

Photocatalytic Degradation Study of Methylene Blue Solutions and Its Application to Dye Industry Effluent

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ABSTRACT

Zinc oxide (ZnO) was used in the photocatalytic decolourisation and degradation study of a dye namely, methylene blue (MB). The effect of the various rate determining parameters like initial dye concentration, catalyst loading, pH of the medium, temperature of the dye solution on the photodegradation of MB were studied in detail. The various thermodynamic and kinetic parameters of the process were evaluated. The MB degradation and its reaction kinetics analysis was utilised in the photocatalytic treatment of an actual effluent collected from an industry manufacturing intermediates for dyes. It revealed that the effluent could be effectively decolourised and degraded by photocatalytic method, without generation of any hazardous wastes or by-products as evident from the considerable reduction in chemical oxygen demand (COD) values.

Keywords: ZnO, photocatalytic degradation, methylene blue, dye effluent

1. INTRODUCTION

Most pollutants in the waste water effluents from industrial or domestic sources comprise of organic chemicals and pathogens which must be removed or destroyed before discharge into the water bodies. Such pollutants prevailing in the ground and surface waters pose irreversible hazards to human and aquatic life. The uncontrolled and heavy discharge of chemicals from industries comprises the major source of water and air pollution. Like any other chemical industry, textile industry is the main source of coloured organic reagents which are called dyes. Dyes are extensively used in the textile industry during dyeing process and the excess dyes are released into the effluent streams as waste after colouring the fabric. The released wastes are nevertheless in highly concentrated and complex state causing difficulty in handling for further treatment. Further most modern synthetic dyes are fairly stable even to the sunlight, with some of them being carcinogenic [1, 2]. Thus the waste water from a textile industry essentially needs an efficient treatment technology which can overcome all the aforesaid challenges giving ultimately clean water for safe disposal. Various conventional methods have been pressed into practice, in the decolourisation and degradation of dyes in the waste namely - biological treatment methods, coagulation, filtration, adsorption by activated carbon, reverse osmosis [3]. Low cost methods such as adsorption by activated charcoal, amongst these have been proven to be effective but incomplete in that they produce large amounts of solid wastages for further disposal thus adding to further pollution and environmental hazards. The other methods which have been proved efficient are not cost-effective [4]. Thus these methods either fail to accomplish the complete degradation, or produce large amount of toxic sludge causing disposal problems.

Thus serious concerns for a better and sufficiently effective alternative which is environment friendly especially in treating the effluent from textile and pharmaceutical disposed waste waters have prompted the development of few advanced oxidation processes (AOP), which are currently in use. Amongst them semiconductor based photocatalytic degradation could be considered as the most efficient [5]. This particular technique involves the use of semiconductor as catalysts which act as the medium of oxidation. Currently, TiO₂ and ZnO are largely deployed as the semiconducting materials suitable in the treatment of pollutants [6]. The semiconductor having a filled valence band and an empty conduction band inherently provides a small band-gap of energy 3 - 3.5 eV. When light falls on the surface of the semiconductor, the photon of threshold energy either equal to or greater than the energy gap, excites (knocks) an electron from the occupied (filled) valence band and promotes it to the unoccupied (empty) conduction band, thus leading to excited state conduction band electrons and positive valence band holes. These charged electrons and holes constitute the charge carriers which can undergo a number of processes namely, (1) they can either recombine radiatively or non-radiatively, dissipating their input energy as heat, (2) the charge carriers can also get trapped into the surface of the catalyst, (3) recombination of the trapped charge carriers, and (4) they can also react, if not undergone recombination, with the electron donors (reducing agents) or acceptors (oxidising agents) adsorbed on the surface of the semiconductor activated under the light [7]. In a recent study it was realized that the photocatalytic behaviour of the semiconductor is mainly due to the trapped electrons and trapped holes. However a competition between all these processes determines the ultimate quantum efficiency of the photoredox reactions on the semiconductor surface. It is also important that the energy band potentials of the semiconductor be compatible with that of the redox potentials of the water/hydroxyl radical couple (2.8 eV) [8]. Several semiconductors have energies of their band gap sufficient for catalysing a wide range of redox reactions. An ideal photocatalyst should be inexpensive, non-toxic, highly photoactive and stable in the conditions in which the pollutant is present. Some examples are TiO₂, WO₃, SrTiO₃, Fe₂O₃, ZnO and ZnS. TiO₂ is the most extensively studied semiconductor found from the literature [9]. It has been found to be the

most promising for photocatalytic destruction of organic pollutants with high stability in aqueous media. The anatase phase of TiO₂ is the material with the highest photocatalytic detoxification compared to the other phase which is called the rutile phase [10].

The advantage of using semiconductor based materials as photoactive catalysts in the detoxification of pollutants is the complete mineralization into environment friendly products, without generation of waste, which is not possible in the case of any other treatment method [11]. The other advantages include easy regeneration, reusability and active under easily available UV-visible photolight. Other than TiO₂ as photocatalyst, studies have been carried out to find the efficiency of other metal oxides. Among the other semiconductors, ZnO appears to be a highly promising photocatalyst and it has a band-gap almost similar to that of the anatase phase of TiO₂ [12, 13].

The main focus of the present work is to use commercially available ZnO in the photocatalytic decolourisation and degradation study of methylene blue (MB). The effect of rate determining parameters like initial dye concentration, catalyst loading, pH of the medium, temperature of the dye solution on the photodegradation of MB were studied in detail. The thermodynamic parameters involved in the degradation process were calculated. The study of MB degradation and understanding the parameters affecting its kinetics, helped in application of the photocatalytic method to the actual effluent collected from the industry that makes intermediates for dyes. It is suggested that the photocatalytic method can be effectively applied to decolourise and degrade the effluent if repeated in multiple steps.

2. EXPERIMENTAL

2.1 Materials

ZnO was procured from Merck, Chemie, Mumbai; MB, H₂SO₄ and NaOH were purchased from Loba Chemicals, Mumbai and double deionized water was used through out the experiment.

2.2 Photocatalytic Degradation

In photocatalytic experiments, MB dye (50 ml) and the catalyst (ZnO), were taken in a beaker and exposed to UV light for up to 180 min. Dye samples of about 5 ml were taken out at a regular interval from the test solution, centrifuged for 4 min at 950–1000 rpm and their absorbance was recorded at 664 nm using a spectrophotometer (Model: Double Beam Spectrophotometer Model 2215, Elico, India). COD was estimated before and after the treatment using potassium dichromate oxidation method. The same photocatalytic experimental set up was employed in the case of effluent collected from the industry manufacturing intermediates for dyes. UV black lamp of intensity 27 W/m² was used which was procured from Sun Electricals, Hyderabad.

3. RESULTS AND DISCUSSION

3.1 Photodegradation reaction kinetics

The present photodegradation process assisted by a ZnO semiconductor was studied by varying the rate determining parameters like concentration of the dye (MB) and temperature. Photocatalytic degradation of dyes generally follows first order kinetics. The corresponding half lives and rate constants were calculated by plotting the log (C₀/C) versus time graphs, whose derived values are presented in Table 1. The kinetic investigation revealed that ZnO induced photocatalysis of MB following first order kinetics.

Table 1

Rate constants and half-lives for different concentrations of MB dye solutions at room temperature

Concentration of Dye (ppm)	Rate constant (k x 10 ⁻²) min ⁻¹	Half-life (t _{1/2}) (min)
35	1.35	51
30	1.82	38
25	2.66	26
10	3.85	18

3.2 Effect of dye concentration

Keeping the catalyst loading concentration constant at 25 mg/50 ml of the dye solution, the effect of varying amounts of the dye was studied on its rate of its degradation (from 10 ppm to 35 ppm) as given in Table 1. With increasing concentration of MB the rate of degradation was found to decrease. This is because as the number of dye molecules increase, the amount of light (quantum of photons) penetrating the dye solution to reach the catalyst surface is reduced owing to the hindrance in the

path of light. Thereby the formation of the reactive hydroxyl and superoxide radicals is also simultaneously reduced. Thus there should be an optimum value maintained for the catalyst and the dye concentration, wherein maximum efficiency of degradation can be achieved.

3.3 Effect of pH on the photodegradation reaction

The photodegradation reaction was also carried out under varying pH conditions from (2 to 11), by adjusting with HNO₃ and NaOH, with ZnO kept at constant amounts of 25mg/50 ml of dye solutions (Fig. 1). The reaction was found to have low rates at neutral ranges of pH. While at higher and lower cases it was found to increase. This implies that alkaline as well as acidic conditions are favourable towards the formation of the reactive intermediates that is hydroxyl radicals is significantly enhanced, which further help in enhancing the reaction rate. On the other hand in neutral medium conditions the formation of reactive intermediates is relatively less favourable and hence less spontaneous.

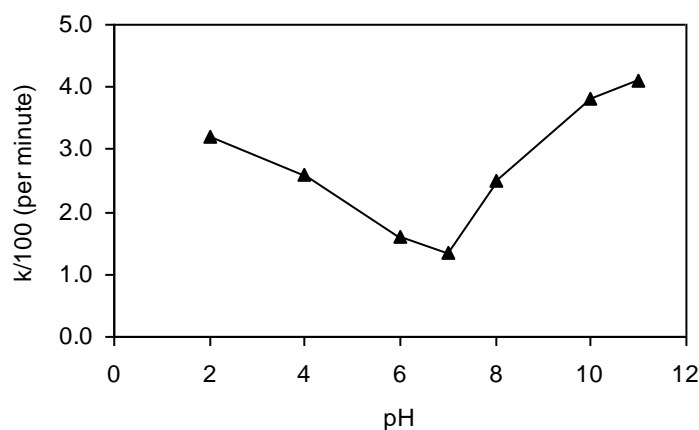


Figure 1. Effect of reaction medium pH on photodegradation of MB solution (35ppm/50 ml)

3.4 Effect of catalyst amounts on the photodegradation reaction

The amount of catalyst was varied from 10mg to 350mg per 50 ml of constant dye solution of 35 ppm concentration. The effect is graphically depicted in Fig. 2.

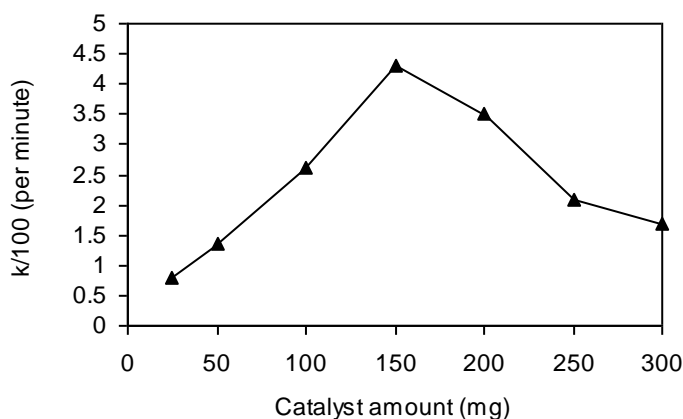


Figure 2. Effect of catalyst amount on photodegradation of dye

We observe that with increasing catalyst amounts the reaction was found to occur faster due to increase in the number of active surfaces on the catalyst. However, beyond 250 mg the reaction rate decreased, which could be due to the hindrance to the pathway of light to reach the dye molecules. Perhaps scattering of light dominates at higher catalyst loadings.

3.5 Effect of temperature on photodegradation reaction

The effect of increasing temperature was observed on the photodegradation of MB dye by varying the temperature from 298 to 328 K, keeping the dye concentration constant at 35 ppm with a catalyst concentration of 25 mg/50 ml. The results are given in Table 2 and graphically evaluated by Arrhenius based temperature dependence of the photocatalytic degradation by a plot of $\log(C_0/C)$ versus $1/T$ (as shown in Fig. 3).

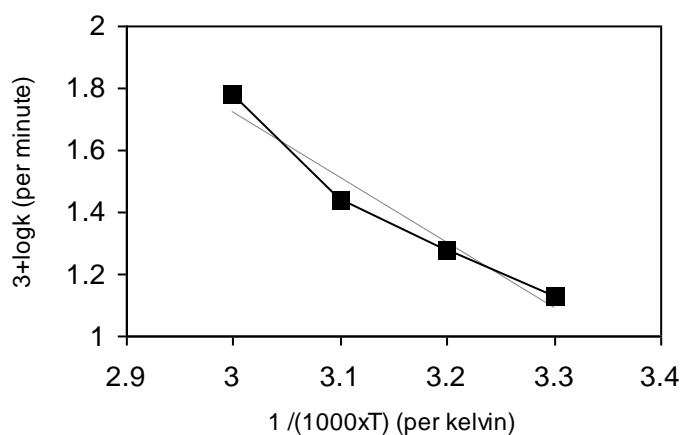
Table 2

Kinetic and thermodynamic parameters for the photocatalytic degradation of MB dye (35 ppm) and ZnO (25mg/50ml) under UV light

T (K)	k (min^{-1}) $\times 10^2$	E_a (kJ mol^{-1})	ΔH^\ddagger (KJ.mol^{-1})	ΔS^\ddagger ($\text{kJ.mol}^{-1}.\text{K}^{-1}$)	ΔG^\ddagger (kJmol^{-1})
298	1.35		37.97		93.79
308	1.67	40.45	37.88	-0.19	96.47
318	2.72		37.80		98.40
328	4.81		37.72		100.03

\ddagger represents activated state

The energy of activation (E_a) was calculated from the slope of the graph. Further other thermodynamic parameters enthalpy of activation, entropy and free energy of activation were also evaluated. The positive energy of activation implies that the reaction is less energy intensive and a spontaneous one. This could be because the activated state is a well solvated structure formed between the dye molecules and the reaction intermediates that is hydroxyl radicals which is also supported by positive entropy of activation.

**Figure 3. Effect of temperature on the photodegradation of methylene blue**

It can be seen that with increasing temperature, the rate of the reaction increases which is due to the reason that increase in temperature helps to speedup the velocity of both the hydroxyl radicals and the dye molecules to interact with each other thus the reaction competes more efficiently with the electron-hole recombination. The following scheme can be proposed for the degradation of the MB dye:



+ mineral salts

3.6 Photodegradation of effluent from industry manufacturing intermediates for dyes

The catalytic photodegradation was also studied for an effluent from an industry manufacturing intermediates for dyes. The results are tabulated in Table 3. The efficiency of degradation was assessed from the experimentally derived chemical

oxygen demand (COD) measured after various times of UV light exposure. It can be seen that there is considerable reduction in the COD values. The drastic lowering in the COD values after 20 hours of exposure is a significant achievement. Further, the reduction in BOD values also signifies the importance of the photocatalytic degradation treatment. The effluent could be completely decolourised and degraded by the use of semiconductor catalysts.

Table 3**Photocatalytic degradation results of effluent collected from a dye industry**

Effluent physico-chemical parameters	Pre-photocatalytic degradation	Post photocatalytic degradation after			
		1 hr	5 hrs	8hrs	20 hrs
COD (mg/L)	3885	2643	1215	665	90
BOD (mg/L)	851	536	206	117	19

4. CONCLUSION

Photodegradation of methylene dye was studied as a model system using powder ZnO catalyst, in order to assess the efficiency of such advanced oxidation technologies in the treatment of effluents from industry manufacturing intermediates for dyes. From kinetic studies it was found that the method of photodegradation is dependent on parameters such as dye concentration, catalyst loadings, temperature and other parameters. Textile effluent with very high initial COD and BOD values was effectively treated using ZnO catalyst. The significant reduction in COD, BOD and decolourization of the effluent suggests that the dye molecules could be completely mineralized with the help of ZnO which is both economically viable and environment friendly.

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