

Treatment of Remazol Brilliant Blue Dye Effluent by Advanced Photo Oxidation Process in TiO_2/UV and $\text{H}_2\text{O}_2/\text{UV}$ reactors

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Abstract: Advanced oxidation processes involving TiO_2/UV and $\text{H}_2\text{O}_2/\text{UV}$ were evaluated for their potential use in decolorization of textile dye effluents. A coil photo reactor, consisting of UV radiation source and a spiral coil coated with TiO_2 , was used to treat synthetic effluent of Remazol Brilliant Blue dye. The TiO_2 coating was performed using the sol-gel technique. The effects of UV radiation, TiO_2 coatings and dye concentration were studied and the results were compared to dye treatment involving H_2O_2 . The maximum dye removal efficiencies were 7.3, 12.2 and 12.5 % for uncoated, single coat and dual coat of TiO_2 , respectively. The decolorization efficiency was inversely related to dye concentration of the effluent. The treatments with UV only, TiO_2 only, UV+ TiO_2 , H_2O_2 only and UV+ H_2O_2 resulted in color reduction of 7.6, 2.3, 12.5, 4.1 and 99.9 % respectively. The maximum decolorization occurred in ≤ 100 min in all cases. The temperature varied from 29.2 to 54.7°C for UV+ TiO_2 treatment and no change in reactor temperature was observed when UV was not used.

Key words: Advanced oxidation, coil reactor, decolorization efficiency, Remazol Brilliant Blue, textile dye effluent, TiO_2 coating, UV radiation.

INTRODUCTION

Textile industries generate 100-170 L dye effluent per kg of cloth processed, which could be characterized by strong color, high COD and wide range of pH^[1]. Synthetic dye effluents emerging from various industrial operations pose great threat to the environment due to risks of toxicity to aquatic organisms in natural water resources and inhibition of photosynthetic activity^[2]. Existing non-destructive treatment methods for industrial effluents comprise various chemical and physical processes, such as chemical-coagulation, electro-coagulation, reverse osmosis, nanofiltration and adsorption^[3-8]. However, these methods concentrate the dye pollutants and necessitate secondary treatment. On the other hand, degradation involving biological processes is not efficient as the synthetic dyes in the effluent are highly structured polymers with low biodegradability^[9-10].

Use of conventional dye wastewater treatment methods are becoming increasingly challenging for existing plants due to recent guidelines adopted by water authorities. The US Department of Commerce has projected a 3.5-fold increase in textile production between 1975 and 2020^[11]. This also indicates that in order to attain this target, the synthetic dyes would be

continually upgraded in terms of both quality and quantity, which would lead to further deterioration of the environment. Current conventional processes sometimes also lead to production of derivative compounds due to reduction under anaerobic conditions which could pose more severe hazard in contrast to original dye^[12]. In order to address these limitations, various researchers have proposed advanced oxidation processes (ozone, H_2O_2 , TiO_2 , ZnO, RuO_2 , SiO_2 , UV radiation, electron-beam irradiation, super critical water, wet air, catalytic wet air and ultrasound) as plausible option for efficient removal of color pollutants from contaminated water^[13-16].

Amongst advanced oxidation methods, TiO_2/UV radiation mediated process hold substantial promise for efficient and complete removal of many synthetic dyes as TiO_2 is the most extensively used photocatalyst^[14,16-20]. TiO_2/UV radiation mediated process lead to heterogeneous photocatalysis, one of the advanced oxidation processes (AOPs). It is an efficient wastewater treatment technique which could result into total mineralization of organics^[21]. It has been suggested that the valence band holes generated by UV photons interact with H_2O or OH^- adsorbed on the catalyst (TiO_2) surface to generate $\bullet\text{OH}$ radical, or with

adsorbed O_2 (on the catalyst surface) to yield $\bullet O_2^-$ and $\bullet OOH$ radicals^[22,23].

The present study was performed to investigate the effect of TiO_2 mediated oxidation of Remazol Brilliant Blue dye under various reaction conditions. The effects of TiO_2 coating, UV radiation and dye concentration on decolorization of dye were studied. Steady-state temperature at different locations of the TiO_2/UV reactor and pH profiles of inlet and outlet dye effluents were also measured. In addition, in order to obtain TiO_2 film on the stainless steel coil used in TiO_2/UV reactor, the sol-gel technique was explored. The effects of H_2O_2 addition and H_2O_2 only were also investigated and the results were compared with the TiO_2 experiments.

MATERIALS AND METHODS

Experimental set-up: The experimental set-up (Fig. 1) consisted of a synthetic dye wastewater feeding and effluent collection system, TiO_2/UV reactors, temperature sensors, pumps and a data acquisition system. The synthetic dye wastewater feeding and effluent collection system consisted of Remazol brilliant blue dye feeding tank, a peristaltic pumps and an effluent collection tank. The dye feeding and effluent collection tanks were made of 4 mm thick Plexiglas pipe of a 200 mm internal diameter and a 435 mm height with volume of about 11 L. The detachable cover and the fixed bottom of each tank were made from 4 mm thick Plexiglas circular plates. A 4 mm diameter port was located on the cover to allow air inlet for pressure equalization during pumping out of the dye wastewater from the tank. The outlet port (4 mm diameter) of the feeding tank was located at 15 mm from the bottom. An agitator having stirring blades (1.5 mm thick and 72 mm in length) of 9 mm diameter and 370 mm length was installed at the center of the

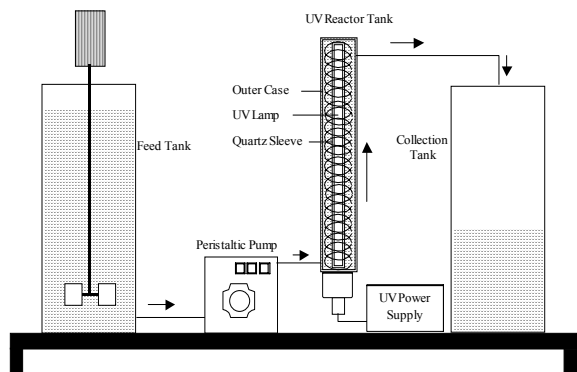
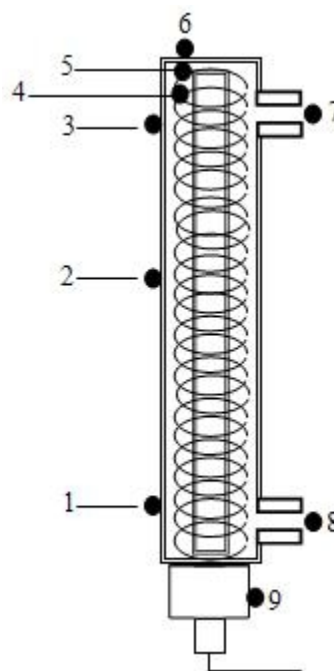


Fig. 1: TiO_2/UV coil reactor setup

feeding tank cover and used to mix the dye. The agitator was driven by an electric motor (model NSI-1 ORS3, Bodine Electric Company, Chicago, IL USA.) mounted on top of the feeding tank cover. Two variable speed peristaltic pumps and Masterflex precision tubings (Digi-Staltic, Masterflex Model 7253-60, head model 77200-50, tubing no. MasterFlex[®] 6404-14 and MasterFlex[®] 6404-13, Barnant Company, Division of Cole Parmer Instrument.Co., Barrington, IL.) were used. The peristaltic pumps pumped the synthetic dye wastewater from the feeding tank into the TiO_2/UV reactors at the required flow rates.

The photo (TiO_2/UV) reactor is shown in Fig. 2. Low pressure mercury lamps with 380 mm arc length, enclosed in a 21 mm outside diameter quartz tube, were



- 1: Temperature on the outside surface of the reactor opposite to inlet
- 2: Temperature on the outside surface of the reactor at the mid height
- 3: Temperature on the outside surface of the reactor opposite to outlet
- 4: Temperature of the reactor head space
- 5: The inside temperature of the reactor top
- 6: Temperature on the outside surface of the reactor top
- 7: The outlet dye temperature
- 8: The inlet dye solution temperature
- 9: The temperature of the lamp socket surface

Fig. 2: Thermocouple locations in the coil reactors

used in the reactors. The inner and the outer diameters of both reactors are 55 and 61 mm, respectively. The 3 mm thick stainless steel chamber provided a gap size (distance between the quartz sleeve and the inner surface of reactor casing) of 17 mm in both reactors. Coils made of stainless steel with a length of 448 mm a thickness of 0.85 mm, an internal diameter of 21 mm and a pitch of 20 mm were used in the reactors. The working volume in each reactor was 840 mL.

A digital data logger (Model 4702-5 E, Cole Parmer, Chicago, IL, USA) and type T thermocouples (Model 8530-75, Cole Parmer instrument company, Chicago, IL, USA) were used in the study to measure the temperature at different sites on the reactors. The thermocouples were placed at nine locations in each reactor (Fig. 2). The temperature sensors (type T thermocouples) were calibrated using ice bath and boiling deionized distilled water. The thermocouples were connected to the data acquisition system individually in different channels and immersed into the ice bath. The thermocouple reading, as temperature in degrees centigrade, was corrected to read zero (offset). The thermocouples were then immersed into the boiling water to calibrate the upper limit. The accuracy of the thermocouples was found to be $\pm 0.4^\circ\text{C}$.

Chemicals: The chemicals used in this study included hydrogen peroxide, Remazol brilliant blue dye, absolute alcohol, tetrabutylorthotitanate ($\text{Ti}(\text{OBu})_4$) and diethanolamine ($\text{NH}(\text{C}_2\text{H}_4\text{OH})_2$). The hydrogen peroxide (H_2O_2 , 30%) was obtained from Fisher scientific (Ca # H-325-500, Fisher scientific, Montreal, Quebec, Canada). The Remazol brilliant blue dye ~50% (1-amino-4-[4-(1-sulfonyl-ethyl-2-sulfoxy)]-2-(9, 10-anthraquinone)-sulfonic acid; disodium salt) was obtained from Sigma (R8001, CAS # 2580-78-1, Sigma-Aldrich Inc., St-Louis, MO, USA). The molecular formula of the dye is $\text{C}_{22}\text{H}_{16}\text{N}_2\text{Na}_2\text{O}_{11}\text{S}_3$ and the structural formula is shown in Fig. 3. Anhydrous ethyl alcohol (100% ethanol) was obtained from Commercial Alcohols Inc., Brampton, Ontario, Canada.

Standard curve: In order to determine the concentration of the Remazol brilliant blue dye using the colorimetric techniques, a standard curve was generated from the standard solution of Remazol brilliant blue dye according to the procedure described by Mahmoud *et al.*^[19]. According to this procedure, the standard solution was prepared by dissolving 0.1 g of the dye in 1000 mL of distilled deionized water at ambient conditions (pH 7 and 25°C). Then, a set of nine solutions with Remazol blue dye concentrations of 10, 20, 30, 40, 50, 60, 70, 80 and 100 mg L^{-1} were

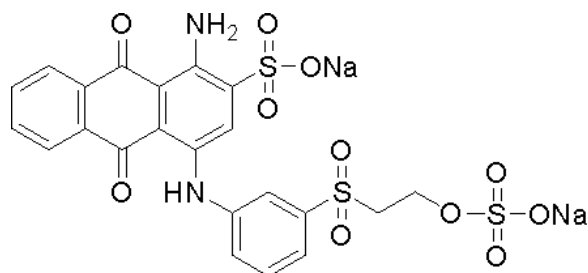


Fig. 3: Molecular structure of remazol brilliant blue R dye

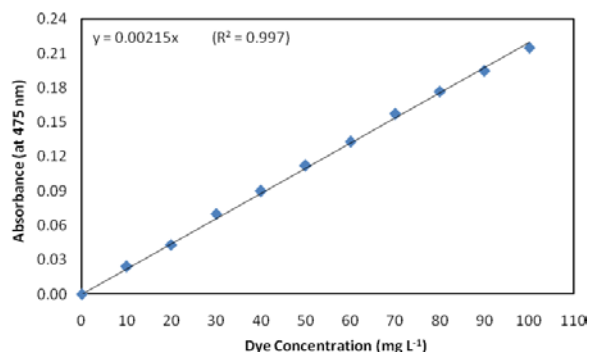


Fig. 4: Absorbance curve for remazol brilliant blue dye solution (pH = 7, 25°C)

prepared. Finally, the absorbance of the solutions thus prepared was measured (in triplicates) using spectrophotometer at 420 nm (Spectronic 601, Fisher scientific, Montreal, Quebec, Canada). The absorbance was then plotted against the known Remazol blue dye concentrations (mg L^{-1}) as shown in Fig. 4. A blank sample using distilled deionized water was used to zero the spectrophotometer.

Sol-gel coating on stainless steel coils: The sol-gel coating was prepared according to the procedure described by Giornelli *et al.*^[24] as shown in Fig. 5. For this, 17.2 mL of tetrabutylorthotitanate ($\text{Ti}(\text{OBu})_4$) 97% and 4.8 mL of diethanolamine ($\text{NH}(\text{C}_2\text{H}_4\text{OH})_2$) 99% were dissolved in 67.28 mL anhydrous ethyl alcohol. The resulting solution was mixed vigorously at room temperature for 2 h on a magnetic stirrer. About 2.7 mL of water and 10 ML of ethanol ($\text{Ti}(\text{OBu})_4:\text{C}_2\text{H}_5\text{OH}:\text{H}_2\text{O}:\text{NH}(\text{C}_2\text{H}_4\text{OH})_2 = 1:25.5:3:1$, molar ratio) were added dropwise to the mixing solution. The resultant alkoxide sols thus formed were left standing at room temperature for 2 h for the hydrolysis reaction to proceed. TiO_2 films on the stainless steel coil were prepared by dipping (15 min) and withdrawing the coil at a rate of 6 mm sec^{-1} . The

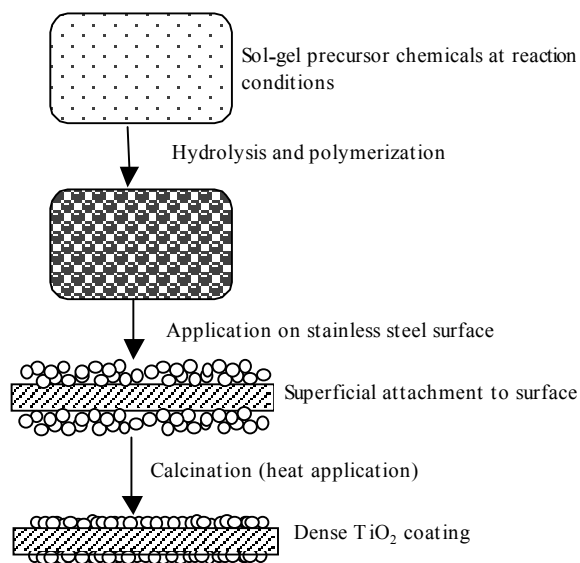


Fig. 5: Sol-gel process for TiO₂ coating on stainless steel^[24]

resulting TiO₂ films coated stainless steel coil was calcined in a furnace at 80°C h⁻¹, up to 100°C during 1 h and then at 900°C for 2 h.

Experimental plan: Four sets of experiments were conducted in this study. The first set of experiments was carried out to study the effects of using UV radiation only (no TiO₂ coating) on the decolorization of Remazol brilliant blue. The coil reactor was operated at a dye concentration of 300 mg L⁻¹ and ten residence times (840.0, 168.0, 84.0, 56.0, 42.0, 28.0, 21.0, 16.8, 14.0 and 8.4 min) which gave flow rates of 1, 5, 10, 15, 20, 30, 40, 50, 60 and 100 mL min⁻¹, respectively. The dye solution was fed into the reactor at ambient temperature (25°C). The sample collection was performed after a minimum of 840 mL of dye effluent was pumped through the reactor.

In the second set of experiments, the effectiveness of the TiO₂ coated coil reactor (different coatings) with UV radiation in removal of Remazol Brilliant Blue dye was evaluated. The coil reactor was operated at a dye concentration of 300 mg L⁻¹ and ten residence times (840.0, 168.0, 84.0, 56.0, 42.0, 28.0, 21.0, 16.8, 14.0 and 8.4 min) which gave flow rates of 1, 5, 10, 15, 20, 30, 40, 50, 60 and 100 mL min⁻¹, respectively. The dye solution was fed into the reactor at ambient temperature (25°C). The sample collection was performed after a minimum of 840 mL of dye effluent was pumped through the reactor.

The third set of experiments was carried out to study the effect of dye concentration (100, 200 and 300 mg L⁻¹) on the decolorization of Remazol brilliant blue using TiO₂ coated coil reactor without UV radiation. The coil reactor was operated at ten residence times (840.0, 168.0, 84.0, 56.0, 42.0, 28.0, 21.0, 16.8, 14.0 and 8.4 min) which gave flow rates of 1, 5, 10, 15, 20, 30, 40, 50, 60 and 100 mL min⁻¹, respectively. The dye solutions were fed into the reactor at ambient temperature (25°C). The sample collection was performed after a minimum of 840 mL of dye effluent was pumped through the reactor.

The fourth set of experiments was carried out to study the effect of using H₂O₂ (at 12.5 mL L⁻¹) only on the decolorization of Remazol brilliant blue at different dye concentrations (100, 200 and 300 mg L⁻¹). The coil reactor was operated at ten residence times (840.0, 168.0, 84.0, 56.0, 42.0, 28.0, 21.0, 16.8, 14.0 and 8.4 min) which gave flow rates of 1, 5, 10, 15, 20, 30, 40, 50, 60 and 100 mL min⁻¹, respectively. The dye solutions were fed into the reactor at ambient temperature (25°C). The sample collection was performed after a minimum of 840 mL of dye effluent was pumped through the reactor.

Experimental procedure: The Remazol brilliant blue dye solutions (100, 200 and 300 mg L⁻¹) were prepared by dissolving the dye (2, 4 and 6 g, respectively) in 20 L of deionized distilled water. The pH of the dye solutions were near 7. The dye solution (with and without H₂O₂) was pumped through the reactors at the required flow rates using the precalibrated peristaltic pumps (Digi-Staltic, Masterflex model 7253-60, head Model 77200-50, tubing no. MasterFlex® 6404-13 and MasterFlex® 6404-14, Barnant Company, Division of Cole Parmer Instrument. Co., Barrington, IL, USA), with the UV lamps in place. The UV lamps were kept on or off depending upon the experiment. The temperature readings were noted down from the data logger. Once the reactor was filled with dye solution, it was left to reach steady state (constant temperature). Samples were collected during the steady state from the reactor outlet. The absorbance of the dye solution samples was measured using a spectrophotometer (Spectronic 601, Fisher scientific, Montreal, Quebec, Canada) at a wave length of 475 nm.

RESULTS AND DISCUSSION

UV radiation only: The decolorization efficiency profile for coil reactor with UV radiation only (no oxidant) is shown in Fig. 6. The reactor was operated at

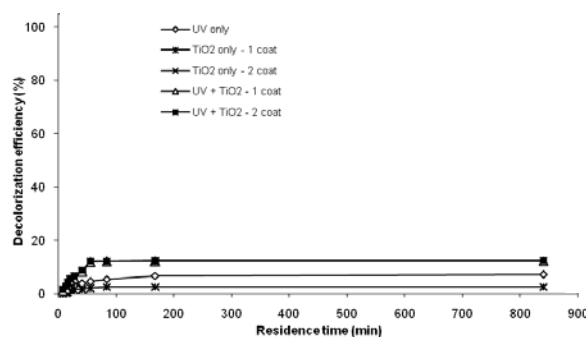


Fig. 6: Effect of UV radiation and TiO₂ coating on decolorization at a dye concentration of 300 mg L⁻¹

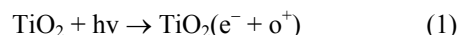
a dye concentration of 300 mg L⁻¹, a pH of 7, a temperature of 25°C and ten different residence times (840.0, 168.0, 84.0, 56.0, 42.0, 28.0, 21.0, 16.8, 14.0 and 8.4 min). Initially, the decolorization efficiency increased with increase in residence time reaching 7.3% at a residence time of 56 min. However, no substantial increment in the decolorization efficiency could be achieved with further increases in residence time.

In the present study, low pressure UV lamps (15 watt) were used. The UV radiation applied for the decolorization of dye wastewater is usually measured in terms of mW-sec⁻² centimeter (mW-sec cm⁻²). The effective UV dose used in this study varied from 30155 to 3015567 mW-sec cm⁻², which was smaller than the UV dose of 2812500-4500000 mW-sec cm⁻² used by Abu Tariq *et al.*^[17] and approximately within the ranges of 35640-39960 mW-sec cm⁻² used by Akyol and Bayramoglu^[21] and 194400-205200 mW-sec cm⁻² used by Mounir *et al.*^[16]. The most commonly employed UV lamps for the wastewater treatment systems are low or medium pressure mercury lamps due to cost concerns^[25]. However, it has been established that many chemical bonds of the targeted organic material cannot be broken directly due to the limitation of wavelengths not matching absorption bonds^[26].

Liao *et al.*^[27] reported that dye solutions exposed to UV radiation only, achieved varying decolorization depending upon type of dye as well as UV intensities and contact time. Therefore, the UV degradation processes must be accompanied with oxidants/photocatalysts such as H₂O₂, TiO₂ or ozone to generate active hydroxyl radicals to initiate auto-oxidation reactions for complete degradation^[28,29]. According to Feng *et al.*^[25], addition of chemicals as oxidants could interfere with the process and thus recommended the application of dielectric barrier discharge (DBD) driven excimer lamps. Depending on

the filling gas, DBD lamps can emit radiation into narrow-band or quasi-monochromatic spectrum with the required specific wavelength with respect to the concerned dye^[30,31].

TiO₂ only: The efficiency of decolorization of Remazol brilliant blue by TiO₂ coated coil reactor in absence of UV radiation is also shown in Fig. 6. A maximum decolorization efficiency of 2.6% was attained at the residence time of 84 min. This low decolorization efficiency could be due to the absence of light source^[14]. Activated by light source, TiO₂ has been reported to be capable of degrading various organic pollutants completely according to the following reaction^[32]:



Where:

$h\nu$ = Radiation energy (mW-sec)

e^- = Strong reducing species

o^+ = Strong oxidizing species

The degradation of organic dye, such as Remazol Brilliant Blue is resulted by the action of hydroxyl radical (OH[•]), which can be formed by the oxidation of the adsorbed water. The complete photocatalytic oxidation reaction result into the final products CO₂ and H₂O^[14]. Furthermore, the quantum yield for the photocatalytic reactions (defined as the number of degraded molecules divided by the number of photons absorbed by the system) is significantly affected by the intensity and wavelength of the radiation^[33].

TiO₂/UV radiation: Several researchers have attempted to treat organic dye effluents using advanced oxidation processes (TiO₂ as catalyst in the presence of visible/UV radiation) with mixed results^[14,16,34]. The possible reasons for low decolorization efficiencies reported by these researchers included: quantity of TiO₂, dye concentration, intensity of UV source used and reactor configuration.

In order to investigate the effect of TiO₂ coating, the coil reactor was operated with single and double coatings of TiO₂ separately in the presence of UV radiation at a dye concentration of 300 mg L⁻¹. The results of decolorization efficiencies obtained with different TiO₂ coatings are shown in Fig. 6. Maximum decolorization efficiencies of 12.2 and 12.5% were achieved at a residence time ≤84 min for the single and double coatings, respectively. Student's t-test was performed on the data to test the differences between

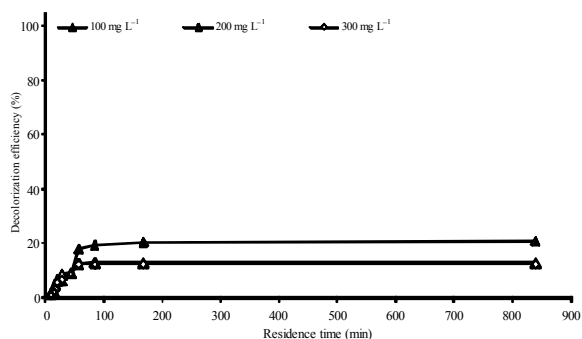


Fig. 7: Effect of TiO₂/UV radiation on decolorization at various dye concentrations

coatings. No significant difference was found at $p > 0.05$. Thus, it was concluded that the number of coatings did not affect the efficiency of decolorization.

The effect of dye concentration (100, 200 and 300 mg L⁻¹) on decolorization efficiency was also investigated. The results are presented in Fig. 7. The decolorization efficiency decreased with increase in dye concentration due to higher effective penetration of UV radiation in the dilute dye solution. The maximum decolorization efficiencies were 20.8, 13.1 and 12.5%, for 100, 200 and 300 mg L⁻¹ dye concentrations, respectively.

Abu Tariq *et al.*^[17] achieved approximately 50 and 70% degradation of the textile dye compounds acid blue (142.3 mg L⁻¹) and xylenol orange (228.2 mg L⁻¹) within 80 min in a TiO₂/UV reactor with TiO₂ suspension, respectively. Akyol and Bayramoglu^[21] reported complete decolorization of the azo-reactive textile dye Remazol Red F-3B (150 mg L⁻¹) in a batch slurry TiO₂/UV reactor. These authors used multiple lamps with constant stirring set-up and applied a centrifugation process to separate TiO₂ catalyst particles after photocatalysis. Mounir *et al.*^[16] were able to decolorize approximately 99% Basic Red 46 (10 and 25 mg L⁻¹) at the end of 2h treatment under sunlight using TiO₂ catalysts fixed on a flexible support.

In the present study, TiO₂ catalyst was fixed on the surface of the stainless steel coil. Although, this eliminated the need for centrifugation step, it resulted in lower quantity of the catalyst in comparison to TiO₂ suspensions used by other authors. The lower decolorization efficiencies for the TiO₂/UV coil reactor used in the present study, in comparison to those reported by Abu Tariq *et al.*^[17] and Akyol and Bayramoglu^[21] could, therefore, be due to lower quantity of TiO₂ catalyst available on the coil. The dye concentration used in the present study was in the range of 100-300 mg L⁻¹. The higher dye concentrations, in

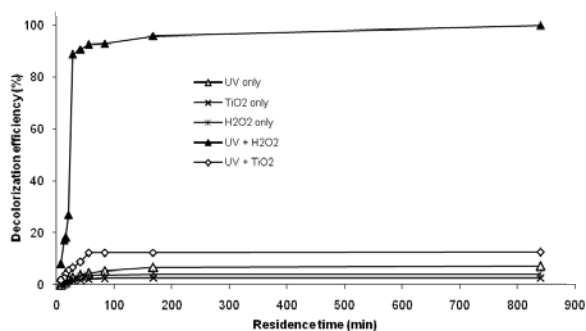


Fig. 8: Effect of UV, TiO₂ and H₂O₂

comparison to that used by Mounir *et al.*^[16] possibly also resulted in lower decolorization efficiency.

H₂O₂ only: A maximum decolorization efficiency of 4.07% was achieved at a residence time of 168 min when H₂O₂ was used in the absence of UV radiation with a dye concentration of 300 mg L⁻¹ as shown in Fig. 8. The low decolorization efficiency was due to limitation of formation of hydroxyl radicals in absence of radiation energy^[34]. The free hydroxyl radical (OH[•]) is produced due to breakdown of H₂O₂ in the presence of radiation energy (UV radiation) as follows:



Photooxidation of the organic aromatic compound Remazol Brilliant Blue dye would require cleavages of functional groups such as amino, anthraquinone, sulfo, sulfonyl, sulfoxy, ethyl and sulfonic acid disodium salt by the free hydroxyl radicals produced from dissociation of H₂O₂^[35]. The decolorization efficiency achieved when using H₂O₂ only was nominal as the H₂O₂ used in the present study contained stabilizer compounds, which limit the dissociation of H₂O₂ under standard conditions. Thus, in the absence of UV radiation, substantial degradation of Remazol Brilliant Blue dye was not observed even at optimal concentration of H₂O₂.

H₂O₂/UV radiation: The decolorization efficiencies increased significantly when H₂O₂ was used in the presence of UV radiation as shown in Fig. 8. A decolorization efficiency of 99.9% was achieved at a residence time of 42 min. The effect of dye concentration (100, 200 and 300 mg L⁻¹) on the decolorization efficiency was also investigated at different residence times (840.0, 168.0, 84.0, 56.0, 42.0, 28.0, 21.0, 16.8, 14.0 and 8.4 min) as shown in Fig. 9. Decolorization efficiencies of 99.92, 99.96 and 99.90%

were achieved at residence time of 42 min for 100, 200 and 300 mg L⁻¹, respectively. This was due to the formation of higher amount of free hydroxyl radicals by the dissociation of H₂O₂ in the presence of UV radiation^[35]. The H₂O₂ concentration in the present study was based on the optimization study of Mahmoud *et al.*^[19]. However, the H₂O₂ concentration could be further reduced for lower dye concentrations. In addition, utilization of moderate to high intensity UV radiation source would also minimize the chemical use.

Temperature profile: Table 1 shows the steady state temperatures at all residence times for single and double coatings of TiO₂ with UV radiation at 300 mg L⁻¹ dye concentration. The temperature on the outside surface of the reactor opposite to outlet increased upto 54.7 °C, while the inlet dye solution temperature was 29.2 °C. The temperature of the reactor decreased considerably with decrease in residence time. The difference in decolorization efficiencies of single and double coatings were not substantial. Therefore, no substantial differences in temperature profiles, due to the heat of the photochemical reaction of dye solution, were observed. Wu *et al.*^[36] reported increase in decolorization of Reactive Blue 15 with temperature using ozone as advanced oxidizing agent due to corresponding increase in volumetric mass transfer coefficient. However, no significant effect on the temperature was observed for UV mediated processes

as most photochemically induced reactions have low activation energy^[37].

The temperatures measured at the steady state conditions of the 2-coat TiO₂/UV reactor using different dye concentrations are shown in Table 2. The temperatures were not affected by the dye concentration.

Table 3 shows the steady state temperature profiles of different locations of the double TiO₂ coatings reactor with and without UV using 300 mg L⁻¹ dye concentration. For the TiO₂ reactor without UV, no significant temperature differences were observed at all locations. However, for the TiO₂ reactor with UV, the

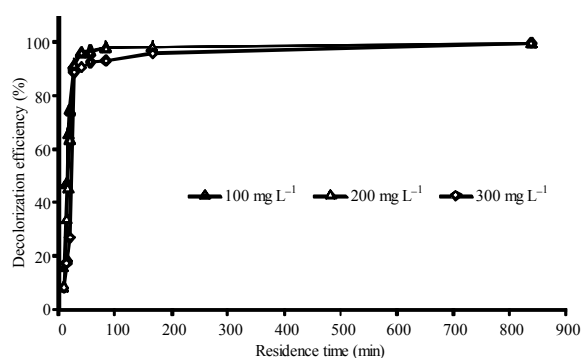


Fig. 9: Effect of H₂O₂/UV radiation on decolorization at various dye concentrations

Table 1: Steady state temperatures measured at different locations of TiO₂/UV coil reactors with different TiO₂ coatings using a dye concentration of 300 mg L⁻¹

Residence time (min)	Location of thermocouples																	
	1		2		3		4		5		6		7		8		9	
	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B
840.0	41.0	39.6	49.5	49.9	54.7	53.3	52.0	52.4	52.4	52.0	49.8	47.1	48.4	49.1	29.2	28.2	30.4	30.5
168.0	34.0	34.0	44.7	43.8	50.2	49.1	48.1	47.8	48.5	47.2	46.5	46.0	50.0	48.1	25.8	26.3	28.5	29.3
84.0	29.8	30.3	37.6	37.8	43.1	43.3	41.5	42.4	42.0	42.0	40.4	41.1	43.7	43.1	25.7	26.2	27.3	28.5
56.0	28.8	28.8	34.7	34.5	39.6	39.6	38.4	39.1	38.8	38.6	37.5	38.0	40.4	39.9	26.1	26.2	27.3	28.2
42.0	27.6	27.8	31.9	32.2	35.2	35.5	34.3	35.1	34.6	34.8	33.6	34.3	35.9	36.1	25.6	26.0	26.8	27.9
28.0	27.2	27.2	30.2	30.3	32.7	32.9	32.2	32.7	32.4	32.4	31.6	32.0	33.4	33.5	25.8	26.1	26.9	27.7
21.0	27.1	26.9	29.3	29.1	31.5	31.1	31.2	31.2	31.4	30.8	30.6	30.6	32.1	31.6	26.1	26.0	26.9	27.4
16.8	27.0	26.3	28.7	28.2	30.6	30.1	30.3	30.2	30.5	29.8	29.9	29.6	31.1	30.4	26.1	25.6	26.7	27.0
14.0	25.7	26.3	27.0	27.7	28.2	28.7	28.4	28.9	28.4	28.5	28.0	28.3	28.6	28.7	24.9	25.7	26.5	26.8
8.4	25.4	25.7	26.2	26.6	28.6	27.9	30.2	30.5	30.3	29.7	29.7	30.4	29.6	28.2	25.0	25.4	26.1	26.4

- 1: Temperature on the outside surface of the reactor opposite to inlet
- 2: Temperature on the outside surface of the reactor at the mid height
- 3: Temperature on the outside surface of the reactor opposite to outlet
- 4: Temperature of the reactor head space
- 5: The inside temperature of the reactor top
- 6: Temperature on the outside surface of the reactor top
- 7: The outlet dye temperature
- 8: The inlet dye solution temperature
- 9: The temperature of the lamp socket surface
- A: The 1- coat TiO₂ reactor
- B: The 2- coat TiO₂ reactor

Table 2: Steady state temperatures measured at different locations of a 2-coat TiO₂/UV coil reactor using different dye concentrations

Residence Time (min)	Location of thermocouples																										
	1			2			3			4			5			6			7			8			9		
	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C
840.0	37.1	36.7	39.6	47.2	43.8	49.9	52.3	46.9	53.3	52.2	47.5	52.4	50.6	47.2	52.0	49.1	46.1	47.1	48.8	48.6	49.1	26.6	26.2	28.2	29.2	29.5	30.5
168.0	34.2	32.8	34.0	44.7	41.2	43.8	50.2	44.2	49.1	49.0	44.6	47.8	48.5	44.3	47.2	47.3	43.2	46.0	47.5	45.5	48.1	26.5	26.1	26.3	29.2	29.2	29.3
84.0	30.2	29.8	30.3	37.9	36.6	37.8	43.3	40.1	43.3	42.6	40.6	42.4	42.2	40.3	42.0	41.3	39.4	41.1	43.9	41.3	43.1	26.3	26.0	26.2	28.1	28.5	28.5
56.0	29.2	28.6	28.8	34.7	34.1	34.5	39.3	37.6	39.6	38.8	38.1	39.1	38.6	37.9	38.6	37.9	37.1	38.0	40.2	39.2	39.9	26.6	26.2	26.2	27.9	28.5	28.2
42.0	28.7	27.8	27.8	32.1	32.1	32.2	36.8	34.8	35.5	36.4	35.3	35.1	36.2	35.0	34.8	34.5	34.5	34.3	37.6	36.2	36.1	26.1	26.1	26.0	27.9	28.2	27.9
28.0	28.3	27.2	27.2	29.9	29.9	30.3	34.3	31.9	32.9	34.1	32.4	32.7	33.8	32.2	32.4	33.4	31.8	32.0	34.9	33.1	33.5	26.1	26.1	26.1	28.0	28.1	27.7
21.0	28.2	27.0	26.9	29.1	29.1	29.1	32.6	31.2	31.1	32.5	31.7	31.2	32.2	31.5	30.8	31.9	31.2	30.6	33.2	32.1	31.6	26.2	26.2	26.0	28.0	28.1	27.4
16.8	28.2	26.8	26.3	28.5	28.5	28.2	31.9	30.0	30.1	32.0	30.5	30.2	31.7	30.3	29.8	31.4	30.0	29.6	32.5	30.7	30.4	26.1	26.1	25.6	28.2	28.2	27.0
14.0	28.0	26.7	26.3	28.2	28.2	27.7	31.3	29.2	28.7	31.5	29.8	28.9	31.1	29.5	28.5	30.9	29.4	28.3	31.7	29.7	28.7	26.1	26.1	25.7	28.4	28.6	26.8
8.4	27.9	26.6	25.7	29.4	27.5	26.6	31.0	28.7	27.9	32.8	30.2	30.5	31.9	29.6	29.7	32.5	29.9	30.4	31.1	28.9	28.2	27.6	26.1	25.4	29.5	29.3	26.4

- 1: Temperature on the outside surface of the reactor opposite to inlet
- 2: Temperature on the outside surface of the reactor at the mid height
- 3: Temperature on the outside surface of the reactor opposite to outlet
- 4: Temperature of the reactor head space
- 5: The inside temperature of the reactor top
- 6: Temperature on the outside surface of the reactor top
- 7: The outlet dye temperature
- 8: The inlet dye solution temperature
- 9: The temperature of the lamp socket surface
- A: at 100 mg L⁻¹ dye concentration
- B: at 200 mg L⁻¹ dye concentration
- C: at 300 mg L⁻¹ dye concentration

Table 3: Steady state temperatures measured at different locations of 2-coat TiO₂ coil reactor without UV using dye concentration of 300 mg L⁻¹

Residence Time (min)	Location of thermocouples																	
	1		2		3		4		5		6		7		8		9	
	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B
840.0	27.2	39.6	27.3	49.9	27.4	53.3	27.7	52.4	27.6	52.0	27.6	47.1	27.6	49.1	26.6	28.2	27.6	30.5
168.0	27.0	34.0	27.0	43.8	26.9	49.1	27.1	47.8	27.1	47.2	27.2	46.0	27.2	48.1	26.8	26.3	27.2	29.3
84.0	26.8	30.3	26.8	37.8	26.7	43.3	26.7	42.4	26.7	42.0	26.7	41.1	26.8	43.1	26.8	26.2	26.9	28.5
56.0	26.5	28.8	26.9	34.5	26.4	39.6	26.8	39.1	26.5	38.6	26.5	38.0	26.7	39.9	26.7	26.2	27.1	28.2
42.0	26.3	27.8	27.0	32.2	26.3	35.5	26.7	35.1	26.4	34.8	26.4	34.3	26.5	36.1	26.6	26.0	27.0	27.9
28.0	26.4	27.2	27.2	30.3	26.3	32.9	26.7	32.7	26.4	32.4	26.3	32.0	26.4	33.5	26.7	26.1	27.1	27.7
21.0	26.3	26.9	27.1	29.1	26.2	31.1	26.5	31.2	26.4	30.8	26.3	30.6	26.3	31.6	26.7	26.0	27.1	27.4
16.8	26.1	26.3	27.1	28.2	26.1	30.1	26.5	30.2	26.1	29.8	26.3	29.6	26.1	30.4	26.7	25.6	27.0	27.0
14.0	26.1	26.3	27.9	27.7	26.1	28.7	26.5	28.9	26.2	28.5	26.3	28.3	26.1	28.7	26.1	25.7	27.2	26.8
8.4	26.1	25.7	29.2	26.6	26.3	27.9	27.7	30.5	27.4	29.7	27.7	30.4	26.3	28.2	26.4	25.4	27.8	26.4

- 1: Temperature on the outside surface of the reactor opposite to inlet
- 2: Temperature on the outside surface of the reactor at the mid height
- 3: Temperature on the outside surface of the reactor opposite to outlet
- 4: Temperature of the reactor head space
- 5: The inside temperature of the reactor top
- 6: Temperature on the outside surface of the reactor top
- 7: The outlet dye temperature
- 8: The inlet dye solution temperature
- 9: The temperature of the lamp socket surface
- A: Without UV
- B: With UV

the temperature increased with residence time due to the removal of the heat produced by UV lamp. However, the temperature measurement could not be correlated with the decolorization efficiency due to the fact that photochemical reactions are effectively not sensitive to temperature changes around ambient values.

pH profile: Table 4 shows the pH values of inlet and outlet of the 2-coat coil reactor at steady state condition

with and without UV radiation. The pH of the dye solution increased from 5.74 to 7.02 when the residence time was decreased from 840 to 8.4 min. However, this pH change could not result in any significant change in decolorization efficiency. In general, the pH profiles also showed an increasing trend with increase in dye concentration as shown in Table 5. The changes in pH with dye decolorization could be mainly attributed to the formation of hydroperoxides (acidic entity) in the reacting solution during dye decolorization process^[17].

Table 4: Inlet and outlet dye pH in TiO₂/UV reactor at different operating conditions

Flow rate (mL min ⁻¹)	Residence time (min)	pH			
		Inlet	A Outlet	B Outlet	C Outlet
1	840.0	5.74	5.53	5.42	5.31
5	168.0	6.41	5.68	5.66	5.96
10	84.0	6.44	5.81	5.73	6.48
15	56.0	6.72	6.09	5.84	6.60
20	42.0	6.84	6.41	5.91	6.65
30	28.0	6.87	6.74	6.34	6.72
40	21.0	6.98	6.69	6.28	6.79
50	16.8	6.99	6.78	6.85	6.84
60	14.0	6.99	6.84	6.90	6.99
100	8.4	7.02	6.85	6.86	7.00

A: 1-coat with UV at 300 mg L⁻¹ dye concentration
 B: 2-coat with UV at 300 mg L⁻¹ dye concentration
 C: 2-coat without UV at 300 mg L⁻¹ dye concentration

Table 5: Inlet and outlet dye pH in TiO₂/UV reactor at different dye concentrations

Flow rate (mL min ⁻¹)	Residence time (min)	pH			
		Inlet	A Outlet	B Outlet	C Outlet
1	840.0	5.74	4.90	4.98	5.42
5	168.0	6.41	5.04	5.18	5.66
10	84.0	6.44	5.62	5.60	5.73
15	56.0	6.72	5.71	5.80	5.84
20	42.0	6.84	5.34	5.84	5.91
30	28.0	6.87	5.86	6.09	6.34
40	21.0	6.98	6.26	6.27	6.28
50	16.8	6.99	6.35	6.51	6.85
60	14.0	6.99	6.40	6.41	6.90
100	8.4	7.02	6.76	6.83	6.86

A: 2-coat with UV at 100 mg L⁻¹ dye concentration
 B: 2-coat with UV at 200 mg L⁻¹ dye concentration
 C: 2-coat with UV at 300 mg L⁻¹ dye concentration

CONCLUSIONS

A coil photo reactor, consisting of a low range UV lamp and a spiral coil coated with TiO₂, was used to investigate the decolorization of a synthetic effluent of Remazol Brilliant Blue dye. The effects of UV radiation, TiO₂ coatings and dye concentration were studied and the results were compared to dye treatment involving H₂O₂. The single TiO₂ coating using sol-gel technique was feasible for the dye treatment. The maximum dye removal efficiencies were 7.3, 12.2 and 12.5% for uncoated, single coat and dual coat of TiO₂, respectively. The decolorization efficiency was inversely related to dye concentration of the effluent. The temperature varied from 29.2 to 54.7°C for UV+TiO₂ treatment and no change in reactor temperature was observed in the absence of UV. The pH profiles showed an increasing trend with increase in dye concentration. The treatments with UV only, TiO₂

only, UV+TiO₂, H₂O₂ only and UV+H₂O₂ resulted in color reduction of 7.6, 2.3, 12.5, 4.1 and 99.9% respectively. The maximum decolorization occurred in ≤ 100 min in all cases.

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