

Photocatalytic Degradation of Methylene Blue in the Presence of TiO₂ Catalyst Assisted Solar Radiation

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Abstract: In this study, degradation of methylene blue (MB) from water was investigated by photocatalysis process in presence of TiO₂ under solar radiation. Some of process parameters such as catalyst loading, initial concentration and pH were examined for influencing on efficiency degradation process. The results showed that pH of solution is acidic to enhance the photocatalytic efficiency was found. However, loading of TiO₂ was found to be 2 g/l as optimal, which the availability of surface to adsorb more molecules of MB was achieved with this loading. Therefore, lower concentration also lead to achieve highest degradation efficiency of MB.

Key words:

INTRODUCTION

About the 1-20 % of dyes production in the world has been discharged to environment from different industries as example textile finishing and dyestuff manufacturing (Mahvi, 2009; El-Sharkawy, 2007). Some of risks from dye in water have been considered for human such as nausea, eyes effects and vomiting (El-Sharkawy, 2007; Lang, 2009).

Methylene blue (MB) is one of pollutant color for environment undesirable which effects on aesthetic of environment (Saqib, 2008; Jain, 2008). As international environmental standards are becoming more stringent (ISO 14001, October 1996), technological systems for the removal of organic pollutants, such as dyes have been recently developed.

Many chemical and physical methods are used for treat, such as chlorination, ozonation (Slokar, 1998) and adsorption, biological (Houas, 1999). Recently, new method of oxidation "advanced oxidation processes" (AOP) has been used as emerging destructive method which going to complete mineralization of pollutant (Herrmann, 1999; Schiavello, 1988; Herrmann, 1993; Bahnemann, 1994; Legrini, 1993). Photocatalytic degradation of methylene blue (MB) from waste water has been studied using Titanium dioxide (TiO₂) thin films (Gao, 2000), and TiO₂ powder in aqueous solution (Sopajaree, 1999). TiO₂ has been reported as a good semiconductor for removal many organic compounds, may due to high oxidation efficiency, complete decomposition process, cheap and nontoxic material (Qamar, 2009; Ba-Abbad, 2012a; Ba-Abbad, 2012 b; Takriff, 2011).

In this work, TiO₂ was used as photocatalyst under direct solar radiation. Effects of some factors such as loading of TiO₂ and concentration of MB on photocatalytic efficiency were investigated in this study.

Experimental:

Materials:

Titanium dioxide (TiO₂) photocatalyst and methylene blue (MB) were supplied from sigma Aldrich. Deionized water was used for preparing all standard solutions.

Photocatalytic Reactor and Experimental Procedures:

All experiments were carried out using 100 ml in cylinder glass reactor. Different amount (1 to 3 g/l) of TiO₂ was added to certain concentration of MB to determine the optimal loading of photocatalytic process. Methylene blue (MB) solution with TiO₂ was stirred for 60 min under the dark condition for adsorption-desorption equilibrium and then exposed to solar light.

A 3 ml from solution was withdrawn every 15min irradiate time and separate the TiO₂ particles by centrifuge. The concentration of clear solution was determined by Perkin Elmer (Lambda 35) UV/VIS spectrophotometer (UV-VIS) equipped under range of absorbance between 200 to 800 nm. The wavelength of absorption and standard calibration for Methylene blue (MB) was 665 nm with R² correlation fit of 0.996. The photocatalytic degradation was calculated based on Eq. (1).

$$\% \text{ Photocatalytic degradation} = \left(\frac{C_0 - C_t}{C_0} \right) \times 100 \quad (1)$$

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Where C_0 (mg/L) is the concentration of MB at $t=0$ min, C_t (mg/l) is the concentration at various intervals of the radiation period.

RESULTS AND DISCUSSION

Photodegradability:

Fig.1 shows the effects of presence of the TiO_2 and solar radiation on photocatalytic degradation of MB. The absorbance spectra of MB at wavelength of 660 nm with interval time was decreased when the TiO_2 and solar radiation presence together.

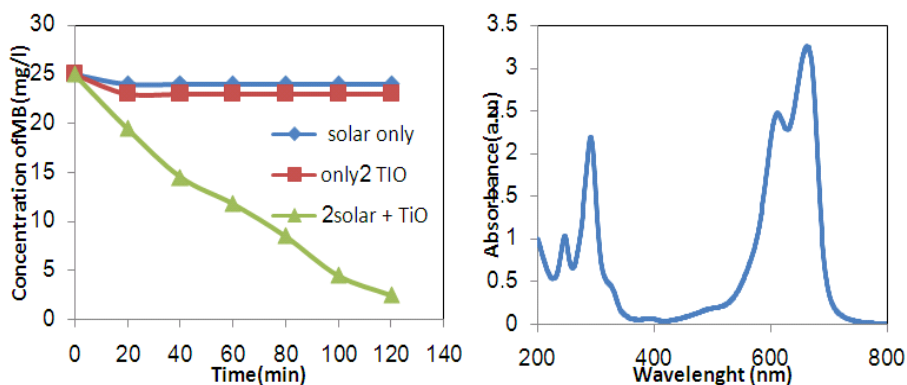


Fig. 1: Effects of TiO_2 and solar on MB degradation efficiency, (b) absorbance of MB with concentration of 25 mg/l, 2 g/l loading of TiO_2 and 120 min.

In the presence of TiO_2 with MB under the dark condition, about 5 % was adsorbed which even after 120 min. The result was negligible when solar was used alone which appeared lower value of degradation. However, in the presence of TiO_2 and solar light, the MB was totally degraded (90 %) within more than 120 minutes. These results confirmed that presence of the solar light was more affected factor especially sunny day as reported previous work (Ba-Abbad, 2012 c; Ba-Abbad, 2012 d).

Effect of pH Solution:

pH solution shows as one of important factor effecting on efficiency of photocatalytic process which has been reported earlier (Hoffmann, 1995; Lewis, 1993). To evaluate the optimum value of pH solution, the experiments was carried out with pH value from 4 to 8.

Fig.2 shows the results of MB degradation, which higher at acidic solution (pH at 4.0) after 2 hr using 25 mg/l as initial concentration. To explain effects of pH solution, the zero point charge (pH_{zc}) of TiO_2 is between 5.8-6.8 (Madhu, 2006), which the adsorption of MB molecules onto the surface of TiO_2 catalyst as important step to start photooxidation reaction.

According to zero point charge (pH_{zc}) of TiO_2 , the surface is positively below pH_{zc} and negatively charge of MB molecules. For this reason, the strong adsorption of MB onto TiO_2 surface at pH solution of 4.0 and highest degradation was found.

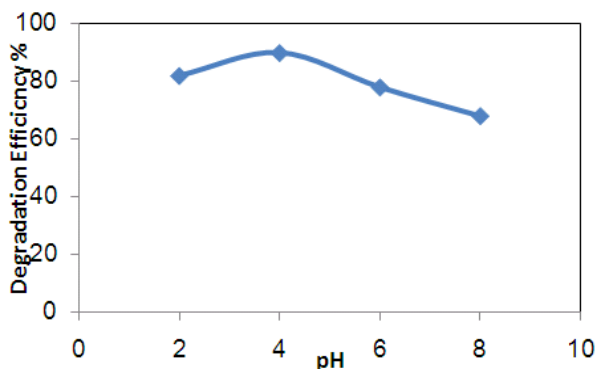


Fig. 2: Effect of pH solution on degradation efficiency of MB with concentration of 25 mg/l, 2 g/l loading of TiO_2 and 120 min.

Effect Loading TiO₂ Catalyst:

Fig. 3 shows effect of different loading of TiO₂ on the MB degradation process. Range between 1 to 3 g/l, 25 mg/l and pH at 4.0 were used to investigate the optimum loading of the catalyst. The photodegradation efficiency increasing with loading was increased from 1 to 2 g/l which completely disappeared MB under 90 min irradiation time.

At same time, decreases of efficiency was observed when the using higher loading of 3 g/l. The main reasons were the increase the turbidity of the suspension TiO₂ catalyst and low light penetration and decreased surface area by agglomeration of catalyst reported earlier studies (Behnajady, 2006; Lathasree, 2004).

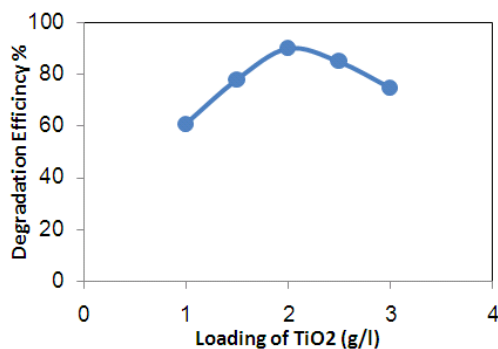


Fig. 3: Effect of the TiO₂ loading on degradation efficiency of MB.

Effect of MB Concentrations:

Different initial concentrations of MB with rang from 12.5 to 50 mg/l were used to evaluate the catalyst activity as shown in Fig.3. The photodegradation efficiency decreases was observed with concentration more than 25 mg/l after 90 min irradiation time. This fact explain as, the adsorption capacity is higher at lower concentration because more active site is available for MB molecules to be adsorbed on the TiO₂ catalyst surface.

At higher concentration which the more and more molecules of MB adsorbed on TiO₂ surface would hinder the hydroxyl radicals generation via adsorption of OH⁻ ions ($H^+ + OH^- \rightarrow \cdot OH$) causes the decrease rate of photodegradation reaction (Augugliaro, 1988; Ba-Abbad, 2013a; Ba-Abbad, 2013b). Therefore, much longer time is required (> 120 minutes) to reach the complete degradation of higher concentrations of MB compared to less than 25 mg/L (Ba-Abbad, 2013c).

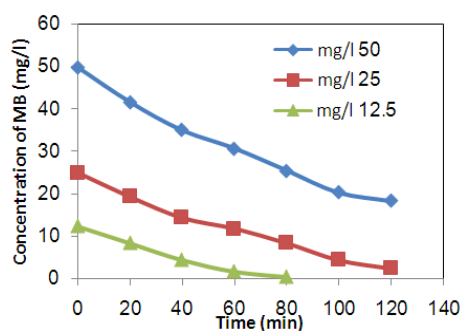


Fig. 4: Effect of concentration of MB on degradation efficiency.

Conclusion:

The photocatalytic degradation of MB was examined using TiO₂ catalyst under direct solar light. Some parameters such as pH of solution, loading of catalyst and concentration were studied for influencing on efficiency of photocatalysis process. A 2 g/l, pH of solution and 25 mg/l concentration were found as optimal conditions of experiment.

The heterogeneous photocatalysis was proved to be as attractive method to remove of pollutants from industrial wastewaters which convert to nontoxic compounds.

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