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UV light Induced Degradation of Methylene Blue Using Various Photocatalysts

M.P. KAUR*, S.K. KANSAL† , M. SINGH‡ and D. SUD
Department of Chemistry, Sant Longowal Institute of Engineering and Technology, Longowal-148 106, India

The present study involves the photocatalytic degradation of Methylene Blue (MeB) employing heterogeneous photocatalytic process with TiO_2 and ZnO. An attempt has been made to study the effect of process parameters *viz.*, amount of catalyst, concentration of dye and pH on photocatalytic degradation of MeB. The experiments were carried out by irradiating the aqueous solutions of dyes containing photocatalysts under UV light. Similar experiments were carried out by varying pH (2-10), amount of catalyst (0.25-2.0 g/L) and initial concentration of dye (5-200 mg/L). The experimental results indicate that the maximum decolorization of dyes occurred with ZnO catalyst and at basic pH.

Key Words: Decolorization, Azo dye, Methylene blue, Photocatalysis, Titanium dioxide, Zinc oxide

INTRODUCTION

The release of colored wastewaters in the environment is a considerable source of non-aesthetic pollution and can originate dangerous by-products through oxidation, hydrolysis or other chemical reactions taking place in the wastewaters phase. Decolorization of dye effluents has therefore received increasing attention. Due to the nature of synthetic dyes, conventional biological treatments are ineffective for decolorization of wastewater containing dyes[1].

In recent years, a very promising treatment method based on the total oxidation of hazardous organic compounds by using advanced oxidation processes (AOPs) has been reported[2,3]. AOPs include photocatalysis systems such as combination of semiconductors and light, and semiconductor and oxidants. Among these processes, heterogeneous photocatalytic systems involving TiO_2/ZnO as catalysts have proven to be more efficient systems[4-7]. In the present study the photodecolorization of methylene blue (MeB) has been carried out using photocatalysts such as TiO_2, ZnO and mixture of TiO_2, ZnO in the ratio 1:1, 3:7, 7:3.

†Department of Chemical Engineering and Technology, Panjab University, Chandigarh-160 014, India
‡Department of Chemical Technology, Sant Longowal Institute of Engineering and Technology, Longowal 148106, India

EXPERIMENTAL

Titania P-25 (surface area 50 m^2/g) was obtained from Degussa. ZnO (5 m^2/g) and Methylene Blue were purchased from Merck, Germany and were used without further purification. Double distilled water was used for preparation of various solutions. pH of the solutions was adjusted with 1 M HCl or 1 M NaOH.Photodecolorization was carried out in specially designed double walled reaction vessels in the UV chamber equipped with 5 UV tubes each of 30 W (Philips) having wavelength 365 nm. Constant stirring of solution was insured by using magnetic stirrers. The temperature was maintained constant throughout the reaction time by circulating the water in the jacketed wall reactor. The spectra were taken with UV-Vis spectrophotometer (Systronics 119); pH meter (Thermo Orion 920A) was used to adjust the pH of the solution.

The photodecolorization experiments were carried out in batch photoreactors at 298 K. In 100 mL of dye solution, photocatalyst was added and suspension was subjected to irradiation. Experiments were carried out under UV light. The aqueous suspension was magnetically stirred throughout the experiment. At different time intervals aliquot was taken out with the help of a syringe and then filtered through Millipore syringe filter of 0.45 μm. Then absorption spectra were recorded and rate of decolorization was observed in terms of change in intensity at λ_{max} of the dye.

Decolorization efficiency (%)

Efficiency = $100 \times (C_0\text{-}C/C_0)$, where C_0 = initial concentration of dye, C = concentration of dye after photoirradiation. Similar experiments were carried out by varying the pH of the solution (pH 2-10), concentration of dye (5-200 mg/L) and catalyst loading (0.25 -2.0 g/L).

RESULTS AND DISCUSSION

Methylene blue is a cationic dye having thiazine group. The photodegradation experiments were carried out under UV light and solar light. Different photocatalysts *viz.*, TiO_2, ZnO and mixture of TiO_2, ZnO in different ratios have been investigated for their decolorization efficiency. Fig. 1 shows typical time dependent UV-VIS spectrum of MeB during photoirradiation with ZnO catalyst. MeB shows absorption peaks at 664 nm in visible region and 291 nm in UV region. The rate of decolorization was recorded with respect to the change in intensity of absorption peaks at 664 nm. The absorption peaks, corresponding to dye diminished and finally disappeared during reaction which indicated the complete degradation of dye. No new absorption bands appeared in

either visible or ultraviolet regions, reflecting that the intermediates had also been degraded leading to complete mineralization of the dye.

Decolorization of methylene blue using various photocatalysts

For the decolorization experiments, one gram of photocatalyst TiO_2, ZnO or their mixtures in different ratios (7:3; 1:1; 3:7) was added to 100 mL of the dye solution and the suspension was subjected to irradiation under UV light at neutral pH and fixed concentration of dye (25 mg/L. Fig. 2 shows the percentage decolorization of MeB with different photocatalysts and their mixture in different ratios. In the presence of TiO_2 and UV light, 53% decolorization of dye was obtained whereas when ZnO was used in place of TiO_2, percentage decolorization of the dye was found to be nearly 100%. The results are in confirmation with earlier findings of using ZnO as an alternative to TiO_2 for the photocatalytic decolorization of azo dyes and proposed that the mechanism of degradation for TiO_2 and ZnO is same[7,8]. The results obtained by using the combination of TiO_2 and ZnO in the ratio 7:3 showed only 60% decolorization whereas in the ratios (1:1 and 3:7), the decolorization was close to the results obtained by using ZnO alone. So the further experiments were performed by using ZnO only.

Decolorization of MeB by ZnO as photocatalyst under UV-light

The experiments were carried out to study the degradation of MeB employing ZnO as catalyst under UV light. Various parameters which effect the decolorization efficiency such as catalyst loading (0.25-2.0 g/L), pH (2-10), initial concentration of dye (5-200 mg/L) for decolorization were assessed under UV light.

Effect of catalyst dose

The effect of catalyst loading on the decolorization efficiency of MeB has been examined by varying its amount from 0.25 to 2.0 g/L. The decolorization efficiency increases with increase in the catalyst dose upto 1 g/L of ZnO (From 60 to 99.5%) and then decreased for 2.0 g/L. The photocatalytic destruction of other organic pollutants has also exhibited the same dependency on catalyst dose. This can be explained on the basis that optimum catalyst loading is found to be dependent on initial solute concentration because with the increase of catalyst dosage, total active surface area increases, hence availability of more active sites on catalyst surface[9,10]. It can be concluded that higher dose of catalyst may not be useful both in view of aggregation as well as reduced irradiation field due to light scattering.

Effect of pH

The color removal efficiency of MeB solution as a function of pH in the range varying from 2-10 was studied. The maximum decolorization was observed (99.8%) at higher pH (pH *ca.*10). Similar findings have been reported by other workers for the photocatalytic decolorization of MeB using TiO_2[5,6]. The decolorization efficiency (%) has been calculated as this might be because of the amphoteric behavior of ZnO. At higher pH, electrostatic interactions between the negative ZnO surface and MeB cations leads to strong absorption and thus enhancing the decolorization rate. In the acidic pH there was poor absorption because the catalyst and dye both are positively charged in the acidic media. Therefore decrease in pH causes decrease in decolorization rate.

Effect of concentration of dye

The results for the effect of the initial concentration (5-200 mg/L) with optimum catalyst loading (1 g/L) and pH-10 of MeB on decolorization rate have been given in Fig. 3. It can be seen that it takes only 2 h for the complete decolorization of dye, for the initial dye concentration of 25 mg/L. For 50 and 100 mg/L of the dye solution, the decolorization was 62 and 51% respectively after 2 h. The possible explanation for this behavior is that as the initial concentration of the dye increases, the path length of the photons entering the solution decreases and in low concentration the reverse effect is observed, thereby increasing the number of photon absorption by the catalyst in lower concentration

Conclusions

Comparison of photocatalytic activity of TiO_2 and ZnO semiconductors has clearly indicated that the ZnO is more active photocatalyst for decolorization of MeB. So it can be concluded that photocatalytic system employing ZnO and UV light has potential to degrade the methylene blue from effluents of textile industries.

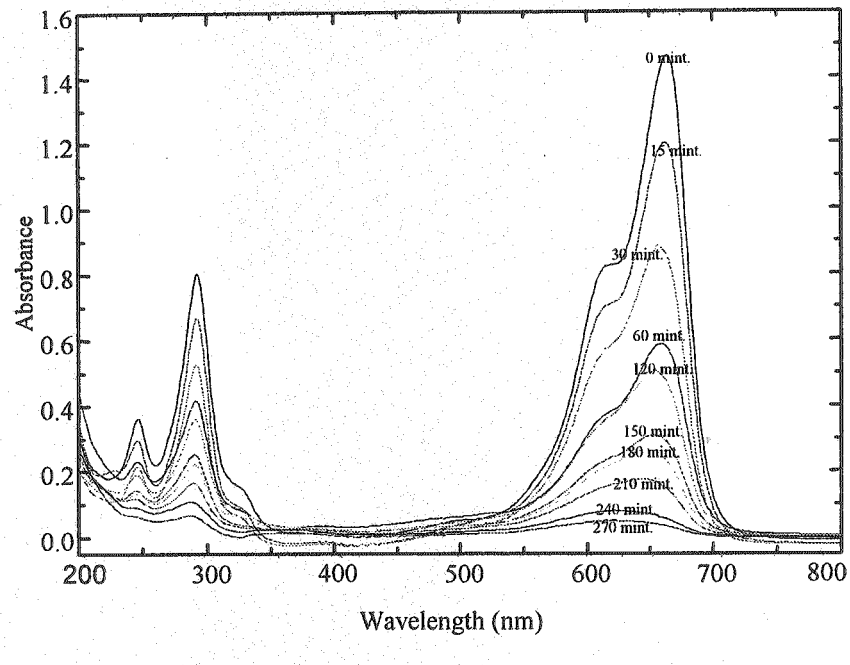

Fig. 1. Time dependent UV-Vis absorption spectra for decolorization of methylene blue

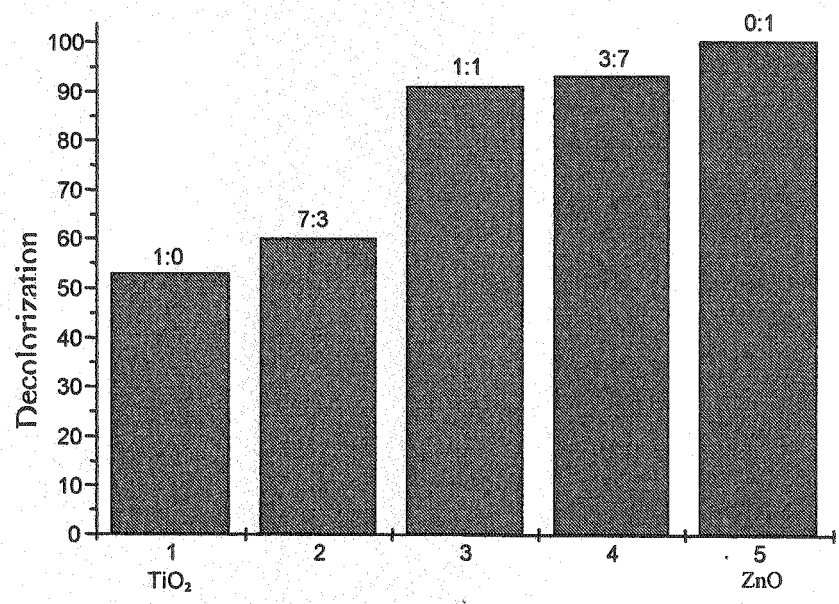

Fig. 2. Effect of various catalysts on decolorization of methylene blue

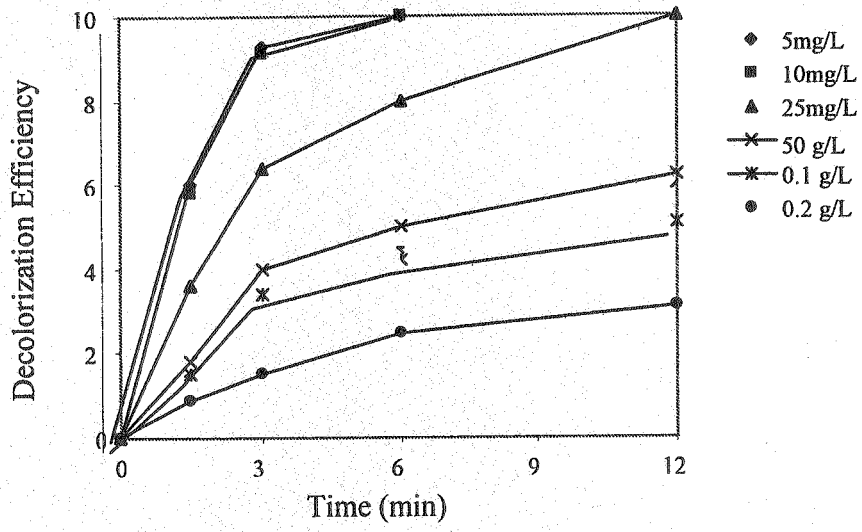

Fig. 3. Effect of initial concentration of methylene blue on decolorization efficiency under UV light

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