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Photo catalytic degradation of methylene blue in aqueous solutions using TiO_2 nanoparticles

Majid Aliabadi[1*], Mohsen Hajiabadi[2]

[1]*Department of Chemical Engineering, Birjand Branch, Islamic Azad University, Birjand, Iran*

[2]*Department of Chemical Engineering, Shahrood Branch, Islamic Azad University, Shahrood, Iran*

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Abstract

Colored wastewater from dyeing and textile industry is one of the most important sources of environmental pollution. Using appropriate methods to remove toxic pollutants from industrial wastewater is necessary for the environment. In the present study, photo catalytic degradation of Methylene blue in aqueous solutions using nanoparticles of TiO_2 was investigated. The effects of operating conditions such as initial dye concentration, solution pH, and catalyst loading and different sources of UV irradiation were investigated. The results revealed that catalyst loading of 0.2 g/l was the optimum and further increase in the TiO_2 loading reduced removal efficiency. In addition, higher degradation rate was observed at pH=5. The order of degradation rate using different sources of UV irradiation was shown to be UV-C > UV-A > UV-LEDs.

***Corresponding Author:** Majid Aliabadi ✉ m.aliabadi@iaubir.ac.ir

Introduction

The worldwide environmental pollution is a threat to the life on the earth. Colors used in the textile industry are the biggest group among synthetic colors soluble in water and are in many varieties considering the type and structure of the color (Al-Momani *et al.*, 2002; Azbar *et al.*, 2004). The spread of colored wastewater into the ecosystem prevents the sunlight from penetrating into the lower layers of water and causes disorder in the aquatic life. Some of these colors and products of their decomposition such as aromatic amines are extremely cancerous (Bauer *et al.*, 2001). These colors are usually toxic and resistant to biological decomposition and are not removable by biological treatment processes.

So far different methods such as coagulation, electrochemical oxidation, activated sludge, reverse osmosis and activated carbon adsorption have been studied. However, these methods do not always provide a complete and economic solution and have their merits and limitations in application. New methods such as advanced oxidation processes especially heterogeneous photo catalysis have been offered to degrade various organic compounds. Photo catalytic degradation as an advanced oxidation process can convert a wide range of toxic organic compounds into harmless inorganic matter such as mineral acids, carbon dioxide and water (Wong *et al.*, 2004).

Implementation of photo catalytic methods for the treatment of textile wastewaters has been examined under different conditions (Cesconeto *et al.*, 2002; Tang *et al.*, 2004). Methylene blue is an aromatic heterocyclic chemical composition with the chemical formula $C_6H_{18}CIN_3S$ and the molecular mass 319.86 that turns blue after it dissolves in water (Lachheb *et al.*, 2002). The molecular structure of Methylene blue is shown in Fig.1.

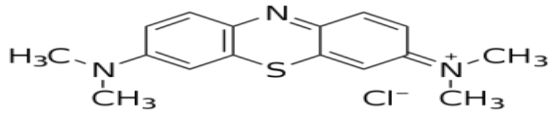

Fig. 1. Molecular structure of Methylene blue.

Titanium dioxide as a semi conductive photo catalyst has been taken into consideration with respect to high chemical stability, cheapness, high photo catalytic activity and non-toxicity. This substance has been used as gas sensors in photochromic tools and as colored sensitized solar cells. It has also been used for degrading different types of compositions with the aid of UV light. The main goal of this study was to investigate the effects of operating conditions such as color concentration, TiO_2 catalyst loading, solution pH and the feasibility of applications of the UV-LEDs as the light source instead of the traditional UV lamps.

Materials and methods

Materials

The catalyst used was P-25 titanium dioxide (TiO_2 80:20% w/w anatase to rutile) with an average particle size of 21 nm and a BET surface area of 50±15 m^2 g^{-1}, supplied by Degussa. The Methylene blue (purity, 99%) was purchased from Merck Co. Ltd. (Darmstadt, Germany). All the other reagents used in this study were analytical grade. Deionized laboratory water was used for making aqueous mixtures.

Experimental and analytical procedures

The experiments were carried out in a slurry batch reactor using 170 mL of the colored solution. In these experiments, different concentrations of Methylene blue (5- 20 ppm) at various catalyst loading (0.05-1 g/l) was aerated and stirred by a steady stream of air. Samples were drawn out from the reactor at desired time intervals during the experiments. The concentration of Methylene blue was determined using a spectrophotometer (Jenway 6305 UV/Vis) by measuring the absorbance at 668 nm wavelength. In this study the removal efficiency of methylene blue was calculated as follows:

$$\text{Removal}\ (\%) = \frac{A_0 - A}{A_0} \times 100$$

where, A_o is the absorbance of the solution before radiation and A is the absorbance of the solution at the time t.

Results and discussion

Effect of catalyst loading

The amount of TiO_2 in the photo catalytic processes is an important factor in the removal of pollutants. Fig. 2. shows the effect of catalyst loading on the removal efficiency of Methylene blue. The experiments were carried out on different amounts of catalyst loading from 0.05 to 1 g/l. As it can be seen, when catalyst loading is increased from 0.05 to 0.2 g/l, the rate of Methylene blue degradation increases. By increasing the catalyst loading more than 0.2 g/l catalyst loading, the removal efficiency decreased due to aggregation of TiO_2 nanoparticles at excess loading, which causes a decrease in the number of surface active sites and increase in opacity and light scattering by TiO2 particles (Ghaly *et al.*, 2011; Kamble *et al.*, 2013). As a result, 0.2 g/l of TiO_2 was selected as the optimum dosage.

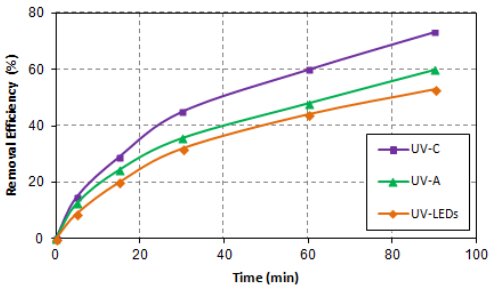

Fig. 2. Effect of TiO_2 loading on the photocatalytic degradation of Methylene blue.

Reaction kinetics shows the information about the rate of reactions and the mechanism of converting reactants into products. Kinetics is determined by concentration of catalyst and substrate. The results of the experiment showed that the photo catalytic degradation of Methylene blue follows first-order kinetics (Table 2.).

Table 2. The effect of TiO_2 loading on the photodegradation rate of Methylene blue solutions.

TiO_2 (g/l)	K_{obs}(min^{-1})	R
0.05	0.014	0.992
0.1	0.010	0.981
0.2	0.013	0.978
0.5	0.012	0.992
1	0.011	0.946

The removal rates of Methylene blue are therefore expressed as:

$$-\frac{dC}{dt} = k_{obs}C \quad (2)$$

Integration of equation (2) results in the following equation:

$$-Ln(\frac{C}{C_0}) = k_{obs}t \quad (3)$$

Where, K_{obs} is the pseudo-first-order rate constant, C is the concentration of Methylene blue at time t, and C_o is the initial concentration of Methylene blue.

Effect of Methylene blue concentration

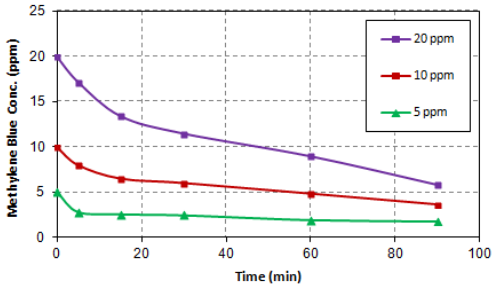

Fig. 3. Effect of methylene blue concentration on photo catalytic degradation.

Fig.3 shows the effect of initial dye concentrations on the removal efficiency of the photocatalytic process. As it can be seen, increasing the dye concentration leads to increasing in the removal efficiency. The effect of the initial concentration of Methylene blue on the degradation rate during the reaction time is presented in Table 3. As can be seen, the highest

photocatalytic degradation rate was occurred in initial concentration of 20 ppm. As a result, the concentration of 20 ppm was selected as the optimum concentration.

Table 3. Effect of initial methylene blue concentration on the photodegradation rate.

Initial conc. (ppm)	K_{obs} (min^{-1})	R
5	0.008	0.671
10	0.011	0.979
20	0.012	0.968

Effect of pH

Solution pH plays an important role in the photocatalytic degradation of Methylene blue. The pH of the solution influences adsorption, catalyst surface charge, oxidation potential, and other physicochemical properties. The effect of pH on the photocatalytic degradation of Methylene blue was examined in the range of pH 3-9 by using initial concentration of 20 ppm and optimum catalyst loading of 0.2 g/l. The effect of pH on the removal efficiency is illustrated in Fig.4.

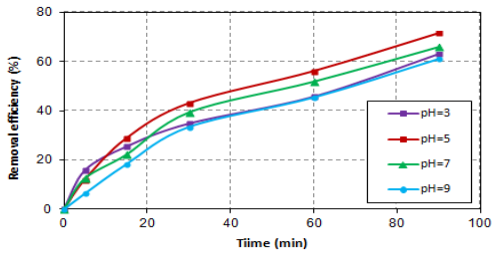

Fig. 4. Effect of pH on the photo catalytic degradation of Methylene blue.

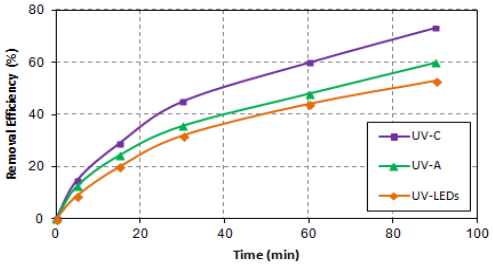

Fig. 5. Effect of different sources of radiation on the photo catalytic degradation of Methylene blue.

As can be seen, the maximum degradation rate of Methylene blue occurs at pH=5.

Table 1. Physical and chemical properties of Methylene blue.

Properties	Value
synonym	methylthionine chloride
Chemical formule	$C_6H_{18}ClN_3S$
Molecular weight	319.86
Melting point	190 °C
Density at 22 °C	1.757 g/cm^3
Solubility in Water at 25 °C	43.6 mg/lit
Maximum wave length	668nm

The first-order reaction rate constants obtained for the photo catalytic degradation of Methylene blue within 90 min irradiation time at different pH values are presented in Table 4.

Table 4. Effect of pH on the photo degradation rate of Methylene blue irradiation time

pH	K_{obs}(min^{-1})	R
3	0.0099	0.969
5	0.0013	0.981
7	0.011	0.983
9	0.010	0.987

Table 5. Effect of different light sources on the photo degradation efficiency of Methylene blue

Light sources	K_{obs}(min^{-1})	R
UV-C	0.013	0.978
UV-A	0.009	0.979
UV-LED	0.008	0.913

Effect of different light sources

The effect of different light sources on the photo catalytic degradation rate is shown in Table 5. and Fig. 5.

The results of experiments indicated that the wavelength of the light used for photo activation has

a significant impact on the dye degradation rate; shorter wavelengths lead to faster degradation. UV-C lamp (254 nm) as a light source resulted in the highest apparent rate constant (K_{obs}=0.013 min^{-1}) in comparison with UV-A lamp (365 nm) and UV-LEDs (400 nm) that may be due to the highest illumination intensity. The degradation rate of Methylene blue using different sources of radiation was as follows: UV-C > UV-A > UV-LEDs

Conclusions

Experimental study was conducted on the photo catalytic degradation of Methylene blue using TiO_2 nanoparticles under UV light radiation. It was observed that initial dye concentration, solution pH, and catalyst loading significantly affect the photo catalytic process. For the configuration used, the optimum ranges of dye concentration (20 mg/l), solution pH (5), and catalyst loading (0.2 g/l) were determined. The order of the degradation rate using different UV radiation sources was shown to be UV-C > UV-A > UV-LEDs. UV-C lamp has the highest apparent rate constant (k_{obs}=0.013min^{-1}) that may be due to the highest illumination intensity. Finally, it can be concluded that photo catalytic process can be used successfully for the treatment of Methylene blue contaminated wastewaters.

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