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Removal of Methylene Blue (MB) Dye from Textile Synthetic Wastewater Using TiO_2/UV-C Photocatalytic Process

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Abstract: Dyes are structurally complex materials which enter the environment due to various textile industry processes like dyeing and cloth completion processes. Methylene blue (MB) is one of the cationic dyes which is now used in textile industry. The aim of this research was to study the efficiency of TiO_2/UV-C photocatalytic process using batch reactor in removing MB from textile synthetic wastewater. In this research, titanium dioxide (TiO_2) nano-particles were used as a photocatalyst in presence of UV-C to remove MB dye. This study was carried out in a batch reactor (useful volume of a sample) on synthetic wastewater with dye concentrations of 15, 30 and 60 mg/L; the effect of some variables including dye initial concentration, TiO_2 nano-particles concentration, radiation time and pH on efficiency of COD and dye removal was studied. Results revealed that removing MB had a direct relationship with radiation time. The best result in removing dye was achieved in concentration of TiO_2=0.9 g/L, pH=3 and time=30 min. As dye concentration increased, speed of dye removal reduced. After dye removal, 47.1% of initial COD decreased too. Photocatalytic process of TiO_2 nano-particles in presence of ultraviolet ray is able to remove dye completely and to reduce COD resulted from dye significantly.

Key words: Photocatalytic process, TiO_2/UV-C, Methylene blue dye, Textile wastewater, Batch reactor

INTRODUCTION

Dyes are a group of complex organic materials which enter the environment due to various processes like dyeing and completion in textile industry. Concerning usages, they are divided into different types of watt, reactive, direct, cationic, acidic, and disperse (Al-Momani, 2002; Xu, 2004). Textile industries produce wastewater with different chemical quality and quantity due to diversity of consumed dyes and production methods. In these industries, a huge amount of colorful wastewater is produced that is usually poisonous, resistant to biodegradation and sustainable in environment; thus, common biological methods aren't effective for removing almost all synthetic dyes due to complex chain structure and dye sustainable nature(Ledakowicz, 2001; Dinçer, 2007). Studies have shown that textile wastewater has low BOD/COD ratio (0.1) which is resulted from non-biodegradability of dyes(Chao, 2002). Discharge of colorful wastewater resulted from textile industries to receiving waters will result in reduced penetration of sunlight, occurrence of eutrophication and interference with receiving water ecology; in addition to decrease photosynthesis of aquatic plants and algae in aqueous environments, it damages environment(Arslan, 2000; Sauer, 2002; Nilsson, 2006). To remove dyes from wastewater, physical, chemical, biological or compound methods can be used. Since dyes are sustainable to bio-degradation, physical and chemical methods like flocculation-coagulation, surface absorption, chemical oxidation and membrane processes are used (López 2004; Tang 2004). Removing pollutants in advanced oxidation process is based on production of Hydroxyl free radicals ($OH^{\bullet}$) with high oxidation power which

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changes most organic chemical compounds to mineral materials (Al-Momani, 2002). These radicals are unstable and completely active and are produced through chemical or photochemical reactions. Free radicals are powerful oxidants and attack molecules of organic materials rapidly and separate a hydrogen atom from structure of organic material (Ledakowicz, 2001; Asadi, 2006; Zahraa, 2006). Advanced oxidation process has significant benefits in comparison with other common treatment methods. However, high expenses related to consumed reactors or required energy are some of its disadvantages. This process can effectively remove dyes (Azbar, 2004; Lucas, 2006). Photocatalytic degradation of dyes using titanium dioxide catalyst along with ultraviolet ray is one of advanced oxidation methods which is being used widely (Jafari, 2004). TiO_2 nano-particles are used in two methods of fixed phase and solution phase as photocatalyst. Both have their own special advantages. Solution phase, however, removes more pollution concentrations compared to the fixed phase. But, since TiO_2 remains in wastewater after treatment, it should be separated from the solvent (Poudyal, 2002). Application of these nano-particles in presence of ultraviolet is one of advanced oxidation processes which has been used in this research to remove MB dye.

MATERIAL AND METHODS

This study is an applied-experimental research which was performed in laboratory scale and in environmental chemistry laboratory of Yazd University of medical sciences. MB dye used in this research is the product of German Merck Company; TiO_2 nano-particles are the product of German Degussa Company (table 1) and other chemical materials used in these experiments are the product of German Merck Company. Properties of MB dye used in this research have been presented in table 2 (Lachheb, 2002; Lee, 2003; Wainwright, 2006).

Ultra sonic bath (Starsonic 18-35, Italy) was used to TiO_2 suspension uniformity. Ultraviolet (UV-C) with two 15-watt lamps (Philips Model) was used as a source of ultraviolet radiation. Peristaltic Pump (OEM Model) and Dolphin EP-30 air pump in reactor were used respectively to circulate and air injection. A plexiglas reactor with a concentric quartz cylinder was used for this experiment. Ultraviolet lamps were placed inside the quartz cylinders. At the end of every step, to remove TiO_2 particles, Buchner funnel with appropriate vacuum device (vacuum pump, model J/B Aurora, IL 60507) and Cellulose nitrate membrane filter (from Sartorius, ø 50 mm), pores ø 0.2 µm were used. Concentration of dye was evaluated using spectrophotometer (UV/Vis Optima SP-3000 Plus, Japan) and COD was evaluated using open reflex method (Clesceri, 2000).

TiO_2 nano-particles were used as catalyst in the presence of UV-C. It was carried out in a batch reactor on synthetic wastewater with concentrations of 15, 30 and 60 mg/L of MB dye. To control temperature of liquid inside the reactor, a glass chamber was used. It was bigger than the reactor and was used as a temperature regulator chamber. To do this, the reactor was placed into the chamber so that cold water flow enters the cooling chamber through the entrance and exits from the other side (Fig.1).

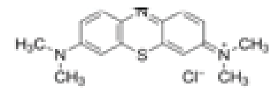
In this research, effect of photocatalyst concentration, pH, dye concentration, and reaction time were examined in dye removal efficiency. Since in various studies different maximum wavelengths have been mentioned for MB dye, to determine maximum wavelength of the given dye (λ_{max}), UV/Vis spectrophotometer was used, and MB dye absorption spectrum was prepared in the scope of 200 to 800 wavelength; based on the resultant absorption spectrum, the λ_{max} of the given dye was determined to be 640 nm (Fig. 2).

Concerning maximum absorption wavelength for the studied dye (λ_{max} =640nm), concentration of dye was evaluated using a standard curve prepared with concentrations of 5, 10, 15, 20, 25 and 30 mg/L (Çiçeka, 2007). In this research, the selected samples were tested randomly in three replications for degradation of dye and examining the effect of other factors in the study; the results are based on the mean of these replicates. To analyze data, median, data standard deviation and correlation test were used.

Table 1: Chemical and physical properties of TiO_2 nano-particles

Characteristics	Unit	Common amount
Specific surface area	m^2/g	50±15
Average initial particle size	nm	21
pH (in 4% mixture)	------	3.5-4.5
Purity degree	%Weight	≥99.5
Al_2O_3	%Weight	≤0.3
SiO_2	%Weight	≤0.2
Fe_2O_3	%Weight	≤0.1

Table 2: Characteristics of methylene blue dye (MB)

Chemical structure	
Type of dye	Cationic
Symbol	MB
Molecular formula	$C_{16}H_{18}N_3SCI$
Molecular weight (g/mol)	319.85
Maximum absorption wavelength (nm)	640

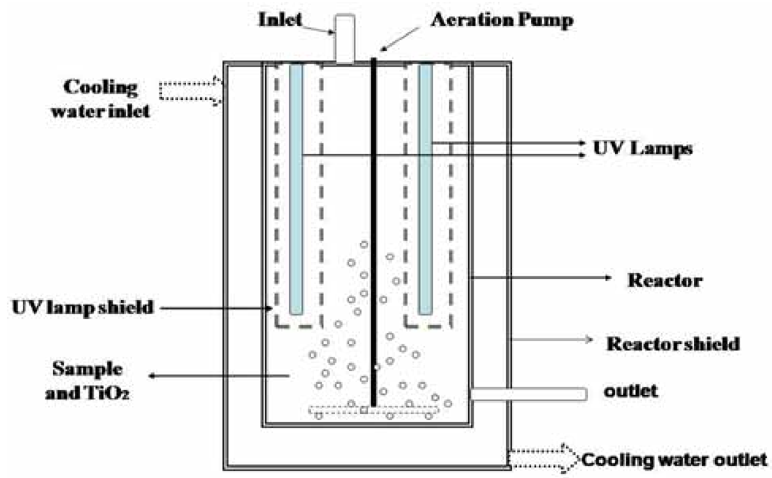


Fig. 1: discrete photocatalytic reactor

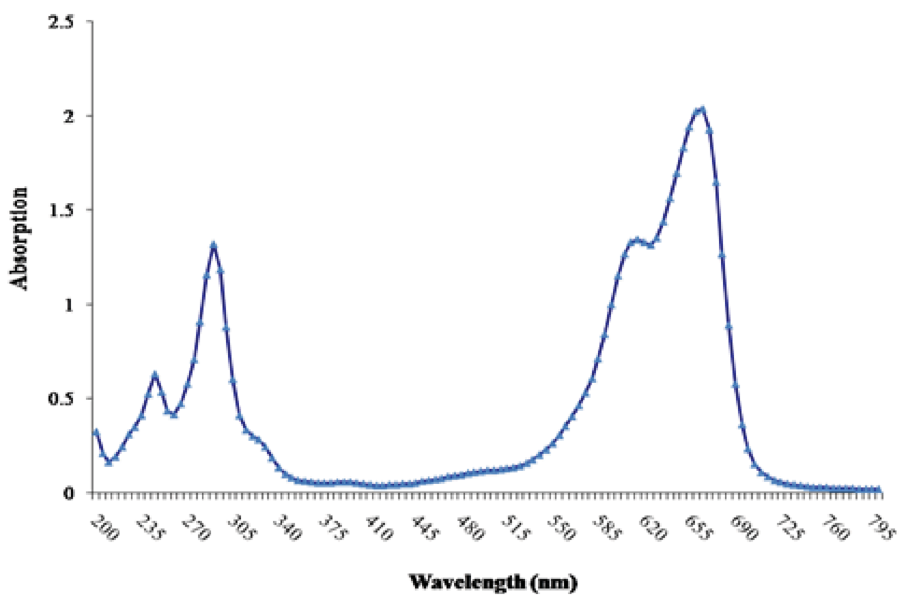


Fig. 2: MB dye absorption spectrum Fig. 3: Effect of TiO_2 concentration on removing dye and COD resulted from MB (dye concentration: 60 mg/L; time: 30min; pH: 3)

RESULTS AND DISCUSSION

To determine the concentration of suitable TiO_2 and its application in removing dye and COD, sample of synthetic wastewater with concentration of 60mg/L and pH =3 was prepared and was placed in the presence of concentrations of 0.3, 0.6, 0.9, 1.2 g/L of TiO_2 for a period of 30 min under the effect of UV-C and photocatalytic process; its data is presented in Fig. 3. According to this figure, as TiO_2 concentration increases, efficiency of removing dye and COD increases too so that for 0.9 g/L of TiO_2 concentration, efficiency of removing dye and COD is 92.2 and 38% respectively; no huge difference can be found in comparison with 1.2 g/l of TiO_2 concentration.

To determine the effect of initial concentration of MB on efficiency of photocatalytic process, dye solution was prepared with concentrations of 15, 30 and 60 mg/L and 0.9 g/L concentration of TiO_2 and pH=3 and was placed for a period of 0 to 30 min in contact with UV-C rays; the results have been presented in Fig. 4. Concerning the efficiency figure, dye removal for synthetic wastewater with initial concentrations of 15, 30 and 60 mg/L and time of 30 min was 99, 98.5 and 92.2 respectively.

Concerning the Fig. 5, removing MB in neutral pH has less efficiency in comparison with acidic (pH: 3) and alkali (pH: 11) conditions. Thus, efficiency of removing dye for synthetic wastewater with initial concentration of 60 mg/L and 30 minutes of time and 0.9 g/L concentration of TiO_2 in pH=3 was 92.2 and in pH=11 was 87.

Comparing efficiency of dye removal in pH=3 for different concentrations of TiO_2 showed that as photocatalyst concentration increases, dye removal increases; but, dye removal efficiency in concentrations of 0.9 and 1.2 had some slight differences. Therefore in this step, effect of concentration of 0.9 g/L of TiO_2 in removing dye and COD resulted from MB with concentration of 60 mg/L was examined and the results have been shown in Fig.6. Concerning the figure, efficiency of removing dye and COD in 15 min was 55% and 18% respectively and it was 92.2 and 38 respectively for 30 min.

Photocatalytic process is a kind of advanced oxidation process; due to low price of treatment operation in comparison with other processes, this process is a great importance for removing organic pollutants. TiO_2 is a relatively cheap and non-poisonous material which is insoluble in water. Due to the importance of removing dye from textile industries wastewater in this research, efficiency of TiO_2 photocatalytic process in removing MB dye, which is now used in textile industries of Iran like blanket making industries, was examined in a batch reactor. In this research, effect of various parameters such as various concentrations of TiO_2 in removing MB was examined. Effect of various concentrations of TiO_2 on the efficiency of removing dye and COD has been shown in Fig.3. Results of this research showed that as TiO_2 concentration increased, decreased initial concentration of dye and increased reaction time of removing dye and COD increased too; they are in agreement with the results of the same studies (An, 2002; Yang, 2005). According to the present study, efficiency of removing dye and COD for concentration of 0.3 g/L of TiO_2 was 49.5 and 6 percent respectively and for concentration of 1.2 g/L was 97 and 42 percent respectively. As shown in Fig.4, increased photocatalyst concentration affects the increased efficiency. Therefore, if photocatalyst concentration increases more than the optimum level, it causes negative effects on the efficiency because catalyst particles inhibit the penetration of optical photons (Kuo, 2001). Results of the present study revealed that dye removal efficiency increased as reaction time increased and as dye concentration decreased; they are in good agreement with the results of the research carried out by Ling et al in 2004. Based on these results, high amounts of dye is absorbed on TiO_2 nano particles in higher concentrations, inhibiting the reaction of dye molecule with free radicals and electron holes. Thus, in higher concentrations of dye, removal efficiency has been decreased (Ling, 2004). As dye concentration increases, transfer of optical photon decreases because optical photons are absorbed by dye before reaching catalyst particles. Also, as concentration and creation of color clots increases, competition for absorbing on substrata increases to; in other words, photocatalyst gets trapped in color flocs (Chakrabarti, 2004). Hoas (2001) reported that MB had the best removal status in neutral and acidic conditions.

For TiO_2 has negative charges in acidic status; and since MB is a cationic dye, dye is absorbed by photocatalyst in these conditions. In alkali conditions, however, TiO_2 gets positive charges and it causes repulsion between photocatalyst and dye (Hoas, 2001). Lee (2002) proposed a different theory and said that since pH_{ZPC} of TiO_2 is about 6.4 in normal status, when pH is less than 6.4, TiO_2 absorbs negative particles but when pH goes higher than 6.4, absorption of negative particles on photocatalyst becomes difficult due to electrostatic repulsive force (Li, 2002). TiO_2 is a suitable photocatalyst and a good substitution for purifying organic pollutants in the recent years; making use of this material is a good and effective technique for complete destruction of undesirable pollutants in liquid and gas phases using artificial light or sun light. Since TiO_2 used as a photocatalyst in this method is spreadable and recyclable, it can be said that UV/TiO_2 process is an environmentally friendly method for removing dye.

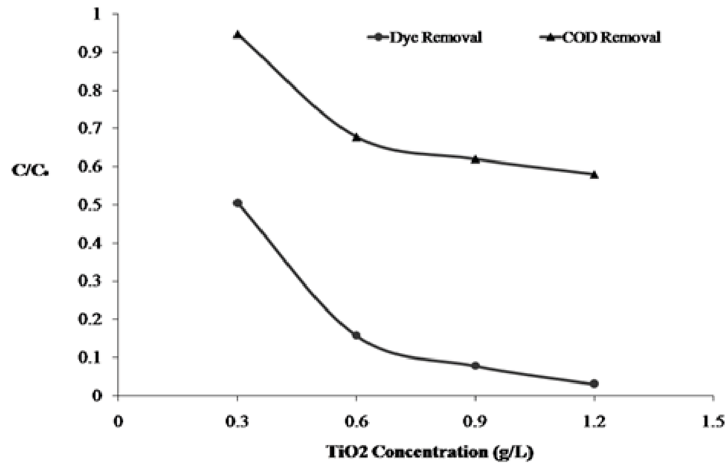


Fig. 4: Effect of dye initial concentration on removing MB dye (TiO_2 concentration: 0.9 g/L; pH: 3)

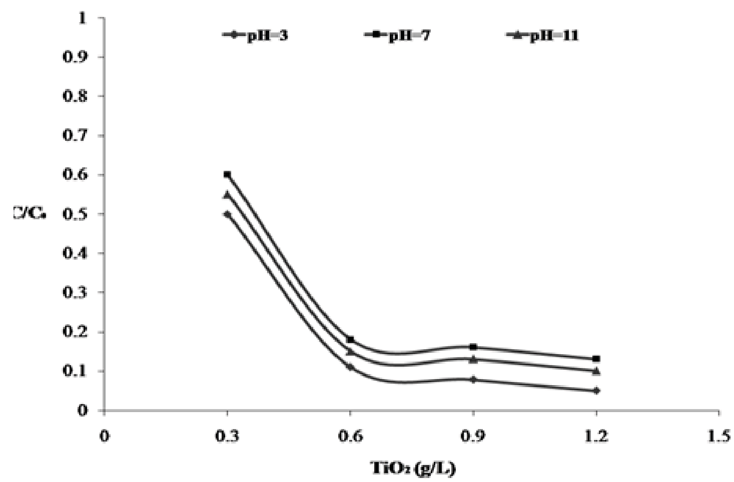


Fig. 5: effect of pH on removing MB dye (dye initial concentration=60 mg/L; time=30min)

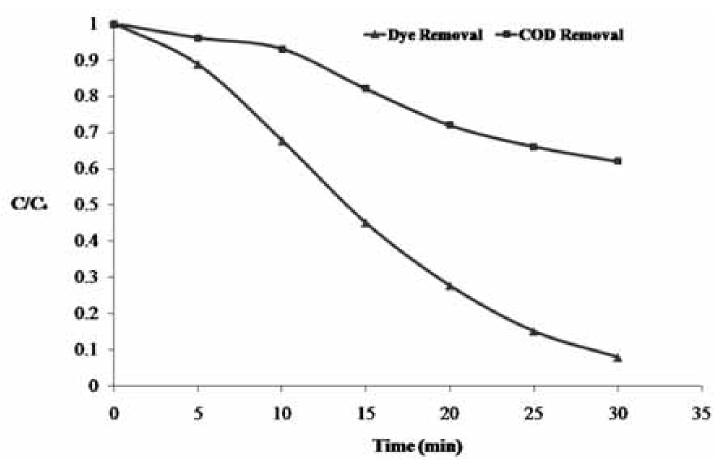


Fig. 6: Effect of reaction time on removing dye and COD resulted from MB (TiO_2 concentration: 0.9 g/L; dye initial concentration: 60 mg/L; pH: 3)

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