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Oxidative degradations of reactive blue 4 dye by different advanced oxidation methods

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ABSTRACT

The degradations of an anthraquinone dye, the reactive blue 4 (RB4), were studied by wet air oxidation (WAO), wet peroxide oxidation (WPO), photocatalytic oxidation, and electro-Fenton (EF) advanced oxidation. The RB4 oxidation was evaluated by the decrease in total organic carbon (TOC) content and concentration. The most efficient method for mineralization of RB4 was WPO, but in all methods TOC removal efficiency was above 75% after 60 min of treatment.

1. Introduction

Textile manufacturing is one of the largest industrial producers of wastewater, which is characterized by strong color, highly fluctuating pH, high chemical oxygen demand (COD), and biotoxicity [1]. Although various traditional methods such as adsorption, coagulation, and biological treatments have been used to treat textile dye wastewater, none of these treatments was satisfactory because of the effluent's high degree of polarity and complex molecular structure [2,3]. Promising results have been achieved using advanced oxidation processes (AOPs) for effluent from the dyeing industry in recent years [4–7]. These processes are based on the production of highly reactive radicals, especially hydroxyl radicals, which promote destruction of the target pollutant until mineralization [8]. The remarkable advantage of AOPs over all chemical and biological processes is that they neither transfer pollutants from one phase to the other nor produce massive amounts of hazardous sludge [9–11].

Advanced oxidation processes include ozonation, photocatalytic degradation, Fenton's reagents (H_2O_2/Fe^{2+}), photo-Fenton, and wet air oxidation (WAO). The photocatalytic system involves illumination of large-bandgap semiconductor particles such as TiO_2 dispersed as slurry in contaminated solution or immobilized film. The interaction between this semiconductor and UV radiation produces electron-hole pairs in the surface of semiconductors. The highly oxidative h_{VB}^+ can react with surface bound H_2O to produce hydroxyl radicals or can directly react with the organic molecules [5,12,13]. Photoactivated periodate ($UV/TiO_2/IO_4^-$ system) was proposed as a novel advanced oxidation method. The periodate ions (IO_4^-) capture released electrons from TiO_2, thus elongating the life of h_{VB}^+ [14–16]. Fenton's reagent is an acidic mixture of hydrogen peroxide and Fe(II). Recently, a new electrochemical advanced process called electro-Fenton (EF) was used successfully to degrade various organic pollutants. Electro-Fenton methods broadly involve the continuous production of hydrogen peroxide by reduction of dioxygen at the cathode in aqueous medium [17–21]. Wet air oxidation can be defined as the oxidation of organic and inorganic compounds in aqueous solution or suspension by air or oxygen. Under oxygen pressure (5–200 bar) at elevated temperature (125–320 °C), this process can completely remove organic pollutants [22,23]. However, the application of WAO under rigorous conditions (high temperature and oxygen pressure) is limited due to the high apparatus requirements, which result in high running costs. Therefore, it is necessary to study this process under mild conditions. If a relatively good performance for the treatment of dye wastewater can be achieved, this WAO process could find widespread use in industry [24]. In order to improve the conditions of such a process, homogeneous or heterogeneous catalysts, and strong oxidant such as hydrogen peroxide were added [22,23,25].

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Nomenclature

AOPs	advanced oxidation processes
COD	chemical oxygen demand (mg/L)
C_0	initial dye concentration (mg/L)
C_t	dye concentration at any time (mg/L)
DE	degradation efficiency
DOC	dissolved organic carbon (mg/L)
RB4	reactive blue 4
TOC	total organic carbon
WAO	wet air oxidation
WPO	wet peroxide oxidation

Reactive dyes are frequently used for the dyeing of cotton, woolen, and polyamide fibers [26]. Under typical reactive dyeing conditions, not all dyes bind to the fabric; depending on the class of dye, up to 50% of the initial dye (up to or exceeding 800 mg/L) remains in the spent dyebath in its hydrolyzed form, which has no affinity for the fabric and results in colored effluent [26,27]. Reactive dyes are known to be non-degradable under the typical aerobic conditions found in conventional biological treatment systems, and adsorb very poorly to biological solids, resulting in residual color in discharged effluents [28–30]. In this study, the oxidative degradation and mineralization of reactive anthraquinone dye, reactive blue 4 (RB4), in aqueous solutions using wet air/peroxide oxidation, UV/TiO_2/periodate, and electro-Fenton systems were investigated. Anthraquinone dyes constitute the second largest class of textile dyes after azo dyes, and are used extensively in the textile industry. Reactive blue 4 was selected for this research based on commercial used and previous frequently research conducted. Recently, many advanced oxidation processes using Fenton's reagent (H_2O_2 and Fe^{2+}) with or without ultraviolet irradiation, heterogenous catalysts such as TiO_2 combined with artificial UV or solar light sources or solar photocatalytic–Fenton system (UV/Fenton/TiO_2), have been evaluated for the decolorization and degradation of BR4 dye. Neppolian et al. reported that direct solar light induced and TiO_2 process achieved complete degradation of 4×10^{-4} M RB4 solution within 8 h in the presence of 300 mg/L of H_2O_2 [31]. Photo-Fenton process under artificial and solar irradiation of BR4 was investigated and the best results were obtained using 1.0 mM ferrioxalate and 10 mM of H_2O_2. Under these experimental conditions, 80% TOC and 100% of color removal were obtained for 0.1 mM RB4 dye in 35 min of solar irradiation [32]. Durán and et al. also reported that photo-Fenton process achieved 75% TOC removal of 20 mg/L RB4 solution after nearly 120 min at pH 2 in the presence of 300 mg/L of H_2O_2 and 4 mg/L of Fe^{2+} [33]. The heterogeneous photocatalytic degradation of RB4 solution under Fenton reagent and TiO_2 assisted by concentrated solar light irradiation using a Fresnel lens was studied [34]. But result showed that mineralization was a slower process, so that a longer time was needed for the complete TOC elimination.

2. Materials and methods

2.1. Materials

Commercial C.I. Reactive Blue 4 (Procion Blue MX-R; Color Index 61205; CAS no. 13324-20-4) was obtained from DyStar (Germany) and used without any further purification. The molecular structure of RB4 ($C_{23}H_{14}Cl_2N_6O_8S_2$) was shown in Fig. 1. It has been estimated that approximately 50% of applied reactive dyes is wasted because of dye hydrolysis in the alkaline dyebath. As a result, typical spent dyebaths contain dyes at a concentration in the range of 10–200 mg/L [4,29]. Therefore, the solution of RB4 was prepared in 100 mg/L initial concentration with distilled water for all the

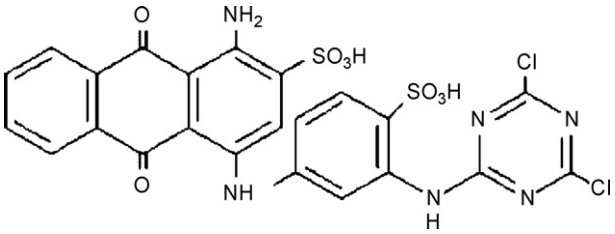

Fig. 1. Molecular structure of reactive blue 4 dye.

treatments. TiO_2 (Anatase form 99.9%) was purchased from Aldrich (USA) with average particle size of approximately 1 μm, specific surface area 8.9 $m^2\,g^{-1}$, and pH_{zpc} approximately 3.8 [35]. A carbon felt electrode (RVG 2000) was obtained from Carbone Loraine (France). All other chemicals, including anhydrous Na_2SO_4, $HClO_4$, H_2O_2, KIO_4, and $Fe(NO_3)_3{\cdot}9H_2O$, were analytical grade. Oxygen was supplied by Tek Oksijen (Mersin, Turkey), in 99.9% purity.

2.2. Oxidation experiments

2.2.1. Wet air oxidation experiments

Wet air oxidation experiments were carried out at various temperatures between 100 and 250 °C with oxygen pressure fixed at 5.05 MPa in a 150 mL stainless steel reactor as shown in Fig. 2. The quantity of dissolved oxygen in water was calculated using an oxygen solubility model for the needed degradation of 100 mg/L RB4 in distilled water [36].

2.2.2. Wet peroxide oxidation

Wet peroxide oxidation (WPO) experiments were carried out at various temperatures between 100 and 200 °C and 35% hydrogen peroxide solution was added to the 150 mL stainless steel reactor, with 1% as void volume.

2.2.3. Photocatalytic oxidation (UV/TiO_2/IO_4^-)

The photocatalytic experiments were run with 150 mL, 100 mg/L aqueous dye solution in a 180 mL cylindrical water jacket Pyrex reactor placed on a magnetic stirrer. The pH of the dye solution was adjusted to 3.00 by the addition of small quantities of 0.5 mM $HClO_4$ solution. Then TiO_2 and KIO_4 were added to the solution. The reaction mixture was sonicated in an ultrasonic bath for 10 min to disperse TiO_2 uniformly in the solution. A mercury vapor UV lamp (UVP-CPQ-7871) that emits its maximum radiation at 365 nm was placed inside the reactor. The intensity of the incident light inside the photoreactor was measured as 0.38×10^{-6} Einstein s^{-1} using a uranyl actinometer [37]. At regular time intervals 26 mL sample aliquots were taken and centrifuged for spectrophotometric analyses. Another experiment under the same conditions was performed for TOC measurements and 3×10 mL sample aliquots were withdrawn from homogeneous 150 mL of solution during treatments.

2.2.4. Electro-Fenton experiments

Electrochemical experiments were performed at constant current with a DC power supply (TT-T-ECHNI-C) in a 250 mL undivided cylindrical glass cell. 0.05 M Na_2SO_4 was used to enhance the conductivity and 0.5 M $HClO_4$ solution was added to bring the pH to 3.0. Electrolyses of 200 mL RB4 solutions were performed on a carbon felt working electrode (50 cm^2 = 12.5 × 4 cm) by applying a constant current of 60, 100, and 200 mA. The counter electrode was Pt gauze (6 cm^2) placed on the center of the cell. The solution was stirred with a magnetic bar. A catalytic quantity of Fe^{3+} (0.2 mM) was added to solutions before starting the electrolysis. Prior to the electrolysis, oxygen gas was bubbled for 15 min to saturate the aqueous solution, which was fed with pure O_2 at 20 mL/min during the experiments.

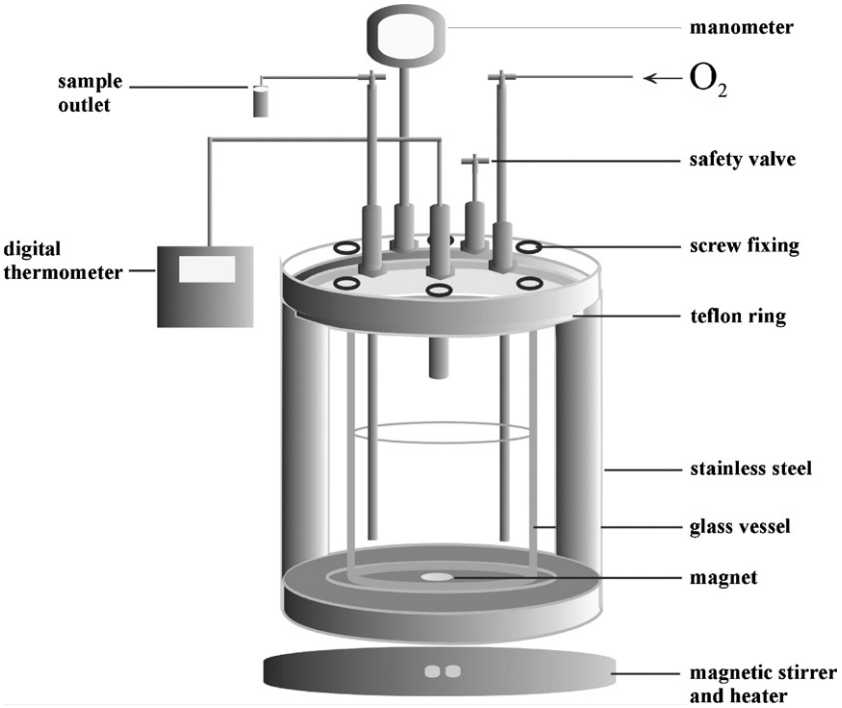

Fig. 2. Schematic illustration of the wet air peroxide system.

Twenty and thirty milliliter samples of aliquots were taken from the dye solution for UV and TOC analyses, respectively, in different experiments. All the samples were filtered through 0.45 μm Titan2 filter before their TOC analysis. All experiments were repeated twice and averages are reported.

2.3. Analytical method

In this study, dye concentration was analyzed spectrophotometrically on a UV–vis spectrometer (Shimadzu UV-160A) at 595 nm by measuring the absorbance of the untreated and treated samples at the maximum wavelength, and the percentage of RB4 degradation efficiency (DE) % was calculated using the following formula:

$$\mathrm{DE}\% = \frac{C_o - C_t}{C_o} 100 \quad (1)$$

where C_o and C_t are the initial and remaining RB4 concentration at given time t, respectively.

The total organic carbon (TOC) of the initial dye solution and samples was determined on a Tekmar-Dohrmann Apollo 9000 analyzer. A calibration curve was prepared using standard solutions of potassium hydrogen phthalate (KHP). An Shimadzu LC-10ADVP model ion chromatograph equipped with a CDD-6A conductivity detector, a Shodex I-524A anion and Shimpack IC-CI cation exchange columns were used to measure nitrate, nitrite, sulfate, chlorine and ammonium ions using 2.5 mM phthalic acid eluent at pH 4 which adjusted with TNs and a total flow rate of 1.2 mL/min for anions; 5 mM nitric acid a total flow rate of 1.5 mL/min for ammonium ion. Generated carboxylic acids were identified by HPLC fitted with a Bio-Rad Aminex HPX 87H column and a 4 mM sulfuric acid solution as mobile phase at 210 nm. Intermediates were identified by gas chromatography–mass spectrometry (GC–MS) with a Thermo Finnigan Trace-Mass system composed of a Thermo Finnigan GC fitted with a RESTEK Rtx-5MS (crossbond 5% diphenyl-95% dimethyl polsiloxane) 0.25 μm, 30 m × 0.25 mm, column and coupled with a Thermo Finnigan Trace-Mass mass spectrometer operating in EI mode at 70 eV. The temperature ramp was 40 °C min^{-1}, 5 °C min^{-1} up to 80 °C and hold time 1 min, then to 280 °C at 4 °C min^{-1} and hold 1 min, and the temperatures of the inlet, transfer line and detector were 250, 250 and 280 °C, respectively. Samples were prepared by the extraction of dye decomposition products with 45 mL of hexane or dichloromethane solvents in three times. Each collected organic solution was then dried with anhydrous natrium sulfate, filtered and its volume reduced to 2 mL to concentrate the remaining products for analysis by GC–MS.

3. Results and discussion

3.1. Degradation experiments

3.1.1. Wet air oxidation

It has been suggested that wet air oxidation occurs through the formation of alkyl, alkyl peroxide radicals, and hydroperoxides, with the third of these being responsible for the autocatalytic decomposition of organic compounds (RH), as shown in Eqs. (2–8) [38].

$$\mathrm{RH} + \mathrm{O_2} \rightarrow \mathrm{R^\bullet} + \mathrm{HO_2^\bullet} \quad \text{(initiation)} \quad (2)$$

$$\mathrm{R^\bullet} + \mathrm{O_2} \rightarrow \mathrm{RO_2^\bullet} \quad \text{(propagation)} \quad (3)$$

$$\mathrm{RO_2^\bullet} + \mathrm{RH} \rightarrow \mathrm{ROOH} + \mathrm{R^\bullet} \quad \text{(propagation)} \quad (4)$$

$$\mathrm{ROOH} \rightarrow \mathrm{RO^\bullet} + \mathrm{OH^\bullet} \quad \text{(autocatalyticdecomposition)} \quad (5)$$

$$\mathrm{RO^\bullet} + \mathrm{RH} \rightarrow \mathrm{ROH} + \mathrm{R^\bullet} \quad \text{(propagation)} \quad (6)$$

$$\mathrm{OH^\bullet} + \mathrm{RH} \rightarrow \mathrm{R^\bullet} + \mathrm{H_2O} \quad \text{(propagation)} \quad (7)$$

$$2\mathrm{ROO^\bullet} \rightarrow \mathrm{ROOR} + \mathrm{O_2} \quad \text{(termination)} \quad (8)$$

These reactions generated organic radicals and other free radicals, which, in turn, initiated chain reactions of dye degradation with the help of dissolved oxygen. Many operating parameters influence the aforementioned formation of free radicals and thus the pollutants degradation rate, among which temperature plays the most important role in the case of sufficient oxygen supply [39].

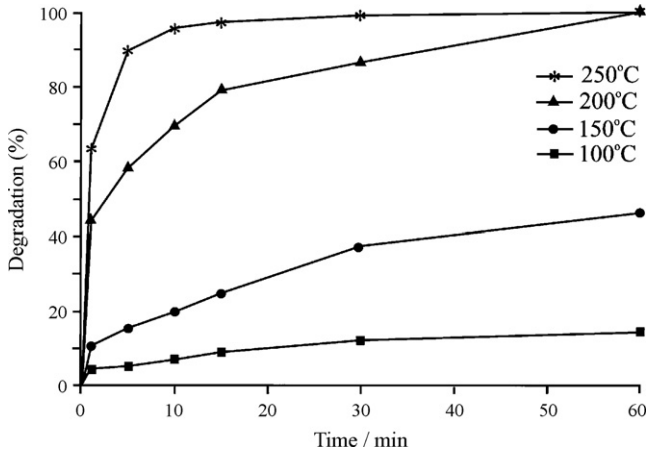

Fig. 3. Effect of temperature on degradation of RB4 in wet air oxidation: $[RB4]_0$ = 100 mg/L, V = 150 mL.

The effect of temperature on degradation after 60 min for wet air oxidation is shown in Fig. 3. In the case of 100 °C, degradation was not effective (15.0%) after 60 min treatment. When the temperature was increased above 100 °C, the degradation was enhanced up to 100%. The degradations were 48.0%, 94.0%, and 100% at 150, 200, and 250 °C, respectively. It can be seen that the removal efficiency was promoted by the increase in temperature due to the enhancement of the hydrothermal reaction and oxygen solubility.

3.1.2. Wet peroxide oxidation (WPO)

WPO experiments were carried out at various temperatures between 100 and 200 °C, and 35% hydrogen peroxide solution was added to the 150 mL stainless steel reactor, with 1% as void volume (Fig. 2). At 100 °C the degradation efficiency reached 92% after 60 min of treatment. With the temperature further rose to 200 °C, the degradation efficiency increased to 100%, which is shown in Fig. 4. Almost complete degradation was reached since first minutes of reaction at 150 and 250 °C. The fast reaction rate of WPO as opposed to WAO is due to the following reasons: (1) H_2O_2 is a stronger oxidant; (2) WPO does not require the transfer of oxygen from the gas phase to the liquid phase as required for WAO. The WPO mechanism may be considered similar to that of Fenton's reaction, with OH• HO_2• or ROO• radicals being the main oxidants depending on the pH of the solution [40].

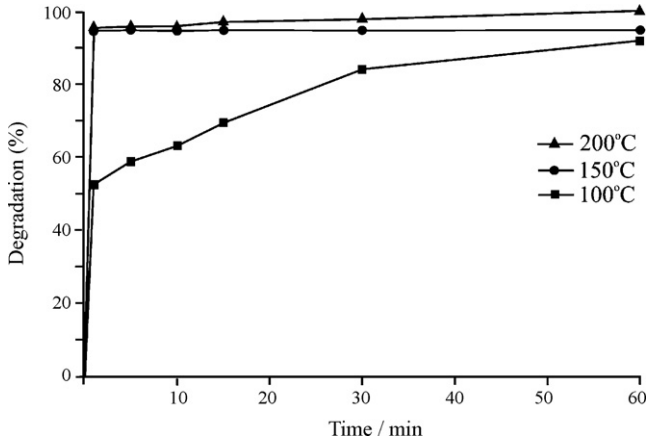

Fig. 4. Effect of temperature on degradation of RB4 by wet peroxide oxidation. $[RB4]_0$ = 100 mg/L, V = 150 mL.

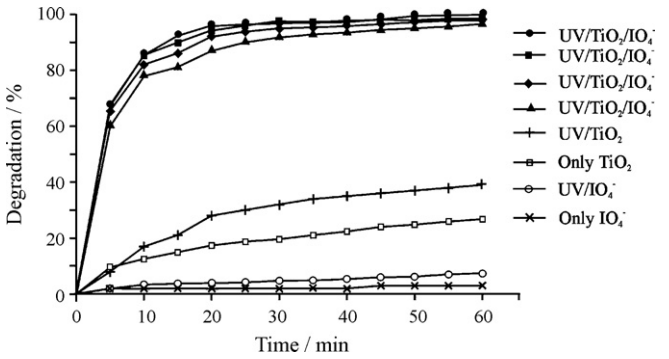

Fig. 5. Degradation % of RB4 solution by: IO_4^- only, TiO_2 only, UV/IO_4^- and UV/TiO_2/IO_4^- systems. TiO_2 = 1 g/L (+, □, ▲, ◊, ■); 2 g/L (●); $[IO_4^-]_0$ = 1 mM (▲); 3 mM (x, ○, ▲, ◊); 5 mM (□, ●); $[RB4]_0$ = 100 mg/L, V = 150 mL, pH 3.0.

3.1.3. UV/TiO_2/IO_4^- process

In the photocatalytic system, the interaction between a semiconductor and UV radiation produces electron-hole pairs in the surface of semiconductors such as TiO_2 (Anatase). The highly oxidative h_{VB}^+ can react with surface bound H_2O to produce hydroxyl radicals or can directly react with the organic molecules [15,37,41].

$$TiO_2 + h\nu \rightarrow e_{CB}^- + h_{VB}^+ \quad (9)$$

$$h_{VB}^+ + H_2O_{(ads)} \rightarrow {}^\bullet OH + H^+ \quad (10)$$

$$\text{Dye} + {}^\bullet OH \rightarrow \text{degradationproduct} \quad (11)$$

$$\text{Dye} + TiO_2(h_{VB}^+) \rightarrow \text{oxidationproduct} \quad (12)$$

$$\text{Dye} + TiO_2(e_{CB}^-) \rightarrow \text{reductionproduct} \quad (13)$$

Fig. 5 shows the decomposition of a 100 mg/L RB4 solution at pH 3 by the UV/TiO_2/IO_4^- system. In the presence of periodate (IO_4^-) alone in the dark, no detectable extent of degradation could be achieved after 60 min treatment. In the UV/IO_4^- process without TiO_2, the degradation efficiency was only 7% after 60 min of treatment. The effects of TiO_2 on degradation of RB4 in the dark and in the UV system were 27% and 39%, respectively. The addition IO_4^- to the UV/TiO_2 system is known to enhance the reaction rate due to IO_4^- capture of released electrons from TiO_2, thus elongating the life of h_{VB}^+ by Eq. (14) [14–16]. Degradation efficiency increased with increasing concentration of periodate from 1 to 5 mM in the presence of 1 g/L TiO_2 suspensions. Degradation of RB4 was 97%, 98%, and 99% after 60 min of treatment for 1, 3, and 5 mM IO_4^-, respectively.

$$IO_4^- + 8e_{(CB)}^- + 8H^+ \rightarrow 4H_2O + I^- \quad (14)$$

The previous research of Gozmen [42] showed that the decomposition slightly increased with increasing periodate concentration from 2 to 5 mM, whereas TOC removal efficiency showed that considerable increase for BR46 dye. However, TOC removal efficiency was decreased at higher concentration periodate due to scavenging the hydroxyl radicals with excess periodate ions by Eq. (15) [41]:

$${}^\bullet OH + IO_4^- \rightarrow OH^- + IO_4^\bullet \quad (15)$$

When the amounts of TiO_2 changed from 1 to 2 g/L in the presence of 5 mM IO_4^- 100% degradation of RB4 was achieved after 50 min of treatment because production of h_{VB}^+ increased with TiO_2. We did not use higher catalyst amounts due to the decreasing effect on degradation. The suitable amount of TiO_2 for the photocatalytic reaction is about 1–3 g/L, although it strongly depends on the type of reactor and TiO_2 powder [43].

3.1.4. Electro-Fenton process

In electro-Fenton methods, H_2O_2 is continuously produced on the cathode by two-electron reduction of dissolved oxygen by Eq.

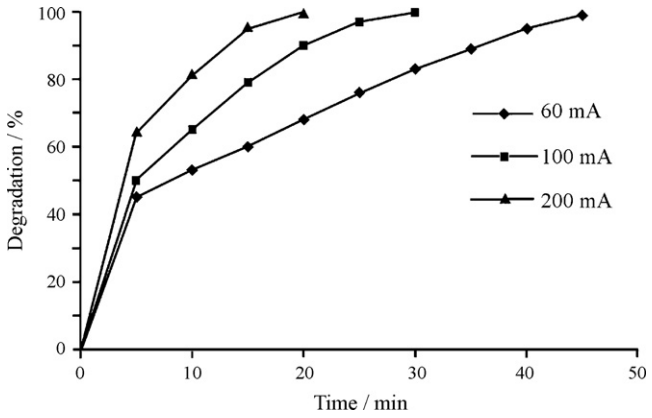

Fig. 6. Degradation of [RB4] solution with the electro-Fenton system. $[RB4]_0$: 100 mg/L, $[Fe^{3+}]_0$: 0.2 mM, V = 200 mL, pH 3.0.

(16) [12,13,18,20]:

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad (16)$$

Ferrous ion is usually added to solution in a catalytic concentration because ferrous ion may also be produced by reduction of ferric ions at the cathode. According to the classical Fenton's reaction hydroxyl radical is produced in the solution [44].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^{\bullet}OH \quad (17)$$

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \quad (18)$$

Fig. 6 shows the degradation of RB4 solution at pH 3 produced in an undivided cell by electro-Fenton in the presence of 0.2 mM Fe^{3+}. Under electro-Fenton conditions, a progressive increase in degradation was observed by increasing the applied constant current from 60 to 100 mA. This trend could be associated with increasing of in situ electrogenerated H_2O_2 concentration. After 20 min of electrolysis at 200, 100, and 60 mA, degradation efficiencies were 100%, 90%, and 68%, respectively. RB4 was slowly degraded at 60 mA and it was completely degraded after the 45 min treatment in this reaction medium.

3.2. TOC removal experiments

The oxidizing power of the four oxidation processes to mineralize RB4 solution was evaluated based on their TOC decay. Fig. 7 shows the TOC decay of a 100 mg/L RB4 solution by wet air oxidation (block A) and wet peroxide oxidation (block B) at different

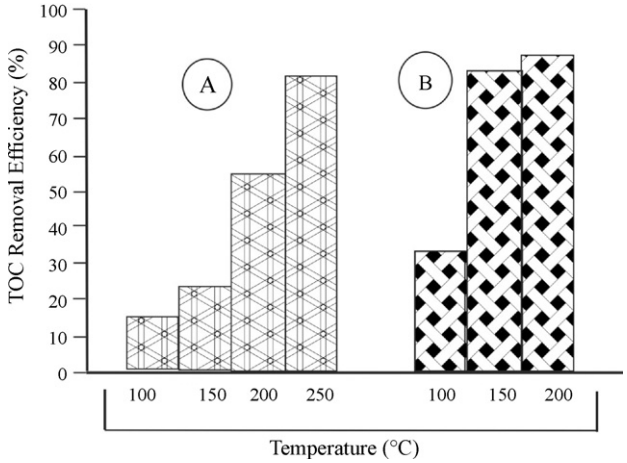

Fig. 7. TOC % Removal of RB4 by wet air peroxide oxidation (A) 5 MPa O_2 (B) H_2O_2 at 60 min. $[RB4]_0$ = 100 mg/L, V = 150 mL.

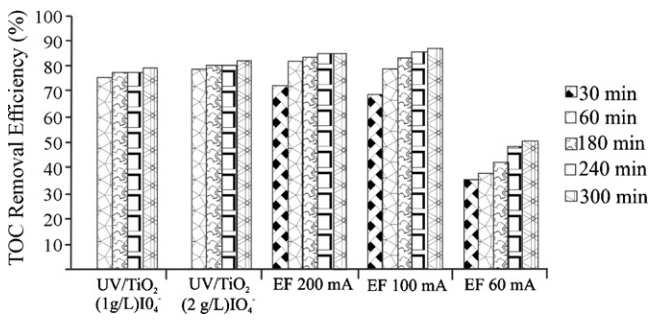

Fig. 8. TOC % Removal of RB4 by the UV/TiO_2/IO_4^- (5 mM) and electro-Fenton systems ($[Fe^{3+}]_0$ = 0.2 mM, 0.05 M Na_2SO_4), $[RB4]_0$ = 100 mg/L, pH 3.0.

temperatures. To make a comparison, RB4 at 100 °C was also investigated, and almost no effective degradation was observed. At the lowest temperature for WAO, the TOC removal efficiency was only 12.6%. A further increase in temperature enhanced the mineralization, which increased significantly to 81.3% when the temperature rose to 250 °C. When using H_2O_2 instead of O_2, there was a very fast increase in the reaction rate. For example, at 100 °C, the TOC removal reached 33%. When the temperature rose to 200 °C at 60 min, the TOC removal efficiency increased significantly to 87%.

An anaerobic experiment was also performed to degradation 100 mg/L RB4 solution for comparison. For that purpose, RB4 solution was purged with nitrogen for removing oxygen. In the anaerobic condition, TOC removal of degradation of RB4 was obtained 45% after 60 min at 250 °C. By helping water dye was degradated in this temperature.

Fig. 8 shows the TOC decay of a 100 mg/L RB4 solution at pH 3 by UV/TiO_2/periodate and electro-Fenton processes. In the UV/TiO_2/IO_4^- system, by adding 5 mM IO_4^- a slight increase in TOC % removal was observed by increasing the concentration of photocatalyst (TiO_2) from 1 to 2 mg/L. After 60 min illumination with 1 g/L TiO_2 and 2 g/L TiO_2, 75% and 79% TOC removal was achieved, respectively. With the increase in the treatment time to 300 min, the mineralization efficiency gradually increased to 78% and 81% for initial TiO_2 concentrations of 1 and 2 g/L, respectively.

In the electro-Fenton system after 30 min of electrolysis, TOC removal efficiencies with 60, 100, and 200 mA constant current were 35%, 68%, and 72%, respectively. The worst mineralization was 50%, obtained with 60 mA for RB4 after 300 min. In the case of 100 and 200 mA, TOC removal efficiency levels were similar (85%) after 300 min of treatment. In the first hour of treatment in both methods, TOC removal was greater than 65%, except with 60 mA in

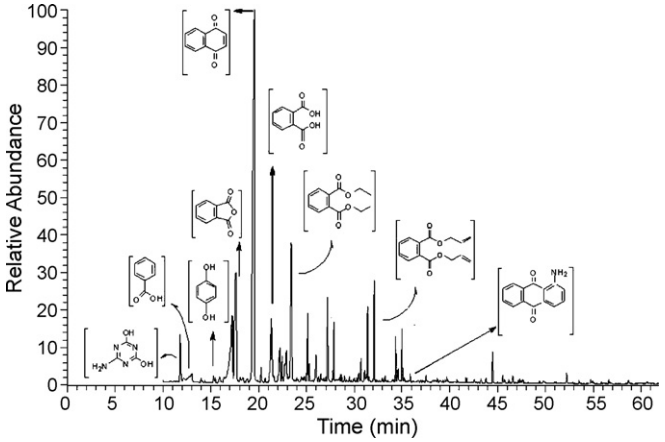

Fig. 9. GC–MS analysis of the organic intermediates of RB4 after 5 min WAO treatment. Reaction condition: T = 200 °C; $[RB4]_0$ = 100 mg/L.

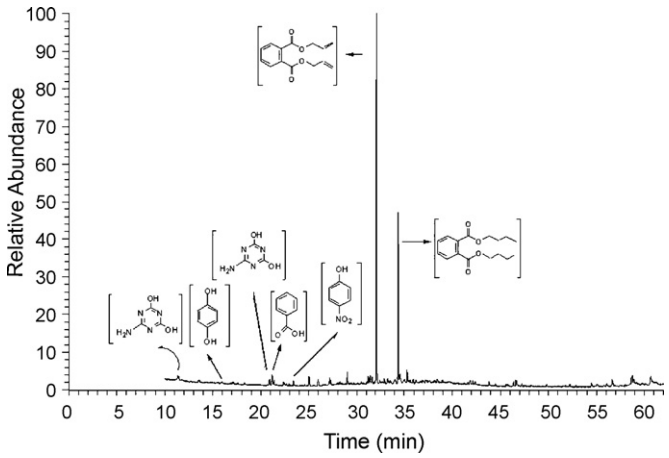

Fig. 10. GC–MS analysis of the organic intermediates of RB4 after 5 h EF treatment. Reaction condition: I = 200 mA; ($[Fe^{3+}]_0$ = 0.2 mM; 0.05 M Na_2SO_4; $[RB4]_0$ = 100 mg/L.

electro-Fenton, but it slowed down after 1 h due to the recalcitrant structural compounds that formed during the degradation.

The above results indicate that WPO, electro-Fenton, and UV/TiO_2/periodate methods were very effective for degrading RB4, an anthraquinone dye. In general, when compared with the other oxidation techniques the capital costs for wet air oxidation are higher, but the processing costs are lower. The capital costs for a wet air oxidation system based on the flow rate, wastewater composition, extent of oxidation and the needed processing conditions [45].

3.3. Identification of degradation intermediates

In this part of the study, organic and inorganic intermediates generated during the degradation of RB4 dye detected by GC-MS, HPLC and IC. The main intermediates identified during WAO and EF treatments of RB4 by GC-MS were shown on GC chromatogram in Figs. 9 and 10. The partial charge showed that the •OH attacks to N-positions on the RB4 structure to form three intermediates groups (A, B and C) in Fig. 11. In part A, because of •OH-addition to N-position, 1-amino-9,10-anthracenedione was found to be initial oxidative product. The benzene rings of this product were further cleaved to yield, alllyl phthalate, diethyl phthalate, 1,4-napthalenedione, phthalic anhydride, 1,2-benzene dicarboxylic acid and benzoic acid by the cooperation of •OH and water. In part B, 4-nitrophenol, hydroquinone and p-benzoquinone were formed after •OH attacks to N-positions. Then the compounds in these parts have broken down into the smaller compounds such as oxalic acid, acetic acid and carbon dioxide that these organic acids were identified by HPLC analysis. In the last part C, two triazine groups, including 2-amino-4,6-dichloro-1,3,5-triazine and 2-amino-4,6-dihydroxy-1,3,5-triazine were identified. The pres-

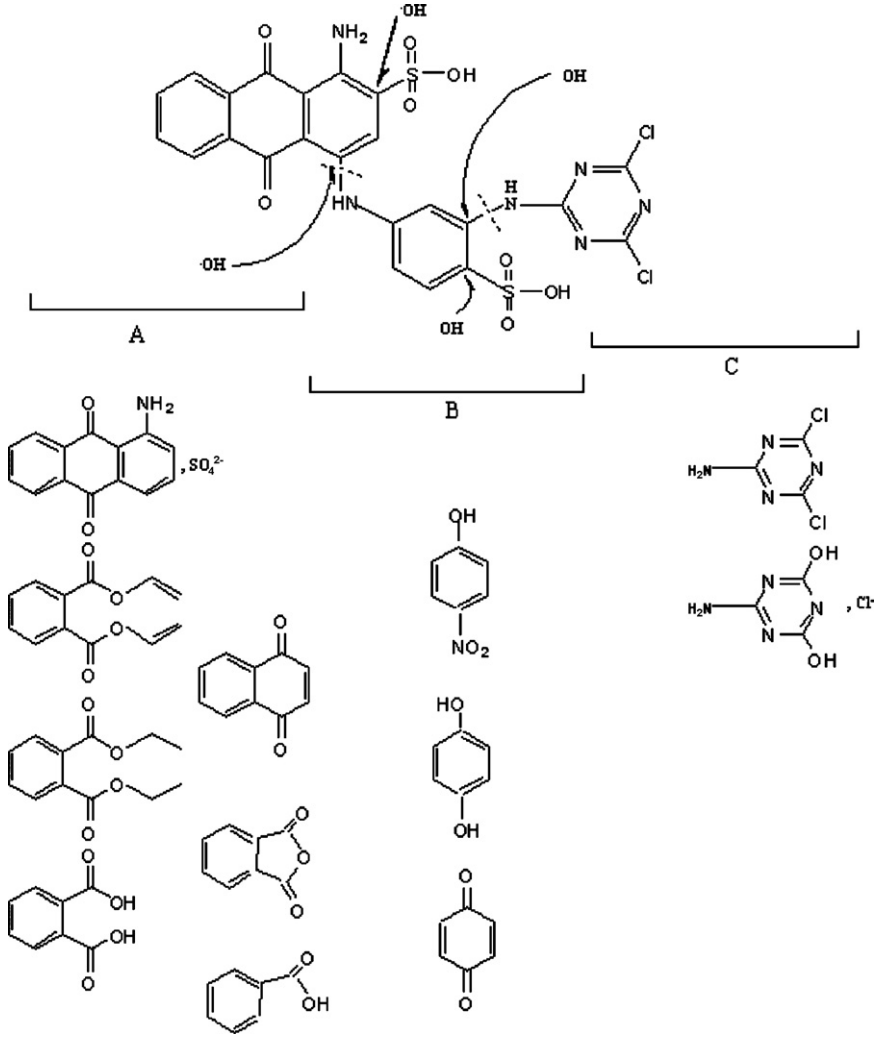

Fig. 11. Proposal of degradation reaction pathway for RB4.

Table 1
Organic intermediates identified by GC–MS.

	EF (1 h) (200 mA)	EF (5 h) (200 mA)	WAO 5 min + 1 h	WPO (5 min)	UV/TiO_2/IO_4^- (5 h)
Napthalene			√		
Benzoic acid			√		
Styrene			√		
2-Methyl napthalane			√		
Hydroquinone	√	√	√		
Phthalic anhydride			√		
Salicylic acid			√		
1-Phenyl-1-propanone			√	√	
1,4-Naphthalenedione			√	√	
1(2H)-3,4-dihydro naphthalenone			√		
3,4-Dimethyl benzoic acid			√		
Diethyl phthalate	√	√	√	√	√
Dibutyl phthalate	√	√	√	√	√
Diallyl phthalate	√	√	√	√	√
2-Amino-9,10-anthracendione			√		
Benzophenone				√	
1,2-Benzenedicarboxylic acid			√		
Phenol 2,4-bis(1,1-dimethylethyl)				√	
Butyl benzene				√	
6-Amino, 2,4-dihydroxy-1,3,5-triazine	√	√	√	√	√
6-Amino, 2,4-dichloro-1,3,5-triazine	√	√			√
4-Nitrophenol		√	√		
Butylparaben		√	√		√

Table 2
Inorganic intermediates identified by IC.

Sample	Cl^-	SO_4^{2-}	NH_4^+ (mg/L)
EF 3 h (200 mA)*	4.64	12.1	<1
EF 5 h (200 mA)*	5.12	12.4	<1
WAO 1 h (200 °C)	7.73	7.5	<1
UV/TiO_2/(5 mM IO_4^-) 3 h	3.78	12.1	<1
UV/TiO_2/(5 mM IO_4^-) 5 h	4.22	14.4	<1

* $LiClO_4$ was used to enhance the conductivity.

ence of these triazine groups after 5 h treatment indicated that they are not completely degradable with photocatalytic and electro-Fenton systems. In Table 1 we summarized identified organic intermediates regarding to applied methods.

The mineralization of RB4 involves the formation of NO_2^-,NO_3^-, SO_4^{2-},Cl^- and NH_4^+ can also be expected. In this study nitrate and nitrite could not be detected, whereas less than 1 mg/L NH_4^+ was detected for all oxidative methods by using ion chromatography, these results are agree with those previously reported [4] with Fenton of RB4. RB4 mineralization involves the formation of sulfate and chlorine ions. However, nitrate ion which has the peak of *m/z* 61.8 was identified via MS in trace amounts after ozonation of reactive Red 120 including triazine group in the previous study [46]. In previous studies nitrate were not detected, the explanation of this phenomenon could be conversation of nitrogen to N_2 [4,33]. Inorganic intermediates generated during the degradation of RB4 by three oxidative methods detected by IC were shown in Table 2.

4. Conclusion

In this study, degradation and mineralization of RB4 dye were investigated using four advanced oxidation methods. Wet peroxide oxidation (WPO) was the most effective and fastest of the methods applied. To achieve TOC removal of 81%, high temperature (250 °C) is necessary in wet air oxidation (WAO), whereas 83% TOC removal was obtained under milder conditions (150 °C) in WPO compared to WAO. When the temperature was increased from 150 to 200 °C, TOC removal efficiency reached 87% after 60 min of treatment in WPO. The oxidation of RB4 by electro-Fenton method was performed at 60, 100, and 200 mA constant currents. The electro-Fenton method with 100 mA can achieve 78% and 85% TOC removal after 60 and 300 min, respectively. The UV/TiO_2/periodate system was the third most effective method for the mineralization of RB4. By this process, which used 5 mM IO_4^- and 2 g/L TiO_2, TOC removal was 79% and 81% after 60 and 300 min of treatment, respectively. These four processes are acceptable, fast, and efficient ways of enhancing the process of destroying textile manufacturing effluent or other organic compounds.

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