

## Decolorization of Remazol Brilliant Blue Dye Effluent by Advanced Photo Oxidation Process ( $H_2O_2/UV$ system)

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**Abstract:** Advanced photo oxidation processes hold great promise for the improved treatment of textile dye effluent. In this study, the effectiveness of a  $H_2O_2/UV$  system for the decolorization of remazol brilliant blue effluent was investigated by examining the optimum conditions for dye removal in two reactors (coil and conventional). The results showed that the coil reactor had a higher temperature profile than the conventional reactor. When the dye was fed into the reactors at  $25^\circ C$ , UV radiation alone was not effective as the decolorization efficiency of the conventional reactor varied from 0.0 to 12.3%, while that of the coil reactor varied from 0.0 to 7.3%, depending on the residence time used. The effect of UV radiation at  $100^\circ C$  was also negligible as the maximum decolorization efficiencies were 4.0 and 3.7% for the conventional and the coil reactors, respectively. Increasing the concentration of  $H_2O_2$  increased decolorization efficiencies of both UV reactors. Dye decolorization also increased with residence time. More than 93% color removal of remazol brilliant blue dye was achieved with a residence time of 56 min and 100% decolorization achieved in 65 min using a  $H_2O_2$  concentration of  $12.50\text{ mL L}^{-1}$ .

**Key words:** Advanced oxidation, textile wastewater, remazol brilliant blue, reactive dye,  $H_2O_2$ , UV

### INTRODUCTION

Color in textile effluents has become particularly identified with the dyeing of cotton products and the use of reactive dyes. Up to 30% of the used dyestuffs remain in the spent dye-bath after the dyeing process<sup>[1]</sup>. The high consumption of reactive dyes, mainly in the cotton industry, causes environmental and aesthetic problems, due to their low degree of exhaustion. A significant percentage (10-40%) of the dye remains in its hydrolyzed and unfixed form in the exhausted dye bath or is removed in the washing liquors<sup>[2]</sup>.

Over 700,000 tons of approximately 10,000 types of dyes and pigments are produced annually worldwide, of which about 20% are in industrial effluents from the textile dyeing and finishing processes<sup>[1]</sup>. Many of these synthetic dyestuffs cannot be treated successfully by conventional methods due to their complex polyaromatic structure and hence cause health problems<sup>[3]</sup>. There is also concern that the aromatic amines, which are formed as metabolites by reductive fission of the azo bond under anaerobic conditions, could pose a more serious toxic hazard than the intact dye molecules<sup>[4]</sup>.

The use of conventional textile wastewater treatment processes imposes new challenges to environmental engineers faced with increasing restrictive effluent quality by water authorities. Conventional treatment such as biological treatment will no longer be acceptable as 53% of 87 colors are identified as non-biodegradable. Pagga and Brown<sup>[4]</sup> reported that the residual colour is usually due to insoluble dyes which have low biodegradability such as reactive blue 21, direct blue 80 and vat violet that have a COD/BOD ratio of 59.0, 17.7 and 10.8, respectively<sup>[5]</sup>. Advanced oxidation processes (AOPs) hold great promise for better treatment of textile dyes<sup>[6]</sup>. The goal of AOPs design is to generate and use hydroxyl free radicals ( $HO^\bullet$ ) as strong oxidants to destroy compounds that cannot be oxidized by conventional oxidants<sup>[7-10]</sup>. The versatility of AOP is also enhanced by the fact that they offer different possible ways for generating  $OH^\bullet$  radicals. Generation of  $OH^\bullet$  is commonly accelerated by combining  $O_3$ ,  $H_2O_2$ ,  $TiO_2$ , UV radiation, electron-beam irradiation and ultrasound. Of these,  $O_3/H_2O_2$ ,  $O_3/UV$  and  $H_2O_2/UV$  hold the greatest promise for oxidizing textile wastewater.

The objectives of the study were to investigate the effectiveness of an advanced oxidation process ( $H_2O_2/UV$ ) for decolorization of remazol brilliant blue effluent and to determine the optimum conditions (temperature, residence time,  $H_2O_2$  concentration and UV reactor type) for dye removal.

## MATERIALS AND METHODS

**Experimental apparatus:** The experimental apparatus (Fig. 1) consisted of a dye feeding and effluent removal system, UV reactors, pumps and a data acquisition system.

The dye feeding and effluent removal system consisted of remazol brilliant blue dye feeding tank, a peristaltic pumps and an effluent collection tank. Each of the dye feeding and effluent collection tanks was made of a 4 mm thick Plexiglas pipe of a 200 mm internal diameter and a 435 mm height, giving capacity of about 11 L. The bottom and cover of each tank were made from 4 mm thick Plexiglas circular plates. The outlet port (4 mm diameter) of the feeding tank was located at 15 mm from the bottom. A mixing shelf having stirring blades (1.5 mm thick and 72 mm in length) of 9 mm diameter and 370 mm length was installed through the center of the feeding tank cover and used to mix the dye. The shaft was driven by an electric motor (model NSI-1 ORS3, Bodine Electric Company, Chicago, USA.) mounted on top of the feeding tank cover. Two variable speed peristaltic pumps and Masterflex precision tubing (Digi-Staltic, Masterflex Model 7253-60, head model 77200-50, tubing no. MasterFlex® 6404-13, Barnant Company, Division of Cole Parmer Instrument.Co., Barrington, IL.) were used. The peristaltic pumps pumped the material from the feed tank into the UV reactors at the desired flow rate.

Two 380 mm arc length low pressure mercury lamps, each enclosed in a 21 mm diameter (OD) quartz tube, were used in two reactors (Fig. 2). The inner and the outer diameter of both reactors are 55 and 61 mm, respectively. A 3 mm thick stainless steel chamber gave a gap size (distance between the quartz sleeve and the inner surface of reactor casing) of 17 mm in both reactors. A coil 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 was used in one reactor. The working volume in each reactor was 840 mL. The outlet of the reactor with coil was 13 mm higher than the outlet of the reactor without coil to compensate for the volume occupied by the coil.

A digital data logger (Model 4702-5 E, Cole Parmer, Chicago, Illinois) and type T thermocouples

(Model 8530-75, Cole Parmer instrument company, Chicago, Illinois) were used in the study to measure the temperature in the reactors. The thermocouples were placed at nine locations in each reactor (Fig. 3): (a) the outside surface of the reactor opposite to inlet, (b) the outside surface of the reactor at the mid height, (c) the outside surface of the reactor opposite to outlet, (d) the reactor head space, (e) inside surface of the reactor top, (f) the outside surface of the reactor top, (g) outlet, (h) inlet and (i) the lamp socket surface. The temperature sensors (type T thermocouples) were calibrated using ice 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 correct the upper limit. The accuracy of the thermocouples was found to be  $\pm 0.4^\circ C$ .

**Reagents:** The chemicals used in this study included hydrogen peroxide and remazol brilliant blue dye. The hydrogen peroxide 30% ( $H_2O_2$ ) 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, Ca # 22-324-7, Sigma, Oakville, Ontario, Canada). The molecular formula of the dye is  $C_{22}H_{16}N_2Na_2O_{11}S_3$  and the molecular-structure is shown in Fig. 4<sup>[11]</sup>.

**Standard curve:** To determine the concentration of the remazol brilliant blue dye using the colorimetric techniques, a standard curve was developed from the standard solution of remazol brilliant blue dye according to the procedure described by Mahmoud *et al.*<sup>[12]</sup>. The standard solution was prepared by dissolving 0.1 g of the dye in 1000 mL of distilled deionized water at ambient conditions (pH of 7 and a temperature of  $25^\circ C$ ). Then, a set of nine solutions with remazol blue dye concentrations of 10, 20, 30, 40, 50, 60, 70, 80 and  $100\text{ mg L}^{-1}$  were prepared. Finally, the absorbance of the prepared solutions was measured (in triplicates) using spectrophotometer (Spectronic 601, Fisher scientific, Montreal, Quebec, Canada). The absorbance was then plotted against the known remazol blue dye concentrations ( $\text{mg L}^{-1}$ ) as shown in Fig. 5. A blank sample was used to zero the spectrophotometer.

**Experimental design:** Three sets of experiments were conducted in this study. In the first set of experiments,

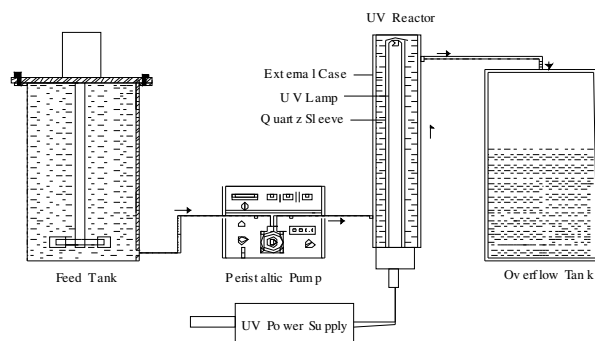


Fig. 1: Experimental setup

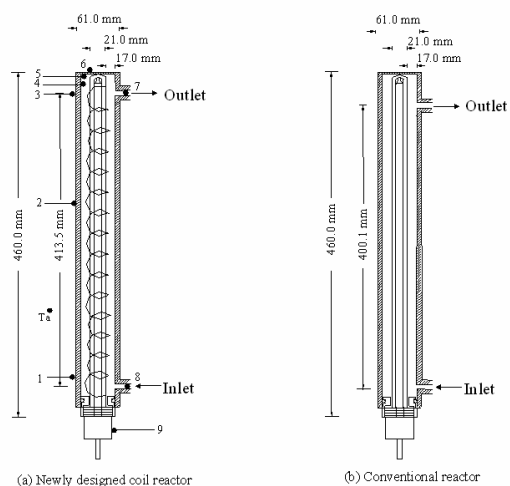
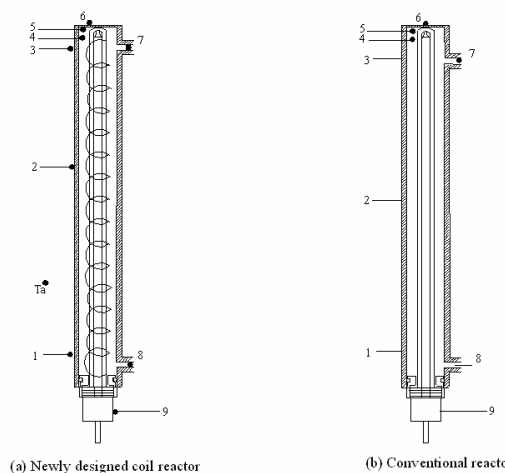


Fig. 2: UV reactors

the performances of the two reactors (coil and conventional) were evaluated 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<sup>-1</sup> respectively. The dye solution was fed into the reactors at ambient temperature (25°C). The experiments were run until the steady state temperature was achieved in each reactor before sampling.

The second set of experiments was carried out to study the effect of temperature on the decolorization of remazol brilliant blue using UV radiation. The two UV reactors were operated at the same residence times (840.0, 168.0, 84.0, 56.0, 42.0, 28.0, 21.0, 16.8, 14.0 and 8.4 min) and the dye solution was fed into the reactor at 100°C.

The third set of experiments were carried out to



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. 3: Location of thermocouples in the two reactors

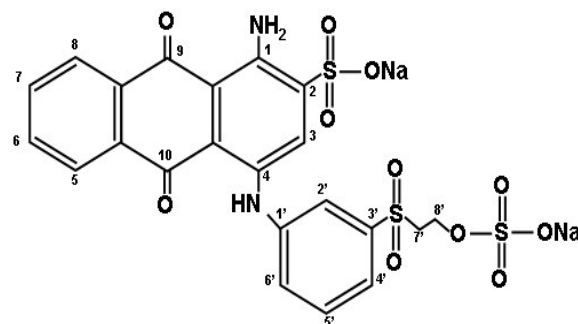


Fig. 4: The molecular-structure of remazol brilliant blue R dye<sup>[11]</sup>

study the combined effects of using H<sub>2</sub>O<sub>2</sub> and UV radiation on the decolorization of remazol brilliant blue. The two UV reactors were operated at the same residence times (840.0, 168.0, 84.0, 56.0, 42.0, 28.0, 21.0, 16.8, 14.0 and 8.4 min). The dye solution was fed into the reactors at ambient temperature (25°C). Seven concentrations (1, 3, 6.25, 12.5, 25, 50 and 75 mL L<sup>-1</sup>) of H<sub>2</sub>O<sub>2</sub> (30%) in the dye solution were investigated.

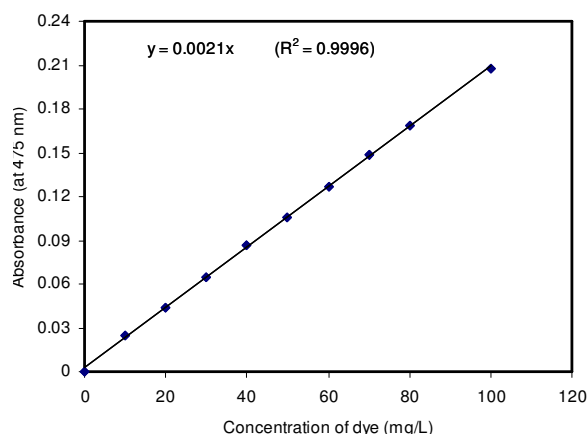


Fig. 5: Standard curve (pH = 7, temperature 25 °C)

**Experimental procedure:** A 20 L volume of the remazol brilliant blue dye solution ( $300 \text{ mg L}^{-1}$ ) was prepared by dissolving (6 g dye in 20 L) in deionized water. The pH of this solution was 7. The dye solution (with and without  $\text{H}_2\text{O}_2$ ) was pumped through the reactors at the required flow rates using the precalibrated peristaltic pump (Digi-Staltic, Masterflex model 7253-60, head Model 77200-50, tubing no. MasterFlex® 6404-13, Barnant Company, Division of Cole Parmer Instrument. Co., Barrington, IL.), while the UV lamp was on. After the reactor was filled with dye solution, it was left to reach steady state (constant temperature). The temperature readings were noted down from the data logger. 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

**Reactor temperature:** The measured steady state temperatures at different flow rates (residence times) for the conventional and coil reactors when fed the dye at temperatures of 25 °C and 100 °C are shown in Tables 1 and 2. The temperatures at all locations in the reactors decreased with the decrease in the residence time, except for the influent temperature (location 8), which remained constant. Generally, the temperatures measured close to the bottom of the reactors were less than the temperatures measured at the top. This was due to the dye being fed at the bottom of the reactor and picking up heat from the UV lamp as it traveled upward to the outlet.

When the dye was fed at 25 °C, the steady state effluent temperature decreased from 40.4 °C to 29.3 °C

and from 41.5 °C to 30.2 °C in the conventional reactor and the coil reactor as the residence time was decreased from 840.0 to 8.4 min, respectively. When the dye was fed at 100 °C, the steady state effluent temperature decreased from 117.7 °C to 111.0 °C and from 122.7 °C to 111.0 °C in the conventional reactor and the coil reactor as the residence time was decreased from 840.0 to 56.0 min, respectively. It was also noticed that the temperatures measured at all the locations in the coil reactor were higher than those measured at similar locations in the conventional reactor. The coil absorbs the heat generated from the UV lamp and increases the heat transfer to the fluid causing higher temperatures.

The results obtained from the present study indicated that increased temperature (from 25 °C to 100 °C) reduced the decolorization efficiency of the UV reactors. Zeynep and Filiz<sup>[13]</sup> reported that increasing the temperature from 15 °C to 50 °C did not change the decolorization efficiency for reactive yellow 15 by Fenton's oxidation. Galindo and Kalt<sup>[14]</sup> reported that the temperature did not significantly affect the decolorization of textile dye by UV radiation and that the photochemical reactions are effectively not sensitive to small changes in temperature in the range 22-45 °C. This is due to the fact that photochemically induced reactions often have a low activation energy<sup>[15]</sup>.

**Effect of UV radiation:** Figure 6 shows the decolorization efficiencies of the two reactors when the dye was fed at 25 and 100 °C. When the dye was fed at 25 °C, the decolorization efficiency of the conventional reactor varied from 0.0 to 12.3%, while that of the coil reactor varied from 0.0 to 7.3%, depending on the residence time used. Although the decolorization increased with increasing the residence time, the results showed that UV radiation was not effective in destroying the dye when it was fed into the reactor at room temperature (25 °C). There was also a negligible effect of UV radiation on the decolorization of remazol brilliant blue in aqueous solution fed into the reactors at 100 °C as the maximum decolorization efficiencies were 4.0 and 3.7% for the conventional and the coil reactors, respectively.

The UV dosage applied to a wastewater is determined by the intensity of the UV radiation and the contact time involved and is commonly expressed in milliwatt-sec per square centimeter ( $\text{mW}\cdot\text{sec cm}^{-2}$ ). Ultraviolet lamps are classified as low, medium or high pressure units<sup>[16]</sup>. The low pressure UV lamps are usually 14 - 35 watts<sup>[17-19]</sup>. The lamps used in this study were 15 watt. Reported studies in the literatures indicated both successes and failures of UV for decolorizing wastewaters. With the exception of

Table 1: Steady state temperatures at different locations when the dye was fed into the reactors at 25°C

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	34.7	35.7	34.8	38.6	40.2	41.5	36.5	37.7	36.2	37.9	36.2	37.6	40.4	41.5	24.1	24.1	37.4	37.3
168.0	34.1	35.6	34.5	37.5	38.5	40.0	34.8	37.5	34.6	37.4	34.4	37.3	38.6	39.7	24.0	24.0	37.2	37.2
84.0	32.0	35.3	32.4	36.9	37.5	38.2	34.5	36.6	34.6	36.9	34.7	37.2	37.8	38.2	24.0	24.0	36.8	36.6
56.0	31.5	31.8	32.0	35.1	37.1	37.7	33.7	36.2	33.6	36.8	33.5	37.2	37.1	37.7	24.0	24.0	35.6	35.5
42.0	30.6	30.9	31.8	34.2	36.3	36.7	33.2	36.0	33.4	35.7	33.2	35.8	36.4	36.9	23.2	23.2	33.3	33.0
28.0	29.0	29.7	30.5	33.3	35.7	36.0	32.0	34.5	32.2	33.9	31.9	34.0	35.8	36.1	23.4	23.4	31.9	31.8
21.0	28.8	29.4	28.5	32.9	33.5	33.9	32.0	34.0	32.1	33.9	31.7	33.2	33.8	34.6	23.4	23.4	30.3	30.5
16.8	27.5	27.5	26.9	31.8	33.0	33.4	29.7	32.9	29.6	32.7	30.0	32.8	33.2	34.6	23.2	23.2	29.6	29.6
14.0	26.0	26.8	26.4	29.0	31.4	32.8	27.9	31.2	28.8	31.6	26.9	31.8	31.6	32.9	23.0	23.0	29.3	29.6
8.4	25.5	26.1	25.3	27.0	28.8	29.3	26.4	30.5	27.4	31.0	26.2	30.6	29.3	30.2	22.3	22.3	28.5	28.9

1 is temperature on the outside surface of the reactor opposite to inlet.

2 is temperature on the outside surface of the reactor at the mid height.

3 is temperature on the outside surface of the reactor opposite to outlet.

4 is temperature of the reactor head space.

5 is the inside temperature of the reactor top.

6 is temperature on the outside surface of the reactor top.

7 is the outlet dye temperature.

8 is the inlet dye solution temperature.

9 is the temperature of the lamp socket surface.

A is the conventional reactor

B is the coil reactor

Table 2: Steady state temperatures at different locations when the dye was fed into the reactors at 100°C

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	116.4	117.5	117.6	118.3	117.7	119.3	113.1	119.9	112.6	116.4	110.2	115.0	117.7	122.7	100	100	48.8	48.8
168.0	115.8	117.3	116.8	117.5	117.0	118.5	110.8	116.1	111.2	115.6	110.0	114.9	116.9	120.5	100	100	48.4	48.5
84.0	114.8	113.1	115.9	116.6	116.4	117.6	110.2	115.1	110.4	113.7	110.0	113.8	116.7	119.2	100	100	46.8	46.9
56.0	112.5	114.0	114.8	115.7	114.8	116.2	110.0	114.2	110.0	113.0	109.5	110.1	115.0	118.8	100	100	46.1	46.3
42.0	111.6	111.4	113.8	114.2	114.0	115.2	110.0	114.0	110.0	113.0	109.4	110.1	114.5	116.0	100	100	46.0	46.7
28.0	110.0	110.8	112.5	113.3	113.2	114.0	110.0	113.5	110.0	112.8	109.1	109.8	113.5	115.0	100	100	45.4	45.5
21.0	109.0	109.6	111.5	111.9	112.5	113.1	110.0	113.0	109.4	112.6	108.9	109.5	112.9	114.0	100	100	45.3	45.4
16.8	107.1	107.8	110.0	110.4	111.9	112.0	110.0	112.5	109.1	112.1	108.4	109.2	112.0	113.2	100	100	45.1	45.0
14.0	106.0	106.9	108.4	109.0	110.3	111.8	109.0	112.1	109.0	111.8	108.2	108.7	111.6	112.0	100	100	45.0	44.9
8.4	105.0	105.2	107.0	107.8	108.2	109.4	109.0	111.3	108.9	111.5	107.9	108.0	111.0	111.2	100	100	44.8	44.7

1 is temperature on the outside surface of the reactor opposite to inlet.

2 is temperature on the outside surface of the reactor at the mid height.

3 is temperature on the outside surface of the reactor opposite to outlet.

4 is temperature of the reactor head space.

5 is the inside temperature of the reactor top.

6 is temperature on the outside surface of the reactor top.

7 is the outlet dye temperature.

8 is the inlet dye solution temperature.

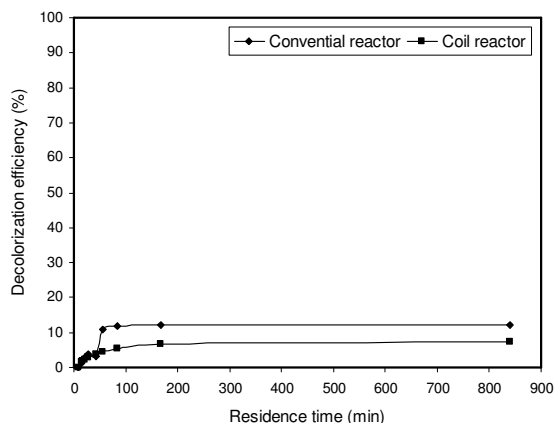
9 is the temperature of the lamp socket surface.

A is the conventional reactor

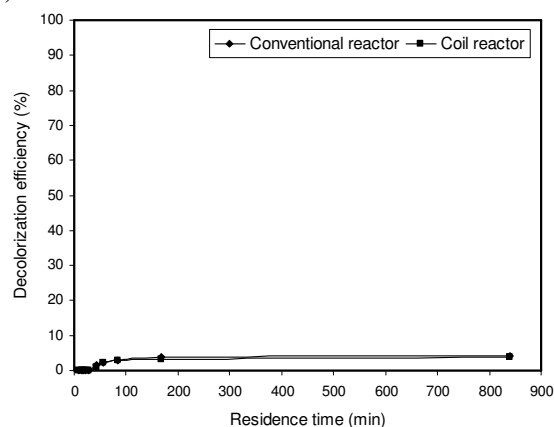
B is the coil reactor

Reactive Black 5, significant decolorization of reactive dyes (with concentrations ranging from 100-300 mg L<sup>-1</sup>) has been achieved at various UV intensities and contact times<sup>[18,20]</sup>. Liao *et al.*<sup>[19]</sup> reported on a textile wastewater color (420 ADMI units) that was reduced nearly 20% (from 160 to 128 mg L<sup>-1</sup>) after 40 min exposure to UV generated with a 14 watt lamp. On the other hand, studies by Ince and Gonenc<sup>[21]</sup> and Shu *et al.*<sup>[17]</sup> indicated that the decolorization of Remazol Black 5 (40 mg L<sup>-1</sup>) and Acid Red 1 and Yellow 23 (20 mg L<sup>-1</sup>) solutions was low when they were exposed to UV radiation.

The remazol brilliant blue dye (C<sub>22</sub>H<sub>16</sub>N<sub>2</sub>Na<sub>2</sub>O<sub>11</sub>S<sub>3</sub>) is an organic aromatic compound containing anthraquinone and amino, sulfonyl, ethyl, sulfoxy groups and sulfonic acid disodium salt<sup>[11]</sup>. Organic compounds (containing carbon) are affected by light and other forms of electromagnetic radiation due to their chemical structure. The degradation process of organic compounds involves the formation of free radicals (short-lived atoms or groups of atoms which are formed by homolytic fission of a covalent bond) and their subsequent reactions as shown in Fig. 7<sup>[22]</sup>. These reactions include: auto-oxidation reactions which



(a) at 25°C



(b) at 100°C

Fig. 6: Effect of UV radiation on decolorization efficiency using conventional and coil reactors

involve the gain of oxygen, loss of hydrogen, or loss of electrons. They occur when covalent bonds (3) absorb radiation of a specific wavelength corresponding to the amount of energy necessary to displace an electron (known as the bond dissociation energy). Certain groups are highly reactive and promote oxidation, such as double bonds between carbon atoms (C=C), carbonyl groups (>C=O) and tertiary hydrogen atoms (>C-). The reactions terminate when free radicals react together to form stable molecules. These reactions lead to products containing polar groups (e.g. hydroxyl, carbonyl and carboxylic acids) and the formation of conjugated systems. Some dyes require a relatively large input of energy to dissociate bonds while others require less energy to dissociate bonds which make them far more vulnerable to UV<sup>[23,24]</sup>.

**Effect of hydrogen peroxide:** Figure 8 shows the combined effects of UV and H<sub>2</sub>O<sub>2</sub> on decolorization of remazol brilliant blue at various residence times and

H<sub>2</sub>O<sub>2</sub> concentrations. The results indicated that decolorization increased when the H<sub>2</sub>O<sub>2</sub> concentration increased. Without H<sub>2</sub>O<sub>2</sub> (UV only), the maximum decolorization efficiencies obtained at a residence time of 840 min were 12.3% for the conventional reactor and 7.3% for the coil reactor. With the addition of H<sub>2</sub>O<sub>2</sub> the decolorization efficiency reached 100% for both reactors.

Analysis of variance was performed on the decolorization efficiency using SPSS 14.0 (SPSS Inc., Chicago, IL) as shown in Table 3. Duncan's multiple range test was also performed on the data in order to test the differences among the levels of each factor as shown in Table 4. This statistical analysis showed that the reactor type, residence time and addition of H<sub>2</sub>O<sub>2</sub> have significant effects on the decolorization efficiency of the dye. There were also significant interactions between the factors.

Table 5 shows the minimum and maximum decolorization efficiency of the conventional and coil reactors at various H<sub>2</sub>O<sub>2</sub> concentrations. The results showed that increasing the concentration of H<sub>2</sub>O<sub>2</sub> increased both the minimum and maximum decolorization efficiencies of both reactors. However, 99.9% decolorization efficiency can be obtained by using 12.5 mL L<sup>-1</sup> H<sub>2</sub>O<sub>2</sub>. Ince *et al.*<sup>[21]</sup> also showed that decolorization increased when the H<sub>2</sub>O<sub>2</sub> concentration was increased, but only to some point beyond which no further decolorization occurred. At increased H<sub>2</sub>O<sub>2</sub> concentrations, the excess can react with hydroxyl radicals already in solution to form water and oxygen<sup>[18, 21]</sup>. The results obtained from both reactors also showed that dye decolorization increases when the residence time is increased. More than 93% color removal of remazol brilliant blue dye is achieved with a residence time of 56 min and a complete decolorization can be achieved in 65 min using H<sub>2</sub>O<sub>2</sub> concentration of 12.50 mL L<sup>-1</sup>. Previous research revealed that sufficient reaction time for dye removal using H<sub>2</sub>O<sub>2</sub>/UV process was found to be subjective. Complete destruction of reactive dyes in 30-90 min have been recorded<sup>[25-28]</sup>. Percowski and Kos<sup>[29]</sup> documented more than 99% color reduction of dye house wastewater after 2 hrs. Shyh-Fang *et al.*<sup>[30]</sup> stated that longer reaction times are more advantageous for color removal. They reported 9% color removal in 10 min and complete color removal in 120 min.

The decolorization mechanism using UV/ H<sub>2</sub>O<sub>2</sub> may follow two steps. The ultraviolet light (UV) causes the dissociation of the H<sub>2</sub>O<sub>2</sub> into two hydroxyl radicals (OH) as follows:



A – Homolytic Bond Cleavage initiated by UV radiation



B – Subsequent radical reactions

1. Initiation

An initiator radical ( $\dot{\text{I}}$ ) removes a hydrogen atom from R-H to form an alkyl radical ( $\dot{\text{R}}$ ):



2. Propagation

An alkyl radical reacts with oxygen to form a peroxy radical ( $\text{RO}\dot{\text{O}}$ ):

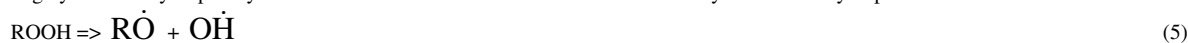


Peroxy radicals react with R-H to form hydroperoxides (ROOH) and alkyl radicals ( $\dot{\text{R}}$ )



3. Chain Branching

Highly reactive hydroperoxy radicals lead to the formation of other free radicals by an auto-catalytic process:



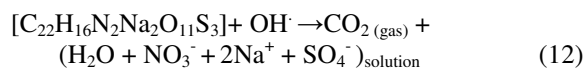
4. Termination

The radical chain ends when two free radicals react together:



Fig. 7: Homolytic bond cleavage and subsequent radical reactions <sup>[22]</sup>

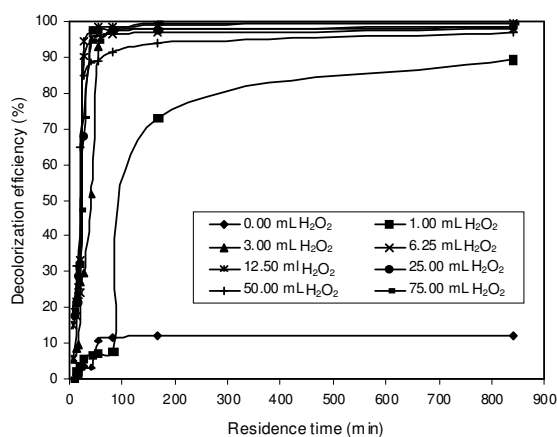
The hydroxyl radicals are strong oxidants that can readily oxidize organic compounds<sup>[21]</sup>. The radicals degrade organic compounds by separating protons to yield organic radical compounds, which lead to either an abstraction of hydrogen atoms or addition to double bonds<sup>[31]</sup>. Colonna *et al.*<sup>[32]</sup> reported that applying UV/H<sub>2</sub>O<sub>2</sub> on dyes containing anthraquinone and sulfonated naphthol rings suggests that nitrogen is evolved at an earlier stage and the azo group and the sulphonic groups are replaced by hydroxyl groups forming polyhydroxylated species. Continuing photooxidation may lead to quinine type compounds and later to aromatic ring cleavage and in the end the main degradation products are sulphate, nitrate, formate and oxalate. When the oxidation is complete, organic compounds end up as CO<sub>2</sub><sup>[33,34]</sup>. Therefore, the equation for complete oxidation of remazol brilliant blue dye can be written as follows:



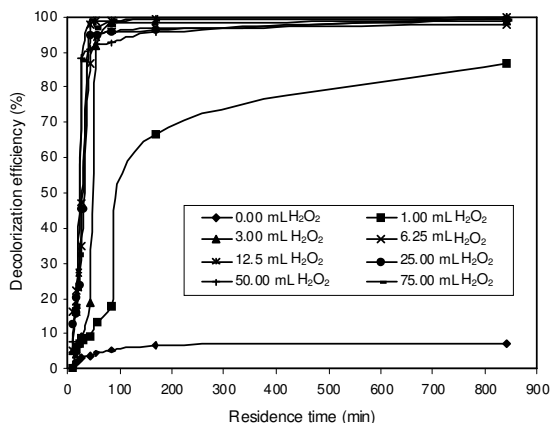
## CONCLUSION

H<sub>2</sub>O<sub>2</sub>/UV treatment for the decolorization of remazol brilliant blue effluent was investigated by

examining the optimum conditions for dye removal in two types of reactor. A higher steady state temperature profile was observed in the coil reactor compared to the conventional reactor. When the dye was fed into the reactors at 25°C, the decolorization efficiency of the conventional reactor varied from 0.0 to 12.3%, while that of the coil reactors varied from 0.0 to 7.3%. At 100°C, the effect of UV radiation was also negligible as the maximum decolorization efficiencies were 4.0 and 3.7% for the conventional and the coil reactors, respectively. Increasing the concentration of H<sub>2</sub>O<sub>2</sub> increased the decolorization efficiencies of both UV reactors. Dye decolorization also increased with residence time. More than 93% color removal of remazol brilliant blue dye was achieved with a residence time of 56 min and 100% decolorization achieved in 65 min using a H<sub>2</sub>O<sub>2</sub> concentration of 12.50 mL L<sup>-1</sup>. The exceptional performance of the combined H<sub>2</sub>O<sub>2</sub>/UV treatment may be attributed to greater



a. Conventional reactor



b. Coil reactor

Fig. 8: Combined effects of UV radiation and H<sub>2</sub>O<sub>2</sub> on decolorization efficiency of remazol brilliant blue

Table 3: Analysis of variance

Source	DF	SS	MS	F	P
Total	497	784689.1			
Model	159	784296.1			
R	1	3254.7	3254.7	2649.41	0.001
T	9	415534.6	46170.5	37584.11	0.001
H	7	233465.5	33352.2	27149.65	0.001
R*T	9	1795.4	199.5	162.39	0.001
R*H	7	1251.9	178.8	145.58	0.001
T*H	63	112768.1	1790.0	1457.09	0.001
R*T*H	63	16225.9	257.6	209.66	0.001
Error	320	393.1	1.2		

R<sup>2</sup> = 98.95

CV = 80.03 %

R = Reactor type

T = Residence time

H = H<sub>2</sub>O<sub>2</sub> concentration

oxidation of the dye due to the increased presence of hydroxyl radicals.

Table 4: Differences among the levels of residence time and H<sub>2</sub>O<sub>2</sub> concentration

Parameter	Level	No. of Observations	Mean	Duncan's Subset
Residence time(min)	8.4	48	9.16	a
	14.0	48	14.24	b
	16.8	48	16.86	c
	21.0	48	28.03	d
	28.0	48	49.03	e
	42.0	48	64.24	f
	56.0	48	75.99	g
	84.0	48	77.66	g
	168.0	48	84.04	g
	840.0	48	86.47	g
H <sub>2</sub> O <sub>2</sub> (mL/L)	0.00	60	4.86	a
	1.00	60	25.04	b
	3.00	60	47.89	c
	6.25	60	61.01	d
	25.00	60	62.94	d
	12.50	60	65.59	d
	75.00	60	67.24	d
	50.00	60	69.99	d

Means with the same letter are not significantly different from one another at the 0.05 level.

Table 5: Effect of H<sub>2</sub>O<sub>2</sub> concentration on decolorization efficiency of remazol brilliant blue

H <sub>2</sub> O <sub>2</sub> level (mL/L)	Conventional reactor		Coil reactor	
	Minimum decolorization (%)	Maximum decolorization (%)	Minimum decolorization (%)	Maximum decolorization (%)
1.00	0.0	89.3	0.0	87.1
3.00	5.7	98.9	5.2	99.1
6.25	5.8	99.0	5.3	99.1
12.50	15.3	99.8	12.6	99.9
25.00	18.0	98.9	13.6	99.9
50.00	19.3	96.9	14.9	99.9
75.00	19.6	99.9	15.7	99.9

Note: Minimum decolorization was obtained at 8.4 min residence time. Maximum decolorization was obtained at 840 min residence time.

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