Journal of Hazardous Materials 177 (2010) 95–102

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Degradation of acid red 97 dye in aqueous medium using wet oxidation and electro-Fenton techniques

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ARTICLE INFO

Article history:
Received 23 June 2009
Received in revised form 21 October 2009
Accepted 12 November 2009
Available online 18 November 2009

Keywords:
Wet air oxidation
Wet peroxide oxidation
Electro-Fenton
Persulfate
Periodate
Bromate

ABSTRACT

Degradation of the acid red 97 dye using wet oxidation, by different oxidants, and electro-Fenton systems was investigated in this study. The oxidation effect of different oxidants such as molecular oxygen, periodate, persulfate, bromate, and hydrogen peroxide in wet oxidation system was compared. Mineralization of AR97 with periodate appeared more effective when compared with that of the other oxidants at equal initial concentration. When 5 mM of periodate was used, at the first minute of the oxidative treatment, the decolorization percentage of AR97 solution at 150 and 200 °C reached 88 and 98%, respectively. The total organic carbon removal efficiency at these temperatures also reached 60 and 80%. The degradation of AR97 was also studied by electro-Fenton process. The optimal current value and Fe^{2+} concentration were found to be 300 mA and 0.2 mM, respectively. The results showed that electro-Fenton process can lead to 70 and 95% mineralization of the dye solution after 3 and 5 h giving carboxylic acids and inorganic ions as final end-products before mineralization. The products obtained from degradation were identified by GC/MS as 1,2-naphthalenediol, 1,1′-biphenyl-4-amino-4-ol, 2-naphthalenol diazonium, 2-naphthalenol, 2,3-dihydroxy-1,4-naphthalenedion, phthalic anhydride, 1,2-benzenedicarboxylic acid, phthaldehyde, 3-hydroxy-1,2-benzenedicarboxylic acid, 4-amino-benzoic acid, and 2-formyl-benzoic acid.

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1. Introduction

In recent years, the textile processing industries are being available in developing countries. Textile dyes are an abundant source of colored organic compounds that present an increasing environmental danger. During dye production and textile manufacturing processes, large quantity of wastewater containing dyestuffs with intensive color and toxicity is introduced into the aquatic systems. Even a small amount of dye in the water (e.g., 10–20 mg L^{-1}) is highly visible, and the water transparency and the gas solubility of water bodies are affected as well. In addition, some dyes can be considered carcinogens or mutagens, and they may also contain various heavy metals that breach environmental standards [1–4]. Traditional treatments involving biological and coagulation/flocculation methods are generally ineffective for total color removal. Therefore, advanced oxidation processes (AOPs) producing high oxidation potential hydroxyl free radicals have often been investigated for organic wastewater treatment, including Fenton's reagents [5,6], ozone [7], electrochemical oxidation (EAOPs) such as anodic oxidation and electro-Fenton [8–10], wet air oxidation (WAO), and catalytic wet air oxidation (CWAO) [11,12]. These processes appear to have the capacity to completely decolorize and partially mineralize the textile industry dyes in a short reaction time, according to the previous studies [13,14] and are considered as a pretreatment step in the conventional biological oxidation for purifying dyehouse wastewaters. Oxygen and hydrogen peroxide are generally used as oxidants. According to the literature, the treatment efficiencies for various dyes using WAO and CWAO vary between 50 and 90% (as COD or TOC removal), at the residence times of 30–240 min in batch or continuous flow reactors [12,15,16]. Electrochemical methods offer many advantages such as low operational cost, be environmentally friendly (its main reagent is an electron), and high mineralization efficiency of various aromatic pollutants, mainly pesticides, dyes, industrial pollutants, and pharmaceuticals [17–20]. Other advantages are related to its versatility, high energy efficiency, amenability of automation and safety because it operates at mild conditions [21]. Electro-Fenton is based on the production of continuous and large amount of hydrogen peroxide in the acidic solution by two-electron reduction of oxygen molecular. Combination of hydrogen peroxide with catalysts such as Fe^{2+}, Fe^{3+}, Cu^{2+}, or Co^{2+} generates the oxidizing agent, $^{\bullet}OH$ from Fenton's or Fenton-like reactions [22,23]:

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad (1)$$

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

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doi:10.1016/j.jhazmat.2009.11.076

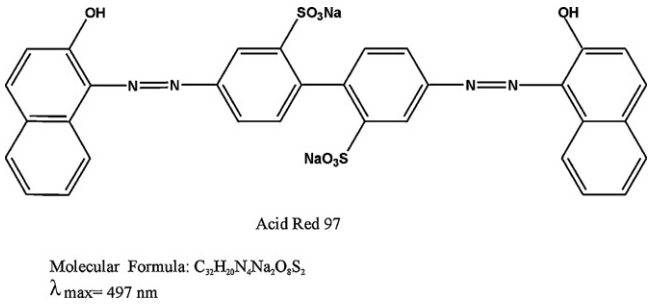

Fig. 1. Molecular structure of acid dye 97.

The main objective of the study is to investigate and compare the removal of AR97 from its aqueous solution by wet oxidation (WO) and electro-Fenton oxidation for the first time in the literature. Furthermore, the effects of important operating parameters in WO such as temperature and type of oxidants (oxygen, persulfate, periodate, bromate, and hydrogen peroxide) and in electro-Fenton such as applied current and amount of Fe^{2+} catalyst on the degradation rate, and mineralization efficiencies have been investigated.

2. Experimental

2.1. Materials

The azo acid dye, acid red 97 (AR97), was selected as the model pollutant because it is not only a biorefractory pollutant but also widely used in the textile and tanning industries. AR97 was supplied by DyStar and was used without further purification. Its chemical structure is given in Fig. 1. A carbon felt electrode (RVG 2000) was obtained from Carbone Loraine. Hydrogen peroxide, potassium periodate, potassium bromate (Merck), and potassium persulfate (Aldrich) were used as oxidants in WO process. Lithium perchlorate (Fluka), perchloric acid (J.T. Baker), and heptahydrate ferrous sulfate (Merck) were obtained as reagent grade. Oxygen was supplied by Tek Oxygen with 99.9% purity. Potassium nitrate and ammonium nitrate (Merck) were used as standards in nitrate and ammonium analyses. Phenol, sodium nitroprusside dihydrate, sodium hypochlorite, and sodium hydroxide (Merck) were used as reagents for spectrophotometric analysis of ammonium ion. Oxalic, maleic, acetic, and formic acids were purchased from Aldrich.

2.2. Oxidation experiment

2.2.1. Wet air oxidation

Wet air oxidation experiments were carried out at various temperatures ranging between 100 and 200 °C with oxygen pressure fixed at 5.0 MPa in a 150-mL stainless steel reactor with a magnetic stirrer as shown Fig. 2. The glass vessel was put inside the reactor and filled with 500 mg L^{-1} (0.72 mM) of AR97 solution. Afterwards stainless steel reactor placed on a magnetic stirrer and heater. Oxygen was supplied through a tube into the liquid phase directly. Typically, the reactor was charged with 150 mL of reaction mixture. The reaction mixture was heated to the desired temperature, and all the valves of the reactor were tightly closed during preheating. When reaching of the desired temperature, 5.0 MPa pure oxygen gas was fed in the reactor in the liquid phase, and its partial pressure was maintained with a gas relief valve. Samples were taken out periodically and analyzed for degradation AR97 by using UV–vis spectrophotometer. The reaction temperature was measured using a thermocouple and controlled using a regulator. After the samples collection treatment, the reactor was cooled to room temperature using a water bath and sampled for TOC and GC–MS analysis of the final effluent in 60 min reaction duration. The quantity of dissolved oxygen in water was calculated using an oxygen solubility model for the needed degradation of 500 mg L^{-1} AR97 in distilled water [24].

2.2.2. Wet peroxide oxidation

Wet peroxide experiments were performed in a 150-mL stainless steel reactor equipped with a magnetic stirrer and temperature control units (Fig. 2). Two different amounts of hydrogen peroxide, 1500 μL and 65 μL, were investigated at 100–200 °C. The first application of WPO of AR97 was realized with 1500 μL (116 mM) of 35% hydrogen peroxide to investigate its degradation power and second 65 μL (5 mM) of 35% hydrogen peroxide solution was added into the 150-mL stainless steel reactor to compare with the other oxidants.

2.2.3. Persulfate, periodate and bromate oxidation

The oxidation experiments were carried out at various temperatures ranging between 100 and 200 °C, and 5 mM of potassium persulfate ($K_2S_2O_8$), potassium periodate (KIO_4), or potassium bromate ($KBrO_3$) was added into the 150-mL stainless steel reactor.

2.2.4. Anaerobic process

An anaerobic experiment was also performed to investigate the degradation rate of 500 mg L^{-1} AR97 solution without using an oxidant. For this, AR97 solution was purged with nitrogen for removing oxygen and then the reactor was filled and heated to desired temperature for degradation.

2.2.5. Electro-Fenton experiments

Electrochemical experiments were conducted in a one-compartment cylindrical cell of 250 mL capacity. The anode electrode was Pt gauze from Aldrich (6 cm^2). The cathode was a carbon felt (50 cm^2 = 12.5 cm × 4 cm). The interelectrode gap was about 1 cm. The cell was filled with 200 mL of AR97 aqueous solution (500 mg L^{-1}). $HClO_4$ (0.5 M) was added to bring the pH to 3.0, and $LiClO_4$ (0.1 M) was used to enhance the conductivity. A catalytic quantity of Fe^{2+} was added to solutions before 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^{-1} during the experiments. The cell voltage was provided with a dc power supply (NEL PS2000 DC). A constant current of 200, 300, or 400 mA was maintained in electro-Fenton experiments. The solution was stirred with a magnetic bar. All experiments were carried

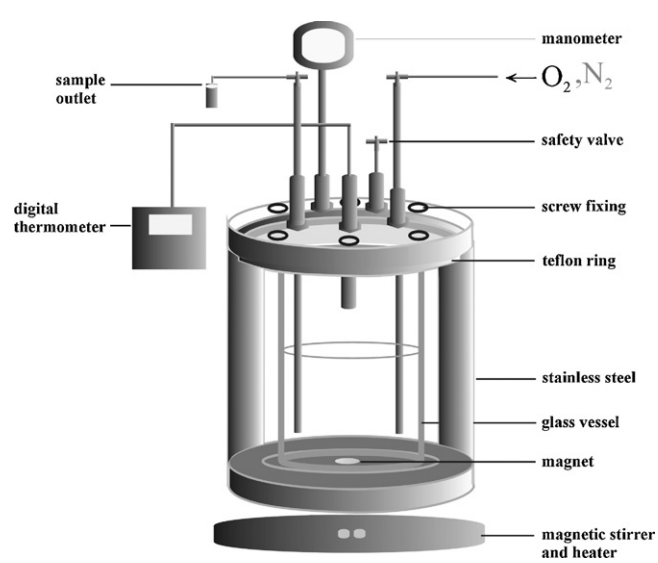

Fig. 2. Schemes of the wet air oxidation system.

out at room temperature. 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 were reported.

2.3. Instruments and analytical procedures

A decrease in the concentration of AR97 was observed from its characteristic absorption at 497 nm, using UV–vis spectrophotometer (Shimadzu UV-160A). After the experiments, the oxidation products were extracted with hexane and, dichloromethane and next the obtained organic solutions were dried with sodium sulfate, filtered, and rotavaporated to about 2 mL. GC–MS analysis was performed on a Thermo Finnigan GC–MS instrument equipped with a RESTEK Rtx-5MS (crossbond 5% diphenyl–95% dimethyl polysiloxane) 0.25 μm, 30 m × 0.25 mm, column. The carrier gas was helium, and the voltage of electron impact ionization was 70 e. The temperature program of the column was set as follows: from 40 to 80 °C, rate = 5 °C min^{-1} and hold time = 1 min; from 80 to 280 °C, rate = 4 °C min^{-1} and hold time = 10 min. The temperatures of the inlet, transfer line, and detector were 250, 250, and 280 °C, respectively. Phenol-hypochloride reaction was used for spectrophotometric determination of ammonia that is a modification of the method of Berthelot [25–27]. Basic reagents (10 g of phenol + 0.05 g of sodium nitroprusside dehydrate) were dissolved in 100 mL pure water. For preparing alkaline hypochlorite solution, 5 g of sodium hydroxide and 8 mL of sodium hypochlorite (4–6%) were added to 100 mL pure water. About 1.0 mL of alkaline hypochlorite reagent was measured into a test tube that contained 2 mL of the sample. Subsequently, 1.0 mL basic reagents were added to the tube. The tube was covered with parafilm, and was shaken vigorously to enable mixing. After 10 min, absorbance was measured at room temperature at 630 nm. A calibration curve was prepared using standard solutions of ammonium nitrate below 2 mg L^{-1} concentration. The samples were diluted 25 times for analysis. The short-chain organic acids were identified by a Perkin–Elmer isocratic HPLC system fitted with a Bio-Rad Aminex HPX 87H column and a 4 mM sulfuric acid solution as mobile phase at 210 nm. The same equipment, using ODS-H-OL (250 cm × 4.6 mm (i.d.)) column and 20 mM KH_2PO_4 with adjusted pH 2.8 with H_3PO_4 as mobile phase, was employed to analyze nitrate ion present in treatment solution at 210 nm. A calibration curve was prepared using standard solutions of potassium nitrate between 0.05 and 0.3 mM. The mineralization of AR97 solutions was monitored by the diminishment of their total organic carbon (TOC), measured on a Tekmar-Dohrmann Apollo 9000 TOC analyzer.

3. Results and discussion

3.1. Wet air oxidation of AR97

The effect of reaction temperature in the range of 100–200 °C was investigated in the WAO of AR97 under 5.0 MPa oxygen pressure and 500 mg L^{-1} initial AR97 concentration. Fig. 3a shows the evolution of decolorization percentage of AR97 solution versus reaction time at three temperatures. It was observed that the temperature has a pronounced effect on decomposition. The decolorization percentages obtained from these curves after 30-min treatments at 100, 150, and 200 °C were 10, 35 and 98%, respectively. These results showed that the reaction temperatures of 200 °C and higher were efficient in the decomposition of AR97. The WAO, in general, accelerates the thermal hydrolysis reaction capable of liquidizing volatile organic solids at the initial stage of reaction. The liquidized organic compounds are then converted to organic acids as intermediates by the sequential oxidation reaction, or decomposed into CO_2 and water [28–30]. The free radical is easily formed at high temperature and oxygen-rich conditions. The free-radical generation consists of O_2 attacking C–H bond of organic molecule. The mechanism of the reactions can be described as follows [31]:

$$RH + O_2 \rightarrow R^{\bullet} + HO_2^{\bullet} \quad (3)$$

$$HO_2^{\bullet} + RH \rightarrow R^{\bullet} + H_2O_2 \quad (4)$$

The free radicals also contribute degradation of organic compounds in the solutions.

3.2. The effects of bromate, persulfate and periodate on the degradation of AR97

Potassium bromate ($KBrO_3$), persulfate ($K_2S_2O_8$), and periodate (KIO_4) were used to investigate the effects of the different oxidants instead of molecular oxygen on the degradation of AR97. Fig. 3b shows the decolorization percentages of AR97 with bromate as an oxidant. The addition of BrO_3^- (5 mM) was a less efficient process especially below 200 °C temperatures than the wet air oxidation because of low oxidizing properties.

As can be seen in Fig. 3c, detectable extent of decolorization of AR97 could be achieved when KIO_4 was added as an oxidant in the process. Periodate can cleave carbon–carbon bonds when both carbon atoms bear an oxygen atom, either in the form of hydroxyl or a carbonyl group. This property is often utilized in molecular biochemistry for the purpose of modifying saccharide rings, because many five- and six-membered sugars often have vicinal diols [32–34]. Moreover, the thermal decomposition of periodate involves the formation of a number of highly reactive radical and non-radical intermediates:

$$IO_4^{\bullet -} + \text{heat} \rightarrow IO_3^{\bullet} + O^{\bullet -} \quad (5)$$

$$O^{\bullet -} + H^+ \rightarrow OH^{\bullet} \quad (6)$$

$$^{\bullet}OH + IO_4^- \rightarrow OH^- + IO_4^{\bullet} \quad (7)$$

These intermediates could contribute to the dye degradation because the radicalic intermediates (with highly electrophilic character) produced from IO_4^- attack the azo groups of the dye molecules causing oxidative destruction [35,36]. The results showed that, in the first 5 min of the oxidative treatment, the decolorization percentages were obtained 45, 90, and 98% at 100, 150, and 200 °C temperatures, respectively.

The effect of the addition of $S_2O_8^{2-}$ (5 mM) on decolorization of AR97 was illustrated in Fig. 3d. Approximately, 98% of starting AR97 solution was decolorized after 8 min at three experimental temperatures. Similar to the case of IO_4^-, the addition of $S_2O_8^{2-}$ to the wet oxidation system resulted in a much higher decolorization than that of O_2 addition. The persulfate anion is the most powerful oxidant of the peroxygen family of compounds and one of the strongest oxidants used in remediation. The standard electrode potential is very high (E° = 2.12 V), but direct reaction of persulfate with most reductants is slow [37]. When solutions of the persulfate are heated, free radicals are formed in aqueous solution:

$$S_2O_8^{2-} + \text{heat} \rightarrow 2SO_4^{\bullet -} \quad (8)$$

Sulfate radical ($SO_4^{\bullet -}$) is a strong one-electron oxidant ($E^{\circ} \approx 2.6$ V) that is used in rapid and deep oxidation of many organic compounds, especially aromatic compounds [38,39], thus benefiting the degradation of both AR97 and its derivative aromatic fragments. Also, sulfate radical reacts with H_2O to produce $^{\bullet}OH$ radicals [40]:

$$SO_4^{\bullet -} + H_2O \rightarrow {}^{\bullet}OH + SO_4^{2-} + H^+ \quad (9)$$

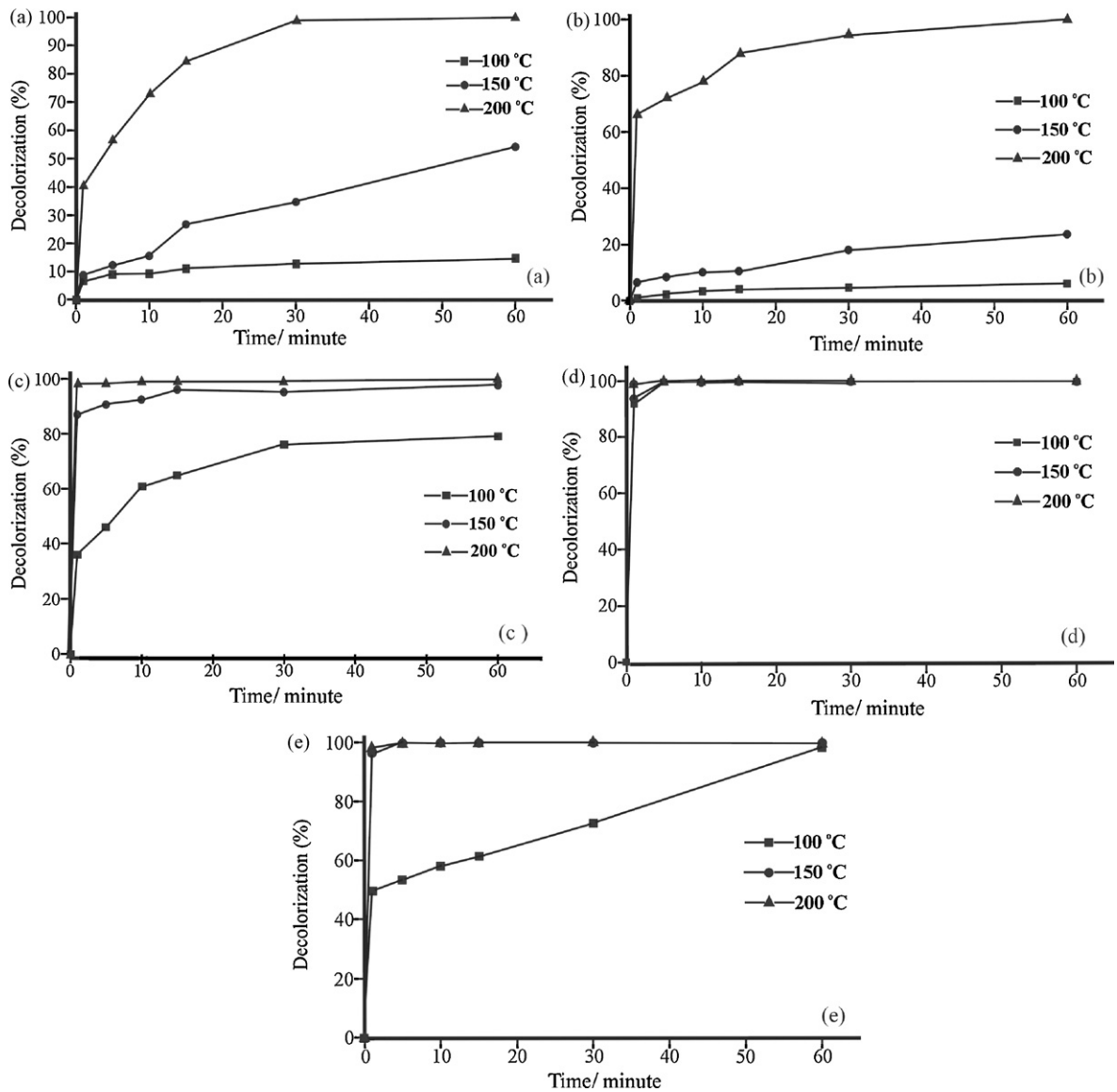

Fig. 3. Effects of temperature and oxidant type on AR97 removal with reaction time in wet air oxidation. $[AR97]_0 = 500\,mg\,L^{-1}$; $V_{dye} = 150\,mL$: (a) O_2 pressure: 5.0 MPa; (b) $[BrO_3^-]_0 = 5\,mM$; (c) $[IO_4^-]_0 = 5\,mM$; (d) $[S_2O_8^{2-}]_0 = 5\,mM$; (e) $[H_2O_2]_0 = 116\,mM$ (1.5 mL, 35%).

Hydroxyl radical and sulfate radical anion are powerful oxidants, which can degrade the AR97 molecules at a faster rate [41]:

$$\text{Dye} + {}^{\bullet}\text{OH} \rightarrow \text{degradation product} \quad (10)$$

$$\text{Dye} + SO_4^{\bullet -} \rightarrow \text{Dye}^{\bullet -} + SO_4^{2-} \quad (11)$$

The direct degradation of AR97 using H_2O_2, BrO_3^-, $S_2O_8^{2-}$, or IO_4^- may be ignored, because no detectable decolorization was observed with 5 mM of each of them after 60 min treatment at room conditions.

3.3. Wet peroxide oxidation of AR97

Oxidative treatment with hydrogen peroxide has emerged as a viable alternative for wastewater treatment with organic load. Hydrogen peroxide (H_2O_2) is a strong oxidant, and its application in the treatment of various inorganic and organic pollutants is well established. Numerous applications of H_2O_2 are known in the removal of pollutants, such as sulfites, hypochlorites, nitrites, organic compounds and chlorine, from wastewater [42,43]. Hence, experiments were also realized with hydrogen peroxide to examine the effect of H_2O_2 (116 mM) on the degradation of AR97 in wet peroxide oxidation system. When the temperature increased up to 150 °C, the decolorization efficiency reached nearly 100% after 5 min of treatment (Fig. 3e). The decolorization rate for the hydrogen peroxide system was similar to that of periodates but more effective than that when O_2 and bromate were used as oxidants. However, persulfate was found to be the most effective oxidant in all of them in wet oxidant system for decolorization percentage of AR97 (Fig. 3a–e).

3.4. TOC removal of AR97 solution with different oxidants

The difference between wet air oxidation and wet peroxide oxidation is that the first one uses a gaseous oxidant and is a two-step process (transfer plus oxidation), and the second one uses a liquid oxidant (hydrogen peroxide), which eliminates gas–liquid mass transfer problems. The process is similar to Fenton reaction, but higher temperatures are employed to enhance TOC reduction [43].

Because temperature is an extremely important variable in the WO process, by increasing the temperature from 100 to 200 °C, a

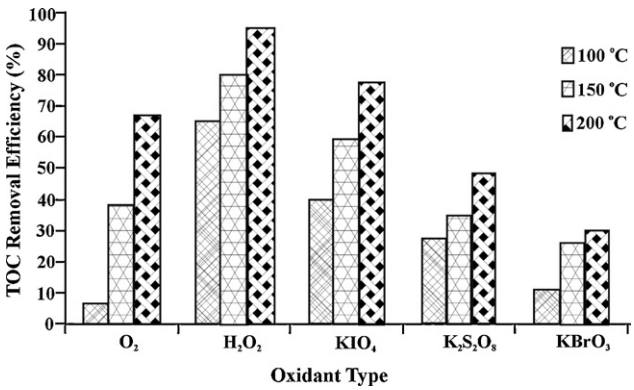

Fig. 4. Effect of temperature on TOC removal after 1 h treatment. $[AR97]_0 = 500\,mg\,L^{-1}$; O_2 pressure: 5.0 MPa; $[H_2O_2]_0 = 116\,mM$ (1.5 mL, 35%); $[IO_4^-]_0 = 5\,mM$; $[S_2O_8^{2-}]_0 = 5\,mM$; $[BrO_3^-]_0 = 5\,mM$; $V = 150\,mL$.

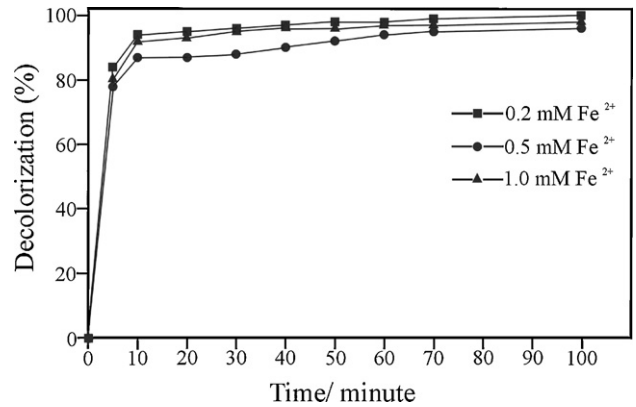

Fig. 5. Effect of Fe^{2+} concentration on AR97 removal with reaction time by electro-Fenton. $[AR97]_0 = 500\,mg\,L^{-1}$; $LiClO_4 = 0.1\,M$; pH 3.0; $V = 200\,mL$; $I = 300\,mA$.

significant increase in the degradation of AR97 was obtained for all of the oxidant systems. To determine the effects of oxidants on TOC removal of AR97 solution, a set of experiments was carried out using 5 MPa of O_2, 5 mM of BrO_3^-, IO_4^-, and $S_2O_8^{2-}$ and 116 mM of H_2O_2 (Fig. 4). For instance, only about 7% TOC was removed at 100 °C, but when the temperature increased to 150 or 200 °C, 38 and 67% TOC removal were achieved in wet air oxidation system, respectively. An experiment was performed in the anaerobic condition to reveal the importance of oxygen in this system; TOC removal of degradation of AR97 was obtained only 12% after 60 min at 200 °C. The efficiencies of the oxidants in TOC removal of AR97 solution were in the order of bromate < persulfate < periodate. While the TOC removal reached only 30% at 200 °C using bromate, in case of periodate it was 78%. From the experimental results, it can be concluded that the wet peroxide oxidation was a more efficient system than the other oxidants which were used in this study at all application temperatures. TOC removal efficiencies were found to be 65, 80, and 95% after 1 h at 100, 150, and 200 °C experimental conditions, respectively. However, hydrogen peroxide concentration was very higher than the other oxidants and hence the experiment was also performed at 200 °C using equal amount of H_2O_2 (5 mM) to compare with the other oxidants. At these conditions, after 60-min treatments, the TOC removal was only 29%. Consequently, based on the results of this work, periodate was recommended as a suitable oxidant in WO system.

3.5. Electro-Fenton oxidation of AR97

Degradation of AR97 was carried out in aqueous solution using electrochemically generated hydroxyl radicals via Fenton reaction due to Eqs. (1) and (2). Fig. 5 shows the comparative decolorization of $500\,mg\,L^{-1}$ AR97 solution with 0.2, 0.5, and 1.0 mM Fe^{2+} at 300 mA constant current. Higher decolorization percentage was obtained when 0.2 mM of ferrous ion was employed as catalyst. The detrimental effect of higher catalyst concentration on the degradation can be explained by scavenging reactions between Fe^{2+} and hydroxyl radicals [42,44].

$$Fe^{2+} + {}^{\bullet}OH \rightarrow FeOH^{2+} \quad (12)$$

$$Fe^{3+} + H_2O_2 \leftrightarrow Fe\text{–}OOH^{2+} + H^+ \quad (13)$$

$$Fe\text{–}OOH^{2+} \rightarrow HO_2^{\bullet} + Fe^{2+} \quad (14)$$

However, the use of 1.0 mM Fe^{2+} slightly favors the decolorization of AR97 solution than that of 0.5 mM Fe^{2+}; this result agreed with the previous studies [45].

Fig. 6 shows the TOC removal results of $500\,mg\,L^{-1}$ AR97 solutions treated by electro-Fenton oxidation for various treatment times, Fe^{2+} concentration, and applied current. A similar TOC removal was observed for 0.2, 0.5, and 1.0 mM Fe^{2+} catalyst. For example, after 5 h of electrolysis, the TOC removals were 94, 89, and 92% for 0.2, 0.5, and 1.0 mM Fe^{2+}, respectively. The effect of applied current on TOC removal was examined using 0.2 mM Fe^{2+} at 300 and 400 mA. It was noted that after 1 h treatment, TOC removal was 43% at 300 mA; while at 400 mA, the TOC removal was 57%.

The mineralization current efficiency (MCE) can show the oxidative efficiency of EF process. MCE was calculated according to [45]:

$$MCE = \frac{\Delta(TOC)_{exp}}{\Delta(TOC)_{theor}} \times 100 \quad (15)$$

where $\Delta(TOC)_{exp}$ is the experimental TOC removal and $\Delta(TOC)_{theor}$ is the theoretically calculated TOC decay at a given time considering that the applied electrical charge (=current × time) required for the complete mineralization of AR97 according to:

$$C_{32}H_{20}N_4S_2O_8Na_2 + 76H_2O \rightarrow 32CO_2 + 4NO_3^- + 2SO_4^{2-} + 2Na^+ + 172H^+ + 166e^- \quad (16)$$

which assumed the consumption of 166 F per mole of AR97.

As can be seen in Table 1, the MCE values decreased, whereas the ROC removal efficiencies increased with increasing applied current. For example, after 5 h of electrolysis of $500\,mg\,L^{-1}$ of AR97 with 0.2 mM of Fe^{2+}, the MCE% values are in an order of 50.30, 36.03, and 27.70% at 200, 300, and 400 mA, respectively. In previous studies, this trend was related to diminished amount of $^{\bullet}OH$ at high current values [46]. Consequently, the low applied current value was preferred for the mineralization of AR97.

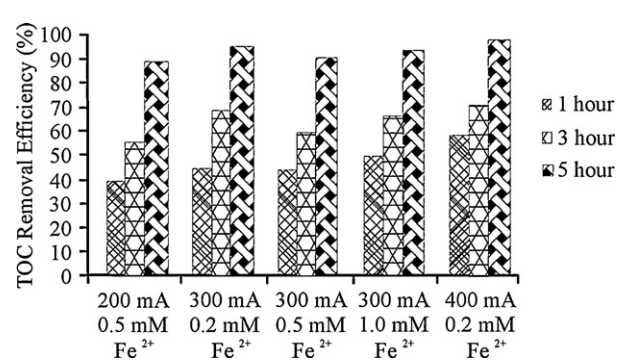

Fig. 6. TOC removal with electrolysis time for AR97 solution in 0.1 M $LiClO_4$ of pH 3.0 by electro-Fenton reaction with different Fe^{2+} concentrations or applied current. $[AR97]_0 = 500\,mg\,L^{-1}$; $V = 200\,mL$.

Table 1
Effect of applied current and amount of Fe^{2+} on TOC removal percentage and corresponding MCE% values.

	TOC removal (mg C L^{-1})	MCE%[a,b]
Applied current (mA)/[Fe^{2+}]$_0$ (mM)		
200/0.2	217	50.30
300/0.2	232	36.03
300/0.5	220	34.15
300/1.0	228	35.30
400/0.2	239	27.70

[a] Electrolysis time: 5 h.
[b] Calculated from Eq. (15).

3.6. Identification of oxidation products of AR97

The metabolites of the AR97 degradation were identified by GC–MS as 1,2-naphthalenediol (**I**), 1,1′-biphenyl-4-amino-4-ol (**II**), 2-naphthalenol diazonium (**III**), 2-naphthalenol (**IV**), 2,3-dihydroxy-1,4-naphthalenedion (**V**), phthalic anhydride (**VI**), 1,2-benzenedicarboxylic acid (**VII**), phthaldehyde (**VIII**), 3-hydroxy-1,2-benzenedicarboxylic acid (**XI**), 4-amino-benzoic acid (**X**), and 2-formyl-benzoic acid (**XI**), which are given in the proposed pathway (Fig. 7). The first step in the degradation of AR97, in either electro-Fenton or wet oxidation processes, is the reduction the azo bonds (–N=N–) leading to the formation of **I**, **II**, **III**, and **IV**. After the azo bond was attacked, most of the nitrogen element went away from the dye structure as NO_3^- and NH_4^+ ions or nitrogen. But the formation of 2-naphthalenol diazonium (**III**) may correspond to attack of hydroxyl radical to ipso position of biphenyl molecule. Benzidine (**II′**) may be formed in oxidation process according to the appearance of 2-naphthalenol (**IV**), but it was not determined as intermediate in the GC–MS analysis. The second step includes the hydroxylation of these intermediates to hydroxylated or poly hydroxylated derivatives, which are in turn oxidized to the quinoid structures (**V**–**XI**). Next, the gradual cleavage of the unstable intermediates leads to the formation of carboxylic acids before conversion to CO_2.

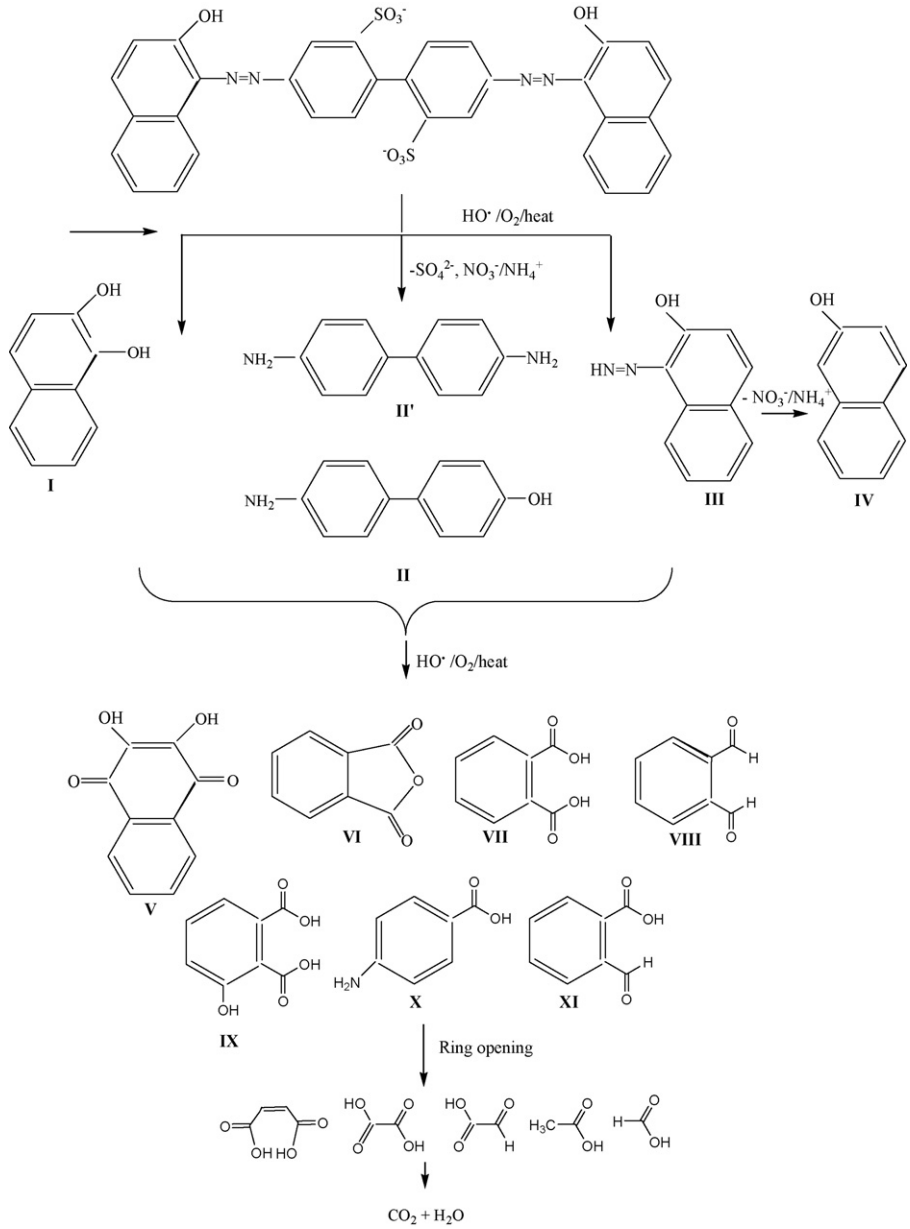

Fig. 7. Proposed pathway of AR97 degradation products.

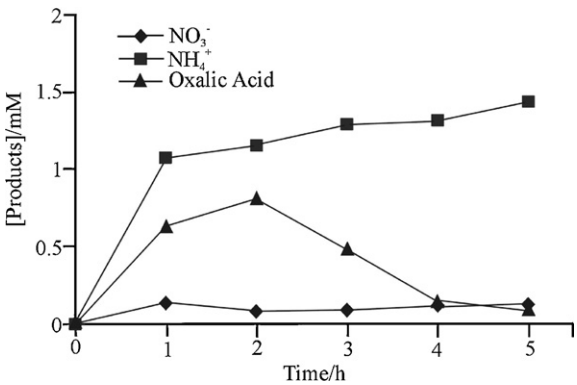

Fig. 8. Degradation products of AR97 during electro-Fenton degradation. $[AR97]_0 = 500\,mg\,L^{-1}$; $[Fe^{2+}]_0 = 0.2\,mM$; $V = 200\,mL$; pH = 3.0; $I = 400\,mA$.

The HPLC identification was carried out by comparison of the retention time and using the standard chemicals. Oxalic, acetic, maleic, glyoxylic, fumaric, and formic acid were used as standards for short-chain organic acids. Oxalic acid was the main carboxylic acid formed by the ring opening reactions of AR97 oxidation products in all treatments. Quantitative analyses of NO_3^- and NH_4^+ ions formed by AR97 mineralization were also realized. The identification of NO_3^- and NH_4^+ ions in treated solution showed that the cleavage of the –N=N– bonds of AR97 due to the oxidation of intermediates containing NO_2 or NH_2 substituents with hydroxyl radicals resulted in releasing of NO_3^- and NH_4^+ ions [47,48]. Evolution of released oxalic acid, NO_3^- and NH_4^+ ions concentrations during electro-Fenton treatment of $500\,mg\,L^{-1}$ AR97 at 400 mA was shown in Fig. 8. From Fig. 8, it can be seen that oxalic acid concentration reached a maximum at the end of 2 h treatment. Concentration of ammonium ions reached 1.44 mM after 5 h treatment. This value corresponded to about 50% of the initial organic nitrogen content of AR97. In contrast, nitrate ion concentration close to 0.12 mM, which corresponded to only 4%, was detected in solution after 5 h treatment. Nitrate and ammonium ion concentrations demonstrated variation in WO systems because of the type of oxidant. For example, when bromate was used as an oxidant at 200 °C after 60 min in WO system, nitrate and ammonium ion concentrations were 0.390 and 0.106 mM, respectively. These values corresponded to 68 and 18.5% of initial nitrogen of AR97. It can be seen that the formation of nitrate ions was preferential in respect of ammonium ions in bromate oxidation of AR97. However, after 60 min at 200 °C using persulfate, the nitrate and ammonium ion concentration in solution were 0.013 (2.3% of initial N) and 0.126 mM (22% of initial N), respectively. The results were different from that of the former values. It can be explained that mineralization of AR97 with persulfate was more influential than that of bromate ions, and hence the formation of nitrate and ammonium ions with persulfate oxidant was lower than bromated ion because the nitrogen in the azo bond was converted to nitrogen gas (N_2).

4. Conclusions

Both wet oxidation and electro-Fenton methods seem to be appropriate to efficiently remove and mineralize the AR97 dye with high initial concentration (i.e., $500\,mg\,L^{-1}$) from aqueous solution. When molecular oxygen was used as an oxidant in wet air oxidation system, the effective degradation or mineralization efficiency was obtained only at high temperature (200 °C). The degradation and mineralization of AR97 depend on the type of oxidant used, and they are increased when hydrogen peroxide is used (116 mM) at even low temperatures (i.e., 100–150 °C). Periodate, persulfate, and bromate were introduced as oxidants in wet oxidation process. To compare the effects of these oxidants with hydrogen peroxide or oxygen, experiments were performed at the same experimental conditions such as amounts of oxidants (5 mM), temperatures, and reaction time. The experimental results showed that periodate as oxidant showed higher ability toward degradation and mineralization of AR97 compared with the others. The efficiencies of the oxidants on TOC removal of AR97 solution were in the order of hydrogen peroxide < bromate < persulfate < periodate. In contrast, the best operative conditions for electro-Fenton are achieved using 0.2 mM Fe^{2+} at low current according to mineralization current efficiency. The TOC removal % using 0.2 mM of Fe^{2+} at 300 mA reached 94 and 67% after 3 and 5 h electrolysis time, respectively. These results show that electro-Fenton is an environmentally friendly technology but needs longer treatment times than wet oxidation methods. Comparative treatment methods, wet peroxide or periodate oxidation, are very effective for degradation of AR97 in a short treatment time, but these methods require high temperatures and operational cost. Therefore, the operational cost of these methods must be optimized using an oxidant like periodate. Aromatic products such as 1,2-naphthalenediol, 1,1′-biphenyl-4-amino-4-ol, 2-naphthalenol diazonium, 2-naphthalenol, 2,3-dihydroxy-1,4-naphthalenedion, phthalic anhydride, 1,2-benzenedicarboxylic acid, phthaldehyde, 3-hydroxy-1,2-benzenedicarboxylic acid, 4-amino-benzoic acid, and 2-formyl-benzoic acid are detected by GC–MS. Generated oxalic acid, ammonium, and nitrate ions were identified during WO and EF treatment and quantified during EF treatment.

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