

# Comparison of the treatment methods efficiency for decolorization and mineralization of Reactive Black 5 azo dye

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## Abstract

Degradation of Reactive Black 5 (RB5), a well-known non-biodegradable disazo dye, has been studied using UV/TiO<sub>2</sub>, wet-air oxidation (WAO), electro-Fenton (EF) and UV/electro-Fenton (UV/EF) advanced oxidation processes (AOPs). The efficiency of substrate decolorization and mineralization in each process has been comparatively discussed by decreases in concentration and total organic carbon content of RB5 solutions. The most efficient method on decolorization and mineralization was observed to be WAO process. Mineralization efficiency was observed in the order of WAO > UV/TiO<sub>2</sub> > UV/EF > EF. Final solutions of AOPs applications after 90 min treatment can be disposed safely to environment. Photocatalytic degradation kinetics of RB5 successfully fitted to Langmuir–Hinshelwood (L–H) kinetics model. The values of second order degradation rate constant ( $k''$ ) and adsorption constant ( $K$ ) were determined as 5.085 mg L<sup>-1</sup> min<sup>-1</sup> and 0.112 L mg<sup>-1</sup>, respectively.

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## 1. Introduction

Dye pollutants from the textile industry are important source of environment contamination. They pose serious environmental problems because of their color, low biochemical oxygen demand (BOD) and high chemical oxygen demand (COD). Azo dyes constitute the largest and most important class of commercial dyes in wastewater. They are mostly non-biodegradable and resistant to destruction by conventional wastewater treatments [1]. Recent studies indicated that toxic and refractory organic compounds including dyes in wastewater can be destroyed by the most advanced oxidation processes (AOPs) [2–5].

Photocatalytic degradation process (UV/TiO<sub>2</sub>) as one of the AOPs is receiving increasing attention because of the low cost and relatively high chemical stability of the catalyst and

the possibility of using sunlight as the source of irradiation [6]. The process is initiated upon UV irradiation of the semiconductor with the formation of high energy electron/hole pairs by exciting an electron from the valence band (VB) to the conduction band (CB):



The highly oxidative  $h_{\text{VB}}^+$  ( $E^\circ = +2.7 \text{ V}$ ) may directly react with the surface sorbed organic molecules or indirectly oxidize the organic compounds via formation of  $\bullet\text{OH}$  radicals [6,7].

Wet-air oxidation (WAO) is an emerging technology for treating wastewaters, which are either too dilute to incinerate or too concentrate or toxic to biologically degrade [8]. It is a process of subcritical oxidation of organic matter in aqueous phase with oxygen (either in pure form or as air) at elevated temperatures (100–350 °C) and at pressures ranging from 0.5 to 20 MPa [9]. This technique is a feasible method to treat various industrial toxic and refractory wastes [10,11].

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There is an increasing interest in the use of electrochemical treatments for the degradation of toxic organic pollutants in waste waters. As one of them, electro-Fenton (EF) has been efficiently applied to degrade some organic compounds [5,12,13].

In this method,  $\bullet\text{OH}$  radicals are produced in the bulk of the solution in the presence of  $\text{Fe}^{2+}$ . Hydrogen peroxide is produced electrochemically upon reduction of oxygen on several electrodes (mercury pool, graphite, carbon-polytetrafluoroethylene  $\text{O}_2$ -fed cathodes). Reaction pathways of production of OH radicals electrochemically can be represented with the reactions given below:



In this system, catalytic reaction can be propagated via  $\text{Fe}^{2+}$  regeneration, which mainly takes place by the reduction of  $\text{Fe}^{3+}$  species with electrogenerated  $\text{H}_2\text{O}_2$ .  $\text{H}_2\text{O}_2$  is produced via reaction (3) by bubbling  $\text{O}_2$  gas through the acidic solution with a small concentration of  $\text{Fe}^{2+}$  or  $\text{Fe}^{3+}$  in the cathodic compartment. The pollutants are destroyed by the action of  $\bullet\text{OH}$  formed in reaction (4).

Some researchers have studied the degradation of Reactive Black 5 (RB5), a well-known non-biodegradable disazo dye, by AOPs. Wang et al. [14] reported that ozonization was effective method for decolorization of RB5, while mineralization was found to be very low by this method. Destruction of RB5 by UV/ $\text{H}_2\text{O}_2$  process was found to be effective on both of decolorization and mineralization [15,16]. Photocatalytic treatment (UV/ $\text{TiO}_2$ ) also observed to be effective method for decolorization and mineralization of RB5 [17]. In addition, RB5 was decolorized effectively by ultrasound and ultrasound/ $\text{H}_2\text{O}_2$  processes [18].

In particular, no published data is available for destruction of RB5 using electro-Fenton and wet-air oxidation. The objective of this study is to compare efficiency of UV/ $\text{TiO}_2$ , electro-Fenton, UV/electro-Fenton and wet-air oxidation treatment methods for decolorization and mineralization of RB5. After each treatment the solution was controlled if it is safely disposable to environment receiving bodies. Additionally, photodegradation kinetics of RB5 in UV/ $\text{TiO}_2$  system was studied and discussed in terms of Langmuir–Hinshelwood kinetics model.

## 2. Materials and method

### 2.1. UV/ $\text{TiO}_2$ experiments

RB5 dye was purchased from Ak-Kim Company (Gaziantep, Turkey) (Fig. 1) and used without further purifi-

cation. Titanium dioxide used was anatase (Aldrich, +99.9%). The light source used was the mercury vapour UV lamp (UVP-CPQ-7871), which emits its maximum radiation at 254 nm. The intensity of the incident light inside the photo reactor, measured as  $0.50 \mu\text{ photons min}^{-1}$  by uranyl actinometer method [19]. RB5 solutions were prepared at various initial concentrations ( $20\text{--}100 \text{ mg L}^{-1}$ ) and necessary pH adjustments were made with  $0.05 \text{ M H}_2\text{SO}_4$  and  $0.05 \text{ M NaOH}$ . The dye solution was placed in the  $220 \text{ mL}$  pyrex reaction tube and mixed with  $0.5 \text{ g L}^{-1}$  titanium dioxide powder. Reaction mixture was sonicated in ultrasonic bath (Lab-line instruments 9314-1) to disperse  $\text{TiO}_2$  uniformly in the solution. During the runs, oxygen gas with  $0.35 \text{ L min}^{-1}$  flow rate was continuously bubbled into dispersion. One milliliter of sampling was carried out at 0, 10, 20, 30, 40, 50, and 60 min of cumulative irradiation times. The samples were centrifuged at 4000 rpm and analyte absorbance in centrifugate was analyzed by Shimadzu UV-2101 PC scanning spectrophotometer at 580 nm. Analyte concentration in centrifugate was determined using a calibration curve with  $0.10\text{--}110 \text{ mg L}^{-1}$  concentration range.

### 2.2. Adsorption test in the dark

Adsorption isotherm of RB5 on  $\text{TiO}_2$  surface was determined by mixing  $50 \text{ mL}$  aqueous solution of dye at various initial concentrations at pH 3 for 30 min in a mechanical shaker. The extent of adsorption on  $\text{TiO}_2$  surface was evaluated in terms of color removal rate (absorbance at 580 nm). Data obtained from the adsorption experiments was fitted to the modified empirical Langmuir equation [20,17]:

$$\frac{C_e}{Q_e} = \frac{1}{K_L} + \frac{a_L}{K_L} C_e$$

where  $C_e$  is the equilibrium concentration of RB5 after 30 min,  $Q_e$  adsorbed dye concentration on  $\text{TiO}_2$  surface, and  $K_L$  and  $a_L$  are isotherm constants for particular solute–solvent combination. The dimensionless separation factor ( $R_L$ ) indicates the shape of the Langmuir isotherm to be either favorable ( $0 < R_L < 1$ ), unfavorable ( $R_L > 1$ ), linear ( $R_L = 1$ ), or irreversible ( $R_L = 0$ ):

$$R_L = \frac{1}{1 + KC_0}$$

$C_0$  in the equation represents highest initial dye concentration ( $\text{mg L}^{-1}$ ).

### 2.3. Electro-Fenton experiments

Graphite felt (RVG 2000) used in electro-Fenton experiments was from Carbone Loraine.  $\text{Fe}(\text{NH}_4)(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  and Nafion 117 were bought from Aldrich. Pure oxygen gas (99.99%) has been bought from different companies. Electrolytic experiments were conducted in a  $300 \text{ mL}$  glass reactor. The platinum gauze anode was separated from the cathode part by using Nafion 117 membrane. The carbon

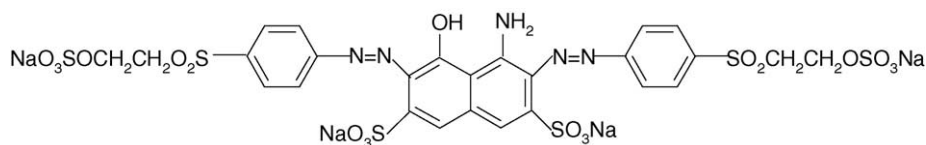


Fig. 1. Chemical structure of non-hydrolyzed form of RB5.

felt (3 cm × 5 cm) was used as working electrode (cathode). Saturated calomel electrode was used throughout the electrolytic experiments as the reference electrode. Controlled potential electrolysis and coulometric measurements were performed by an EG&G Par model 273A electrochemical system. In a typical electrolytic experiment, following the addition of the metal salt into pH 3 solution of RB5, O<sub>2</sub> gas was bubbled through the solution for 20 min and then −0.55V/SCE constant cathodic potential was applied to the system, while O<sub>2</sub> gas bubbling was continued throughout the electrolysis. Fe<sup>2+</sup>/RB5 = 3 (mol/mol) ratio was used for all EF experiments. Predetermined amounts of aliquots were withdrawn from the system at certain time intervals. Each aliquot of solution withdrawn from the system has been analyzed immediately by UV–vis spectrophotometer.

#### 2.4. Wet-air oxidation experiments

Oxidation of RB5 solutions was carried out in the high pressure Hastelloy reactor (4740 Series, Parr Instrument, USA) that has an effective volume of 71 mL. The gas inlet, pressure gauge and on-off Hoke valve were mounted on top of the head. The connection of the system elements was made with 0.25 in. o.d. tubing.

The operating pressure of the oxidation reaction was controlled by a gauge above the head of reactor. Bottled oxygen was used as the oxygen supply for the oxidation reaction. The oxygen partial pressure was kept at 17 bar in all experiments. Desired reaction temperature was provided by heating the reactor in a eutectic salt bath whose components were 53% KNO<sub>3</sub>, 40% NaNO<sub>2</sub>, and 7% NaNO<sub>3</sub>. The temperature was controlled by PID heat controller (Elimko, Turkey) to keep temperature of salt solution with in ±3 °C of set point.

In a typical WAO experiment, 50 mL of the RB5 dye solution was placed into the reactor. After the reactor was sealed, it was pressurized by supplying oxygen gas and heated to the desired temperature by immersing into the eutectic salt bath.

The operating temperature varied between 200 and 300 °C. The oxidation reactors were agitated by a shaker in eutectic salt bath at 150 cycles/min. Because of batch type, the reactor does not allow to sampling for analysis at various time intervals. Therefore, the experiments were repeated at various time intervals for all temperatures. At a certain reaction time, reactor was cooled rapidly up to room temperature; gas effluent depressurized slowly and reactor was unsealed. The solution of this experiment was one sampling. WAO runs were carried out at three different temperatures

(200, 250, and 300 °C) at various reaction times. The solutions were analyzed by UV–vis spectrophotometer and TOC analyzer.

#### 2.5. Mineralization of the RB5 solutions during AOPs

Mineralization of the RB5 solutions during AOPs treatment was followed by measuring the total organic carbon using Tekmar Dohrmann Apollo 9000 instrument. In a typical application, an aliquot of 10 mL was withdrawn from the reaction medium at certain intervals. In electro-Fenton application, 10 mL solution was filtered through glass frit to get rid of carbon contamination from the carbon felt used as electrode in electrolytic experiments. In UV/TiO<sub>2</sub> application, 10 mL solution was centrifuged at 4000 rpm to remove TiO<sub>2</sub> catalyst. The samples were ignited at 700 °C on platinum-based catalyst, and the carbon dioxide formed was swept by pure oxygen as the carrier gas through a non-dispersive infrared (NDIR) detector.

#### 2.6. Toxicity test

*Pseudomonas putida* growth inhibition test was applied according to the procedures described in the ISO protocol (ISO, 1995) [21]. The inhibition effect of degradation products of RB5 was determined by the increase of turbidity of bacterial cultures. The mineral medium composed for the test was as follows: 125 mg L<sup>−1</sup> NaNO<sub>3</sub>; 30 mg L<sup>−1</sup> K<sub>2</sub>HPO<sub>4</sub>; 15 mg L<sup>−1</sup> KH<sub>2</sub>PO<sub>4</sub>; 500 mg L<sup>−1</sup> D(+)-glucose monohydrate; 50 mg L<sup>−1</sup> MgSO<sub>4</sub>·7H<sub>2</sub>O, and 0.0125 mg L<sup>−1</sup> iron(III)citrate. The pH was adjusted to 7.4 ± 0.1. The mineral medium was mixed with the sample. The result was compared with the turbidity of the control culture incubated under the same conditions, but without degradation products, after 18 ± 1 h incubation duration at 26 ± 1 °C. Turbidity measurement of the bacterial biomass grown in the samples was performed on a Shimadzu UV-2101 PC Scanning spectrophotometer at 600 nm. Because this wavelength is close to absorption wavelength of RB5 (580 nm), the solution was centrifuged at 4000 rpm first and then the precipitate was washed with water to remove dye solution. The same amount of water was added to bacterial mass and turbidity measurement of this solution was performed at 600 nm. Toxicity test experiments for each applied methods were run in three replicates. The percentage of cell multiplication inhibition was calculated in conformity with the ISO standard (ISO, 1995) for all samples.

### 3. Results and discussion

#### 3.1. UV/TiO<sub>2</sub>

##### 3.1.1. The effect of pH on photocatalytic degradation of RB5

The effect of pH on photocatalytic degradation of RB5 was illustrated in Fig. 2. The experiments were carried out with 40 mg L<sup>-1</sup> dye concentration at pH of 3, 5, 7, and 9 for 30 min reaction time. Decomposition of RB5 was obtained under 30% level at each pH for 30 min illumination time. Complete degradation was achieved at pH 3 at the end of 20 min reaction time. It was observed that increasing pH of the solution resulted in decrease of the decolorization rate of RB5 with exception at pH 7. Adsorption and agglomeration are two important factors on photocatalytic degradation of RB5 and these factors strongly depend on pH of the solution. The zero point charge pH (pH<sub>ZPC</sub>) for anatase TiO<sub>2</sub> used in this study is approximately 4 [22,23]. Therefore, catalyst surface was positively charged at acidic medium and negatively at basic medium. Repulsion between positively charged surfaces prevents the agglomeration of the catalyst particles at acidic medium. Since, the dye has sulfonate groups in its structure, which are negatively charged, the acidic solution favors adsorption of the dye molecules onto TiO<sub>2</sub> surface. As a result of that, decolorization efficiency increased via reaction of dye molecules with •OH radical on the surface of TiO<sub>2</sub> catalyst. As pH of the solution was increased, the adsorption of dye molecules onto catalyst surface decreased. Therefore, decolorization level was observed to be lower at basic pH medium (pH 9). Because catalyst surfaces were more negatively charged than that of at pH 7 agglomeration might be less. Thus, decolorization of the dye at pH 9 was observed to be higher than that of at pH 7.

##### 3.1.2. Photocatalytic degradation and kinetics of RB5

When photocatalytic degradation of RB5 was performed at varying initial concentrations (20, 40, 60, 80, and 100 mg L<sup>-1</sup>) at pH 3, the results demonstrated that the more diluted was the initial solution the faster was the degradation (Fig. 3).

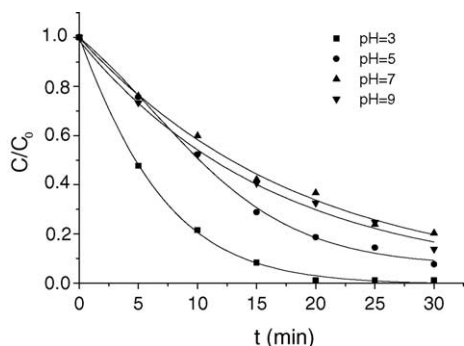


Fig. 2. UV/TiO<sub>2</sub> photocatalytic degradation of RB5 at various pH ( $C_0 = 40 \text{ mg L}^{-1}$ ,  $\text{TiO}_2 = 0.5 \text{ mg L}^{-1}$ ).

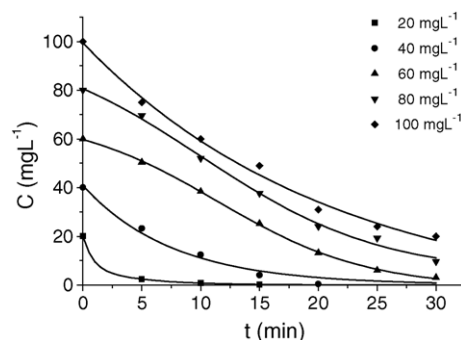


Fig. 3. Degradation of RB5 at various initial concentrations by UV/TiO<sub>2</sub> application (pH 3,  $\text{TiO}_2 = 0.5 \text{ g L}^{-1}$ ,  $\text{O}_2 = 0.5 \text{ L min}^{-1}$ ).

At 20 mg L<sup>-1</sup> initial dye concentration, all dye solution was degraded at 15 min illumination time. In case of 100 mg L<sup>-1</sup> initial concentration, 80% degradation was achieved at the end of 30 min reaction time. The amount of photoactive sites on TiO<sub>2</sub> surface has decreased due to adsorption of the organic compound and its degradation products in concentrated solutions. Therefore, degradation rate has decreased [24,25].

The kinetics Langmuir–Hinshelwood (L–H) model which was modified by Heredia et al. [26], was used to analyze the photodegradation kinetics of dye. According to L–H kinetics second order decomposition rate of organic compound can be expressed as:

$$r = k' \Phi_{\text{OH}} \Phi_{\text{OC}}$$

In this equation,  $r$  is the initial degradation rate,  $k'$  the surface second order rate constant, and  $\Phi_{\text{OH}}$  and  $\Phi_{\text{OC}}$  are the fractions of sites covered by hydroxyl radicals and by organic compounds, respectively. Second order kinetics equation can be written in terms of a pseudo-first order kinetic constant as follows [26]:

$$\frac{1}{k_{\text{obs}}} = \frac{1}{k''K} + \frac{C_0}{k''}$$

where  $k_{\text{obs}}$  is pseudo-first order kinetic constant,  $k''$  the second order rate constant, and  $K$  is the adsorption constant. When initial concentrations are plotted versus  $1/k_{\text{obs}}$ , the rate constant and the adsorption equilibrium constant can be calculated. Kinetics of RB5 was analyzed using  $-dc/dt = k_{\text{obs}}C$  kinetic equation. Pseudo-first order rate constants were calculated from slope of plot of  $\ln(C/C_0)$  versus time for each concentration (Fig. 4).

Half-life ( $t_{1/2}$ ) and pseudo-first order kinetic rate constants with various initial concentrations of RB5 are given in Table 1. The oxidation rate constants have decreased due to increasing adsorption constants. The values of half-life for RB5 depended on initial concentrations were range between 1.8 and 12.2 min<sup>-1</sup>. The same relation was observed for pseudo-first order rate constants and their range was determined between 0.379 and 0.057 min<sup>-1</sup>.

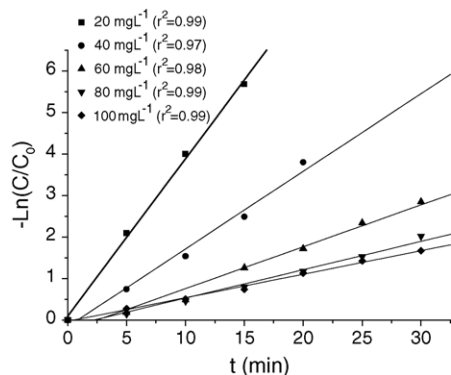


Fig. 4. Linear transforms:  $\ln C/C_0$  vs. time for the decomposition of RB5 during UV/TiO<sub>2</sub> application.

Table 1  
Pseudo-first order rate constants and half-life during AOPs applications

AOPs methods	First order ( $k_{obs}$ ) (min <sup>-1</sup> )	$t_{1/2}$ (min)
UV/TiO <sub>2</sub> (mg L <sup>-1</sup> )		
20	0.379	1.8
40	0.187	3.7
60	0.101	6.9
80	0.068	10.2
100	0.057	12.2
WAO (°C)		
300	0.406	1.7
250	0.168	4.1
200	0.092	7.5
EF (mg L <sup>-1</sup> )		
20	0.197	3.5
40	0.095	7.3
60	0.035	19.9
80	0.022	30.8
100	0.019	36.1

Fig. 5 shows that the plot of  $1/k_{obs}$  versus  $C_0$  forms a straight line according to the modified L–H model with the regression coefficient of 0.983. The second order rate constant ( $k'$ ) and adsorption constant ( $K$ ) were calculated as  $5.085 \text{ mg L}^{-1} \text{ min}^{-1}$  and  $0.112 \text{ L mg}^{-1}$ , respectively.

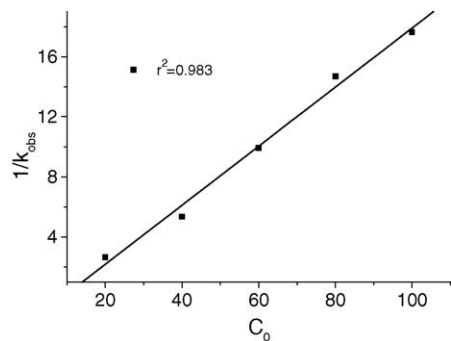


Fig. 5. Determination of adsorption equilibrium constant and second order rate constant for adsorption of RB5 on TiO<sub>2</sub>.

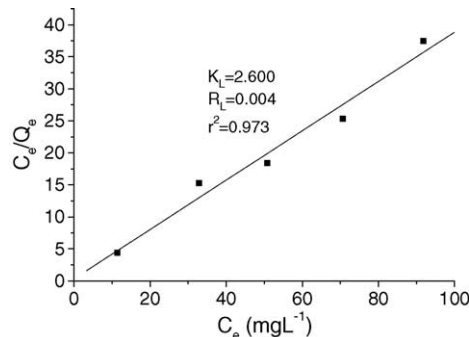


Fig. 6. Establishment of Langmuir monolayer adsorption constant for adsorption of RB5 on TiO<sub>2</sub> at pH 3.

### 3.2. Adsorption of RB5 on TiO<sub>2</sub> in the dark

$C_e/Q_e$  versus  $C_e$  plot and Langmuir parameters obtained from this plot are shown in Fig. 6. Langmuir adsorption constant ( $K_L$ ) and the separation factor ( $R_L$ ) were calculated as  $2.600 \text{ L mg}^{-1}$  and  $0.004$ , respectively. From the data in Fig. 6, it is seen that adsorption constant of various initial concentrations of RB5 over TiO<sub>2</sub> at pH 3 was nearly 23 times higher than the adsorption constant which was calculated by using the kinetic model. The both adsorption constants calculated for Reactive Red 120 azo dye was found to be close in previous work [2]. However, these values highly differed for RB5 which has smaller molecular size and higher polarity than Reactive Red 120. The dimensionless separation factor ( $R_L$ ) indicates that the shape of the Langmuir isotherm was favorable since  $0 < R_L < 1$  [27].

### 3.3. Degradation of RB5 by wet-air oxidation

The effect of temperature on the decolorization of  $40 \text{ mg L}^{-1}$  RB5 solution by wet-air oxidation is shown in Fig. 7. The decolorization rate has been enhanced markedly by increasing the temperature from 200 to 300 °C at constant 17 bar of oxygen partial pressure. At 10 min treatment time, RB5 was decolorized 56, 87, and 100% at 200, 250, and 300 °C, respectively. Because of application at the higher operation temperature causes increase in the operating cost

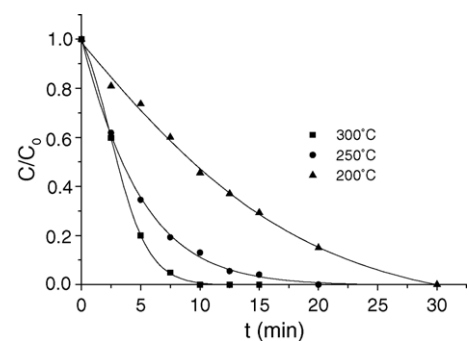


Fig. 7. Degradation of RB5 at various operation temperatures by wet-air oxidation ( $C_0 = 40 \text{ mg L}^{-1}$ ;  $P_{O_2} = 17 \text{ bar}$ ).



of the technique, decolorization of RB5 by WAO at 250 °C appears to be more practical comparing with 300 °C. The substrate was decolorized completely at the end of 20 min treatment time at this temperature.

The temperature has been also major effect on the reaction rate and half-life ( $t_{1/2}$ ) of the organics [28]. When the temperature was enhanced 50 °C, which is from 200 to 250 °C,  $t_{1/2}$  had decreased from 7.5 to 4.1 min. When temperature was increased with the same magnitude again, which was from 250 to 300 °C,  $t_{1/2}$  had decreased from 4.1 to 1.7 min (Table 1).

### 3.4. Degradation of RB5 by electro-Fenton application

Fig. 8 shows decolorization of 250 mL of various initial concentrations of RB5 acidic solutions (20–100 mg L<sup>-1</sup>) by electro-Fenton process. Decolorization rate increased with increasing electrolysis time for all various concentration of RB5 under -0.55V/SCE constant cathodic potential applied to the system at 30 °C for 30 min.

As can be seen, a reversed proportion was observed between initial concentrations of RB5 and decolorization rates (Table 1). Decolorization rate was decreased from 0.197 to 0.019 min<sup>-1</sup> with increasing initial concentration from 20 to 100 mg L<sup>-1</sup>. After 30 min EF treatment, RB5 was decomposed completely at 20 mg L<sup>-1</sup> initial concentration and 94% at 40 mg L<sup>-1</sup> initial concentration. In case of 60, 80, and 100 mg L<sup>-1</sup> initial concentrations decolorizations were observed 50% and less. Half-life ( $t_{1/2}$ ) at various initial concentrations increased with increasing initial concentration. When initial concentration increased from 20 to 40 mg L<sup>-1</sup>,  $t_{1/2}$  was increased from 3.5 to 7.3 min that was 2.1 times higher than initial value. At higher concentration,  $t_{1/2}$  ratio was low, for instance; it was 1.55 when concentration was increased from 60 to 80 mg L<sup>-1</sup> and it was 1.17 when concentration was increased from 80 to 100 mg L<sup>-1</sup>.

The consumed charges for decolorization of RB5 during 30 min electro-Fenton treatment were calculated as 1.21, 1.28, 1.36, 1.42, and 1.51 mF for 20, 40, 60, 80, and 100 mg L<sup>-1</sup>, initial concentrations, respectively.

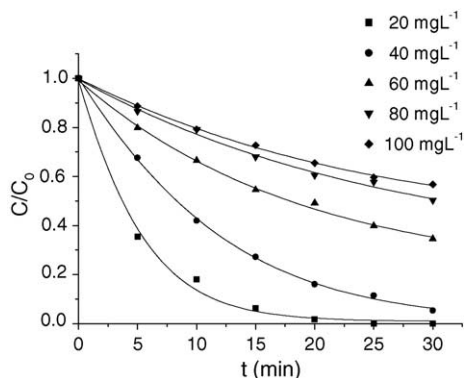


Fig. 8. Degradation of various aqueous solutions of RB5 at various initial concentrations by EF application.

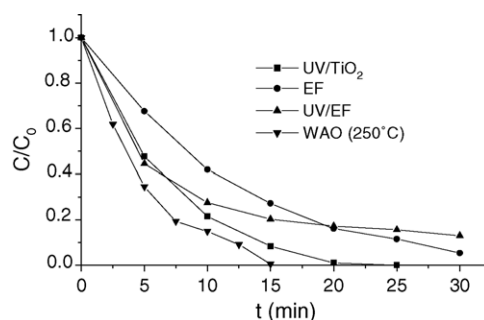


Fig. 9. Degradation of RB5 by various AOPs (RB5 = 40 mg L<sup>-1</sup>).

### 3.5. Comparison of efficiencies of AOPs for degradation of RB5

Decolorization efficiencies of UV/TiO<sub>2</sub>, EF, UV/EF, and WAO treatments were compared by running the experiments with 40 mg L<sup>-1</sup> initial concentration of RB5. The results were illustrated in Fig. 9. Degradation levels for these applications were observed in 80–100% range for 30 min treatments.

WAO which was carried out at 250 °C and UV/TiO<sub>2</sub> treatments, found to be efficient methods for complete decolorization of RB5 at 15 and 20 min treatment time, respectively. When UV light was used with EF process (UV/EF) decolorization was observed higher until 20 min treatment than conventional EF process. After 20 min, conventional EF process exhibited more efficiency for decolorization of RB5. Finally, decolorization efficiency was observed to be in the order of WAO > UV/TiO<sub>2</sub> > EF > UV/EF at the end of the 30 min treatment.

### 3.6. Mineralization of the RB5 using different AOPs

Mineralization of 100 mg L<sup>-1</sup> RB5 solutions during AOPs treatment was followed by measuring total organic carbon (TOC) contents of the samples. Fig. 10 shows the decrease of TOC percent versus time for different AOPs.

The fastest mineralization was obtained with WAO oxidation process with 77% efficiency. Mineralization with UV/TiO<sub>2</sub> system was also observed to be efficient (71% mineralization). EF and UV/EF treatments were found to be less efficient methods on mineralization of RB5 with 20 and 29%

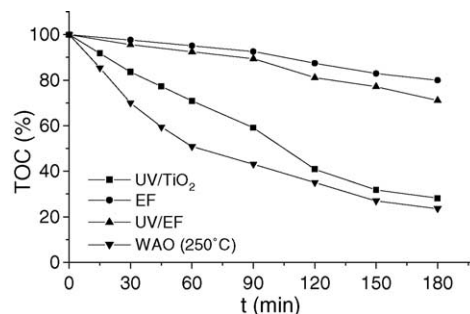


Fig. 10. TOC decreases of RB5 aqueous solutions during various AOPs applications ( $C_0 = 100 \text{ mg L}^{-1}$ ).

mineralization, respectively. Combination of UV light with electro-Fenton process promoted the mineralization of RB5 only by 9%. Although WAO was observed to be most effective method complete mineralization was not achieved at the end of the 180 min treatment. Some researchers were observed similar results for WAO process, i.e. even at 300 °C, organic materials were not completely mineralized because stable intermediates such as acetic acid were formed [29].

Graphite structure is composed of unsaturated aromatic rings which may be very active for reaction with  $\bullet\text{OH}$  radicals. Graphite felt, which was used as a working electrode (cathode) in EF application, might reduce the degradation efficiency via competition between graphite and RB5 molecules for reaction with  $\bullet\text{OH}$  radicals [30]. Although  $\bullet\text{OH}$  radicals might have been produced excessively in EF system, important part of the radicals was consumed by graphite felt. Therefore, the degradation level of TOC in EF and UV/EF processes was observed to be lower than the other methods.

### 3.7. Comparison of the toxicity for degradation products of RB5 by using AOPs

The toxicity of intermediates was determined by cell growth inhibition test technique. The results were illustrated in Fig. 11. No bacterial growth inhibition was observed for RB5 solution at  $t=0$ . According to the results of inhibition experiments, the primary products formed at the first 15 min in all AOP applications were implied to have toxicity. The toxicity of these products and secondary or tertiary products were decreased gradually dependence on oxidation time. However, intermediates yielded at UV/TiO<sub>2</sub> and WAO processes were shown slightly higher toxicity than the others after 45 min, and then decreased by increasing oxidation time. Since bacterial inhibition change trends for the AOP applications were different, RB5 might have been degraded with different mechanisms. As a result of that, different intermediates with different toxicity patterns were formed. Because of having low toxicity, there would not be any risk when solutions of RB5 treated by these AOPs methods for 90 min were disposed to the appropriate environmental receiving bodies.

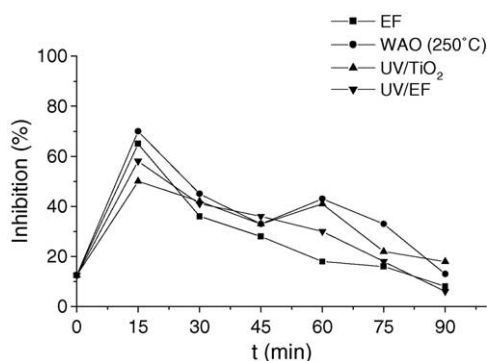


Fig. 11. Bacterial inhibition of intermediates produced during various AOPs applications.

## 4. Conclusion

UV/TiO<sub>2</sub>, electro-Fenton, wet-air oxidation, and UV/electro-Fenton advanced oxidation processes have been studied and compared with a view to decrease in the pollutant concentration for the degradation of Reactive Black 5 azo dye in aqueous solution. Among all applied AOPs processes wet-air oxidation process was found to be most effective method for decolorization and mineralization of RB5. In this process 77% of TOC removal has been achieved at 250 °C for 180 min treatment. UV/TiO<sub>2</sub> was the second effective process on mineralization of the dye with 71% of TOC removal. Because possibility of agglomeration was very low at acidic pH, UV/TiO<sub>2</sub> process was exhibited high efficiency at acidic pH medium for photocatalytic degradation of RB5. In this process, the surface second order rate and surface adsorption constant were calculated as 5.085 mg L<sup>-1</sup> min<sup>-1</sup> and 0.112 L mg<sup>-1</sup>, respectively.

Although EF was effective method on decolorization of RB5 only 20% mineralization was achieved by this process. When EF system was supported with UV light, mineralization was increased only upto 29%.

Toxicity measurement of the samples showed that final solutions of AOPs applications after 90 min treatment were disposable safely to environment because of having intermediates with low toxicity.

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