is essential for life, is contaminated by chemical and microbiological contaminants; thus, poses a problem. Dyes are extensively used in the textile industries. These industries produce large volume of coloured dye effluents, which are toxic and non-biodegradable[1]. Dyes create several environmental pollution problems by releasing toxic and potential carcinogenic substances into the aqueous phase. Various chemical and physical processes such as precipitation, adsorption by activated carbon, reverse osmosis and ultrafiltration can be used for colour removal from textile effluents[2-5]. Each methods has its own advantage and disadvantage. Above methods are non-destructive and only transfer the non biodegradable matter into sludge giving rise to a new type of pollution[6-8]. Advanced

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oxidation processes are of ample interest for the effective oxidation of a wide variety of dyes[9]. AOPs include photocatalysis systems such as combination of semiconductor and light. Most of the photo catalytic studies utilise TiO_2 as photocatalysts[10]. Many attempts have been to study photocatalytic activity of different semiconductors such as SnO_2, ZrO, CdO and ZnO[11-13].
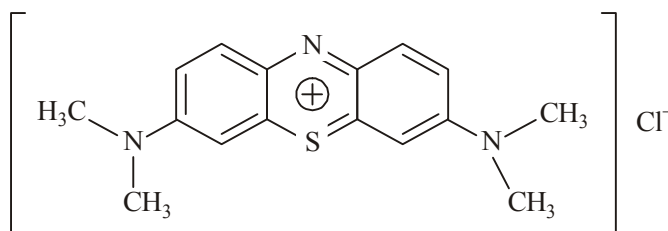
Structure of methylene blue dye
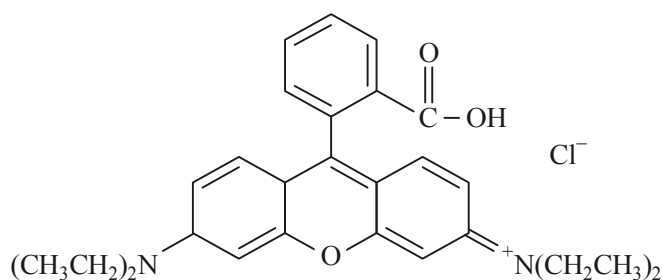
Structure of rhodamine B dye

Dyes can be degraded in the presence of photocatalyst upon irradiation with visible light because of their absorption in visible light. Rhodamine B is a basic dye. It is used to dye wool, cotton, silk and paper. Methylene blue is very important member of thiazine family and most commonly used in dyeing, printing, leather building of tissues, staining of DNA and other important biological purposes. The release of these dyes and their products in the environment cause toxicity problems. So an attempt has been made to study the decolorization of these dyes.

In this study, the semiconductor copper oxide is used for decolouring the aqueous solution of rhodamine B (RB) and methylene blue (MB). Copper oxide is grey in colour and shows wide band gap (2.2 eV) and thus, it is suitable for photodegradation in visible light.

EXPERIMENTAL

Stock solutions of methylene blue and rhodamine B were prepared by dissolving their 0.0479 g and 0.0442 g, respectively in 100 mL double distilled water so that the concentration of dye solution were 1.0×10^{-3}M. In case of methylene blue, 1.2 mL of 0.001 dye solution was taken in a beaker and 23.8 mL of doubly distilled water was added. Then copper oxide (0.13 g) in solid form was added in beakers. Similarly, 1.0 mL of rhodamine B solution was taken in a separate beaker and 24 mL of doubly distilled water and 0.12 g copper oxide was added.

Then the reaction mixture was exposed to light. A 200 W tungsten lamp (Philips) was used for irradiation. The absorbance of solutions was measured at λmax – 664 nm and 544 nm for methylene blue and rhodamine B, respectively at regular time intervals using UV-visible spectrophotometer (Systronics Model 106). The pH of the solution was measured by a digital pH meter (MAC 512). The desired pH of solution was adjusted by addition of previously standardized 0.1 N sulphuric acid and 0.1 N sodium hydroxide solutions. The intensity of light at various distances was measured by Suryamapi (CEL Model SM 201). A water filter was used to cut off thermal radiations.

RESULTS AND DISCUSSION
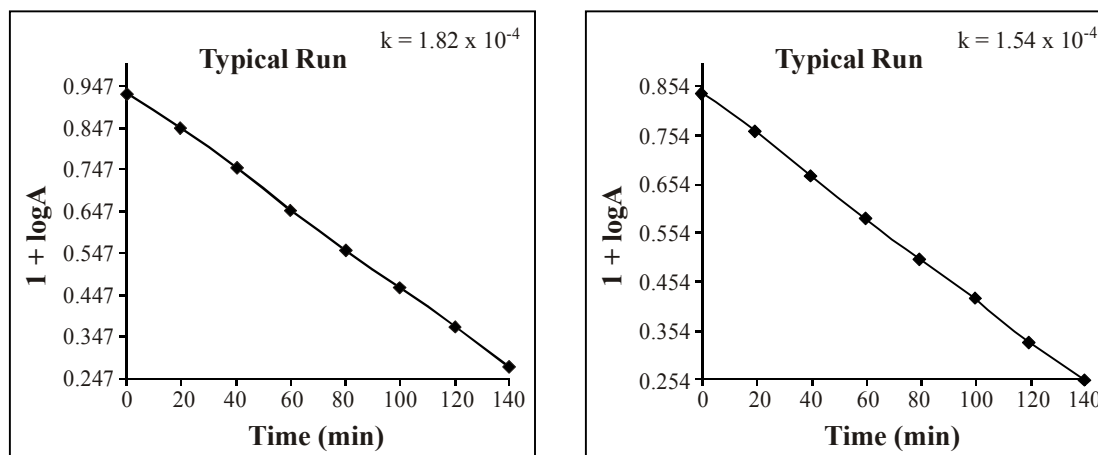
The phtocatalytic bleaching of methylene blue and rhodamine B in the presence of copper oxide semiconductor at different time intervals was observed at λmax 664 nm and λmax 544 nm, respectively. The results for typical run are given in Table 1. It was observed that the absorbance of solution decreases with increasing time intervals, which indicates that both dyes are photocatalytically degraded on irradiation (Control experiments were also

performed, which indicated that dyes degrades only in the presence of photocatalyst and light). A plot of 1 + log A versus time was linear and follows pseudo first order kinetics. The rate constant was measured using following expression.

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

Table 1: A typical run

[Methylene blue] = 4.0 × 10⁻⁵ M, pH = 10.0 Copper oxide = 0.13 g Intensity of light = 60 mW cm⁻²		[Rhodamine B] = 3.5 × 10⁻⁵ M, pH = 8.5 Copper oxide = 0.12 g; Intensity of light = 60 mW cm⁻²	
Time (min.)	**1 + log A**	**Time (min.)**	**1 + log A**
0	0.930	0	0.843
20	0.844	20	0.760
40	0.750	40	0.671
60	0.652	60	0.584
80	0.551	80	0.502
100	0.462	100	0.422
120	0.370	120	0.330
140	0.274	140	0.254

Effect of pH variation

The effect of pH on the rate of photocatalytic bleaching of methylene blue and rhodamine B was investigated in the pH range (7.0 to 11.0). It is evident from the data that the rate of photocatalytic bleaching of MB and RB increases with increasing pH. This increase in the rate of photodegradation may be due to the more availability of OH ions at higher pH values. These OH ions will generate more OH radicals by combining with holes. These hydroxide radicals are responsible for photocatalytic degradation. But after a certain value of pH (pH = 10.0 for MB and pH = 8.5 for RB), a further increase in the pH of medium decreases the rate of photocatalytic degradation. It may due to the fact that the dye does not remain in its cationic form due to greater concentration of OH ions and as such, the reaction rate decreases. The results are reported in Table 2.

Table 2: Effect of pH

[Methylene blue] = 4.0×10^{-5} M Copper oxide = 0.13 g Intensity of light = 60 mW cm^{-2}		Rhodamine B = 3.5×10^{-5} M Copper oxide = 0.12 g Intensity of light = 60 mW cm^{-2}	
pH	**k × 10^4 (sec^{-1})**	**pH**	**k × 10^4 (sec^{-1})**
7.5	1.00	7.0	0.84
8.0	1.12	7.5	0.94
8.5	1.24	8.0	1.18
9.0	1.40	8.5	1.54
9.5	1.55	9.0	1.20
10.0	1.82	9.5	1.11
10.5	1.52	10.0	0.89
11.0	1.20	-	-

Effect of dye concentration

The effect of concentration of methylene blue and rhodamine B on the rate of reaction was observed. It is clear from the results (Table 3) that as the concentration of dye was increased, the reaction rate also increases due to increase in number of molecules participating in the reaction. But after the optimum value of concentration 4.0×10^{-5} M and 3.5×10^{-5} M for MB and RB, respectively, the rate of reaction decreases. This may be explained on the basis that the dyes will start acting as internal filter and does not allow light to reach the semiconductor surface.

Effect of amount of semiconductor

The amount of photocatalyst is also likely to affect the rate of photodegradation of dyes. Here, different amounts of photocatalyst were used. It has been observed that initially the rate of reaction increases with an increase in an amount of semiconductor but after a optimum value, it becomes almost constant. This may be due to the fact that the exposed surface area increases on increasing the amount of semiconductor but after a certain limit, if the amount of semiconductor was increased further, there will be no increase in the exposed surface area of the photocatalyst.

Table 3: Effect of dye concentration

pH = 10.0 Copper oxide = 0.13 g Intensity of light = 60 mW cm^{-2}		pH = 8.5 Copper oxide = 0.12 g Intensity of light = 60 mW cm^{-2}	
[Methylene blue] $\times 10^5$ M	**k $\times 10^4$ (sec^{-1})**	**[Rhodamine B] $\times 10^5$ M**	**k $\times 10^4$ (sec^{-1})**
2.0	1.20	2.0	1.09
2.5	1.34	2.5	1.19
3.0	1.50	3.0	1.33
3.5	1.62	3.5	1.54
4.0	1.82	4.0	1.31
4.5	1.60	4.5	1.21
5.0	1.50	5.0	1.82

Table 4: Effect of semiconductor

[Methylene blue] = 4.0×10^{-5}M, pH = 10.0 Intensity of light = 60 mWcm^{-2}		[Rhodamine B] = 3.5×10^{-5}M, pH = 8.5 Intensity of light = 60 mWcm^{-2}	
Amount of semi-conductor (g)	**k $\times 10^4$ (sec^{-1})**	**Amount of semi-conductor (g)**	**k $\times 10^4$ (sec^{-1})**
0.10	1.09	0.10	1.09
0.11	1.13	0.11	1.14
0.12	1.46	0.12	1.54
0.13	1.82	0.13	1.53
0.14	1.82	0.14	1.53
0.15	1.82	0.15	1.53
0.16	1.82	0.16	1.52

Effect of light intensity

The effect of light intensity on the photocatalytic degradation of dyes has been observed by varied the distance between the light source and the exposed surface of the

reaction mixture. The intensity of light at each distance was measured by Suryamapi (CEL Model SM 201). The rate of decolourization was accelerated as the intensity of light was increased. Increase in light intensity will increase the number of photons striking per unit area of semiconductor powder. The rate of reaction increased up to 60.0 mW cm^{-2} but above this, the rate decreases due to the thermal effects caused by increase in intensity.

Table 5: Effect of light intensity

[Methylene blue] $= 4.0 \times 10^{-5}$ M, pH $= 10.0$ Copper oxide $= 0.13$ g		[Rhodamine B] $= 3.5 \times 10^{-5}$ M, pH $= 8.5$ Copper oxide $= 0.12$ g	
Intensity (mWcm^{-2})	**k $\times 10^4$ (sec^{-1})**	**Intensity (mWcm^{-2})**	**k $\times 10^4$ (sec^{-1})**
10.0	1.02	10.0	1.01
20.0	1.19	20.0	1.09
30.0	1.25	30.0	1.12
40.0	1.39	40.0	1.18
50.0	1.41	50.0	1.21
60.0	1.82	60.0	1.54
70.0	1.45	70.0	1.11

Mechanism

On the basis of the observations, tentative mechanism has been proposed for the degradation of methylene blue or rodamine B in the presence of copper oxide and light may be as –

$$(Dye) \xrightarrow{h\nu} {}^1(Dye)^* (\text{Singlet exited state}) \qquad \dots(1)$$

$$^1(Dye)^* \xrightarrow{ISC} {}^3(Dye)^* (\text{Triplet exited state}) \qquad \dots(2)$$

$$SC \longrightarrow e^-(CB) + h^+(VB) \qquad \dots(3)$$

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

$$^3(Dye)^* + {}^\bullet OH \longrightarrow \text{Products} \qquad \dots(5)$$

Dye absorbs light radiation of suitable wavelength and it goes to its excited singlet state. It then undergoes intersystem crossing (ISC) to give the triplet state of the dye. On the other hand, the semiconducting copper oxide also utilizes the radiant energy to excite its electron from valence band to the conduction band; thus, leaving behind a hole.

The hole abstracts an electron form OH^- ions generating $^\bullet OH$ radical. Now the excited dye is oxidized by $^\bullet OH$ free radical to give the products. The participation of $^\bullet OH$ radical was confirmed by the use of scavanger, 2-propanol, which stops the bleaching reaction almost completely.

CONCLUSION

Copper oxide is an effective photocatalyst for photobleaching of dyes methylene blue and rhodamine B.

ACKNOWLEDGEMENT

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