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REMOVAL OF METHYLENE BLUE DYE FROM TEXTILE SIMULATED SAMPLE USING TUBULAR REACTOR AND TiO_2/UV-C PHOTOCATALYTIC PROCESS

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ABSTRACT
In this study, photocatalytic degradation of methylene blue was examined using different concentrations of TiO_2 nano-particles (diameters less than 21 nm) and ultraviolet (UV-C) radiation in a tubular reactor. Different concentrations of catalyst (0.3-1.2 g/L), different pH conditions (3, 7 and 9) and dye concentration (15, 30 and 60 mg/L) as well as sample rotation level (125 mL/min) were studied. The sample passed 1-7 times through the quartz reactor exposed to UV-C ray (constant intensity = 2.8 mW/cm^2) (every rotation time was 8 min). Results of this research showed clearly that methylene blue is significantly degradable by TiO_2 and UV-C radiation. Increasing dye concentration resulted in decreased efficiency and thus, as more samples passed through quarts tube, removal efficiency increased. Methylene blue with concentration of 15 mg/L and after 7 rotations in the reactor (56 min) was removed with the efficiency of 98%. Subsequent to dye removal, 47% of initial COD decreased simultaneously.

Key words: Tubular reactor; TiO_2 photocatalytic process; Methylene blue; Dye

INTRODUCTION
Paper, dyeing, plastic and textile industries use color for dyeing their products and thus use a huge amount of water which results in the production of a dye-containing wastewater with hazardous effects on the environment (Lachheb, 2002; Gregorio, 2006; Sreedhar, 2006; Bidhendi, 2007). At present, 100000 different types of dyes with annual production rate of 7×10^5 are produced. Among them textile industries consume about 36000 ton/year dye, 10 to 20 percent of which remains in wastewater (Espulgas, 2002; Gregorio, 2006). Degradation of organic materials existing in the environment which occurs according to the above process with radiation of ultraviolet on the surface of titanium dioxide is called photocatalytic reaction of TiO_2 (Awitor, 2008; Vijay, 2009). Basis of TiO_2/UV photocatalytic process is the semi-conduct optical stimulation of TiO_2 as a result of electromagnetic ray absorption. TiO_2 has an energy band of 3.2 eV which can be activated by radiation of UV in the wavelength of 387.5 nm. On the earth surface, sunlight begins in the wavelength of 300 nm and only 4-5 percent of solar radiation

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may be used by TiO_2 .
In photocatalytic reactions, surface area and number of active places used by the catalyst for absorbing pollutants, play an important role in degradation level. Among known catalysts like ZrO_2, ZnO and TiO_2, high efficiency of TiO_2 has been approved and confirmed in many studies. TiO_2 is not poisonous and has high stability and very good performance and is also cheaper (Fujishima, 2000; Awitor, 2008).
An advantage of photocatalytic method includes low temperature, low expenses and also radically low level of energy consumption in this method. These factors have caused the photocatalysts to be used in commercial scales (Rezaee, 2008; Rajeswari, 2009).
A significantly great number of researches and articles have been published regarding removal of dangerous and poisonous compounds from water, wastewater and air, using photocatalytic methods, which imply the importance of the mentioned method in removing pollutants (Chen, 2003; Gao, 2008; Xiu, 2009; Zhang, 2010).
The aim of this research was to study the efficiency of TiO_2/UV-C photocatalytic process using tubular reactor in removing methylene blue from textile synthetic wastewater.

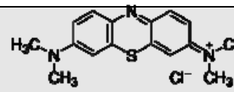
MATERIALS AND METHODS

This study was an applied-experimental research which was performed in laboratory scale in the environmental chemistry laboratory of Yazd University of Medical Sciences. Methylene blue (MB) dye used in this research was a product of German Merck Company; TiO_2 nano-particles were provided from German Degussa Company (Table 1). Other chemical materials used in these experiments were purchased from Merck Company, Germany.
Properties of MB dye used in this research are presented in Table 2 (Lachheb, 2002; Lee, 2003).
Ultrasonic bath (Starsonic 18-35, Italy) was used for TiO_2 suspension uniformity. Ultraviolet (UV-C) with two 15-watt lamps (Philips Model) was used as the source of ultraviolet radiation (with constant intensity = 2.8 mW/cm^2). Peristaltic pump (OEM Model) and Dolphin EP-30 air pump were used respectively for air circulation and injection. Sample (synthetic wastewater) storage tank was made of quartz. At the end of every step in order 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). The experiments were carried out in a tubular reactor for synthetic wastewater with concentrations of 15, 30 and 60 mg/L of MB. The reactor consisted of three different parts: UV source, reaction tube and mixture chamber. UV source consisted of two lamps (15 W); reaction tube was placed in a parallel way between two lamps and the tube was built of quartz (diameter: 15 mm and length: 460 mm), (Fig. 1).
A peristaltic pump pushed the sample through the reaction tube with discharge rate of 125 mL/min. The capacity of storage tank was 1L. Lamps and reaction tube were covered by aluminum foil in order to prevent ray dispersion. Also, mixture chamber was aerated and mixed by the pump. In this research, effect of different pH conditions, photocatalyst concentration, dye concentration, number of sample rotations and aeration level, on

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	%w	≥99.5
Al_2O_3	%w	≤0.3
SiO_2	%w	≤0.2
Fe_2O_3	%w	≤0.1

Table 2: Characteristics of methylene blue dye

Chemical structure	
Type of dye	Cationic
Symbol	MB
Molecular formula	$C_{16}H_{18}N_3SCl$
Molecular weight (g/mol)	319.85
Maximum absorption wavelength	640

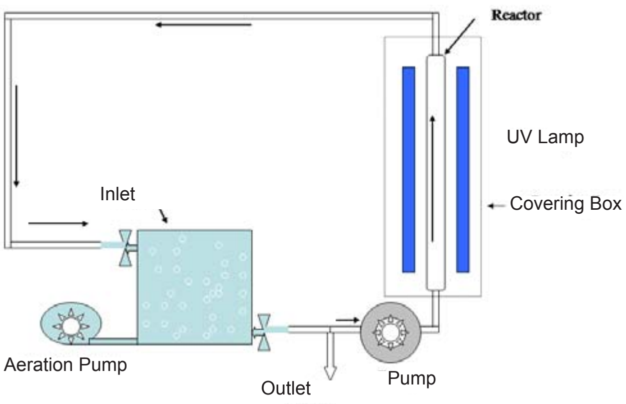


Fig. 1: Tubular photocatalytic reactor with rotatory flow

dye removal efficiency were studied.

The temperature was almost constant during the experiments (23–24°C). Since in various studies, different maximum wavelengths have been mentioned for MB dye, in order to determine the 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 nm; based on the resultant absorption spectrum, the λ_{max} of the

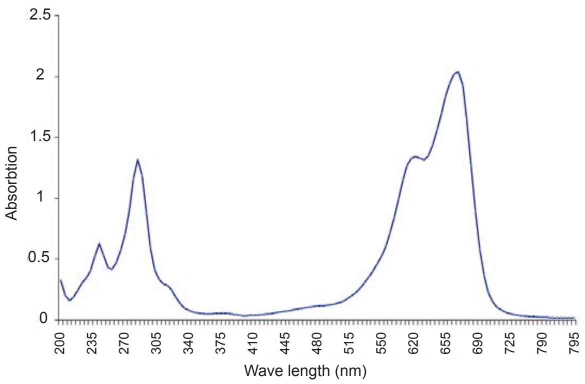


Fig. 2: MB dye absorption spectrum

given dye was determined to be 640 nm (Fig. 2). Other part of the experiments was done to study the effect of rotation level of sample on removal efficiency. Pump discharge rate was regulated on 125 mL/min; in other words, after 8 minutes, total volume of the sample passed through the quartz reactor. To determine the effect of rotation on efficiency of dye removal, the passage of the sample was examined 1-7 times separately. The effect of aeration on the removal efficiency was also examined. For this purpose 0.5, 1 and 2 cm^3 air was injected into the reactor by the pump.

RESULTS

Effect of pH

Experiments were carried out in different pH conditions (3, 7 and 9). Results are given in Fig. 3 and show that as pH increased, the efficiency of catalyst for degrading dye decreased as well.

Effect of TiO_2 concentration on MB and COD

In order to study the effect of various concentrations of photocatalyst, the experiment was carried out with different concentrations of photocatalyst (0.3-1.2 g/L, in accordance with

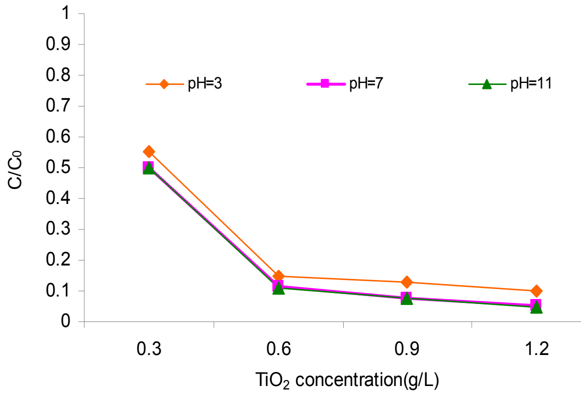


Fig. 3: Effect of different pH on dye removal

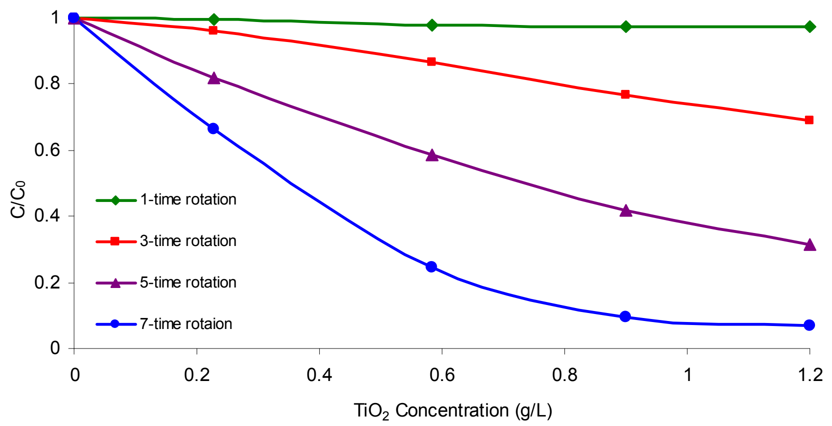


Fig. 4: Effect of different TiO_2 concentration (MB=60 mg/L; pH=7)

similar study) and rotation flow of 125 mL/min. Results are give in Fig. 4, which show that when TiO_2 concentration increased to 0.9 g/L, dye degradation increased as well. For higher concentrations exceeded 0.9 g/L, opacity resulted from TiO_2 powder increased in the reactor and penetration of UV ray into the reactor, decreased.

Effect of MB concentration
Experiments were carried out in different MB concentrations (with TiO_2=1.2 g/L and pH=7). Results are given in Fig. 5 and show that as dye concentration increased, the efficiency of catalyst for degrading dye decreased as well.

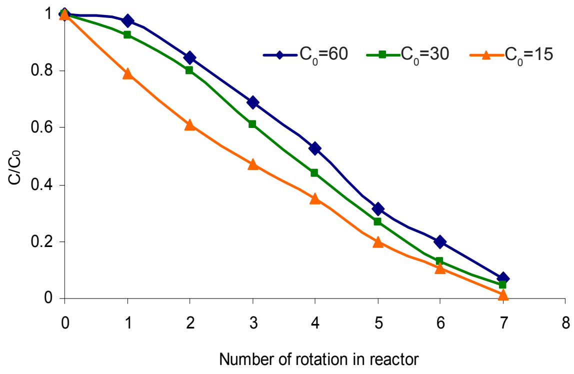


Fig. 5: Effect of different MB concentration (TiO_2=1.2 g/L; pH=7)

Effect of rotation in the tubular reactor
Fig. 6 shows that as rotations increased, level of MB degradation increased radically and after 56 minutes (7 rotations) degradation reached its maximum.

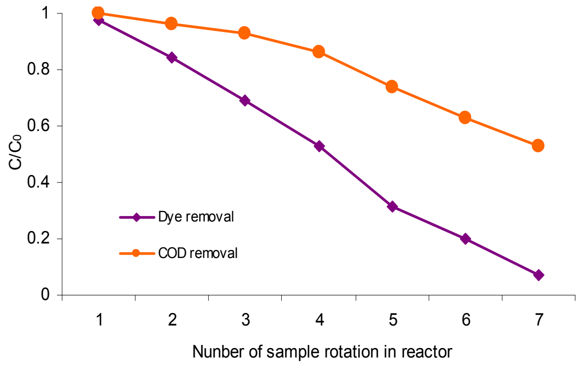


Fig. 6: Effect of rotation in the tubular reactor (TiO_2=1.2 g/L; MB=60mg/L; pH=7)

Effect of aeration rate
As shown in Fig. 7, in 56 minutes (7 rotations), with 2 m^3/s aeration, removal efficiency with initial concentration of 60 mg/L was 93%, comparing to 71% in non-aeration condition.

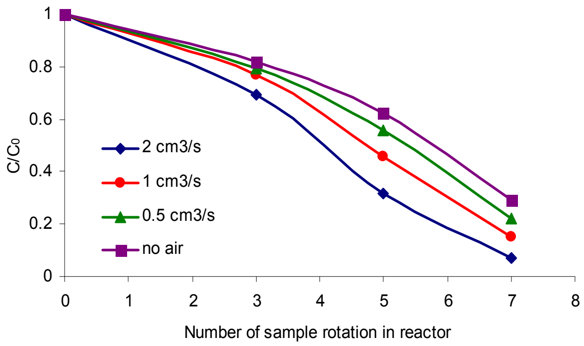


Fig. 7: Effect of aeration on dye removal efficiency (TiO_2=1.2 g/L; MB=60 mg/L; pH=7)

DISCUSSION

Effect of pH

As shown in Fig. 3, the degradation rate of MB increased with increase in pH; however, the difference was not significant between 7 and 9. Consequently, pH=7 was selected as the optimum value. Optimum pH values for photocatalytic degradation according to different studies have been reported between 1.5 and 11 (Yu, 2007; Saquiba, 2008). Akpan stated that in alkaline condition, OH° are easier to be generated by oxidizing OH available on TiO_2 surface, therefore the efficiency is increased (Akpan, 2009). On the other hand in alkaline condition there is a Coulombic repulsion between the negative charged surface of photocatalyst and the hydroxide anions. This status could prevent the OH° formation and therefore decline the photoxidation process (Fox, 1993).

Effect of TiO_2 concentration on MB and COD removal

As it is shown in Fig. 4, after seven rotations dye degradation reached 90% with concentration of 0.9 g/L. No significant difference was found between removal efficiency in two concentrations of 0.9 and 1.2 g/L. The optimum TiO_2 concentration range for photocatalytic degradation of dyes in various studies have been reported between 0.055 (Liu, 2006) to 12.5 g/L (Sun, 2006). Generally, increase in concentration of TiO_2 increases the number of active sites on the photocatalyst surface, which in turn increases the number of OH° radicals. Besides, when the TiO_2 concentration increases to higher than the optimum value, the degradation rate declines due to the interference of the light by the suspension (Chakrabarti, 2004; Konstantinou, 2004).

Effect of MB concentration

As it is shown in Fig. 5, with increasing MB concentration the efficiency of catalyst for degrading dye decreased. When dye concentration increases, number of dye molecules absorbed on catalyst surface increases too (Lee, 2003). Also, increased concentration results in reduction of UV radiated on photocatalyst particles and also reduction in production of OH°; finally, it causes reduced efficiency of dye removal (Toor, 2006).

Effect of rotation and aeration rates

As shown in Figs. 6 and 7, the increase in rotation and aeration rates has helped in increasing the efficiency of process higher, which may be due to more exposure of sample to UV, more mixing and higher reaction of photocatalyst with the dye. In photocatalytic process, electron is produced by optical photons and creation of holes in photocatalyst surface. Oxygen is one of the most abundant and the cheapest gas which, in this process, can trap electrons in hydroxyl radical. Therefore, solvent oxygen available in sample can significantly increase removal efficiency. Concerning hydroxyl radical formation, it has been proved that creation of electron holes and production of free electrons are the main reasons of formation of these active radicals. Available solvent oxygen increases the production of hydroxyl radical(Ming, 2000).

As solvent oxygen increases, MB $(H_2)^+$ formation increases as well. Mils showed that low surface area of solvent oxygen has a negative effect on removal efficiency. In other words, in small oxygen surfaces, methylene blue is oxidized and tends to restore again and change to MB (Mills, 1999).

Overally, results of this study showed that this process may be considered as an alternative for dye removal.

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