USE OF LEAD CHROMATE FOR PHOTOCATALYTIC DEGRADATION OF METHYLENE BLUE

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ABSTRACT

The photocatalytic degradation of Methylene blue has been studied in the presence of lead chromate as a photocatalyst. The effect of different parameters like pH, concentration of Methylene blue, amount of lead chromate and light intensity on the rate of degradation was observed. A tentative mechanism for this reaction has been proposed involving oxidation by hydroperoxyl radical.

Key words: Methylene blue, Lead chromate, Photocatalytic, Degradation.

INTRODUCTION

A wide variety of organic contaminants are introduced into the water resources from industrial effluents, agricultural runoff and chemical spills. Their toxicity & stability to natural decomposition and persistence in the environment has been the cause of much concern to the societies and regulation authorities around the world. Thus, development of some appropriate method for the degradation of contaminated drinking, ground, surface waters and wastewaters containing various toxic or nonbiodegradable compounds seems necessary.

The biggest consumers of water are textiles, tannery, electroplating and pulp & paper industries and therefore, these industries are also considered mostly responsible for creating water pollution. Photocatalytic degradation has emerged as an efficient process for degradation of organic pollutants, which are present in the effluents released by these industries.

The photocatalytic bleaching of methylene blue was carried out by Ameta et al.[1] in the presence of semiconducting iron (III) oxide. The degradation was observed spectrophotometrically. The effect of various operating variables like pH, concentration of dyes, amount of semiconductor, light intensity, particle size, stirring, etc. was observed on the rate of the reaction. Methylene blue (MB) degradation has also been investigated by Houas et al.[2] in aqueous heterogeneous suspensions. Removal of the colour by TiO_2/UV-based photocatalysis was simultaneously oxidation of the dye, with an almost complete mineralization of

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carbon, nitrogen and sulfur heteroatoms into corresponding counter parts CO_2, NH_4^+, NO_3^- and SO_4^{2-}, respectively was observed. Successive hydroxylations of aromatic ring lead to clevage of the aromatic ring.

The effects of synthesis conditions (metal concentration, precursor flow rate and O_2 dispersion) during flame-spray pyrolysis (FSP) and annealing post- treatment on the characteristics and photocatalytic activities of ZnO nanoparticles have been investigated by Mekasuwandumrong et al.[3] The larger particle size of ZnO nanoparticles exhibited higher photocatalytic activities in the degradation of Methylene blue dye. The degradation rate over FSP-ZnO (47.0 nm) was observed to be 1.7 and 7.2 times higher than those of the commercially available photocatalysts Degussa P-25 and JRC-TiO$_2$, respectively. The better photocatalytic performance of the FSP-ZnO was correlated with the improved crystalline quality of ZnO nanoparticles.

Photodegradation of Methylene blue using the TiO_2/Ti electrode under different experimental conditions was investigated by Li et al.[4] in presence of UV. Chemical oxygen demand (COD) removal was also observed. The prepared electrode mainly consisted of anatase TiO_2 nanoparticles on its surface and exhibited a superior photocatalytic activity. The COD removal during the photodegradation of methylene blue by TiO_2/Ti mesh electrode was 97.3%.

UV/titanium dioxide degradation of two xanthene dyes, Erythrosine B (Ery) and Eosin Y (Eos), was studied by Pereira et al.[5] in a photocatalytic reactor. Photocatalysis was able to degrade 98% of Ery and 73% of Eos and results in removal of 65% chemical oxygen demand. It was revealed that it is a pH dependent the process and better results were obtained under acidic conditions, which may be due to the electrostatic attraction caused by the opposite charges of TiO_2 (positive) and anionic dyes (negative).

The photocatalytic degradation of a series of six acid dyes (Direct red 80, Direct red 81, Direct red 23, Direct violet 51, Direct yellow 27, and Direct yellow 50) has been compared in terms of color removal, mineralization, and toxicity (Lactuca sativa L. test) after photocatalysis on immobilized titanium dioxide by Byberg et al.[6] The dyes were examined at their natural pH and after hydrolysis at pH 12. The hydrolysis decreases the efficiency of color removal strongly. Full mineralization takes much longer reaction time than color removal, and toxicity is only very partially reduced.

Wang et al.[7] studied the photocatalytic degradation of Methylene blue over poly-*o*-phenylenediamine/TiO$_2$ composite (PoPD/TiO$_2$) photocatalysts in presence of simulated solar light. The effect of operational parameters, i.e. pH of the solution, photocatalyst content, irradiation time, initial MB concentration, and temperature, on the photocatalytic degradation efficiency was observed and the results obtained were fitted with Langmuir-Hinshelwood model to investigate the degradation kinetics. The PoPD/TiO$_2$ composites exhibit significantly higher photocatalytic activity than that of pure TiO_2 on the degradation of MB aqueous solution under visible light irradiation.

The photocatalytic degradation of synthetic dye solution of reactive blue 2 was investigated by Rashidi et al.[8] using UV irradiation in aqueous suspension of nanotitania as photocatalyst and H_2O_2 as electron acceptor in a slurry photoreactor. The optimum conditions of decolorization were determined by observing the effect of influential parameters like initial dye concentration, catalyst quantity, hydrogen peroxide concentration, pH value and UV light intensity. The mineralization was considered significant with regard to the obtained values of total organic carbon (TOC) analysis (92.52%) and chemical oxygen demand analysis (94.05%).

Photocatalytic degradation of Methyl orange and Methylene blue has been carried out by heterogeneous photocatalytic process using TiO_2 as semiconductor by Mehra and Sharma[9]. The effect of

process parameters like concentration of dye and pH on photocatalytic degradation of Methyl orange and Methylene blue was observed.

Chakrabarti and Dutta[10] have explored the potential of a common semiconductor, ZnO as an effective catalyst for the photodegradation of two model dyes: Methylene blue and Eosin Y. A 16 W lamp was used as the source of UV-radiation in a batch reactor. Substantial reduction of COD, and removal of colour was also achieved

Ranjith and Kumar[11] synthesized ZnO nanostructures of different morphology (Rods, spindles, stars and buds) successfully by co-precipitation method. The photocatalytic degradation of Methylene blue in aqueous solution under UV-irradiation was investigated with different ZnO nanostructures. The photocatalytic experiments reveal that the spindle like nanostructures showed faster photocatalytic activity as compared to the rods, stars and buds like nanostructures.

Nanoparticles of zinc sulfide as undoped and doped with manganese, nickel and copper were used by Pouretedal et al.[12] as photocatalysts in the photodegradation of Methylene blue and Safranin as color pollutants. Photoreactivity of doped zinc sulfide varied with dopant, mole fraction of dopant to zinc ion, pH of solution, dosage of photocatalyst and concentration of dye. The maximum degradation efficiency was obtained in the presence of $Zn_{0.98}Mn_{0.02}S$, $Zn_{0.94}Ni_{0.06}S$ and $Zn_{0.90}Cu_{0.10}S$ as nanophotocatalysts. The highest degradation efficiency was obtained in alkaline pH (11.0). In the optimum conditions, the degradation efficiency was 87.3-95.6 and 85.4-93.2 for Methylene blue and Safranin, respectively.

Barjasteh-Moghaddam and Habibi-Yangjeh[13] prepared ZnS nanoparticles in aqueous solution of a room-temperature ionic liquid (RTIL), which were used for the photocatalytic degradation of Methylene blue and the results were compared with that of commercial ZnS. The optimum value of pH and catalyst dose was found to be 9.5 and 0.6 g L^{-1}. It was found that the photodegradation of MB follows a pseudo first-order kinetics.

Photocatalytic degradation of the Methylene blue dye was studied in distilled water (laboratory conditions) and sea water (field condition) by Sawant et al.[14] using Indian edible chuna (Calcium oxide/hydroxide) as a photocatalyst. It was observed that the photocatalytic degradation of Methylene blue dye in sea/saline water is very slow as compared to that in distilled water. This may be due to the fact that salts present in the sea water hinder the photocatalysis process by reducing the direct contact between the photocatalyst and dye.

IUPAC name of Methylene blue is 3,7-bis (dimethylamino)- phenothiazin-5-ium chloride trihydrate. Its molecular formula and molar mass is $C_{16}H_{18}N_3SCl.3H_2O$ and 373.91 g/mol, respectively. It is soluble in water. It appears as a solid, odorless and dark green powder. It has many uses in a range of different fields, such as biology and chemistry. Methylene blue is often used as a cationic dye in textile industries. It is also used as a redox indicator in analytical chemistry.

EXPERIMENTAL

0.0374 g of Methylene blue 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 stock solution was further diluted. The absorbance of Methylene blue solution was determined with the help of a spectrophotometer at λ_{max} = 665 nm. The dye solution was divided in four beakers.

- The first beaker containing Methylene blue solution was kept in dark.
- The second beaker containing Methylene blue solution was exposed to light.

- The third beaker containing Methylene blue solution and 0.10 g lead chromate was kept in dark, and

- The fourth beaker containing Methylene blue solution and 0.10 g lead chromate was exposed to light.

These beakers were kept for 3-4 hours and then the absorbance of each solution was measured with the help of a spectrophotometer. It was observed that the absorbance of solutions of first three beakers remained virtually constant, while the solution of fourth beaker showed a decrease in its initial value. This observation suggests that this reaction requires both; the presence of light as well as semiconductor lead chromate. Therefore, this reaction is a photocatalytic reaction in nature and not chemical or photochemical.

A solution of 1.10×10^{-5} M methylene blue was prepared in doubly distilled water and 0.10 g of lead chromate was added to it. The pH of the reaction mixture was adjusted to 6.5 and then this solution was exposed to a 200 W tungsten lamp at 50.0 mWcm^{-2}.

It was observed that there was a decrease in absorbance of methylene blue solution with increasing time of exposure. A linear plot between 1 + log A v/s time was obtained, which indicates that the photocatalytic degradation of methylene blue follows pseudo-first order kinetics. The rate constant for this reaction was measured with the help of following equation-

$$k = 2.303 \times \text{slope} \qquad \qquad \text{…(1)}$$

A typical run has been presented in Table 1.

Table 1: A Typical run

pH = 6.5   Lead Chromate = 0.10 g
[Methylene Blue] = 1.10×10^{-5} M   Light Intensity = 50.0 mWcm^{-2}

Time (min.)	Absorbance (A)	1 + log A
0.0	0.490	0.6902
15.0	0.457	0.6599
30.0	0.426	0.6294
45.0	0.412	0.6149
60.0	0.384	0.5843
75.0	0.376	0.5752
90.0	0.351	0.5453
105.0	0.324	0.5105
120.0	0.309	0.4899
135.0	0.288	0.4594
150.0	0.275	0.4393
165.0	0.260	0.4149
180.0	0.243	0.3856

Rate constant (k) = 6.49×10^{-5} sec^{-1}

Effect of pH

The pH of the solution may also affect the degradation of Methylene blue. The effect of pH on the rate of degradation of Methylene blue was investigated in the pH range 5.0 - 10.0. The results are reported in Table 2.

Table 2: Effect of pH

[Methylene Blue] = 1.10×10^{-5} M   Light Intensity = 50.0 mWcm^{-2}

Lead chromate = 0.10 g

pH	Rate constant (k) $\times 10^5$ (sec^{-1})
5.0	3.29
5.5	4.65
6.0	5.73
6.5	**6.49**
7.0	5.94
7.5	5.02
8.0	4.87
8.5	4.05
9.0	3.89
9.5	3.54
10.0	3.07

It has been observed that the rate of photocatalytic degradation of Methylene blue increases as pH was increased and it attained optimum value at pH 6.5. On further increasing pH, the rate of the reaction was decreased. This behavior may be explained on the basis that as pH was increased, there is greater probability for the formation of oxygen anion radicals ($O_2^{\bullet -}$). These are produced from the reaction between O_2 molecule and electron (e^-) in conduction band of the semiconductor. As the optimum pH is in acidic range, this super oxide anion radical will combine with proton forming $HO_2^{\bullet}$ radical. With the formation of more $HO_2^{\bullet}$ radicals, the rate of photocatalytic degradation of the dye increases. Above pH 6.5, a decrease in the rate of photocatalytic degradation of the Methylene blue was observed, which may be due to the fact that cationic form of Methylene blue is converted to its neutral form, which faces no attraction towards the negatively charged semiconductor surface due to adsorption of $^-$OH ions.

Effect of dye concentration

The effect of dye concentration was observed by taking different concentrations of Methylene blue. The results are summarized in Table 3.

It was observed that the rate of photocatalytic degradation of dye increases on increasing the concentration of Methylene blue up to 1.10×10^{-5} M. It may be attributed to the fact that as the concentration of the Methylene blue was increased, more dye molecules were available for excitation and consecutive energy/electron transfer and hence, an increase in the rate of degradation of the dye. There was a decrease in degradation rate on increasing the concentration of dye above 1.10×10^{-5} M. This may be because of the fact that after a particular concentration, the dye may start acting as an internal filter and it will not permit the

sufficient light intensity to reach surface of the photocatalyst at the bottom of reaction vessel.

Table 3: Effect of Methylene blue concentration

pH = 6.5   Light intensity = 50.0 mWcm^{-2}

Lead chromate = 0.10 g

[Methylene blue] × 10^5 M	Rate constant (k) × 10^5 (sec^{-1})
0.60	4.77
0.70	5.00
0.80	5.46
0.90	5.98
1.00	6.22
1.10	**6.49**
1.20	6.04
1.30	4.92
1.40	3.83
1.50	3.08

Effect of amount of semiconductor

The amount of semiconductor may also affect the degradation of dye and hence, different amounts of lead chromate were used. The results are reported in Table 4.

Table 4: Effect of amount of lead chromate

pH = 6.5   Light Intensity = 50.0 mWcm^{-2}

[Methylene Blue] = 1.10 × 10^{-5} M

Lead chromate (g)	Rate constant (k) × 10^5 (sec^{-1})
0.02	2.39
0.04	3.06
0.06	4.12
0.08	5.22
0.10	**6.49**
0.12	6.48
0.14	6.47
0.16	6.48

The rate of reaction was found to increase on increasing the amount of semiconductor, lead chromate. The rate of degradation reached to its optimum value at 0.10 g of the photocatalyst. Beyond 0.10 g, the rate of reaction become almost constant. This may be explained on the basis that as the amount of semiconductor was increased, the exposed surface area of the semiconductor also increases. However, after a particular value (0.10 g), an increase in the amount of semiconductor will only increase the thickness of layer of the

semiconductor and not its exposed surface area. This was confirmed by taking reaction vessels of different sizes. It was observed that this point of saturation was shifted to a higher value for vessels of larger volumes while a reverse trend was observed for vessels of smaller capacities.

Effect of light intensity

The effect of light intensity on the photocatalytic degradation of Methylene blue was also investigated. The light intensity was varied by changing the distance between the light source and the exposed surface area of semiconductor. The results are given in Table 3.5.
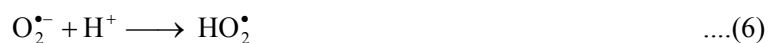
Table 5: Effect of light intensity

pH = 6.5	Lead Chromate = 0.10 g
[Methylene Blue] = 1.10×10^{-5} M	

Light intensity (mWcm^{-2})	Rate constant (k) $\times 10^5$ (sec^{-1})
20.0	3.67
30.0	4.87
40.0	5.39
50.0	**6.49**
60.0	6.33
70.0	6.28

These data indicate that photocatalytic degradation of Methylene blue was enhanced with the increase in intensity of light, because an increase in the light intensity will increase the number of photons striking per unit area per unit time of photocatalyst surface. There was a slight decrease in the rate of reaction as the intensity of light was increased beyond 50.0 mWcm^{-2}. Therefore, light intensity of medium order was used throughout the experiments.

Mechanism

On the basis of these observations, a tentative mechanism for photocatalytic degradation of methylene blue dye has been proposed as follows:

$$^1MB_0 \xrightarrow{h\nu} {}^1MB_1 \qquad ....(2)$$

$$^1MB_1 \xrightarrow{ISC} {}^3MB_1 \qquad ....(3)$$

$$SC \xrightarrow{h\nu} e^-(CB) + h^+(VB) \qquad ....(4)$$

$$e^- + O_2 \longrightarrow O_2^{\bullet-} \qquad ....(5)$$

$$O_2^{\bullet-} + H^+ \longrightarrow HO_2^{\bullet} \qquad ....(6)$$

$$HO_2^{\bullet} + {}^3MB_1 \longrightarrow \text{Leuco MB} \qquad ....(7)$$

$$\text{Leuco MB} \longrightarrow \text{Products} \qquad ....(8)$$

Methylene blue absorbs radiations of desired wavelength and it is excited giving its first excited singlet state. Further, it undergoes intersystem crossing (ISC) to give its more stable triplet state. Along with this, the semiconducting lead chromate (SC) also utilizes this energy to excite its electron from valence band to the conduction band. This electron can be abstracted by oxygen molecule (present in the form of dissolved oxygen) generating superoxide anion radical ($O_2^{\bullet-}$). This anion radical will react with the proton to form $HO_2^{\bullet}$ radicals as the medium is acidic. $HO_2^{\bullet}$ radicals will oxidize Methylene blue to its leuco form, which may ultimately degrade to products. $^{\bullet}OH$ radical does not participate as an active oxidizing species in the degradation of methylene blue as the rate of degradation was not affected reasonably in presence of hydroxyl radical scavenger (2-propanol).

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