



Comparative mineralization of Basic Red 18 with electrochemical advanced oxidation processes

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Abstract: In this study, the role of electrochemical oxidation processes, including the electro-Fenton, the electro-persulfate (PS), and the electro/FeII/PS processes, in the removal of Basic Red 18 (BR18) from aqueous solutions was investigated. It was found that the electro-PS process successfully removes colour, but after 5 h, it produced only 75 % mineralization. In the same conditions, more effective mineralization was achieved by the electro/FeII/PS process than by the electro-Fenton method. At pH levels of 3.0 and 5.7, very effective mineralization results were produced by the electro/FeII/PS process. Moreover, the maximum mineralization current efficiency values were obtained by the electro/FeII/PS process. The mineralization efficiency of the electro/FeII/PS process was determined to be 97 % under the following conditions: BR18 initial dye concentration of 100 mg L⁻¹, pH of 5.7, contact time of 5 h, PS concentration of 10 mM, Fe²⁺ concentration of 0.2 mM, and a sodium sulfate concentration of 0.05 M.

Keywords: advanced electro-oxidation processes; Fenton; persulfate; azo dye; decolourization.

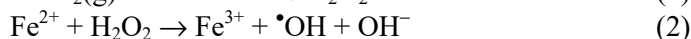
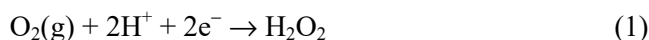
INTRODUCTION

The electrochemical advanced oxidation processes (EAOPs) have recently attracted the increasing attention due to their environmental compatibility, versatility, high efficiency in the removal of recalcitrant organic pollutants, and operational safety, based on the fact that they are performed in mild conditions and degrade pollutants in wastewater by generating very powerful radicals.¹ Electro-Fenton (EF), photoelectro-Fenton (PEF), electro-persulfate (EPS) and electro/Feⁿ⁺/persulfate (E/Fe/PS) processes are some of the most efficient EAOPs. In the EF process, hydrogen peroxide is electrogenerated at the cathode of the cell to achieve the O₂ gas reduction.² The hydroxyl radicals are generated by the Fenton

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reaction between Fe^{2+} and H_2O_2 . The hydroxyl radicals ($\bullet\text{OH}$) are non-selective, and very powerful oxidants ($E(\bullet\text{OH}/\text{H}_2\text{O}) = 2.80 \text{ V}_{\text{SHE}}$):

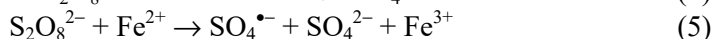


The addition of a catalytic amount of Fe^{2+} is sufficient because it is continuously regenerated from the reduction of Fe^{3+} at the cathode:

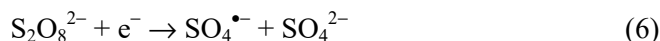


In PEF, the EF process is enhanced by irradiation with artificial UV-A light^{3,4} or sunlight^{1,5,6} to degrade end products – Fe(III)–organic acid complexes – that hinder complete mineralization.

Persulfate possesses high solubility, good stability, and high reactivity ($E = 2.1 \text{ V}$) and causes less intensive damage to the ecological functions of soil after treatment.^{7,8} Sulfate radicals ($\text{SO}_4^{\bullet-}$) play an important role in oxidation techniques as the hydroxyl radical has a high redox potential ($E = 2.6 \text{ V}$). This radical can be generated by the activation of persulfate with a transition metal, heat, base, H_2O_2 , UV or ultrasound (US) as follows:^{7,9-14}



In the EPS process, sulfate radicals result from cathodic reduction as follows:^{15,16}



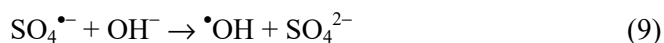
Furthermore, persulfate anions can be regenerated from the anodic oxidation of sulfate ions, as follows:¹⁷



Basically, the electro/Fe/PS process combines the EPS process with Fe^{2+} to activate persulfate. When the energy required for the activation of persulfate with ferrous ion to yield sulfate radicals is $12 \text{ kcal} \cdot \text{mol}^{-1}$,¹⁸ $33.5 \text{ kcal} \cdot \text{mol}^{-1}$ is required for thermal activation.¹⁹ Although iron is cheap and non-toxic, it cannot be remediated after the reaction shown in Eq. (5) occurs, which necessitates the use of greater quantities of iron salt. In the electro/Fe(II)/persulfate method, Fe^{2+} can be reproduced *via* cathodic reduction, so that low concentrations can be used.¹⁵ The excess ferrous ions may act as radical scavengers; therefore, the ion dosage must be optimized. Sulfate radicals may enter into different reactions and thereby cause the return of other oxidants, particularly $\bullet\text{OH}$ and H_2O_2 .⁷ Under alkali conditions, Eq. (9) has an important rate constant as compared to Eq. (8) shown below:²⁰⁻²²



* 1 kcal = 4184 J



When comparing the two radicals, the sulfate has a higher chance of reacting with organic pollutants at acidic pH levels owing to its longer life time (30–40 μs)¹¹ than that of $\bullet\text{OH}$ (20 ns).²³ Moreover, the oxidation potential of $\bullet\text{OH}$ increases as pH decreases.^{15,24} Apart from these properties, the sulfate radicals have high solubility and are stable and effective over a wide pH range. As such, they are more effective in the degradation of recalcitrant organic compounds than the hydroxyl radical.²⁵ Sulfate radicals have a different mechanism for reacting with organic pollutants than that of hydroxyl radicals – they remove their electrons to produce an organic radical cation,²⁶ whereas hydroxyl radicals attach to C=C bonds or abstract hydrogen from the C–H bond.²⁷ Besides being a highly effective oxidant, the sulfates are not categorized as a pollutant by US EPA as long as its concentration does not exceed 250 mg L^{-1} .^{28–30}

The electro/FeII/PS process was used by Zhang *et al.*³¹ to enhance the removal of organic contaminants (CODs) from landfill leachate (initial COD of 1900 mg L^{-1}). Based on the energy consumption analysis results, the optimum time was selected as 60 min and a 62.2 % COD removal was achieved when the PS concentration was 62.5 mM, Fe^{2+} concentration was 15.6 mM, initial pH was 3.0, and the current density was 13.89 mA cm^{-2} .³¹ Dinitrotoluenes (DNTs) were mineralized in the industrial wastewater using an electro-activated persulfate process in the range of 303–318 K and various nitrogen/oxygen dosages by Chen *et al.*³² In their study, DNTs were almost completely removed under the following optimal conditions: electrode potential of 6 V, temperature of 318 K, N_2 dosage of 150 mL min^{-1} , pH of 0.5, and a PS concentration of 1.7 wt. %. The authors also found that the hydrogen peroxide was electro-generated by the cathodic reduction of oxygen and the anodic oxidation of water made only a minor contribution toward the elimination of DNTs.³² The removal efficiency of bisphenol A showed a tendency to increase when the PS concentration was increased from 1 to 10 mM, but no further increase in the PS concentration was found to improve the mineralization by the electro/ Fe^{3+} /peroxydisulfate process.¹⁵

The textile industry is one of the largest polluters in the world. After the dyeing process, it is estimated that 10–15 % of the dye passes into the wastewater stream.³³ In the textile industry, approximately 40–65 L of wastewater is released per kg of product.³⁴ In this study, the performance of the EF, EPS and electro/FeII/PS processes in an O_2 or N_2 medium was compared at two different pH levels (3.0 and 5.7) and the decolorization and mineralization of the model pollutant Basic Red 18 (BR18) at room temperature was monitored. BR18 is a cationic azo dye that is commercially used in the textile industry for fiber dyeing. More than 50% of all the dyes produced in worldwide are azo dyes.¹⁸ Both azo dyes and their degradation products (*e.g.*, aromatic amines) are quite toxic and

mutagenic and carcinogenic effects in organisms as well as they can cause environmental pollution.¹⁸

EXPERIMENTAL

BR18 (cationic, MW: 426.34 g mol⁻¹, molecular formula C₁₉H₂₅Cl₂N₅O₂) textile dye was supplied by the DyStar Textile firm and was used as received. Properties of BR18 dye are given in the Supplementary material to this paper (Table S-I). Analytical grade potassium persulfate (K₂S₂O₈), ferrous sulfate (FeSO₄·7H₂O), *t*-butyl alcohol (TBA) and methanol were purchased from Merck. The supporting electrolyte chemical anhydrous sodium sulfate was also obtained from Merck at 99.9 % purity. Sulfuric acid (Merck) was used to regulate the solution pH. Dye solution was prepared with ultra-pure water with 18.2 Millipore ohms. Oxygen and nitrogen gases were supplied by Linde (Mersin, Turkey) at 99.9 % purity.

Electrochemical cell and apparatus

A one-compartment electrochemical cell with a 300 mL capacity and a stabilized power supply were used for all the electrolytic experiments. As a cathode, a carbon felt electrode (Carbone Lorraine, France) with a 3D shape and 60 cm² physical surface area were used. For the anode, Pt gauze electrode (9 cm²) was purchased from Aldrich. In all cases, the anode was set up in the centre of the electrochemical cell and the carbon felt cathode was placed in the inner wall of the cell as the interelectrode gap was ~1 cm. All the experiments were performed at a constant current provided by a DC power supply (NEL PS2000 DC). The cell was filled with 200 mL of aqueous solution containing 100 mg L⁻¹ BR18 and 0.05 M Na₂SO₄. The electrolysis experiments were performed either with the pH adjusted to 3.0 by adding 0.5 M H₂SO₄, or at the initial pH (5.7). A stoichiometric quantity of Fe²⁺ and/or K₂S₂O₈ was added to solutions prior to electrolysis. Moreover, prior to the electrolysis (15 min), pure oxygen or nitrogen gas at a rate of 20 mL min⁻¹ was bubbled during the experiments. In addition, for the purpose of comparison, gas was not used in some experiments. The solution was stirred with a magnetic bar and all experiments were conducted at room temperature. The experiments were repeated twice, and the averages of the results were calculated.

To determine the concentrations of the dye solutions based on the characteristic absorption at 488 nm, a UV-Vis spectrophotometer (Shimadzu UV-160A, Japan) equipped with a quartz cell with a 1.0 cm path length was used. The dye removal efficiency was calculated from the determined concentrations.

The mineralization of the solutions was monitored by the decay of their total organic carbon (TOC), as measured using a Tekmar-Dohrmann Apollo 9000 TOC (USA) analyzer.

RESULTS AND DISCUSSION

Electro-Fenton (EF) experiments

The degradation of the azo dye, BR18, was performed by the EF process at different current values (100, 200, 300 and 400 mA). The colour removal in the solution was found to accelerate with an increase in the applied current (Fig. 1a). When 300 and 400 mA currents were applied to the EF system, the decolourization efficiency reached 100 % after 15 min. After the application of 300 mA current for 1, 3 and 5 h, the mineralization efficiencies were 52, 72 and 86 %, respectively (Fig. 1b). Although the mineralization efficiency was enhanced with an increase in the applied current from 100 to 300 mA, no enhancement in the

mineralization was produced by further increases. The decline in TOC removal efficiency has been explained by the increasing rate of wasting reactions:³⁵

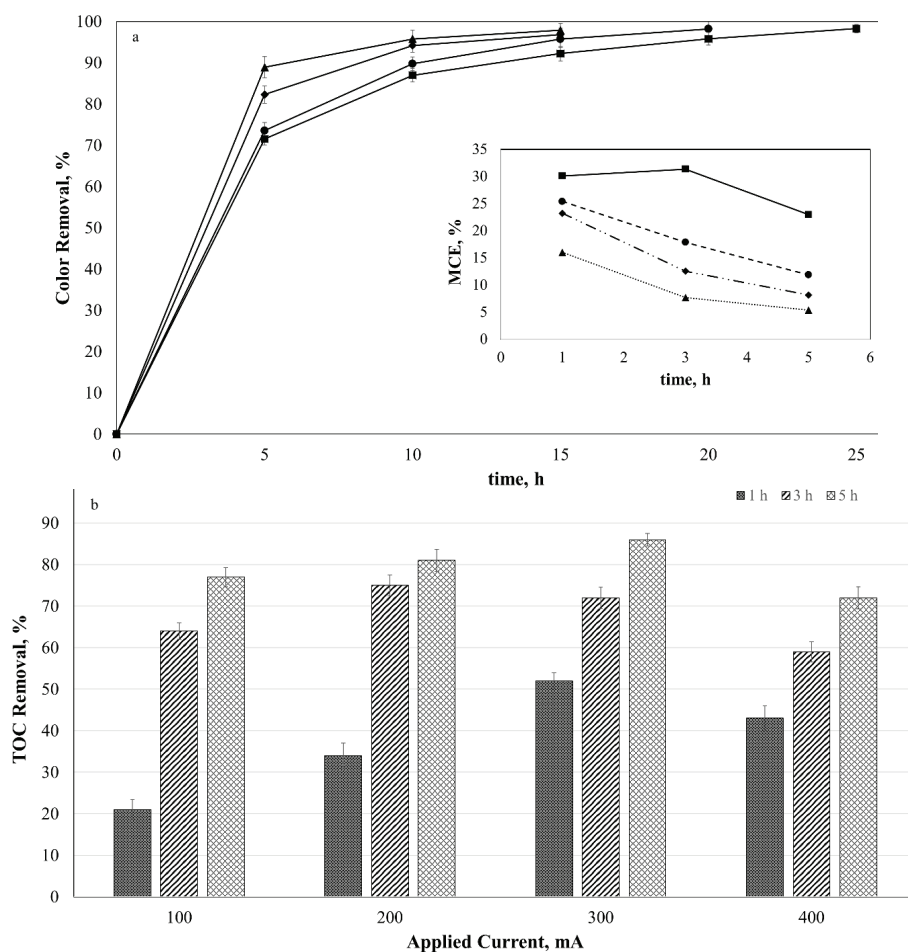
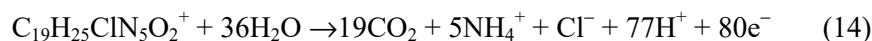


Fig. 1. The effect of the applied current on a) decolorization efficiency (100 mA, ■; 200 mA, ●; 300 mA, ◆; 400 mA, ▲), b) mineralization efficiency (total organic carbon (TOC) removal) during the treatment of BR18 solution by Electro-Fenton ([BR18] = 100 mg L⁻¹, [Fe²⁺] = 0.2 mM, [Na₂SO₄] = 0.05 M, pH 3.0).

The mineralization reaction of BR18 by electrolysis, which involves its conversion into carbon dioxide, chloride ions, and ammonium ions, is expressed by Eq. (14):



From the measured *TOC* values, the mineralization current efficiency (*MCE*) was estimated as a percentage by Eq. (15):³⁶

$$MCE = \frac{100nFV_s\Delta(TOC)_{\text{exp}}}{4.32 \times 10^7 mIt} \quad (15)$$

where *n* is the number of electrons in Eq. (15), *F* is the Faraday constant (96487 C mol⁻¹), *V_s* is the solution volume (L), $\Delta(TOC)_{\text{exp}}$ is the experimental *TOC* decay (mg L⁻¹), 4.32×10^7 is a conversion factor (3600 s h⁻¹ × 12000 mg C mol⁻¹), *m* is the number of C atoms in BR18, *I* is the applied current (A), and *t* is the electrolysis time (h).

The mineralization capacity of the process was determined by calculating its *MCE*. The changes in the *MCE* percentage over time with respect to the applied current are shown in the inset panel of Fig. 1a. In the EF process, *MCE* values of 30, 25, 23 and 16 % were obtained for current values of 100, 200, 300 and 400 mA after the first 60 min of electrolysis, respectively. In the EF experiments, a decrease in the *MCE* values was caused by higher currents. While the *MCE* showed no significant change between 1–3 h at 100 mA, it dropped after this time and reached 25 % at 5 h. For the other applied current values, the *MCE* gradually decreased after 1 h until the end of the 5 h electrolysis period. This behaviour can be explained by the increase in the parasitic reactions, which are the discharge of O₂ at the anode and the evolution of H₂ at the cathode, competing with the formation of H₂O₂ (Eq. (1)).

All the *MCE* values were observed to continuously decrease during the electrolysis over time. This situation can be explained by increasing the low molecular organic matter content owing to degradation and mineralization. These degradation products such as short-chain carboxylic acids are resistant to mineralization. An increase in the tendency for Fe ions to react with •OH or short-chain carboxylic acids, to give complexes, was observed at low aromatic concentrations.³⁷ As a result, the yield of mineralization can decrease with high current and time in the EF process.

Electro/Fe²⁺/PS experiments

First, an experiment to investigate the combined effect of Fe²⁺/S₂O₈²⁻ without electrolysis was conducted. In this case, a *TOC* removal efficiency of only 20 % was obtained after 5 h, the details of which are provided in Supplementary material (Table S-II). In addition, the colour removal in the solution was incomplete even after 5 h of electrolysis.

The effects of the electro/FeII/PS and electro/PS systems was investigated at pH levels of 3.0 and 5.7 (without adjustment) using O₂ gas during electrolysis.

As can be seen in Fig. 2a, the BR18 decolorization time was shortened in the following order: electro/FeII/PS/pH 3.0 < electro/FeII/PS/pH 5.7 = electro/PS/pH

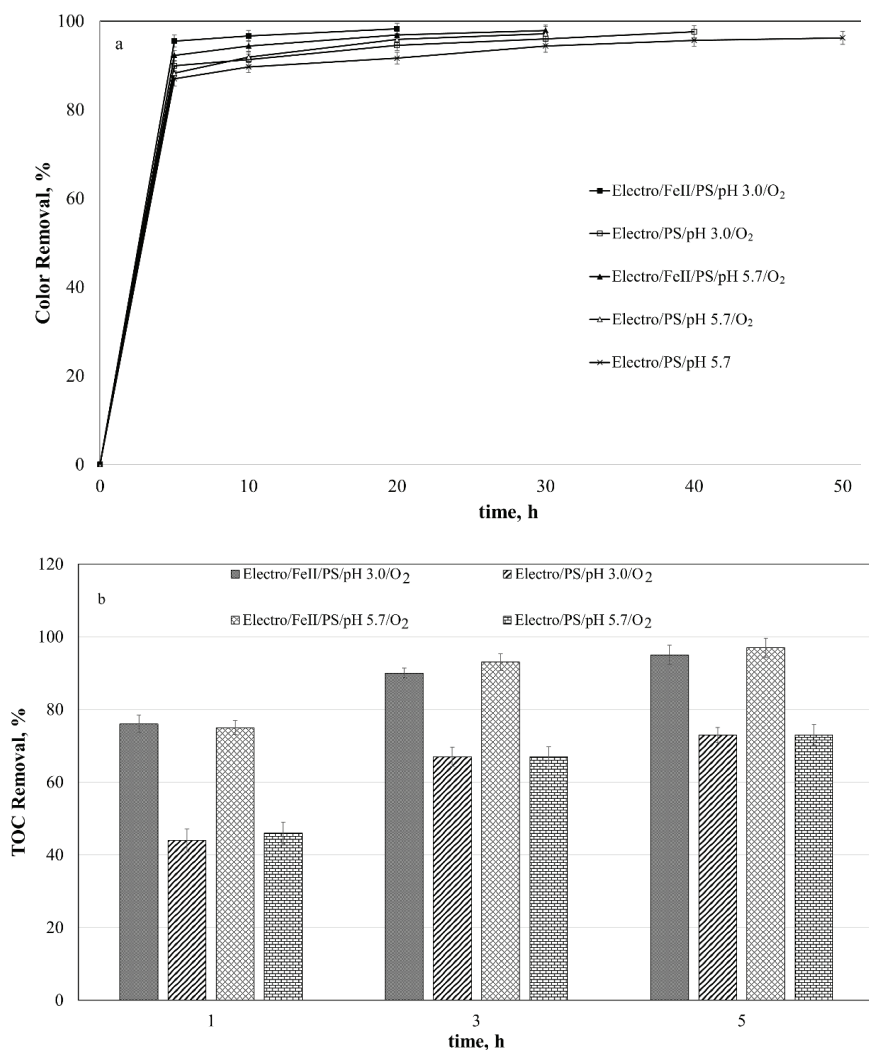


Fig. 2. The results of: a) decolorization and b) mineralization of BR18 solution at 300 mA by electro-PS ([PS] = 10 mM) and electro/FeII/PS ($[\text{Fe}^{2+}] = 0.2 \text{ mM}$, [PS] = 10 mM) processes.

5.7 < electro/PS/pH 3.0. Moreover, the efficiencies of the electro/PS and electro/FeII/PS processes in the mineralization of the BR18 solution are shown in Fig. 2b. Based on the analysis results, it was observed that the electro/PS systems have nearly the same TOC removal efficiencies at each pH values (Fig. 2b). The obtained TOC removal values by oxidation in the electro/PS/pH 3 or pH 5.7/O₂

processes were 44–46, 67 and 73 % after 1, 3 and 5 h, respectively. Sulfate radicals were generated *via* the cathodic reduction of the PS anions,^{15,16,32} and the PS anions could be simultaneously regenerated from the anodic oxidation of the sulphates,¹⁷ as given in Eqs. (6) and (7). Meanwhile, the dissolved O₂ in the solution was reduced at the cathode to form hydrogen peroxide. A PS/H₂O₂ oxidant system was proposed by Block *et al.* (2004),³⁸ but studies have shown the hydrogen peroxide activation of persulfate to be less efficient.³⁹

When the mineralization efficiencies of the EPS and electro/FeII/PS processes were compared under the same conditions, an improvement in the TOC removal efficiency with the electro/FeII/PS process was observed. An increase in the TOC removal (31 %) by the addition of ferrous ions to the solution was obtained at pH 3.0 for 1 h, and nearly 23 % after 3 and 5 h. In this case, the hydroxyl radical may be produced by the EF process in addition to the electroreduction of the PS and the activation of the PS by the ferrous ions continuously regenerated from the reduction of Fe³⁺ at the cathode, as shown in Eq. (3). For a more effective result, it may be necessary to increase the PS concentration. From previous studies, it was observed that when using the electro-activated persulfate method to remove various organic contaminants such as DNTs and aniline, a range of 1.7–3.0 wt.% of persulfate and a temperature of 318 K are needed in acidic conditions.^{32,40}

The electrolysis experiments were performed at two different pH values. For one, pH 3.0 was selected because that has been determined to be the optimum pH value for the EF process. The second was selected as pH 5.7, which was the pH value of the dye solution without any adjustment. Using the electro/FeII/PS/O₂ process at both pH values, more success was achieved in terms of colour removal and mineralization efficiency than when using the electro/PS/O₂ process (Fig. 3a and b). The relatively high TOC removal efficiency values of 75, 93 and 97 % were obtained at pH 5.7 in the electro/FeII/PS/O₂ process after 1, 3 and 5 h, respectively. In fact, only a 2 % improvement was observed compared to the results at pH 3.0 (Fig. 2b). The previous studies showed a neutral pH to be the most suitable for the sulfate radical-based oxidation;⁴¹ however, the scavenging of sulfate radicals by themselves or by protons and protonation of PS have been performed at low pH levels:^{22,42–44}



The mineralization efficiency of the BR18 solution by the electro/FeII/PS and EPS processes in which N₂ gas is bubbled through the solution is shown in Fig. 3. Under this condition, smaller reductions in the TOC removal % were observed compared to those for O₂ gas. These small declines in the TOC removal efficiency may be attributed to the fact that the major oxidant for mineralization

are the sulfate radicals via the electro-reduction of PS anions. The oxygen supplied from anodic oxidation of water remained usable for the production of hydrogen peroxide.⁴⁵

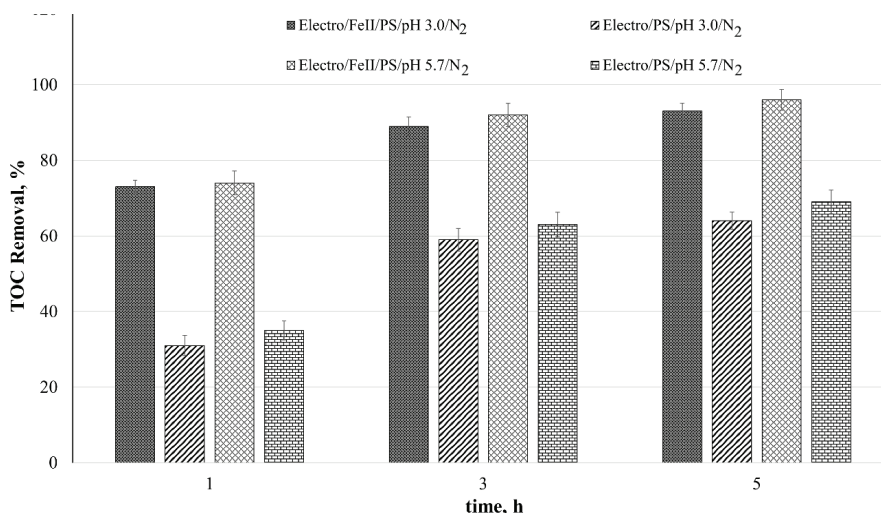


Fig. 3. The result of mineralization of BR18 solution at 300 mA by electro-PS processes ([PS] = 10 mM) and electro/FeII/PS ([Fe²⁺] = 0.2 mM, [PS]=10 mM).

To verify our results, the TOC removal efficiencies when no gas was bubbled through the solution were obtained (Fig. 4). From the results, it was observed that the bubbled N₂ gas decreased the amount of dissolved oxygen in the solution, which caused a decrease in the mineralization due to the decrease in the hydrogen peroxide production (Fig. 3). Despite the high specific surface area of the carbon felt cathode, the PS anions and oxygen compete to be absorbed at the surface for conversion into sulfate radicals and hydrogen peroxide. In the absence of gas, the observed TOC removal was higher than those in which N₂ or O₂ was bubbled, especially during the first hour. Although persulfate and ferrous ions could provide with only 1 % of mineralization after 1 h without electrolysis (Table S-II), owing to the activation of PS with both Fe²⁺ (continuously produced at the cathode) and cathodic reduction, a synergistic effect was observed on the mineralization of the BR18 solution.

Different radical scavengers were used to determine the effectiveness of the radical species in electro-oxidation processes. *t*-Butyl alcohol (TBA) and methanol acted as radical scavengers for hydroxyl and sulfate radicals, respectively. It is known that the kinetic constant for sulfate radicals and methanol ($3.2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$) is greater than that for TBA ($4.0 \times 10^5 - 9.1 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$).^{46,47} The mole ratio of 500:1 of the radical scavenger/PS was used.⁴⁷ After a 5 min electrolysis period, the colour removal of BR18 with and without radical scavengers was observed in

Fig. 5. A 20 % reduction in colour removal was observed for both the presence and absence of TBA in the first 5 min. As observed, the hydroxyl radical was the predominant species at pH 3.0. When using the radical scavengers at pH 5.7, a decrease in the formation of the hydroxyl radicals was observed in the analysis results. The hydroxyl radical formation by the sulfate radicals at all pH values, by the reaction shown in Eq. (8), has been reported by many previous studies. The electro-activated PS oxidation was reported to be significantly faster than that of PS alone by Lee *et al.*⁴⁸ and Chen *et al.*⁴⁰ In addition, the generation of sulfate radicals by electro-activated persulfate consisting of hydroxyl radicals at pH 3.0 and 30 °C has been achieved using a platinum anode and cathode.^{40,48}

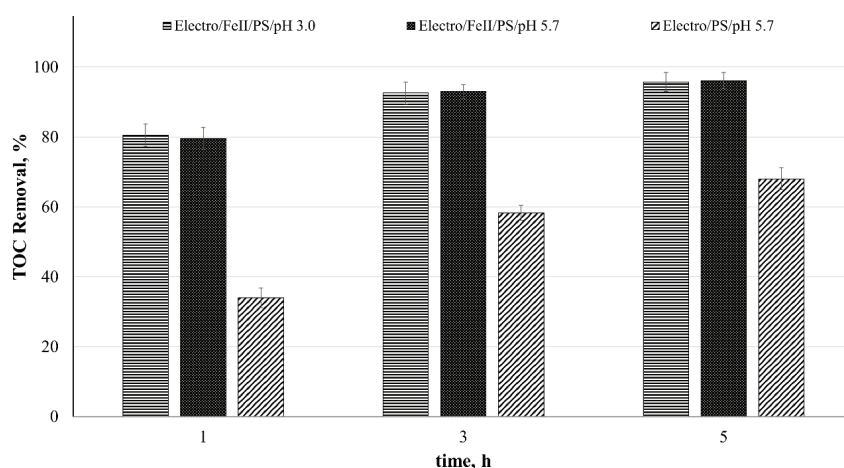


Fig. 4. The result of mineralization of BR18 solution at 300 mA by electro-PS ([PS] = 10 mM) and electro/FeII/PS processes ($[\text{Fe}^{2+}] = 0.2 \text{ mM}$, [PS] = 10 mM) without bubbling gas.

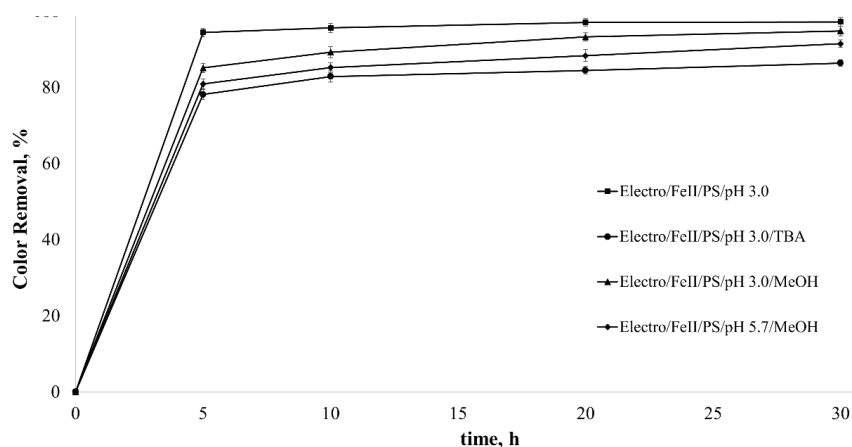


Fig. 5. Effect of reactive radical scavengers on the decolorization of BR18 by electro/Fe(II)/PS process ($[\text{Fe}^{2+}] = 0.2 \text{ mM}$, [PS] = 10 mM).

The *MCE* values over time for the electro/FeII/PS and electro/PS processes at different pH values, and with and without the use of gas, are shown in Fig. 6. When the *MCE* values of the electro/FeII/PS processes were compared with those of the EPS processes under the same conditions, at the beginning of electrolysis, higher mineralization current efficiency was obtained by the electro/Fe/PS processes. This can be explained by the subsequent generation of sulfate radicals by the activation of PS with Fe^{2+} owing to the cathodic reduction of Fe^{+3} . This idea was also supported by the higher TOC resolution achieved by electro/FeII/PS processes.

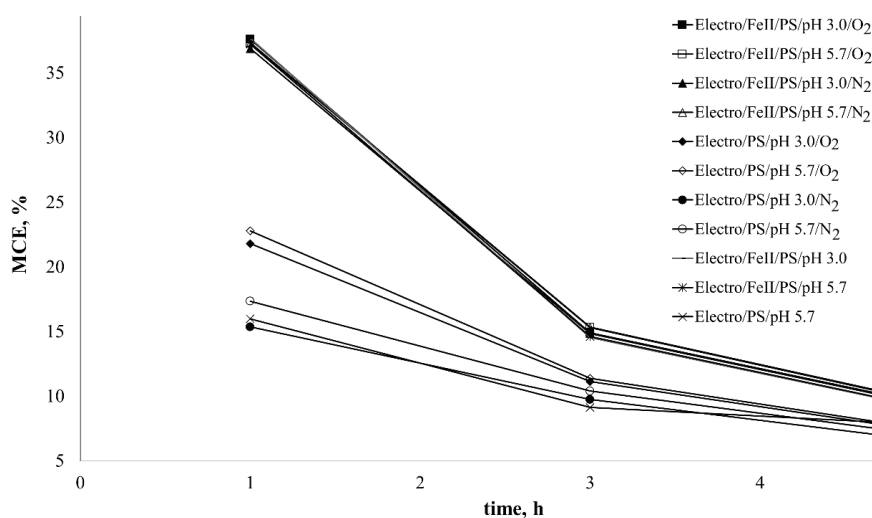


Fig. 6. Evolution of the mineralization current efficiency (*MCE*) during the treatment of BR18 ($I = 300 \text{ mA}$, $[\text{Fe}^{2+}] = 0.2 \text{ mM}$, $[\text{PS}] = 10 \text{ mM}$).

CONCLUSIONS

The electro/FeII/PS process was found to be a more effective method for the reducing of organic pollution than the EF and EPS processes. Compared with the EF process, the promising results at close to neutral pH values were yielded by this process. The efficiency of the electro/FeII/PS processes with respect to the mineralization indicates that a synergistic effect is yielded by the activation of PS (with both electro-reduction and Fe^{2+}) and EF process. The mechanism of $\text{SO}_4^{\bullet-}$ reaction with compounds was expected to differ from that of $\bullet\text{OH}$ based oxidation. In this process, it was observed that the formation of Fe-carboxylic acid complex product, which limits the completion of the mineralization in the EF process, is prevented and the mineralization is obtained at higher yields. From the results, it was observed that 93 % TOC can be removed from BR18 solution (100 mg L^{-1}) at room temperature at a PS concentration of 10 mM, an Fe^{2+} concentration of 2 mM, an initial pH of 5.7, a constant current of 300 mA, and a react-

ion time of 3 h. In this study, very low concentrations of PS and ferrous ions were maintained as compared to those in the literature. It was found that the TOC removal efficiency increased by decreasing the applied current in EF. The maximum *MCE* values were observed when using the electro/FeII/PS oxidation processes.

SUPPLEMENTARY MATERIAL

Properties of BR18 and *MCE* and TOC removal values for BR18 different oxidation methods are available electronically at the pages of journal website: <http://www.shd.org.rs/JSCS/>, or from the corresponding author on request.

ИЗВОД

УПОРЕДНА МИНЕРАЛИЗАЦИЈА BASIC RED 18 УНАПРЕЂЕНИМ ПРОЦЕСОМ ЕЛЕКТРОХЕМИЈСКЕ ОКСИДАЦИЈЕ

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У овој студији је испитивана улога процеса електрохемијске оксидације који су обухватили електро-Фентон, електро-персулфат (PS) и електро/Fe(II)/PS процесе, у уклањању Basic Red 18 (BR18) из водених раствора. Нађено је да електро-PS процес успешно уклања ову боју, али је након 5 сати произвео само 75 % минерализације. При истим условима је постигнута делотворнија минерализација процесом електро/Fell/PS него електро-Фентон методом. При рН нивоима 3,0 и 5,7 остварена је врло делотворна минерализација електро/Fell/PS процесом. Штавише, максимална минерализација по искоришћењу струје остварена је електро/Fell/PS процесом. Ефикасност минерализације електро/Fell/PS процесом је била 97 % под следећим условима: BR18 почетна концентрација 100 mg L⁻¹, рН 5,7, време контакта 5 h, PS концентрација 10 mM, концентрација Fe²⁺ 0,2 mM, а концентрација Na-сулфата 0,05 M.

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