

## Comparing the photocatalytic process efficiency using batch and tubular reactors in removal of methylene blue dye and COD from simulated textile wastewater

Sajad Rahimi, Ali Poormohammadi, Behnam Salmani,  
Mohammad Ahmadian and Mina Rezaei

### ABSTRACT

The aim of this study was photocatalytic degradation of methylene blue (MB) dye using titanium dioxide nanoparticles simulated using ultraviolet in batch and tubular reactors. In this study, the effect of different concentrations of titanium dioxide nanoparticles in the photocatalytic process on MB degradation was examined in batch and tubular reactors. The effect of dye concentration, titanium dioxide nanoparticle concentration and aeration level were examined on the process efficiency. Results showed that the removal of MB dye was directly related to the radiation time. The best removal efficiency of dye and chemical oxygen demand (COD) in the batch reactor was 100% and 42.2%, respectively, while it was 93% and 47.8% in the tubular reactor (in 1.2 g/L of titanium dioxide nanoparticles at 60 min). Moreover, as dye concentration increased, dye removal rate decreased. Making use of the batch model to remove dye and COD is more efficient and can be used on a larger scale due to the required removal efficiency and wastewater discharge standards.

**Key words** | batch reactor, methylene blue dye, photocatalyst, photocatalytic, titanium dioxide, tubular reactor

**Sajad Rahimi**

**Behnam Salmani**

Social Development and Health Promotion  
Research Center,  
Kermanshah University of Medical Sciences,  
Kermanshah, Iran

**Ali Poormohammadi**

Department of Environmental Health Engineering,  
Faculty of Health,  
Hamadan University of Medical Sciences,  
Hamadan, Iran

**Mohammad Ahmadian**

Department of Environmental Health Engineering,  
School of Public Health, Bam University of Medical  
Sciences,  
Bam, Iran

**Mina Rezaei** (corresponding author)

Iranian Academic Center for Education, Culture  
and Research (ACECR), Branch of Amirkabir,  
Iran  
E-mail: m.rezaei\_eng@yahoo.com

### INTRODUCTION

Textile industries use large amounts of water (Neppolian *et al.* 2002) and are the major consumers. The amount of water consumed in these industries is between 25 and 250 cubic meters per ton of product (according to the type of production process) (Marković *et al.* 2015). Dyes are a group of complex organic matters which enter the environment as a result of various activities such as dyeing and completion in textile industries (Moussavi *et al.* 2013). An ideal way to treat water and wastewater involves degrading all toxic materials without discharging harmful materials from the treatment process, which must be effective regarding expenses and resources. Biological treatment, aeration, adsorption on activated carbon, burning and ozonation processes are practically ineffective in the treatment and removal of resistant organic materials because these

materials are resistant to biodegradation and are not degradable. These methods are expensive, and the oxidation processes are not sufficient for degrading various pollutants. In addition, the production of toxic byproducts and environmental risks are other considerations discussed in this regard (Patel *et al.* 2015). Based on their usages, these materials are categorized into watt, reactive, direct, cationic, acidic and disperse types (Azbar *et al.* 2004; Xu *et al.* 2004). Textile industries produce wastewaters with chemical quality and quantity due to dye variations and production methods. In these industries, large quantities of dyeing wastewater is produced that is often toxic, resistant to biodegradation and stable in the environment. Due to the complex cyclic structure and resistant nature of dyes, common biological methods are not effective in the removal

of most synthetic dyes (Dinç *et al.* 2007; Soares *et al.* 2015). Studies have shown that textile wastewater has low biochemical oxygen demand (BOD) to chemical oxygen demand (COD) ratio (0.1) which is as a result of the non-biodegradable nature of dyes (Sauer *et al.* 2002). Discharge of dyeing wastewater from textile industries to receiving waters results in reduced sunlight penetration, eutrophication and interference in the ecology of receiving waters. In addition to affecting the intensity of photosynthesis of aquatic plants and algae in the aqueous environment, it damages the environment (Zhan & Tian 1996; Nilsson *et al.* 2006; Samadi *et al.* 2015). These factors have led to the increased tendency to use photocatalysts commercially and on a large scale (Poudyal & Clark 2002; Jafari 2004; Seid-Mohammadi *et al.* 2016). A large number of studies have been recently carried out on the removal of dangerous toxic compounds from air, water and wastewater using photocatalytic methods (Clesceri Lenore *et al.* 2000; Lachheb *et al.* 2002; Lee *et al.* 2003; Wainwright & Byrne 2006). Previous studies have shown the importance of the above-mentioned method of removal of pollutants (Lachheb *et al.* 2002; Jafari 2004). The photocatalytic process is a type of advanced oxidation process. It is considered as an important process for removing organic pollutants due to its low cost of treatment operation. Photocatalytic decomposition of dye using titanium dioxide catalyst along with UV is one of the advanced oxidation methods which is increasing in application (Poudyal & Clark 2002). TiO<sub>2</sub> nanoparticles are used as a photocatalyst in two stationary phase and solution phase methods. Both techniques have their own advantages. However, the solution phase removes more concentration of pollutants than the stationary phase, but it must be separated from the solution because titanium dioxide remains in the effluent after treatment (Lachheb *et al.* 2002). Titanium dioxide is a relatively inexpensive material which is non-toxic and insoluble in water. The titanium dioxide photocatalytic process is currently used in Iranian textile industries such as blanket-weaving industries, in both batch and tubular reactors. The aim of this study was to evaluate and compare two tubular and batch reactors as well as to examine the possibility of using the photocatalytic system to help titanium dioxide with ultraviolet (UV-C) radiation for removing methylene blue (MB) dye and COD from synthetic wastewater.

## MATERIALS AND METHODS

### Materials

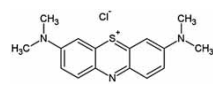
Devices used in this study included a pH meter (Hach-HQ40D), an ultrasonic bath (Starsonic 18–35, Italy), a 15-watt UV-C lamp (Philips) with an irradiation intensity of 22.5  $\mu\text{W}/\text{cm}^2$ , a peristaltic pump (OEM Model), an air pump (Dolphin EP-30), a magnetic stirrer (Frago Hs 102) and a spectrophotometer (UV/Vis, Optima SP-3000 Plus, Japan). Chemicals used in this research were MB dye (Merck Co., Germany) (Table 1) and titanium dioxide (Degussa P25) of Anatas Type made in Germany (in the form of powder) (Figure 1). Other chemicals were purchased from Merck Co.

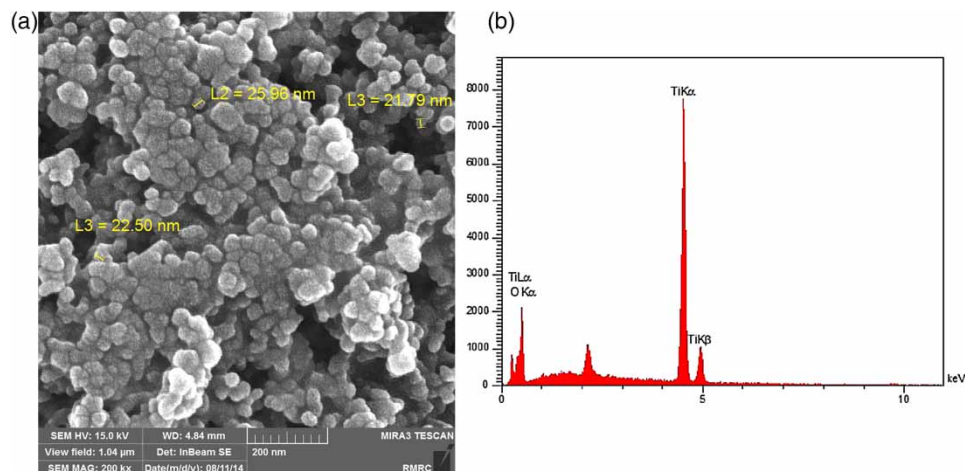
### Preparation of batch and tubular reactors

To make the batch reactor, a cylindrical glass chamber with a useful volume of 1 L was used. In order to control the temperature of the liquid inside the reactor, a larger Plexiglas chamber in the shape of a cubic column was designed and used as a temperature regulator chamber. The reactor was placed inside the chamber, so cold water could enter the cooling chamber through the inlet and could exit from the other side. UV lamps were first placed inside a quartz tube and were then immersed inside the reactor using arms; thus, the lamp could be used in a submerged form and sufficient contact was obtained with the liquid inside the reactor (Figure 2).

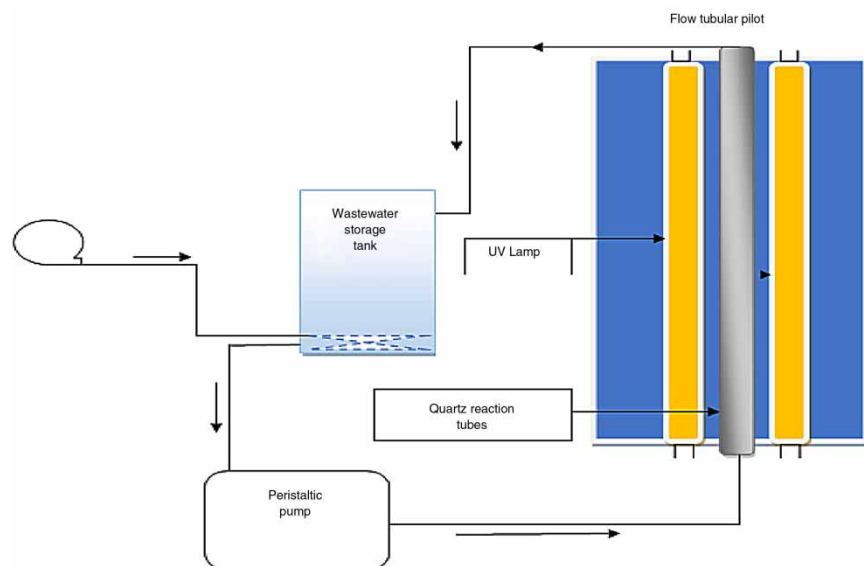
To make the tubular reactor, cubic Plexiglas was used as a sample storage chamber; a tubular quartz glass with a volume of 81.2  $\text{cm}^3$  was used as a reaction tube, which

**Table 1** | Characteristics of MB dye

Parameter	Value
Chemical structure	
Dye type	Cationic
Abbreviation	MB
Chemical formula	C <sub>16</sub> H <sub>18</sub> N <sub>5</sub> ClS
$\lambda_{\text{max}}$ (nm)	640
Molecular weight (g/mol)	319.85



**Figure 1** | Characterization of TiO<sub>2</sub>. (a) Scanning electron microscopy (SEM); (b) energy dispersive X-ray spectroscopy (EDX).

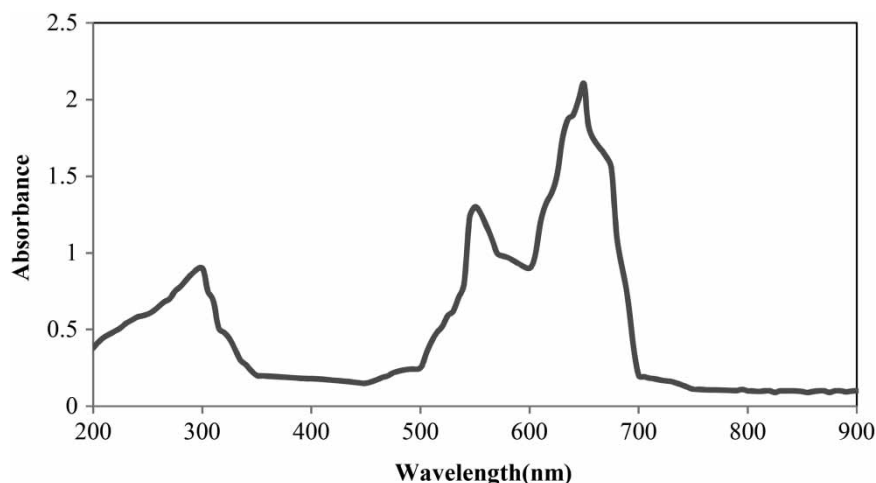


**Figure 2** | Batch and tubular reactors used in this study.

was placed between two UV lamps (diameter: 15 mm; length: 460 mm). The reactor's useful volume was 1,000 mL. In both reactors, two 15-watt lamps were used. The aeration method was used to mix the samples inside the reactor. A peristaltic pump guided the sample from the mixture tank with a discharge of 125 mL/min. Therefore, it took the sample 8 minutes to completely pass through the tube. To prevent the scattering of radiation in the laboratory, the reactor was covered with an aluminum plate. The

ultrasonic bath was used to ensure uniform TiO<sub>2</sub> suspension (Cıçek *et al.* 2007).

Since the wavelength of maximum adsorption of MB dye is different in various articles, the spectrophotometer UV/Vis was used to determine the wavelength of maximum dye adsorption ( $\lambda_{\text{max}}$ ); the adsorption spectrum of MB dye was prepared at the range of 200–800 nm. Based on the obtained absorption spectrum,  $\lambda_{\text{max}}$  of the above-mentioned dye was 640 nm (Figure 3).



**Figure 3** | Adsorption spectrum of MB dye.

## Study variables

Variables examined in this study included pH, contact time, concentration of titanium dioxide, concentration of MB dye, reactor type and COD. Experiments were carried out at a pH of 3, 7 and 11 and at a contact time of 5, 15, 30 and 60 minutes. Various concentrations of titanium dioxide (0.3, 0.6, 0.9 and 1.2 g/L) and different concentrations of MB dye (15, 30 and 60 mg/L) were used. At the end of each step of the study, to remove titanium dioxide particles, a vacuum pump (J/B Aurora, IL 60507), a Buchner funnel and a cellulose nitrate filter (Sartorius) with pores of 0.2 micron were used. To measure dye concentration and COD, the spectrophotometer (UV/Vis, Optima SP-3000 Plus, Japan) and the open reflux method were used, respectively.

## RESULTS AND DISCUSSION

Tables 2 and 3 show the effects of various parameters, such as different concentrations of titanium dioxide, on the removal efficiency of MB dye and COD. Comparing dye removal efficiency at different concentrations of titanium dioxide showed that the dye removal efficiency increased with the increase in photocatalyst concentration. However, dye removal efficiency showed a slight difference at concentrations of 0.9 and 1.2 of titanium dioxide. According to Table 2, dye removal efficiency in batch and tubular reactors was 15.2% and 3.5%, respectively, after 5 min of reaction time, while it was 100% and 93%, respectively, after 60 min of reaction time. The results of the present study showed that the removal efficiency of dye and COD increased with the increase in  $\text{TiO}_2$  concentration and

**Table 2** | The effect of contact time on dye removal at different  $\text{TiO}_2$  concentrations (dye concentration: 60 mg/L, pH: 7)

$\text{TiO}_2$ concentration (mg/L)	Dye removal (%)							
	Time: 5 min		Time: 15 min		Time: 30 min		Time: 60 min	
	Batch	Tubular	Batch	Tubular	Batch	Tubular	Batch	Tubular
0.3	10.2	0.4	42.2	4	86.6	38.2	99	74.3
0.6	13.3	2	46.5	12.5	88.8	49.9	99.9	76.2
0.9	15.1	3	54.4	20	90.1	56.6	100	90.7
1.2	15.2	3.5	55	21.7	92.2	60	100	93

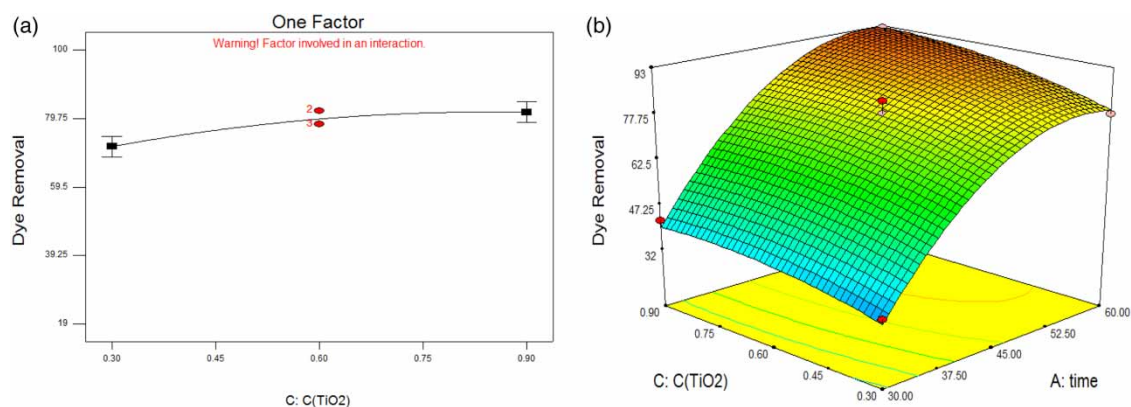
**Table 3** | The effect of titanium dioxide concentration on COD removal at different contact time (dye concentration: 60 mg/L, pH: 7)

TiO <sub>2</sub> concentration (mg/L)	Dye removal (%)							
	Time: 5 min		Time: 15 min		Time: 30 min		Time: 60 min	
	Batch	Tubular	Batch	Tubular	Batch	Tubular	Batch	Tubular
0.3	3.5	2	7.7	4.5	28.8	7.7	37.7	33.3
0.6	4	2.7	8	4.7	30.3	7.8	39.9	39.8
0.9	5.5	2.7	9.9	5.9	36.6	8.3	40.1	44
1.2	5.5	3.3	10.2	6.4	38	9	42.2	47.8

reaction time (Figure 4). This result is consistent with the results of similar previous studies (Kuo 2001; An & Zhu 2002). Based on the obtained results, the removal efficiency of dye and COD was 99% and 37.7%, respectively, in the batch reactor at the concentration of 0.3 g/L of titanium dioxide, while it was 74.3 and 33.3% in the tubular reactor. Concerning concentration of 1.2 g/L of titanium dioxide and contact time of 60 min, the removal efficiency of dye and COD was 100% and 42.2%, respectively, in the batch reactor, while it was 93 and 47.8% in the tubular reactor. As indicated in Table 4, increased photocatalyst concentration (up to a certain concentration) played a role in increasing removal efficiency. If the photocatalyst concentration exceeded the optimal limit, it had a negative effect on the removal efficiency because catalyst particles prevented penetration of light photons (Chakrabarti & Dutta 2004). The increase of process efficiency with titanium dioxide dosage can be attributed to the increase in reactive radicals for degradation of dye and COD. Asgari *et al.* (2013) reported that the catalytic ozonation efficiency

increased with bone charcoal dosage as a catalytic in the ozonation process.

To determine the effect of the initial concentration of MB dye on the efficiency of the photocatalytic process, experiments carried out at various concentrations of MB dye in the range of 15–60 mg/L and a titanium dioxide concentration of 1.2 g/L and pH of 7. It was then exposed to UV-C rays for 5–30 min (Table 4). According to the table, after 30 min, the process efficiency for dye removal in synthetic wastewater with an initial concentration of 15 mg/L, 30 mg/L and 60 mg/L was 97.7%, 94.2% and 92.2%, respectively, at the batch reactor, while it was 66.7%, 64% and 60%, respectively, at the tubular reactor. As can be seen, by increasing the initial dye concentration the photocatalytic process efficiency decreased. This phenomenon may be due to the fact that during the photocatalytic process only a limited amount of hydroxyl radical is produced, so the process cannot remove or degrade a high amount of pollutants more than a certain concentration. Another suggested reason for this is the large amounts of dye that were adsorbed

**Figure 4** | (a) Dye removal change with TiO<sub>2</sub> concentration change; (b) effect of TiO<sub>2</sub> nanoparticle dose to one factor in batch reactor (C<sub>initial</sub> Dye: 60 mg/L, pH: 7).



**Table 4** | The effect of initial dye concentration on dye removal (TiO<sub>2</sub> concentration: 1.2 g/L, pH: 7)

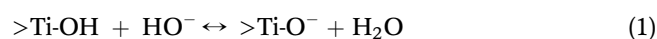
Time (min)	Dye removal (%)					
	Dye concentration: 15 mg/L		Dye concentration: 30 mg/L		Dye concentration: 60 mg/L	
	Batch	Tubular	Batch	Tubular	Batch	Tubular
5	48.8	22.5	30.8	8.3	15.2	3.5
15	83.3	39.9	77.1	22	55	21.7
30	97.7	66.7	94.2	64	92.2	60
60	100	98.3	100	96	100	93

on titanium dioxide nanoparticles at higher concentrations and prevented the dye molecules from reacting with free radicals and the electron holes. Therefore, the removal efficiency decreased at higher concentrations of dye (Chakrabarti & Dutta 2004). Moreover, light photon transition decreased with increasing dye concentration because light photons are adsorbed by dye before they can reach the catalyst particles. Also, as the concentration increased and dye clots appeared, the adsorption on the substrate increased; that is, the photocatalyst was trapped inside dye clots (Ming 2000). These results are consistent with the results of Ling & Mohamed (2004).

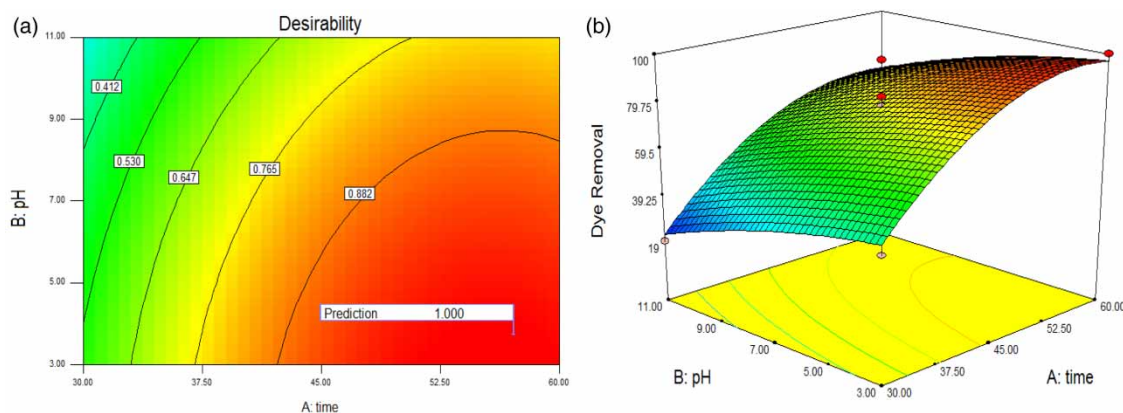
Figure 5 shows that after 60 min of contact time, removal efficiency increased from 58.5 to 98% with decreasing pH values from 11 to 3. The results clearly indicate that as pH decreased, removal efficiency increased noticeably.

In other words, the solution pH affected the way the TiO<sub>2</sub> surface was ionized and caused amphoteric behavior of TiO<sub>2</sub>

nanoparticles at different conditions (Papadam *et al.* 2007). This behavior could change the process oxidation power. Results showed that decomposition of MB followed first order reaction in both reactions.  $R^2$  values reported in Table 5 also confirm this. Concerning the slope of diagram  $\ln C/C_0$  in terms of contact time, apparent speed constants ( $k_p$ ) could be easily achieved at any level of initial concentration. Comparing apparent speed constants in both reactors showed that the efficiency of the batch reactor was higher in degrading MB than the tubular reactor. The effect of pH on the photocatalytic process efficiency with various catalyst nanoparticles is related to the point of zero charge ( $\text{pH}_{\text{zpc}}$ ) and structures of catalyst. The isoelectric point of TiO<sub>2</sub> was reported to be in the range of 5.9–7.5 (Bahnmann *et al.* 2007). Also, the effects of pH on the efficiency of the photocatalytic process of TiO<sub>2</sub> nanoparticles were as a result of TiO<sub>2</sub> amphoteric behavior and weakness of the oxide power of the holes produced in basic conditions (Hoffman *et al.* 1995). Titanium atoms are functionalized by primary hydrates and then placed on the surface of titanium dioxide nanoparticles (as  $>\text{Ti-OH}$ ). Moreover, solution pH affects the surface ionization in the titanium dioxide nanoparticles according to Equations (1) and (2) (Papadam *et al.* 2007):



According to Equation (1), at pH values higher than the isoelectric point, the surface of titanium dioxide

**Figure 5** | (a) Dye removal change with pH change; (b) effect of pH to one factor in batch reactor (C-initial Dye: 60 mg/L, pH: 7).

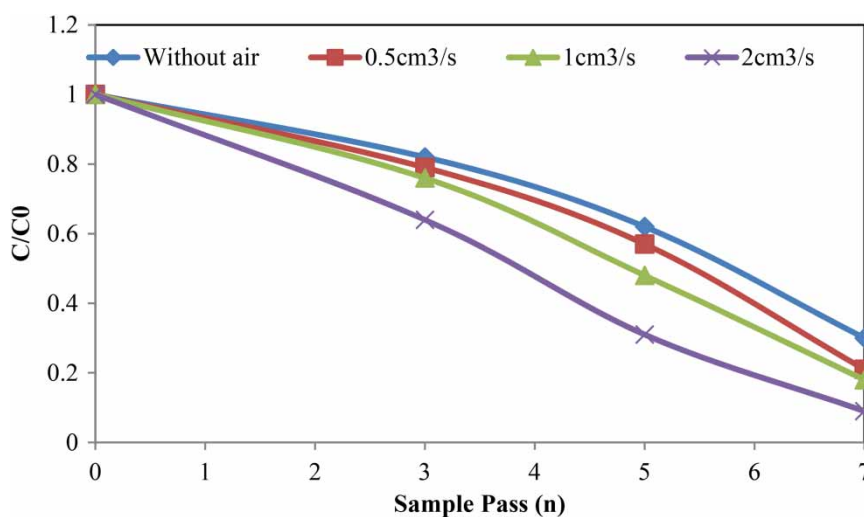
**Table 5** | The apparent rate constant of decomposition of MB in tubular reactors and batch (T: 25 °C, I: 15 W/m<sup>2</sup>)

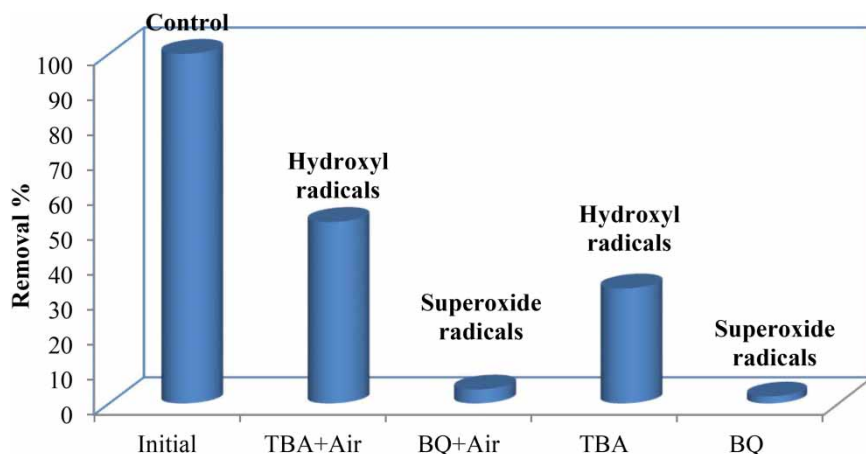
Batch reactor			Tubular reactor		
MB initial concentration (ppm)	$k_p(\text{min}^{-1})$	$R^2$	MB initial concentration (ppm)	$k_p(\text{min}^{-1})$	$R^2$
15	0.0058	0.948	15	0.002	0.948
30	0.0045	0.952	30	0.002	0.928
60	0.004	0.981	60	0.0017	0.948

nanoparticles adsorbs hydroxide ions and becomes negatively charged. On the other hand, at acidic conditions, the surface of the titanium dioxide nanoparticles get positively charged due to the presence of protons. Therefore, the efficiency of the photocatalytic process is related to the electrostatic attraction and repulsion between the catalyst surface and pollutant (Ishibashi *et al.* 2000).

In this study, the effect of aeration was also tested on dye reduction; 0.5, 1 and 2 cm<sup>3</sup>/s of air was injected into the reactor by a pump. As shown in Figure 6, the maximum removal efficiency increased with an increasing amount of injected air. At an initial MB concentration of 60 mg/L, contact time of 60 min and air flow of 2 cm<sup>3</sup>/s, the removal efficiency was 93%, while it was 71% without aeration. Therefore, aeration has a significant effect on the photocatalyst process and can increase the process efficiency. This can be attributed to the role of dissolved oxygen in

the production of hydroxyl radicals. In the photocatalytic process, an electron was produced by light photons and creation of a hole on the photocatalyst surface. Oxygen is abundant, available and a cheap gas which is capable of trapping electrons in the hydroxyl radical. Therefore, dissolved oxygen in the sample significantly increased the removal efficiency. Concerning formation of hydroxyl radicals, it has been proved that the main reason for the formation of active radicals is the creation of electron holes and production of free electrons; dissolved oxygen increases the production of hydroxyl radicals (Mills & Wang 1999). As the amount of dissolved oxygen increased, formation of MB (H<sub>2</sub>)<sup>+</sup> also increased. Rahimi showed that low levels of dissolved oxygen had a negative effect on removal efficiency (Mills & Wang 1999). In other words, at low levels of oxygen, MB dye was oxidized and changed into MB.

**Figure 6** | Effect of aeration (TiO<sub>2</sub>: 1.2 g/L, MB concentration: 60 mg/L, pH: 7).



**Figure 7** | The effects of hydroxyl and superoxide radicals in the removal of MB in the photocatalytic process (CMB: 60 mg/L, pH: 3,  $\text{TiO}_2$ : 0.9 gr/L, air: 2  $\text{cm}^3/\text{s}$ ).

### Effects of hydroxyl radical, superoxide, holes and electrons on removal of MB

In this part of the experiment the amount of hydroxyl radicals and superoxide was investigated using tetra-butyl alcohol (TBA), and benzoquinone (BQ). First, the optimal dose of TBA and BQ was calculated and then the removal efficiency of MB under optimal conditions of aerated and non-aerated photocatalytic processes were examined.

The optimal doses of TBA and BQ were 11 mg/L and 2.2 mg/L, respectively. According to Figure 7, under aerated conditions, the contribution of the hydroxyl radical and superoxide radical in removal efficiency were 52% and 4%, respectively.

### CONCLUSIONS

The present study has explored the efficiency of the photocatalytic processes in MB removal using titanium dioxide nanoparticles simulated using UV-C in batch and tubular reactors. The results indicate that the system efficiency decreased with an increasing titanium dioxide concentration higher than the optimal concentration (0.9–1.2 g/L) and with increasing dye concentration. The dye removal efficiency was increased by increasing the number of rotations of samples in the tubular reactor. The best removal efficiency of dye and COD in the batch reactor was 100% and 42.2%, respectively, while it was 93% and 47.8% in

the tubular reactor (in 1.2 g/L of titanium dioxide nanoparticles at 60 min). Since titanium dioxide used as a photocatalyst in this study could be recycled and separated, it could be said that the UV/ $\text{TiO}_2$  process was an environmentally friendly method for dye removal from textile dye wastewater.

### REFERENCES

- An, T. C. & Zhu, X. H. 2002 Feasibility study of photo electrochemical degradation of methylene blue. *Chemosphere* **46**, 897–903.
- Asgari, G., Seid Mohammadi, A., Mortazavi, S. B. & Ramavandi, B. 2013 Investigation on the pyrolysis of cow bone as a catalyst for ozone aqueous decomposition: kinetic approach. *J. Anal. Appl. Pyrolysis* **99**, 149–154.
- Azbar, N., Yonar, T. & Kestioglu, K. 2004 Comparison of various advanced oxidation processes and chemical treatment methods for COD and color removal from a polyester and acetate fiber dyeing effluent. *Chemosphere* **55**, 35–43.
- Bahnemann, W., Muneer, M. & Haque, M. M. 2007 Titanium dioxide-mediated photocatalysed degradation of few selected organic pollutants in aqueous suspensions. *Catalysis Today* **124** (3), 133–148.
- Chakrabarti, S. & Dutta, B. K. 2004 Photo catalytic degradation of model textile dyes in wastewater using ZnO as semiconductor catalyst. *J. Hazard. Mater.* **112**, 269–278.
- Çiçek, F., Ozer, D., Ozer, A. & Özer, A. 2007 Low cost removal of reactive dyes using wheat bran. *J. Hazard. Mater.* **1–2**, 408–416.
- Clesceri Lenore, S., Greenberg, A. E. & Eaton, A. D. 2000 *Standard Methods for the Examination of Water and Wastewater*. 20th edn. American Public Health Association, Washington, DC, USA.



- Dinç, A. R., Güneş, Y. & Karakaya, N. 2007 Coal-based bottom ash (CBBA) waste material as adsorbent for removal of textile dyestuffs from aqueous solution. *J. Hazard. Mater.* **14**, 529–535.
- Hoffman, M. R., Martin, S., Choi, W. & Bahnemann, D. 1995 Environmental applications of semiconductor photocatalysis. *Chem. Rev.* **95**, 69–96.
- Ishibashi, K., Fujishima, A., Watanabe, T. & Hashimoto, K. 2000 Quantum yields of active oxidative species formed on TiO<sub>2</sub> photocatalyst. *J. Photochem. Photobiol. A Chem.* **134**, 139–142.
- Jafari, J. A. 2004 Simultaneous photo-oxidative degradation of EDTA and extra-oxidative recovery of copper from industrial effluents. *J. Iran Chem. Chem. Eng.* **23**, 65–71.
- Kuo, W. S. 2001 Photocatalytic decolorization of methylene in water. *Chemosphere* **77**, 145–157.
- Lachheb, H., Puzenat, E., Houas, A., Ksibi, M., Elaloui, E., Guillard, C. & Herrmann, J. M. 2002 Photocatalytic degradation of various types of dyes in water by UV-irradiated titania. *Appl. Catal. B.* **39**, 75–90.
- Lee, J. H., Nam, W. S. & Kang, M. S. 2003 Design of two types of fluidized photo reactors and their photo-catalytic performances for degradation of methyl orange. *Appl. Catal. A* **244**, 49–57.
- Ling, C. & Mohamed, A. 2004 Photo degradation of methylene blue dye in aqueous stream. *J. Teknologi.* **40**, 91–103.
- Marković, D., Šaponjić, Z., Radoičić, M., Radetić, T., Vodnik, V., Potkonjak, B. & Radetić, M. 2015 Sonophotocatalytic degradation of dye C.I. Acid Orange 7 by TiO<sub>2</sub> and Ag nanoparticles immobilized on corona pretreated polypropylene non-woven fabric. *Ultrason. Sonochem.* **24**, 221–229.
- Mills, A. & Wang, J. 1999 Photobleaching of methylene blue sensitized by TiO<sub>2</sub>. *Photochem. Photobiol.* **127**, 123–134.
- Ming, L. Y. 2000 Treatment of dye aqueous solution by UV/TiO<sub>2</sub> process with applying bias potential. *Water Sci.* **36**, 189–106.
- Moussavi, S. P., Ehrampoush, M. H., Mahvi, A. H., Ahmadian, M. & Rahimi, S. 2013 Adsorption of humic acid from aqueous solution on single-walled carbon nanotubes. *Asian J. Chem.* **25** (10), 5319–5324.
- Neppolian, B., Choi, H. C., Sakthivel, S., Arabindoo, B. & Murugesan, V. 2002 Solar light induced and TiO<sub>2</sub> assisted degradation of textile dye reactive blue 4. *Chemosphere* **46**, 1173–1181.
- Nilsson, I., Möller, A., Mattiasson, B., Rubindamayugi, M. S. T. & Welandar, U. 2006 Decolorization of synthetic and real textile wastewater by the use of white-rot fungi. *Enzyme Microb. Technol.* **38**, 94–100.
- Papadam, T., Xekoukoulotakis, N. P., Poullos, I. & Mantzavinos, D. 2007 Photocatalytic transformation of Acid Orange 20 and Cr(VI) in aqueous TiO<sub>2</sub> suspensions. *J. Photochem. Photobiol. A Chem.* **186**, 308–315.
- Patel, T. L., Patel, B. C., Kadam, A. A., Tipre, D. R. & Dave, S. R. 2015 Application of novel consortium TSR for treatment of industrial dye manufacturing effluent with concurrent removal of ADMI, COD, heavy metals and toxicity. *Water Sci. Technol.* **71** (9), 1293–1300.
- Poudyal, K. & Clark, D. 2002 Titanium dioxide photocatalysis of metals. Enve 436-01. *Bull. Hazard. Waste Manage.* **2002**, 1–4.
- Samadi, M. T., Zolghadrnasab, H., Godini, K., Poormohammadi, A., Ahmadian, M. & Shanesaz, S. 2015 Kinetic and adsorption studies of reactive black 5 removal using multi-walled carbon nanotubes from aqueous solution. *Pharm. Chem.* **7** (5), 267–274.
- Sauer, T., Cesconeto, N., Jose, H. J. & Moreira, R. F. P. M. 2002 Kinetics of photocatalytic degradation of reactive dyes in a TiO<sub>2</sub> slurry reactor. *J. Photochem. Photobiol. A* **149**, 147–154.
- Seid-Mohammadi, A., Asgari, G., Poormohammadi, A., Ahmadian, M. & Rezaeivahidiand, H. 2016 Removal of phenol at high concentrations using UV/Persulfate from saline wastewater. *Desalin Water Treat.* **57** (42), 19988–19995.
- Soares, P. A., Batalha, M. S., Souza, M. G. U., Boaventura, R. A. & Vilar, V. J. 2015 Enhancement of a solar photo-Fenton reaction with ferric-organic ligands for the treatment of acrylic-textile dyeing wastewater. *J. Environ. Manage.* **152**, 120–131.
- Wainwright, M. & Byrne, M. N. 2006 Phenothiazinium-based photobactericidal materials. *Photochem. Photobiol. B* **96**, 227–230.
- Xu, X. R., Li, H. B., Wang, W. H. & Gu, J.-D. 2004 Degradation of dyes in aqueous solutions by the Fenton process. *Chemosphere* **57**, 595–600.
- Zhan, H. & Tian, H. 1998 Photocatalytic degradation of acid azo dyes in aqueous TiO<sub>2</sub> suspension 1. The effect of substituents. *Dyes Pigm.* **37**, 231–239.

First received 26 October 2015; accepted in revised form 28 December 2015. Available online 10 February 2016