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PHOTOCATALYTIC DEGRADATION OF METHYLENE BLUE USING CALCIUM OXIDE

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ABSTRACT

The present study involves the photocatalytic degradation of methylene blue by heterogeneous photocatalytic process using Calcium oxide (CaO) as semiconductor. Progress of the reaction was recorded spectrophotometerically. The effect of various operational parameters such as pH, concentration of dye, amount of semiconductor and light intensity have been studied. Kinetic studies reveal that the photocatalytic process follows pseudo-first order kinetics. A tentative mechanism for the photocatalytic degradation of methylene blue was proposed.

Key words: Photocatalytic degradation, Methylene blue, Calcium oxide.

INTRODUCTION

Widespread contamination of soil as well as ground and surface water by synthetic dyes used for textile dyeing and other industrial application causes severe ecological problems. Most of these compounds are toxic, mutagenic or at least cause an aesthetic problem in receiving water and soil[1]. A variety of physical, chemical and biological methods employed for removal of synthetic dyes have been described. However, most current physico-chemical methods are quite expensive, rather inefficient or have operational problems[2]. Physico-chemical methods such as coagulation/flocculation, activated carbon adsorption and reverse osmosis techniques have been developed in order to remove the colour. However, the later methods can only transfer the contaminants (dyes) from one phase to the other leaving the problem essentially unsolved[3,4]. The use of one individual process may often not be sufficient to achieve complete decolorization. Therefore, attention has to be focused on techniques that can lead to the complete destruction of the dye molecules. This had led to the study of other methods. Photocatalysis, which is one of the Advanced Oxidation Processes, is a new method used to mineralize dye compounds[5,6].

Heterogeneous photocatalysis with titanium dioxide as a semiconductor has proven to be an efficient process for elimination of a large number of dyes from textile wastewater[7]. The photocatalytic activity of silver doped TiO_2 was tested by photocatalytic degradation of C. I. acid red 88- as a modal compound from mono azo textile dye by Behnajady et al.[8]. Homogenous photocatalytic degradation of two azo dyes mono azo dye acid orange 10 and di azo dye acid red 114 with UV/H_2O_2 process was investigated by Abo Farha[9]. Photocatalytic degradation of a textile azo dye, acid orange 8 in aqueous solution has been investigated

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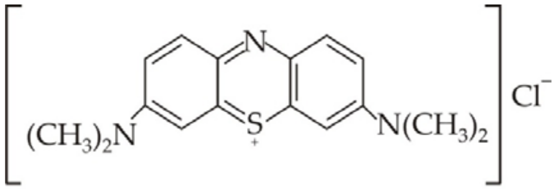
under visible light using TiO_2 as catalyst by Mehta et al.[10] The photocatalytic degradation of indigo carmine dye was studied using hydrothermally prepared TiO_2 impregnated activated carbon (TiO_2 : Ac) by Subramani et al.[11] The photodegradation of malchite green, a cationic triphenylmethane dye is examined under different pH values and amounts of TiO_2, by Chen et al.[12] The photocatalytic degradation of five dyes has been investigated on dynamic solar pilot plant using non-woven fibers coated with TiO_2 as photocatalyst by Barka et al.[13] Performances of solar photocatalytic pilot plant using TiO_2 were investigated for removal of azo dye by Zayani et al.[14] Photocatalytic degradation of methylene blue was examined using TiO_2 nano-particles by Ehrampoush et al.[15] Seven azo dyes were photocatalytically degraded in TiO_2 suspension by Tanaka et al.[16] The photocatalytic degradation of acid orange in aerated aqueous TiO_2 dispersion has been studied under visible light irradiation by Stylidi et al.[17] The photocatalytic degradation of azo dyes has been reviewed using TiO_2 as photocatalyst by Konstantinou and Albanis[18]. The photocatalytic decomposition of C. I. acid yellow 17 was investigated using TiO_2 photocatalyst by Liu et al.[19]

EXPERIMENTAL

Methylene blue is 3,7-bis(dimethylamino)-phenothiazin-5-ium chloride.



Structure of Methylene blue

This dye belongs to the class of thiazene dye at room temperature. It appears as a solid, odorless, dark green powder. Its molecular formula is $C_{16}H_{18}N_3SCl$ (molecular weight = 371.91). The colour of the dye solution in water is blue. It absorbs at 663-667 nm (665 nm).

0.0372 g of methylene blue (MB) was dissolved in 100.0 mL of doubly distilled water so that the concentration of dye solution was 1.0×10^{-3} M. It was used as a stock solution. This solution was further diluted as desired. The optical density of this dye solution was determined with the help of a spectrophotometer. Then, it was divided into four parts.

(i) The first beaker containing only dye solution was kept in dark.

(ii) The second beaker containing only dye solution was kept in sunlight.

(iii) 0.40 g of semiconductor calcium oxide was added to the third beaker containing dye solution and was kept in dark, and

(iv) 0.40 g of semiconductor calcium oxide was added to the fourth beaker containing dye solution and was exposed to sunlight.

These beakers were kept for four hours and then the optical density of solution in each beaker was measured with the help of a spectrophotometer. It was observed that the solution of first three beakers had the same optical density while the solution of fourth beaker had a decrease in its initial value of optical density. The above experiment confirms that the reaction between methylene blue and semiconductor powder is neither thermal nor photochemical but it is a photocatalytic reaction.

Methylene blue, calcium oxide, sodium hydroxide, sulphuric acid and other chemicals employed in the present study were of analytical grade chemicals. 1.00×10^{-3} M solution of methylene blue was prepared in volumetric flask with doubly distilled water and stored as a stock solution. The photocatalytic degradation of methylene blue was observed by taking dye solution of 2.0×10^{-5} M and 0.40 g of CaO. Irradiation was carried out keeping the whole assembly exposed to a 200 W tungsten lamp (Philips, light intensity = 70.00 mWcm^{-2}). The intensity of light was measured with the help of a solarimeter (SM CEL 201). The pH of the solution was measured by the digital pH meter (Systronics Model 335). The desired pH of solution wad adjusted by the addition of previously standardized 0.1 N sulphuric acid and 0.1 N sodium hydroxide solutions. The optical density (OD) was measured by visible absorption spectroscopy (Systronics Model 106), under the necessary conditions that the sample solutions are free from photocatalyst particles and impurity. Controlled experiments were also carried out to confirm that reaction is photocatalytic in nature.

The photocatalytic degradation of methylene blue using CaO as photocatalyst under visible light was investigated by visible absorption spectroscopy, and most kinetic measurements were performed at room temperature (298 K). The concentration of dye in the form of optical density before and after photocatalytic degradation was measured at 665 nm. A 200 W tungsten lamp (Philips) was used as the visible light source. A water filter was used to cut-off thermal radiations. The progress of the photocatalytic reaction was observed by taking optical density at regular time intervals.

The change in absorbance at the λ_{max} value versus the irradiation time was measured. A typical run is presented in Fig. 1. It was observed that the optical density of methylene blue solution decreased in presence of the photocatalyst and light. The optimum condition was obtained at [Methylene blue] = 2.0×10^{-5} M, light intensity = 70 mWcm^{-2}, pH = 6.5, CaO = 0.40 g.

The plot of 2 + log O. D. Vs exposure time was a straight line (Fig. 1), which indicates that the reaction followed pseudo first-order kinetics. The rate constant (k) for the reaction was determined from the expression k = 2.303 × slope. A value of $k = 6.20 \times 10^{-4}$ s^{-1} was determined for this reaction in the optimum conditions.

Table 1: Typical run

pH = 6.5
CaO = 0.40 g
[Methylene blue] = 2.00×10^{-5} M
Light Intensity = 70.0 mWcm^{-2}
Temperature = 298 K

Time (min.)	Optical Density (O. D.)	2 + log O. D.
0.0	0.884	1.9465
10.0	0.611	1.7860
20.0	0.421	1.6243
30.0	0.297	1.4728
40.0	0.202	1.3054
50.0	0.139	1.1430
60.0	0.096	0.9823
70.0	0.067	0.8261

Rate constant (k) = 6.20×10^{-4} sec^{-1}

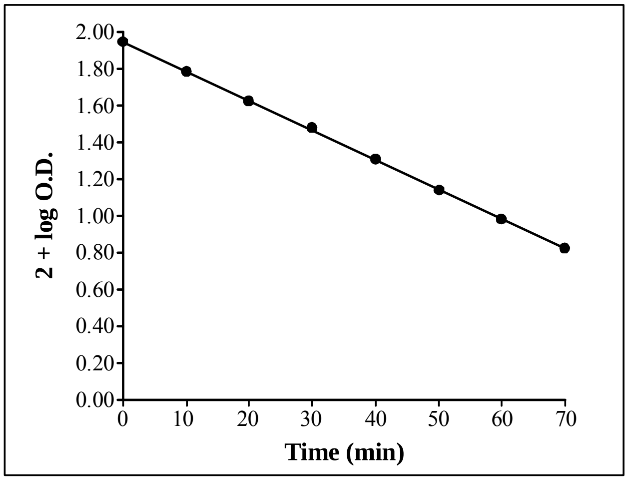


Fig. 1: Typical run

Effect of pH

The effect of pH on the rate of photocatalytic degradation of methylene blue was investigated and reported in Table 2 and graphically presented in Fig. 2. It is evident from the data that the degradation rate of methylene blue increases with increasing pH of solution upto to 6.5 and above this value of pH, the rate of photocatalytic degradation of methylene blue starts decreasing. This behaviour may be explained on the basis that an increase in the rate of photocatalytic degradation may be due to the increased availability of OH^- ions at higher pH value. OH^- ions will generate more hydroxyl radicals ($^\bullet OH$) by combining with holes, which are considered responsible for the photocatalytic degradation. Above pH value 6.5, more OH^- ion will compete with the electron rich dye for adsorption on semiconductor surface. Sidewise, the OH^- ions will make the surface of the semiconductor negatively charged and as a consequence, the approach of methylene blue molecules to the semiconductor surface will be retarded due to repulsive force between two negatively charged species (OH^- ions and the electron rich dye). This will result into a corresponding decrease in the rate of photocatalytic bleaching of methylene blue at higher pH value i.e. pH > 6.5.

Table 2: Effect of pH

[Methylene blue] = 2.00×10^{-5} M Light Intensity = 70.0 mWcm^{-2}
CaO = 0.40 g Temp. = 298 K

pH	k × 10^4 (sec^{-1})
3.0	3.39
4.0	3.61
5.0	4.40
5.5	5.29
6.0	5.39
6.5	**6.20**
7.0	3.61
7.5	3.53
8.0	3.39
8.5	2.86

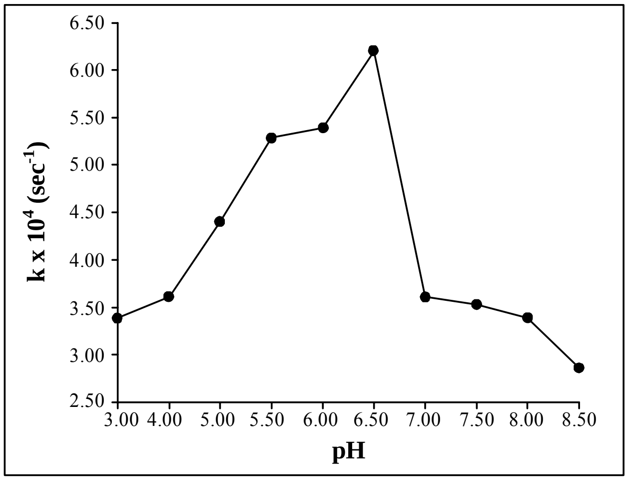


Fig. 2: Effect of pH

Effect of dye concentration

The effect of dye concentration on the rate of reaction was also studied by using different concentrations of the methylene blue solution. The results are given in Table 3 and graphically presented in Fig. 3.

Table 3: Effect of dye concentration

pH = 6.5 Light Intensity = 70.0 mWcm^{-2}
CaO = 0.40 g Temp. = 298 K

[Methylene blue] x 10^5 M	k × 10^4 (sec^{-1})
0.50	4.83
1.00	4.97
1.50	5.42
2.00	**6.20**
2.50	3.31
3.00	2.60

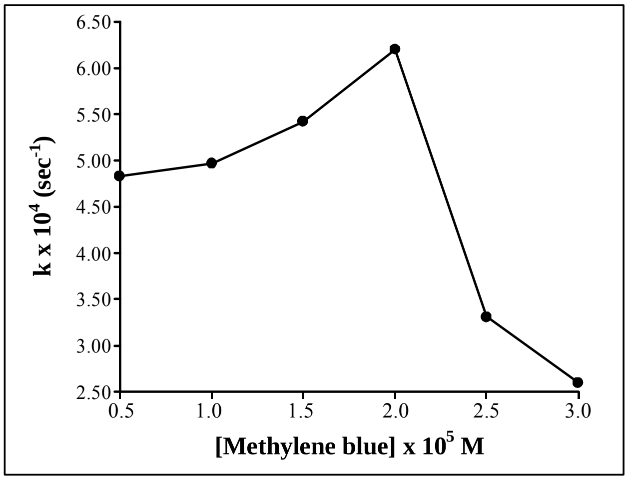


Fig. 3: Effect of dye concentration

It was observed that the rate of photocatalytic degradation increases with increase in the concentration of the dye upto 2.00×10^{-5} M. It may be due to the fact that as the concentration of dye was increased, more dye molecules were available for excitation and consecutive degradation. 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 started acting as a filter for the incident light and it does not permit the desired light intensity to reach the photocatalyst surface; thus, a decrease in the rate of photocatalytic bleaching was observed.

Effect of amount of CaO

The effect of amount of CaO powder on the rate of photocatalytic degradation of methylene blue was also observed. The results are reported in Table 4 and graphically presented in Fig. 4. It was observed that the rate of reaction increases with increase in the amount of CaO upto 0.40 g. Beyond 0.40 g the rate of reaction becomes almost constant.

This may be due to the fact that as the amount of semiconductor was increased in the initial state, the exposed surface area of the semiconductor also increases but after this limiting value (0.40 g) any increase in the amount of semiconductor will not increase the exposed surface area but only the thickness of the semiconductor layer. This was also confirmed by using reaction vessels of different dimensions.

Table 4: Effect of amount of CaO

[Methylene blue] = 2.00×10^{-5} M pH = 6.5
Light Intensity = 70.0 $\mathrm{mWcm^{-2}}$ Temp. = 298 K

CaO	$k \times 10^4$ ($\mathrm{sec^{-1}}$)
0.10	3.86
0.20	5.42
0.30	5.53
0.40	**6.20**
0.50	6.09
0.60	5.99
0.70	6.10

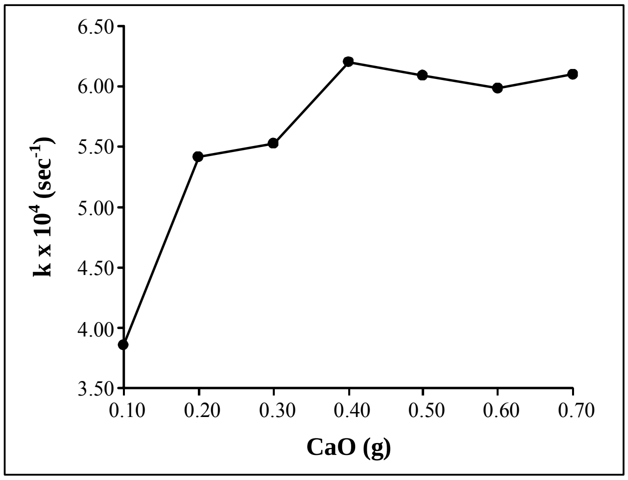


Fig. 4: Effect of amount of CaO

Effect of light intensity

The effect of light intensity on the rate of photocatalytic degradation of methylene blue was observed. The results are reported in Table 5 and graphically presented in Fig. 5.

The data indicate that the degradation action was accelerated as the intensity of light was increased, because any increase in the light intensity increase the number of photons striking per unit time per unit area of the photocatalyst powder. An almost linear behaviour between light intensity and the rate of reaction was observed. However, higher intensities were avoided due to thermal effects.

Table 5: Effect of light intensity

[Methylene blue] = 2.00×10^{-5} M pH = 6.5
CaO = 0.40 g Temp. = 298 K

Light intensity ($mWcm^{-2}$)	**$k \times 10^4$ (sec^{-1})**
20.0	2.62
30.0	2.89
40.0	3.35
50.0	4.00
60.0	6.01
70.0	**6.20**

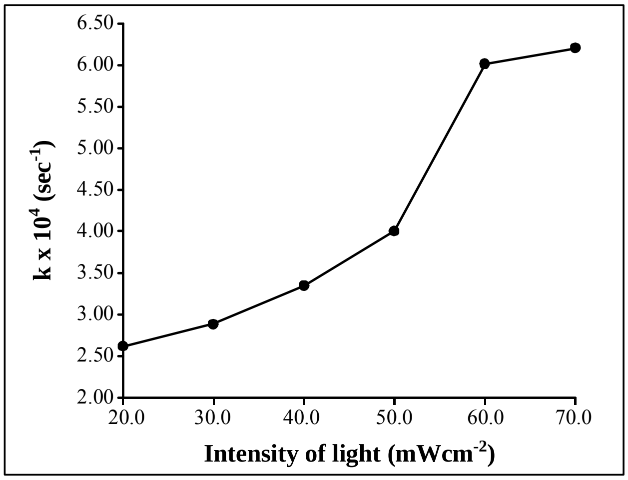


Fig. 5: Effect of light intensity

Mechanism

On the basis of experimental observations, a tentative mechanism for photocatalytic degradation of methylene blue may be proposed as :

$$^1\mathrm{Dye}_0 \xrightarrow{h\nu} {}^1\mathrm{Dye}_1^* \qquad ....(1)$$

$$^1\mathrm{Dye}_1^* \xrightarrow{ISC} {}^3\mathrm{Dye}_1^* \qquad ....(2)$$

$$\mathrm{CaO} \xrightarrow{h\nu} \mathrm{CaO}\,[\mathrm{h}^{+}(\mathrm{VB}) + \mathrm{e}^{-}(\mathrm{CB})] \qquad \text{....(3)}$$

$$\mathrm{OH}^{-} + \mathrm{CaO}(\mathrm{h}^{+}) \longrightarrow {}^{\bullet}\mathrm{OH} + \mathrm{CaO} \qquad \text{....(4)}$$

$$^{3}\mathrm{Dye}_{1} + {}^{\bullet}\mathrm{OH} \longrightarrow \mathrm{Products} \qquad \text{....(5)}$$

When the solution of the dye was exposed to light in presence of CaO, the $^{1}Dye_{0}^{-}$ molecules were excited to first excited singlet state ($^{1}Dye_{1}^{-}$). Then these excited molecules are transferred to the triplet state through intersystem crossing (ISC). On the other hand, the semiconductor CaO also absorbs photons and as a result electron-hole pair is generated. The OH^{-} will react with hole of the semiconductor to generate $^{\bullet}OH$ radicals and these radicals will convert the dye molecules into products, which are colourless. The participation of $^{\bullet}OH$ radicals as an active oxidizing species was confirmed by carrying out the same reaction in presence of some hydroxyl radical scavengers like 2-propanol, where the rate of degradation was drastically reduced.

CONCLUSION

Photocatalytic degradation of methylene blue was investigated using CaO as a semiconductor. Various parameters such as (dye concentration, CaO loading, pH values) were tested. This work demonstrates that photocatalysis is a very effective technology for degradation of methylene blue dye. Also, there is 60% reduction in the COD of dye solution after photocatalytic degradation.

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